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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 Ph.D. laureates having a common background and specialized qualifications in advanced research areas. The knowledge and skills of a Ph.D. in Materials Engineering enable graduates to pursue their career in the Manufacturing industry, given its quest for innovation in the production, processing, application and conservation of traditional materials, and for the development of innovative materials allowing radically new, currently unforeseeable applications. Moreover, the background deriving from full-time activity both in research and in education also qualifies the Ph.D. graduates for an academic career. Several graduates from the Materials Engineering Programme have been able to secure post-doctoral research positions at high-ranking universities and research Institutes.

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MECHANICAL CHARACTERIZATION AND MODELLING OF A NOVEL CONTINUOUS GLASS FIBERS-POLYDIMETHYLSILOXANE SOFT COMPOSITE: FROM MATERIAL PREPARATION TO LOAD COUPLING EFFECTS

Tiziana Baldelli - Supervisor: Francesco Briatico Vangosa

After the World War II, the development of new composite materials has raised an increasing interest. Several composites have been developed over the years, characterized by different constituent materials and types of reinforcement depending on their application field. Among them, fiber-reinforced polymers (FRPs) found wide applications in structural field or as an alternative to conventional materials in the design of structures, such as wind turbines, airplane parts or automobile frames. At the same time fiber-reinforced composites with elastomeric matrices, FREs (fiber-reinforced elastomers), also developed. In these composites, the elastomeric matrix, while characterized by good performance in flexibility, damping and absorption, is limited by its low strength and stiffness, which prevent its application in those fields where load bearing is required. The integration of rigid reinforcing elements into elastomeric matrices would allow their mechanical properties to be improved, partially maintaining the flexibility that characterize elastomers. In recent years, with the growth of the field of soft robotics, the interest for FREs increased, particularly for biomimetic applications, trying

to mimic the behavior of natural being from locomotion and morphing to the development of prosthetics or exoskeletons. Elastomeric composites, capable of meeting the required characteristics of light weight, load bearing capability and high deformability are very promising for this kind of applications. Especially for soft robotics applications, the combination of elastomers with properly oriented reinforcements (e.g., continuous fibers) can generate composites with strongly direction-dependent properties that lead to the possibility to obtain complex deformation responses in the presence of simple stimulus (Fig.1). For example, in the so called smart soft composites (SSCs), the application of an external simple stimulus, provided by an embedded active component, usually shape memory alloys that respond to
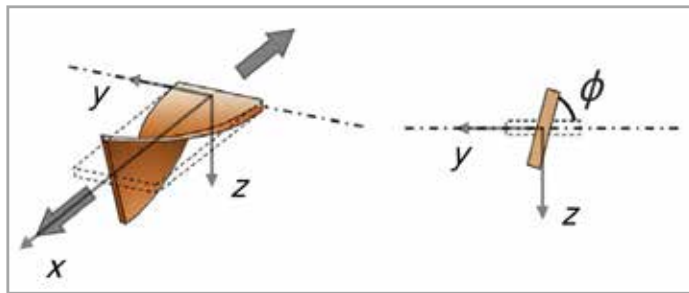
mechanical, thermal, or electrical inputs, can enable responses that could not be achieved neither by traditional isotropic materials nor by anisotropic stiff advanced composites. The complex displacements that are obtained in response to the applied simple stimulus are the result of an appropriately design of the orientation of the fibers and of the high deformability of the matrix. The orientation of the fibers determines the type of response that the FREs will experience upon application of a stimulus due to load-coupling effects common to all anisotropic materials. The high deformability of FREs makes possible to exploit a wide range of movements required by different applications which could not be achieved by conventional FRPs, which are characterized by much stiffer matrices, even with the application of low-intensity stimuli. The state of the

art on the development of these stimulus-responsive materials with load-coupling effects is still quite limited. An extensive understanding of the deformation mechanisms of fiber-reinforced elastomers as well as a suitable characterization method for determining their mechanical response is not present.

The present work aims to expand the knowledge of fiber-reinforced elastomers. In particular, a study of a continuous glass fibers (GF) reinforced polydimethylsiloxane (PDMS) will be presented. The first part of the work is centered on a deep characterization of the PDMS matrix and on how its processability and its mechanical properties are influenced by the production process and the relevant process parameters. The work then proceeds with the characterization of the glass fiber-polydimethylsiloxane
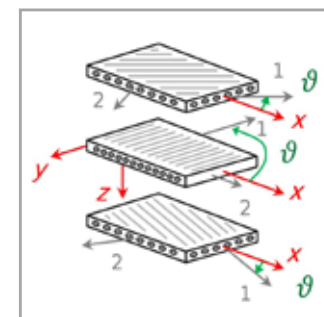

Fig.1 - Example of complex deformation obtained from the application of a simple stimulus.

composite according to the classical approach typically adopted for the characterization of fiber-reinforced polymers, that is, characterizing a thin layer of composite material with mono-oriented continuous fibers, the so-called lamina. According to the classical approach, once the properties of the single lamina are known, the behavior of any laminate composed of stacked lamina (Fig.2) can be predicted. This study aims to explore to what extent this approach could also applied to FREs, which are characterized by a nearly incompressible, highly deformable soft elastomeric matrix with a modulus on the order of MPa and by fibers with a modulus on the order of tens of GPa, that is moduli that differ more than four orders of magnitude, resulting in a level of anisotropy never explored in traditional composites. Quasi-static tensile tests on unidirectional and symmetric-balanced laminates are performed to evaluate the four independent elastic constants necessary to describe the behavior of a lamina at small strains and micromechanical models are proposed to predict the elastic constants varying the fiber volume fraction. The results are compared with those of typical traditional rigid matrix

composites, and the differences are discussed. Then, an example of a complex response obtainable with a particular lamination sequence will be presented, and the experimental results will be compared with the theoretical prediction obtainable by applying the classical approach. The peculiar strongly non-linear behavior of symmetric-balanced laminates up to large strain is then studied. Finally, the response of antisymmetric laminates to a uniaxial load is investigated, and a large extension-twisting coupling is showed and compared with the predictions of classical lamination theory and simple finite element simulations.

This work can be considered a solid foundation for the characterization of the behavior of fiber-reinforced elastomers and support the study of more complex models for predicting their behavior.

Fig.2 - Laminate composed of stacked laminae properly oriented.

MICROMETRIC-SCALE, NON-DESTRUCTIVE INVESTIGATION OF DIFFUSION PROCESS IN TURBID MATERIALS

Alessandra Botteon - Supervisor: Claudia Conti

Tutor: Chiara Castiglioni

The PhD project focused on the non-destructive investigation of materials, mainly of the Cultural Heritage field, that possess a concentration gradient created by the diffusion of a substance (agent) in a turbid matrix.

During diffusion processes, the agent distributes in the matrix up to a certain depth, following a defined concentration profile. Since concentration profile and penetration depth of agents can affect the major physical and mechanical properties of materials, the study of their distribution into matrices is important for materials characterization, quality control and for monitoring their performance over time.

In several situations, the diffusion involves relatively small volumes of the material (from microns to millimeters in depth), and in those case a micro-scale resolution study of agent-matrix systems becomes essential.

Non-destructive methods performed on the intact sample or object, without resorting to a cross-sectional analysis, present several advantages including faster quality control processes and the possibility of applying different analytical techniques on the same (and unaltered) area. This is extremely useful when dealing with unique or precious samples or objects, as it typically happens in Cultural Heritage field.

The measurements were performed using micro-spatially offset Raman spectroscopy (micro-SORS), an emerging technique that combines conventional macro-scale SORS with microscopy, permitting the study of the subsurface molecular composition at the micrometre-scale directly from the surface of the material, at depths beyond the reach of conventional confocal Raman microscopy. The sub-surface Raman photons can be detected by enlarging ('defocusing micro-SORS') or separating ('full micro-SORS') excitation and collection zones (Fig.1). Compared to other non-destructive analytical techniques, micro-SORS offers the great advantages of high chemical selectivity and easy access.

The research was mainly focused on materials encountered in the Cultural Heritage field, including plasters and stuccos treated with ammonium oxalate (AmOX) or Paraloid B72.

A systematic investigation of micro-SORS potentials and limitations were carried out using mock-up samples with controlled characteristics, namely penetration depth of the agent, its concentration on the surface and its concentration profile inside the matrix. The results of the experiments showed a decrease of the agent/matrix Raman intensity ratio (H) with the increase of the defocusing distance or the spatial o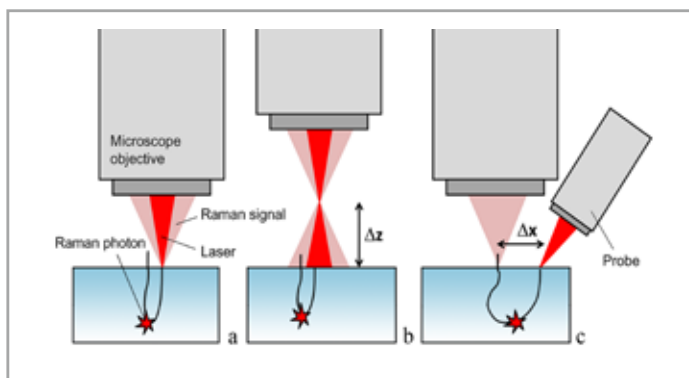ffset. The trend of this intensity decrease was found to be related to the penetration depth of the agent, a parameter that is crucial for the evaluation of treatment efficacy (Fig.2).

Additionally, it was demonstrated that micro-SORS is not dependent on the initial concentration of the agent applied to the surface, and this characteristic makes micro-SORS suitable for comparing materials that have a different amount of agent on the surface, a common situation in conservation field. A preliminary application of principal component analysis (PCA) provided promising results, that encourage further exploration on the use of statistical multivariate analysis on micro-SORS spectra. The data interpretation was supported by an analytical, physical model, that was designed to simulate the scattering of light and the Raman photons collection in micro-SORS measurements, thus providing analytic expressions which describe the relationship between normalized agent/matrix intensity ratio (H) of micro-SORS spectra and the concentration profile of an agent dispersed in the turbid medium. Micro-SORS was able to characterize the diffusion behaviour of Choline-Chloride-Urea (Ch-Ch-U), an innovative and eco-friendly deep eutectic solvent (DES), used for the removal of protein-based coatings from painted surfaces. Different cleaning procedures were tested, demonstrating that the gel is able to control the solvent release and it has better retention capacity compared to more traditional solvent-soaked cotton swabs.

A case study was included in the experimentation: plasters treated with AmOX collected from a historical building, Palazzo Besta in Teglio (SO, Italy), were analysed obtaining relevant information about newly formed oxalates distribution inside the plaster matrix, paving the way for the use of micro-SORS as a routine method for non-destructively evaluating conservation products distribution and treatments efficacy (Fig.3).

Additionally, dye sensitized solar cells (DSSC) photo-electrode was investigated for quality control purposes, demonstrating the applicability of the procedure to a wider range of situations also outside heritage science field.

Fig.1 - Conventional Raman (a) and micro-SORS variants: defocusing, with indication of the defocusing distance Δz, (b) and full micro-SORS, with indication of the offset Δx (c).
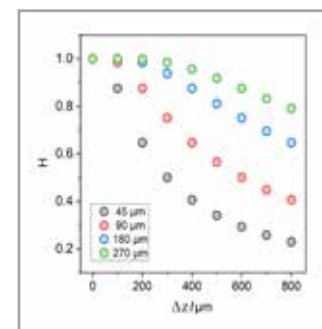

Fig.2 - Agent/matrix normalized intensity ratio (H) for samples with different penetration depths of the agent (45-270 μm), plotted against defocusing distance (Δz).

Fig.3 - Palazzo Besta (a) and detail of the treated painted plasters (b).

COMPUTATIONAL MODELLING OF THE CHEMICAL PHENOMENA IN PARTIAL DISCHARGES

Giacomo Buccella - Supervisor: Giovanni Dotelli

Polyethylene is one of the simplest polymeric materials used in electric power industry due to its low cost and effective dielectric features. For instance, it is largely used in high voltage electric power cables. Unfortunately, this material undergoes wear and ageing. Using AC power supplies, one of the main causes of deterioration is the treeing, i.e. a series of internal cavities formed in the polymeric matrix. The dielectric strength within the cavities is low and this triggers the occurring of internal discharges which propagates the treeing itself (Fig 1A).
In order to improve the correlation between measures and ageing conditions, we aimed at estimating, by means of first-principles calculations, a series of physico-chemical parameters. The latter are often very uncertain and play a key role in the modelling of internal discharges based on partial differential equations (Fig 1B).
Most of the unknown parameters are strictly related to chemical processes. Therefore, the purpose of this work has been to outline a significant part of the chemical mechanisms involved in internal discharges and treeing process, for estimating the related parameters. In particular, we focused on: discharge triggering through Schottky effect, plasma chemistry, surface-gas interactions for chemical ageing (Fig 2) and successive carbon layer formation (Fig 3).
In this thesis, we obtained the modelling of different phenomena that play a key role, at the microscopic level, in the deterioration process of PE in contact with a plasma. This problem is linked to the PDs in electrical engineering. In particular, we performed first-principles calculations (Density Functional Theory) to better understand the chemical processes involved in the treeing. The quantum mechanical description was, then, employed to obtain a series of parameters to be integrated in a macroscopic model conceived to investigate the plasma dynamics and gas-surface interactions in technically relevant geometries.
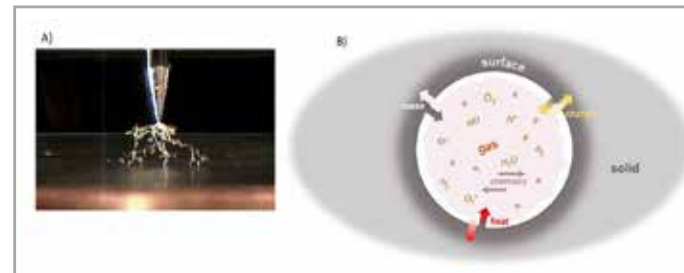

Fig. 1 -A) Treeing structure obtained by a metallic electrode embedded in a PE sample; B) scheme of the general model based on PDE: an arbitrary gas mixture confined in aspherical geometry interacting with a solid insulator domain.
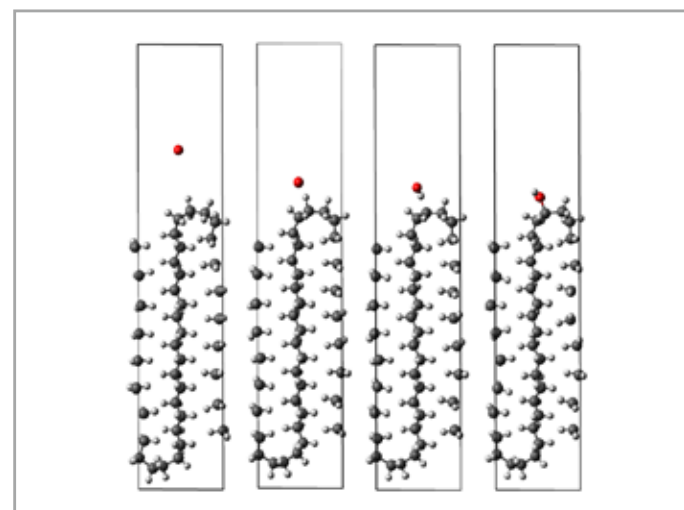

Fig.2 - Snapshots of a molecular dynamics simulation reproducing the formation of a hydorxil group a polyehtylene surface.
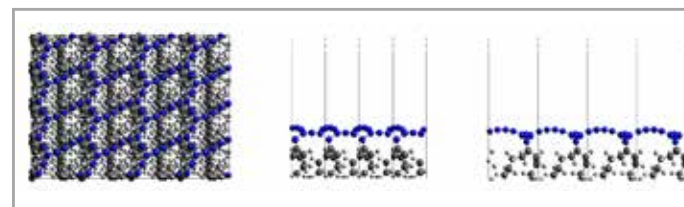

Fig. 3 - Example of carbonic structure formed after the impact of carbon-rich fragments on polyehtylene. In this case, ring structures are clearly visible (blue atoms).

PULSED ANODIZING TREATMENTS TO INCREASE THE CORROSION RESISTANCE OF CP TITANIUM IN ACIDIC ENVIRONMENT

Luca Casanova - Supervisor: Marco Ormellese

Tutor: Maria Pia Pedeferri

Titanium and its alloys offer a great opportunity and reliability when applied in those industrial applications where the contact with an aggressive solution, or the occurrence of too serious consequences in case failure, limit the use of other common structural materials like iron or aluminum. For those reasons common fields of Ti implementation, listed in order of market demand, are: aerospace, chemical, nuclear, and naval industry. In all cases, the contact with acidic environments can severely affect the protective properties of the thin oxide layer that naturally grows on the metal. This is particularly true when dealing with sulfuric acid often present, for example, in the stratosphere where airliners fly or during metal pickling and synthesis of several chemicals like fertilizers. Followed from those observations, electrochemical surface treatment, like plasma electrolytic oxidation (PEO), offers a great deal to improve surface properties upon the growth of a thick (even several microns) and hard conversion coating. The aim of this research is to optimize PEO surface treatments for titanium grade 2 tested for corrosion resistance in a solution of hot concentrated sulfuric

acid (typically 10 %v/v at 60 $^\circ$C, a common environment adopted in metal pickling applications). In the first part of the thesis, the role of the main technological parameters, like frequency and amount of cathodic polarization, was investigated according to a detailed characterization made possible upon the use of transmission electron microscopy (TEM). This allowed to probe the material structure, at the scale of the nanometers, according to the use of electron energy loss spectroscopy (EELS) and to construct component maps (**Fig.1**) (each component identified with a color code) based on automatic structural discrimination performed by a script developed in Python. Detailed structural maps were constructed improving knowledge about the barrier layer, i.e., the morphological region of PEO oxides directly in contact

with the metal and responsible for the corrosion resistance, and the porous region, i.e., the oxide portion directly in contact with the external environment. The application of a direct current (DC) regime favored the establishment of a barrier layer composed by a three-layer structure, as in **Figure 1a**, typical of the natural oxide formed on titanium in atmosphere and composed of: TiO (in light blue), immediately in contact with the metallic substrate, Ti_2O_3 (in purple) and mixed Ti^{3+}/Ti^{4+} bearing oxide phases (in green and orange). On the other hand, the use of pulsed PEO with hybrid duty cycles, repeated at high frequency (1000 Hz), allowed to limit the amount of oxygen vacancies and to promote the formation of the most thermodynamically stable TiO_2 polymorph, i.e., rutile (in red) as in **Figure 1b**.

The latter verifications were found to be fundamental in characterizing the corrosion response of the coatings, particularly in acidic environments, where the presence of electronic defects can favour protons reduction and consequent atomic hydrogen ingress inside the oxide layer. The corrosion mechanism was investigated through the use of electrochemical impedance spectroscopy (EIS) allowing to extract proton diffusivities of oxides produced according to different PEO conditions. Accordingly, a clear correlation between technological parameters, synthesized materials, and corrosion response was established.
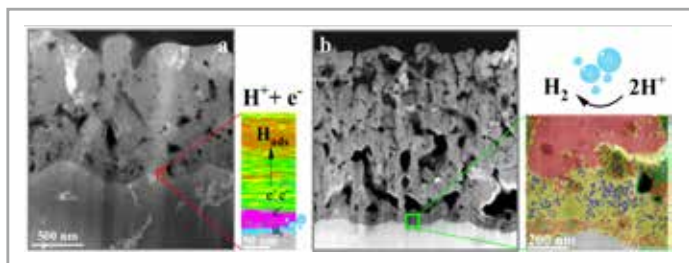

Fig. 1 -TEM images and EELS characterization of titanium oxide produced by PEO in a DC and b pulsed regime.

STRUCTURE-PROPERTY RELATIONSHIPS OF N-TYPE DOPED SEMICONDUCTING POLYMERS: A STUDY BASED ON VIBRATIONAL SPECTROSCOPY, ELECTROCHEMICAL AND MORPHOLOGICAL INVESTIGATION

Ilaria Denti – Supervisor: Gianlorenzo Bussetti

Tutor: Chiara Castiglioni

Polymeric semiconductors represent a thrilling group of organic materials with outstanding properties that has proven, over the years, to be adaptable to many research fields. These materials performances are heavily dependent on their electronic, molecular and super-molecular structure, which is affected by doping processes and doping mechanism. The constant search for new materials and better performances of existing devices needs to be supported by a deep understanding of the charge transport properties of both p-type and n-types polymers, pristine and doped. Among many techniques available to unveil the polymers properties and characteristics, this dissertation focuses on vibrational spectroscopies (Raman and infrared), which we used in searching structure-property relationships upon the formation of charge defects through doping of n-type organic materials (polarons and bipolarons). Moreover, fundamental aspects of doping kinetics and environmental factors will be unveiled in this work, focusing on both chemical and electrochemical doping. First, evidence of charge defect localization and hopping-type charge transport mechanism in chemically doped P(NDI2OD-T2), a pioneer n-type polymer, is provided. Vibrational spectroscopy is proved to be a powerful tool to monitor the polaron formation in doped polymers: infrared spectra were used in this chapter to individuate distinct polaronic features in doped samples, different from the dopants or the polymer fingerprints (**Fig.1**). At high dopant/polymer molar ratio, these new vibrational transitions are of the same intensity (dipole strength) of the pristine bands and can be nicely modeled by a radical anion localized on the NDI unit. Resonant Raman spectra add more information, showing how, by changing probing wavelength, we can tune the response of the polymer and highlight different building blocks. The spectra acquired at 1064 nm, which allow focusing on the T2 unit, were unaffected by the doping even at high concentrations of dopant. Spectra acquired at 514 nm (and 632 nm) showed major changes and new polaronic features. Calculations agreed with the data, further confirming that the T2 is not playing an active role in the formation of the charge
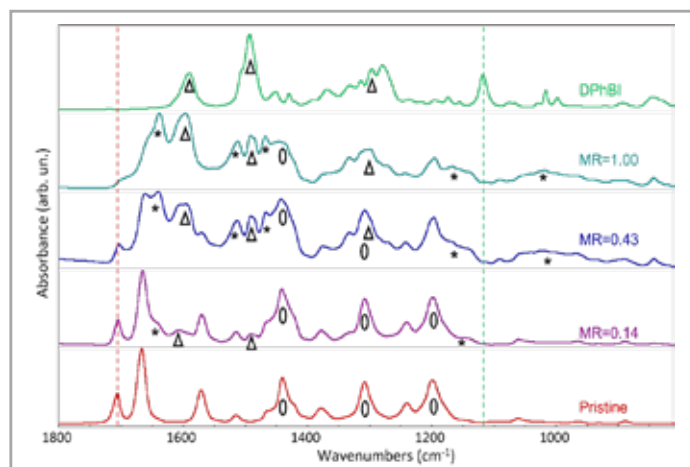

Fig. 1 - From bottom to top, pristine spectra of P(NDI2OD-T2) (red), doped annealed spectra with different dopant/polymer ratio (purple MR=0.14, blue MR=0.43 and dark green MR=1.00), dopant spectra (DPhBI, light green)

defect. The extreme localization of the polaron on the NDI unit and the torsional angle between the NDI unit and the thiophene are responsible of the interchain nature of the charge transport mechanism in n-type polymers. Chemical doping kinetics is further exploited regarding the effect of annealing time and temperature. To characterize these effects on a multiscale, complementary techniques are used, such as Grazing Incident Wide X-ray Scattering (GIWAXS), which probes the material morphology. The most interesting finding of this work is that 1H-benzimidazoles dopants of P(NDI2OD-T2) are already active at room temperature, showing an increase in conductivity of 3 orders of magnitude. The finding parallels by GIWAXS and infrared in-situ measurement, indicating that the charge defect is already formed at room temperature. The annealing has a further effect on the conductivity, doubling the conductivity value in conjunction with a morphology refinement. The important conclusion of the in-situ infrared dataset is that the charge transfer/polaron formation process takes place spontaneously but has a rather slow kinetic in thick films at ambient temperature. Interestingly, we showed here that in absence of oxygen, which can give rise to competitive reactions, an incipient doping is observed also immediately after the casting of the film from the polymer/dopant solution. The GIWAXS data, obtained for thin spin coated films, show that the crystalline structure changes upon doping from face-on to edge-on, as well as giving intercalation sites for the dopant, in between the polymer backbones. increases, explaining why the conductivity for these samples presents lower values.

Several aspects of the electrochemical doping are analyzed, such as the influence of environmental oxygen on polaron and bipolaron formation, as well as the type of electrolyte; in addition, the reversibility of electrochemical doping is investigated. The study on electrochemically doped samples is pursued through in-situ Raman spectroscopy coupled with an electrochemical characterization. Signature Raman bands ascribed to the polaron and bipolaron are individuated through in situ measurements. The measurements were performed under different experimental conditions, using different electrolytes. Regardless of the electrolyte composition and acidity, similar vibrational features are individuated, with slight changes in the voltage onset. The main differences are highlighted by saturating the electrolyte with an inert gas or oxygen. The Raman data show that oxygen hinders the formation of the bipolaron even at high voltages applied. This is probably due to side reaction happening in the electrolyte, such as the formation of hydrogen peroxide. A direct comparison with the chemically doped P(NDI2OD-T2) spectra confirms that the bipolaron formation does not take place in this case. In the last case, this could be due to several factors, such as the segregation of the dopant at high doping levels in the chemically doped samples. Differently, electrochemical doping can give rise to bipolarons formation and Raman measurements in resonance with the bipolaron absorption, show changes in the vibrational bipolaronic features. So far, the analysis of the Raman features ascribed to polarons and bipolarons has been done by means of empirical correlations of the spectroscopic data collected, while Quantum Chemical modelling is required for a detailed vibrational assignment of the polaronic/bipolaronic Raman peaks and for the rationalization of their modulation with the excitation wavelength. It is worth noting that the polaronic Raman bands are independent from the doping method, namely the marker bands are the same for chemical and electrochemical doping and they do not depend on the chemical dopant species nor on the ions involved in the electrochemical process. For the above reasons, we can confidently correlate doping induced Raman bands the formation of charged defects on the polymer chain, characterized by their peculiar vibrational features.

PRODUCTION AND CHARACTERIZATION OF SELF-LUBRICATING METAL MATRIX COMPOSITES FOR SLIDING ELECTRICAL CONTACT IN AEROSPACE APPLICATIONS

Marco Freschi - Supervisor: Giovanni Dotelli

The work aimed to investigate materials characterized by high electrical conductivity and wear resistance to be employed in sliding electrical contacts for the aerospace field.

The research focused on conductive self-lubricating metal matrix composites. In particular, copper was employed as the metallic conductive matrix to ensure the required electrical conductivity, and different lubricating second phases were investigated. The main scope of the reinforcements was to ensure a lubricating effect to the composite, decreasing wear and extending the components lifetime. The investigated materials belonged to the families of the transition metals dichalcogenides and the carbon-based materials, namely molybdenum disulfide, tungsten disulfide, and different graphene nanoplatelets. All these materials are characterized by a layered structure that facilitates sliding in the presence of shear stresses, decreasing the friction coefficient. Moreover, they promote the formation of a tribofilm at the interface between the sliding surface, further decreasing wear and improving the tribological performance. The employed materials were analyzed and characterized through granulometry, thermogravimetry, X-ray diffractometry, and Raman scattering spectroscopy. The investigation of the effects of the variables of the employed production method allowed the optimization of the operative conditions during the metal powder metallurgy procedure, namely ball-milling duration, load, and maintenance time span during the pressing step, sintering temperature, and the addition of secondary treatments, like double pressing and double sintering. The reinforcement concentration was optimized, looking for the best trade-off between the mechanical, electrical, and tribological properties.

After the sintering process, the density, wettability, electrical resistivity, and hardness were analyzed. The tribological assessment was performed by micro-scratch test and wear test. The resulting tracks were analyzed by scanning electron microscopy and confocal laser scanning microscopy to evaluate the wear mechanisms, the specific wear rate, and the wear coefficient of the different composites.
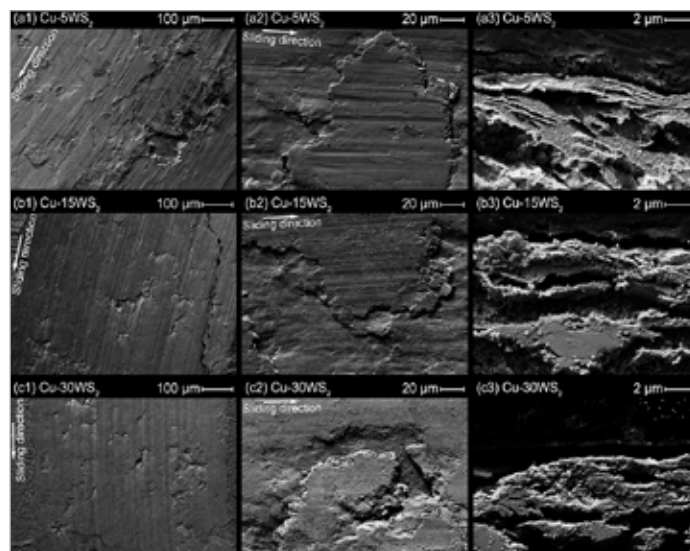
The obtained results indicated a decrease in friction coefficient thanks to the presence of the solid lubricants and the enhancement of the wear conditions, with a lower specific wear rate and wear coefficient. On the one hand, the use of a low percentage of solid lubricant determined a decrease of friction coefficient during the micro-scratch and wear tests, but it did not modify the severe wear regime; on the other hand, an excess of solid lubricant determined a worsening of the tribological performances, due to the production of a significant volume of debris and a strong increase of electrical resistivity. The analysis of composites made with molybdenum disulfide highlighted the possible improvement due to the use of the nanometric solid lubricant compared to the micrometric one. Moreover, an additional pressing step showed a further improvement in the material mechanical properties.

Different graphene nanoplatelets were tested; the one with the lowest surface area exhibited the best results with a low weight concentration. Nevertheless, the adhesion problem with the metal matrix should be further investigated as it may be one of the leading causes that generate a high volume of undesired debris. A deep analysis of the composites with tungsten disulfide found that the most promising composites are those produced with 10 wt% of reinforcement after a ball-milling of two hours. This combination reached a satisfying electrical conductivity and lowered the wear coefficient and specific wear rate of the composite compared to the pure copper sample. Nevertheless, they remained in the same order of magnitude, indicating the same wear regime. The evaluation of the effects of different sintering temperatures, additional pressing and sintering steps found out that the increase of the sintering temperature determined an increase of the porosity within the composite material, especially at the interface between the metal matrix and the solid lubricant reinforcement, worsening the wear behavior. The additional pressing step introduced defects and dislocations that determined a work-hardening of the composite material, improving the tested properties. A second sintering step relaxed the deformed lattice of the metallic matrix, and part of the observed improvement was lost.

The further analysis evaluated the synergetic effect of employing multiple reinforcements, namely tungsten disulfide, inorganic fullerene of tungsten disulfide, and graphene nanoplatelets. These composites strongly decreased the wear coefficient and the specific wear rate, lowering the severity of the wear conditions and moving to a mild regime of unlubricated sliding contact. In particular, the use of the two structures of tungsten disulfide outperformed in all the tested properties compared to the other analyzed materials. This project was sponsored by and performed in collaboration with Logic S.p.A.
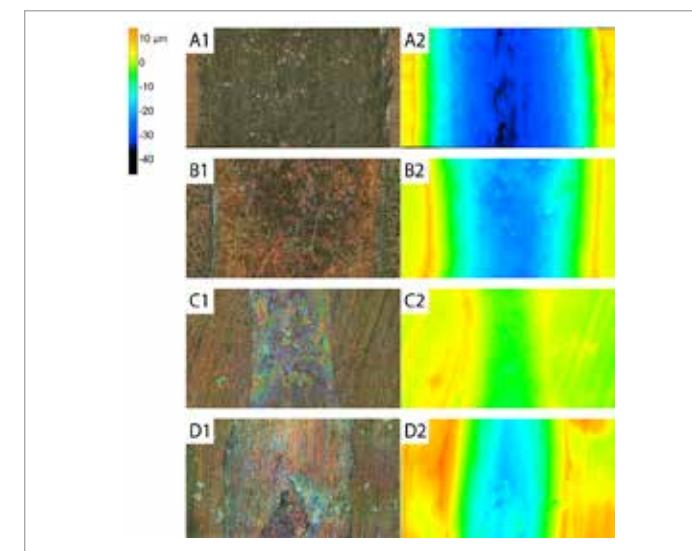

Fig. 1 - SEM images of the wear tracks of Cu-XWS$_2$ composites: Cu-5WS$_2$ (a), Cu-15WS$_2$ (b), and Cu-30WS$_2$ at 400x (1), 1500x (2), and cross-section at 20000x (3).

Fig.2 - Optical microscopy (1) and CLSM (2) images at 20x magnification of the wear tracks of the samples: (A) Copper, (B) Cu-WS$_2$, (C) Cu-WS$_2$-IF, and (D) Cu-WS$_2$-IF-GNP.

FABRICATION OF ENERGY STORAGE MICRODEVICES AND THEIR APPLICATION ON TEXTILES

Eugenio Gibertini - Supervisor: Luca Magagnin

Many experts agree that the future of wearables is smart fabrics and wearable electronics will be directly embedded in our clothes in the form of microdevices, yarns and fibers rather than external gadgets. The next transition from the classical flexible but rigid wearable electronics to the new textile-based one, is laying the foundations of a new technological field that was recently termed as "Textronic". If one hand embedded textile-based sensors for human health monitoring gained tremendous attention because of their potentiality to bring healthcare to a next level accomplishing the new paradigm of predictive diagnostic approach, all of these microdevices necessarily require the development of a new highly miniaturized eco-system of textile-based electronic devices as communication, luminescent, energy harvesting and energy storage working on demand as micro-power source. In particular, the hot theme of energy storage is posing the development of new energy storage devices as a fundamental key also in the field of Textronic. Recently, great advances have been made in micro-fabrication of energy storage devices such as capacitors and batteries.

However, the state of art is still unripe and further improvements about materials, technologies and strategies are needed. This thesis work belongs to the framework of energy storage applied to fabrics in order to achieve textile-based microdevices for wearable electronics applications. The study investigated very different materials, synthesis and fabrication techniques. In fact, due to the almost countless combinations of techniques and materials for energy storage application, a transversal approach was adopted rather than focusing on a single material, technology or strategy. The approaches proposed in the experimental works tried to overcome the main limitations identified in the state-of-art on this research field, with a particular attention to develop scalable strategies for both electrode synthesis and micro-device fabrication. The main advantages as well as main limitations for the case of study proposed were pointed out. The thesis work was structured in six chapters. The first chapter introduces the main concepts of energy storage, wearable electronics and the new paradigm of wearable electronics applied to textile (Textronic). Device architectures, integration strategies and main requirements were described in details. The second chapter provides an overview of the state of art of energy storage for Textronic applications, particularly focused on the 1D/2D devices, materials and electrode fabrication strategies. The following chapters are experimental, describing the different approaches and materials that were investigated in order to obtain energy storage micro-devices able to be integrated in textiles. In terms of electrode design and configuration, two macro-areas were investigated as the development of (a) 1D wire-shaped and fibrous electrodes and (b) 2D planar microdevices. A fibrous shaped microcapacitor was proposed, based on a new material combination of PEDOT:PSS loaded in wet-spinned Kevlar nanofibers (KNF)
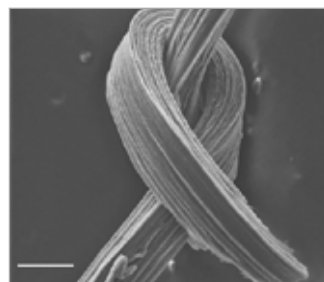
resulting in a PEDOT:PSS@KNF composite fibres. The easy approach here proposed allowed easy production of wire-shaped conductive, mechanically robust and flexible electrodes with good electrochemical storage properties. A textile-based symmetric microcapacitor was demonstrated by sewing the PEDOT:PSS@KNF electrodes onto a fabric substrate. Coupled with PVA/H3PO4 gel polymer electrolyte, the textile microcapacitor showed considerable volumetric capacitance and remarkable life cycle. In a second work we tried to address a common lack found in the state of art about fibrous-shaped energy storage device, namely the incompatibility of 1D electrodes (mainly made of
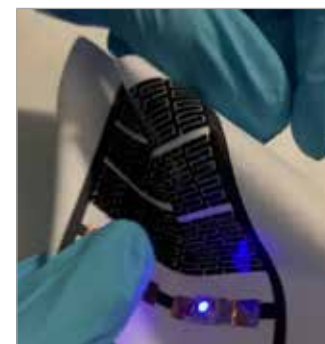

Fig. 1 - SEM image of a knotted PEDOT:PSS@KNF wire-shaped electrode.

carbon nanostructures) with conventional textile machining techniques. Moreover, coating techniques commonly employed for loading active materials on these 1D electrodes usually allow only few cm-long devices because they involve complex, long-lasting or hardly scalable procedures. We then proposed an innovative route to produce meter-long thread electrodes to be employed in Zn/Ag battery chemistry. A custom-made setup allowed the continuous electrodeposition of Zn, Ni and Ag on commercially available conductive Ag-plated nylon thread. The as obtained Zn@Ag and Ni@Ag thread electrodes were successfully integrated in textile substrates by embroidery technique. Coupled with an in-situ crosslinked alkaline gel-polymer electrolyte, the embroidered Zn@Ag/Ni@Ag textile microbattery showed satisfactory energy storage performances and their feasibility in textronic application was demonstrated. Finally, inkjet printing of $Ti_3C_2T_x$ MXene was investigated as suitable technique to obtain textile-based microcapacitors. Other then $Ti_3C_2T_x$ MXene aqueous ink formulation, a new inkjet-printable UV-curable electrolyte precursor was proposed to obtain all-inkjet-printed

Fig.2 - All-inkjet-printed array of Ti3C2Tx MXene microcapacitors on a fabric substrate powering on a blue led.

microcapacitors on textile. The effect of printing parameters as well as the geometrical parameters of the textile-based $Ti_3C_2T_x$ MXene microcapacitors were investigated. Arrays of all-inkjet-printed microcapacitors were demonstrated to be suitable as energy storage and micro-power supply units, able to switch on a blue led under various deformation conditions. In general, all the optimized microdevices fabricated showed that the developed strategies and materials are feasible for energy storage and micro-power source applications in Textronic.

HUMIDITY-RESPONSIVE LAYERED SELF-ACTUATOR

Shiva Khoshtinat - Supervisor: Claudia Marano

Co-Supervisor: Valter Carvelli, Tutor: Giovanni Dotelli

Towards the development of a low-cost humidity-responsive self-actuator (Fig.1), this project aimed to exploit the dimensional variation mismatch between a hygroscopic material (as an active layer for coating) and a non or less-hygroscopic substrate, due to changes in the humidity level of the environment. For this goal, a cellulose-based polymer, namely a cellulose acetate (CA), was chosen as a highly hygroscopic material. The path to achieve the project's goal was divided into three main steps:

• Providing a systematic procedure of hygroscopic membranes production,

• Characterization of the membranes' intrinsic features that contribute to the bi-layered behavior.

• Development of a comprehensive finite element model that takes advantage of the characterized intrinsic properties of the hygroscopic material for the prediction of self-actuator response to variation of humidity level which could be used for a proper design of the humidity-responsive self-actuator.

A systematic investigation of cellulose acetate membrane fabrication to produce the appropriate membrane for the project's intended purpose was performed. The effect of the type of solvent adopted for CA solution preparation, CA concentration, casting process, and solvent evaporation method was analyzed. After optimizing the manufacturing process of cellulose acetate membranes, surface morphology, thermal, and mechanical properties of the membranes were studied.

The hygroscopic behavior of CA membrane was investigated to identify the parameters governing the moisture diffusion process. Material properties such as moisture diffusion coefficient, moisture concentration at saturation and moisture absorption induced expansion were evaluated.

The moisture diffusion in cellulose acetate membranes has been investigated via gravimetric measurements and the dependency of the CA moisture concentration at saturation on the environment's humidity level was characterized. Within a wide range of the experimental campaign for thickness and relative humidity level, an analytical model was utilized to fit the sigmoidal non-Fickian behavior of moisture diffusion in cellulose acetate membranes, taking into account the influence of induced relaxation by moisture at the membrane's surface. While the models currently used to simulate diffusion are not able to reproduce the non-Fickian moisture diffusion process in highly hygroscopic materials, a COMSOL Multiphysics-based finite element model capable of predicting the sigmoidal moisture diffusion by taking into account the effect of induced relaxation, membrane thickness, and relative humidity is proposed in this study (and Fig.3).

The moisture absorption induced expansion of cellulose acetate membranes has been characterized via Thermomechanical Analysis (TMA). A correlation between the relative humidity, affecting the equilibrium moisture concentration, and the related expansion was defined. A finite element model that combines the moisture diffusion process and the hygroscopic deformation induced in the membrane was proposed.

Finally, the response of a humidity-responsive bilayer self-actuator consisting of the characterized cellulose acetate membrane as active layer and a non-hygroscopic substrate made of a commercial adhesive tape (Tesa ® 64621) was investigated. The evolution of bending curvature induced in the bilayer composite by an environment humidity variation has been well predicted by the finite element model (Fig.4).

The main findings of this research revealed some fundamental aspects:

• Highly hygroscopic materials such as cellulose acetate, in this research, demonstrate a peculiar non-Fickian moisture diffusion;

• despite conventional assumptions, both the concentration at saturation (C_{sat}) and the hygroscopic strain (ε_{hygro}) exhibit non-linear relationships with the environment's relative humidity at constant temperature for the studied cellulose acetate;

• for highly hygroscopic materials the coefficient of hygroscopic expansion may be humidity dependent.

The finite element model presented in this research, on the other hand, appears to be the first numerical study successful to describe the sigmoidal moisture diffusion kinetics of cellulose acetate and couple the non-Fickian diffusion with mechanical deformation for prediction of the induced hygroscopic strain. This comprehensive model, which successfully describes the evolution of bending curvature induced by variation in humidity in a layered self-actuator over time, not only has the potential to be extended to other cellulose-based or highly hygroscopic materials, but it also has the potential to be used as a design tool for the fabrication of this new generation of humidity-responsive self-actuators.

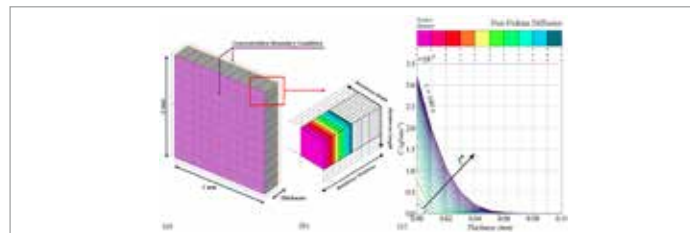Fig. 1 - A humidity-responsive self-actuator.

Fig. 2 - Finite element model for the simulation of the non-Fickian moisture diffusion in highly hygroscopic materials, a) geometry, boundary conditions and discretization of the sample, b) elements set to monitor the concentration at each time increment, c) predicted moisture concentration distribution through the thickness for a non-Fickian moisture diffusion.
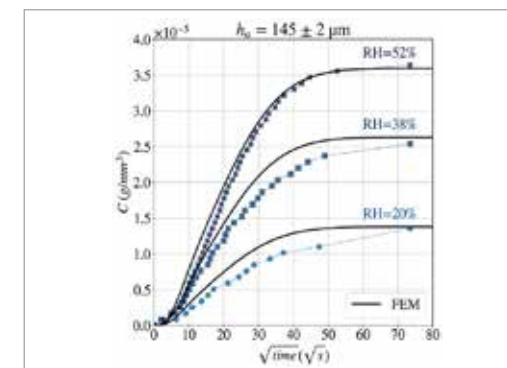

Fig. 3 - Prediction of the non-Fickian moisture absorption (continuous lines) in a CA membrane at three different level of relative humidity and experimental data (symbols).
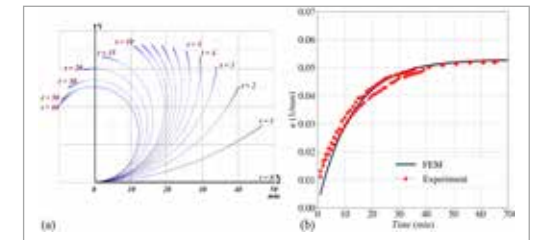

Fig. 4 - a) finite element simulation for Self-actuator deformation prediction, (b) comparison between experimental data and numerical modeling (FEM).

SPECTROSCOPIC ANALYSIS OF SNOW SURFACES IN RELATION TO THE PHYSICO-CHEMICAL AND MECHANICAL BEHAVIOR OF DIFFERENT KINDS OF SNOW

Ettore Maggiore – Supervisor: Matteo Tommasini

Tutor: Paolo Maria Ossi

Snow is an important component of the cryosphere as it regulates the global climate and it constitutes a source of fresh water used both as drinking water and to produce hydroelectrical energy. Furthermore, the practice of winter sports also depends on the presence of snow in mountain resorts, which guarantees a source of livelihood for local businesses. In this thesis I carried out a study of snow in two different (but interrelated) research areas: (i) Raman spectroscopy applied to the study of different types of snow, and (ii) friction between snow and materials for winter sports. Due to metamorphism, the morphology and size of the snow grains on the ground change over time. This process leads to the formation of types of snow that are distinct from each other by size and shape of the snow grains and particle aggregation. Generally, in a snowpack different snow layers coexist. The distinction and characterization of the different types of snow is important in assessing the mechanical stability of a snowpack (thus establishing the risk of an avalanche release). In the first part of my research, I studied

different types of snow both in the laboratory and on field with Raman spectroscopy, focusing on the analysis of the OH-stretching region. In the laboratory I found out that the characteristics of the Raman spectrum of snow are different from those of ice at the same temperature (Fig.1). This is due to the different arrangement of the water molecules in the solid state between the surface sites and the bulk sites. Indeed, at the surface water molecules are less hydrogen-bonded to each other than they are in the bulk, and they form the so-called

quasi-liquid layer. The higher the surface/volume ratio of the snow sample the higher the spectral differences with respect to bulk ice. Based on this feature it is possible to distinguish the Raman spectra of different kinds of snow characterized by a distinct granulometry, thus a different value of the Specific Surface Area (SSA). I carried out Raman measurements directly on field. In collaboration with alpine guides, we identified the different layers of a snowpack, and we acquired Raman spectra on the same snow layers. By comparing
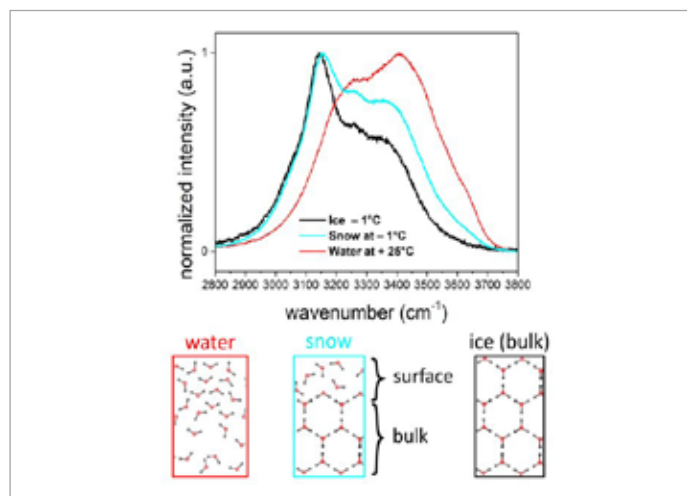

Fig. 1 - Comparison between the Raman spectra of liquid water at 25°C, bulk ice at -1°C and snow at -1°C in the OH-stretching region. On the right are schematically represented the dispositions of the water molecules in the liquid and the solid state. In the case of snow, the presence of the quasi-liquid layer at the surface is highlighted.

the spectra of different kinds of snow belonging to distinct layers of a snowpack, we were able to distinguish freshly fallen snow (smaller average grain size) from metamorphized snow (larger average grain size). In the laboratory I studied how the Raman spectrum of snow is affected by the presence of different amounts of liquid water. The aim was to associate the changes of snow Raman spectrum to the Liquid Water Content (LWC) of snow. LWC is an important parameter for the determination of the stability of a snowpack and the prediction of the water runoff following the melting of snow. Finally, I carried out experiments at Elettra Sincrotrone Trieste in which I performed UV Raman Spectroscopy on liquid water and snow. I compared the spectra acquired with a 532 nm laser source with those acquired by using monochromatic sources in UV-C range (between 250 nm and 200 nm). The results showed that by using excitation sources with progressively

increasing energy in the explored wavelength range, it is possible to selectively excite the sub-bands associated with weakly hydrogen-bonded water molecules.

The second activity of the thesis is related to the study of the friction between snow and materials for ski bases. The ski base is the component of a ski that glides on snow. Currently, ski bases are made of Ultra High Molecular Weight Polyethylene (UHMWPE). This material has a low friction coefficient on snow (a desirable feature for ski bases) however it undergoes wear when skiing in the presence of debris or abrasive snow. This implies that a ski pair has a relatively short service life (on average four years in ski rentals). A possible solution to increase the service life of a ski is the use of a metallic base that is harder, therefore more wear resistant than UHMWPE. In this context, in the second part of my research activity, I studied how the friction between snow and AISI 301 changes after

the exposure of the metallic surface to an ultra-short laser pulse treatment (duration between 247 fs and 7 ps) which alters the surface morphology obtaining the so-called Laser Induced Periodic Surface Structures (LIPSS). In our case we obtained LIPSS consisting of micrometer-sized parallel ripples aligned perpendicularly to the polarization direction of the incident laser radiation. The presence of LIPSS reduces the interaction between AISI 301 and liquid water, as it is evidenced by contact angle measurements (Fig.2). By using a custom-made snow tribometer we measured the friction coefficient as a function of the sliding speed between snow and the different steel and UHMWPE samples. As shown in Figure 2, the friction coefficient of UHMWPE is the lowest. The friction coefficient of bare AISI 301 increases as a function of the sliding speed, whereas the presence of LIPSS reduces the friction between AISI 301 and snow.
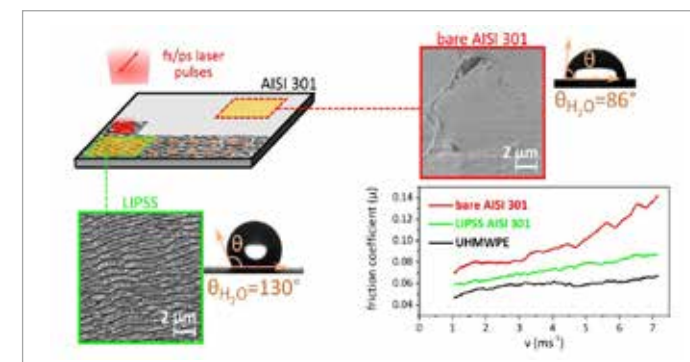

Fig. 2 - LIPSS formation upon the interaction with ultra-short laser pulses. The SEMs of AISI 301 before and after the laser treatment are shown. The respective static contact angle values are also reported. The graph shows the trend of the friction coefficients of bare AISI 301, LIPSS treated AISI 301 and UHMWPE as a function of the sliding speed on snow at -10°C.

EX SITU AND IN SITU CHARACTERIZATION OF AN INNOVATIVE AND SUSTAINABLE BIO-BASED BUILDING MATERIAL: HEMP-LIME

Chiara Moletti – Supervisor: Giovanni Dotelli

Bio-based building materials are innovative solutions developed to reduce the huge environmental impact of the building sector. The related emissions are due to the production of materials and the operation (e.g., heating and cooling) of buildings. In this framework, research focuses on materials characterized by sustainable production processes and good insulation properties, able to improve the energy efficiency of buildings. Bio-based materials are promising candidates to replace traditional ones; they contain agricultural biomasses that are used as raw materials for building purposes. Consequently, their production process adheres to the principles of circular economy since it enables the recovery and valorisation of material that otherwise would have been a waste. Once installed, these materials can provide excellent thermal and acoustic insulation thanks to the porosity and hygroscopicity of the vegetal aggregates.

The present research focused on hemp-lime, a bio-based material obtained by mixing hemp shives, a mineral binder and water. The vegetal aggregates derive from the by-product of the industrial hemp crop that is a woody stem; through a simple procedure called scutching, the stem is cut into particles with controlled granulometry called hemp shives or hurds. The mineral binder is typically lime-based and constitutes the matrix of the final composite material. The proportion among hemp shives and binder depends on the final application (e.g., plasters, prefabricated blocks, in situ casting). The research activity was carried out in collaboration with ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development). The focus of the project was the determination of the properties of hemp-lime produced by an Italian company; this included the evaluation of the performances of the material in Mediterranean climatic conditions.

During the project, hemp-lime walls were monitored in laboratory and in situ to study their hygrothermal performances. The experimental campaigns were performed a few months after the walls construction and 3 years later to assess the effect of the material maturation on its hygrothermal performances. In parallel to these tests, periodic characterization analyses were performed via X-Ray Diffraction (XRD) and thermogravimetry (TG-DTG) to investigate the evolution of the carbonation of the binder. This reaction is crucial for the development of the hygrothermal properties, mechanical strength, and durability of hemp-lime. For this reason, a chemical analysis was performed to study further the proceeding of carbonation in different material formulations. In addition, sorption isotherms and thermal conductivity of hemp-lime were measured in laboratory to implement the numerical simulations. These were performed with the software WUFI® which simulates the hygrothermal behavior of building envelopes in a dynamic regime. Furthermore, mechanical tests were carried out to determine the behavior at failure of hemp-lime and to estimate the modulus of Young of different formulations used to produce prefabricated blocks. Among the analysed samples, the one used to produce the walls mentioned before was also studied. Such experiments were carried out with a triaxial set-up to test the material in conditions as similar as possible to the service ones. Eventually, the analysis of the environmental performances of hemp-based building products was performed according to the Life Cycle Assessment (LCA) methodology. The latter considered the quantification of carbonation advancement derived from the experimental characterization of hemp-lime.

Hemp-lime blocks showed satisfactory hygrothermal performances in Mediterranean climatic conditions; this behavior developed over time with the proceeding of the binder carbonation, evidenced by the characterization of the material. In terms of mechanical properties, the experimental results confirmed the possibility of using hemp-lime with a non-loadbearing function solely due to its low modulus of Young. The LCA analysis proved the good environmental performances of hemp-lime that further improve when the binder-to-aggregate ratio is lower (e.g., formulations for infill or plasters).

SYNTHESIS AND CHARACTERIZATION OF TITANIUM BASED BINARY SURFACE ALLOYS MADE THROUGH PVD AND LEHCEB TECHNIQUES

Federico Morini - Supervisor: Massimiliano Bestetti

Tutor: Silvia Franz

The aim of this work is the synthesis of binary alloys based on commercially pure Ti, obtained through the magnetron sputtering deposition of Nb, W and Ta and then alloyed with the aid of Low Energy High Current Electron Beam (LEHCEB). A first study was done on the thermophysical events happening due to the effect of LEHCEB, analyzing different single metal to predict the formation of the surface alloys. COMSOL simulations were helpful to investigate and compute the effect of this treatment, considering different voltages and number of pulses.

These alloys are then chemically and mechanically characterized. In particular, the main features depend on the graded chemical composition and on their thickness, that is around tens of microns, making them surface films with enhanced mechanical properties. XRD analysis were useful to study the presence of metastable phases, formed for the high temperatures reached during the synthesis process and then due to the high melting and cooling rate. SEM and EDS analysis were employed to evaluate the chemical composition of the surface and of the cross section, together with

the morphology. GDOES analysis helped to evaluate the thickness of the surface alloys and their composition, investigating how deep is the deposited material after the LEHCEB treatment. Regarding the mechanical tests, microindentation tests was useful to know mechanical properties as Vickers microhardness and elastic modulus, while wear test gave the friction coefficient.

Low energy (10 – 40 keV) high current (10 – 25 kA) electron beam (LEHCEB) is a technique for surface treatment of materials, which is able to deliver large quantity of energy in short time within a thin layer. Furthermore, the relatively low energy density

and short pulse duration (2 – 4 μs) of the beam allow to release the beam energy within a thin surface layer (0.1 – 10 μm), causing the melting and the selective evaporation of the treated material. The heat transferred to the underlying layers of the material leads to fast heating and cooling rates (up to 109 K/s), giving structure and phase modifications that could not be possible in steady-state conditions. LEHCEB technique allows the modification of the chemical composition and mechanical properties of the outermost surface layer. This effect is possible because LEHCEB treatment change both lattice parameters and
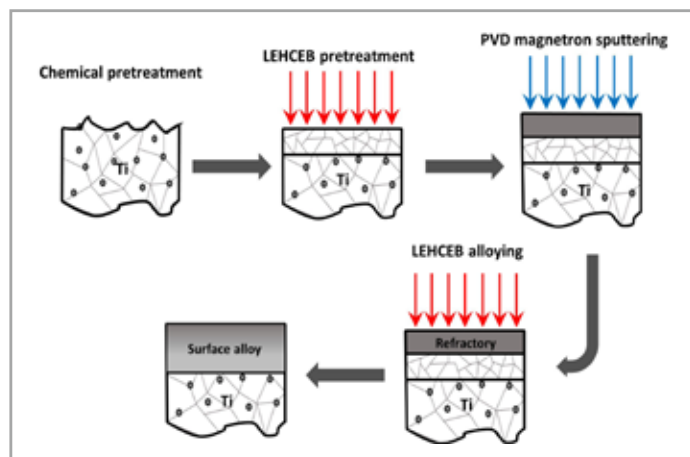
crystal structure with the formation of metastable phases. Another effect of LEHCEB is the chemical recombination of different components, due to the preferential evaporation of low melting ones, and the further surface supersaturation of higher melting ones. This technique could be coupled with magnetron sputtering physical vapor deposition (PVD). In this way thin film of different metal could be deposited onto different substrates and then alloyed together. Low Energy High Current Electron Beam will induce different modification to treated metals, mostly in terms of microstructure, hardness and corrosion resistance. The ultrafast solidification is also capable of the formation of nanostructured layer, with the reduction of crystallites size, and the formation of modified layer of different thickness, which depends on the working parameters (i.e. applied accelerating voltage, delivered energy and number of pulses). This treatment is a surface hardening method, as Ti is subjected to a reduction of grain size and microstructure modifications, with the formation of martensitic α' phase. The change in microstructure and the relative reduction in the grain size leads to a change in different properties of c.p. Ti after LEHCEB irradiation. Another way to deal with Ti and to improve its mechanical properties is to alloy it with other metals. LEHCEB is capable to melt different layer of metals and let the interdiffusion, with the formation

of a surface thin alloy with graded composition.

A 2-dimensional sample was considered through COMSOL Multiphisics to predict the behavior of the material, with partitioned mesh on the first few microns of the outermost surface layer. It was considered a rectangular shape, simulating temperature and stress field in the first micron below the surface. Melting threshold and melt thickness was evaluated as a function of the energy density provided by the accelerated electrons of LEHCEB, for both single and multiple pulses. it was necessary to compute the treatment at different energy densities to understand the behavior of different metals when treated with LEHCEB. Simulations were set considering the operation parameter of RITM-SP LECHEB, in particular with a pulse duration of 2.5 μs, an initial temperature of 293 K and a power density of the beam equal to 8×10^{10} W/m2.

One way to improve the surface properties of Ti is to alloy it with other metals as Nb, W and Ta. Ti-Nb was easy to synthetize, because Nb is characterized by a melting threshold close to the one of Ti. In this way it was possible to have the interdiffusion of Nb more in depth, with a thickness in the order of 6 to 10 μm. The average Nb content goes from 4 to 8 at%. From the point of view of phase composition, there is the presence of different metastable phases, in particular α' and α". Both of them are the main responsible of the increased

mechanical properties, as the Vickers microhardness showed an increase, passing from 225 HV of c.p. Ti to 375 or 750 HV, depending on the treatment; the friction coefficient slightly decreased and is similar to the one of Ti, going to 0.4/0.6. Ti-W is characterized by the presence of β phase, which could coexist with αTi in the case of incomplete melting and mixing. The amount of W presents in different alloys varies from 10 to 25 at%, in a defined thickness from 1.5 to 7 μm. W is present in a graded composition if the treatment is suitable for the synthesis of the alloy, while is inhomogeneous when the treatment is too light and there is not the mixing process. Furthermore, the presence of β phase and the formation of Ti-W alloy influence the mechanical properties: Vickers microhardness was in a range from 750 to 1300 HV and the friction coefficient from 0.2 to 0.5 (vs 0.8 of c.p. Ti). Ti-Ta surface alloys is characterized by metastable phases, passing from α' and α" with low content of Ta (i.e. low level of homogenization) to β when Ta is well mixed and alloyed with the substrate. The content of Ta varies from 5 to 15 at% and the thickness of the alloy from around 4 to 6 μm. Also in this case, the presence of Ta in different amount influences the mechanical properties, with a trend similar to the one of Ti-Nb. Ta is interesting because of its low friction coefficient. In particular, Ti-Ta surface alloy is characterized by a Vickers microhardness around 800 HV and a friction coefficient of 0.5.

Fig.1 - Schematic view of the synthesis of surface alloys through PVD+LEHCEB process.

REMEDIATION OF DEGREASING WASTEWATERS BY MEANS OF COMBINED ELECTROCHEMICAL AND BIOLOGICAL PROCESSES

Emanuele Oddo – Supervisor: Marco Derudi

Combined electrochemical and biological processes have been thoroughly studied for a sound variety of effluents – which does not include degreasing wastewaters, though. Anodic oxidation stands out as electrochemical process, as it is easy to operate, requires no dosing of chemicals (e.g., for pH adjustment) and produces no sludges. Due to the relevant power input of AO for complete mineralization, a coupling with bioremediation and a proper selection of the anode material are mandatory to achieve satisfactory removal efficiency while limiting the energy costs. Boron-doped diamond (BDD) electrodes are currently considered as the best performing anodes thanks to their unique properties (hardness, chemical and electrical stability, wide potential window, etc.), and they are reported to be particularly effective in the non-selective oxidation of organics. Hence, the aim of the thesis has been to firstly study anodic oxidation as a stand-alone process for the remediation of control and model solutions and then to implement the coupling with an activated sludge bioreactor (Fig.1) to assess the performances of the combined processes for the remediation of

synthetic and real effluents. Firstly, anodic oxidation was investigated with control solutions containing target pollutants, namely gallic acid and its derivatives and two non-ionic surfactants (cocamide DEA and GENAPOL X-80), using a commercially available BDD electrode. It was shown that the electrode can effectively destroy all contaminants in less than 60 min, even for low current densities (25-50 mA cm^{-2}) and that gallic acid degradation proceeds via an apparent 1st order kinetics (i.e., mass-transfer regime), with pyrogallol as the main intermediate. Next, AO was applied to model solutions containing several organic acids (gallic, tannic, butyric, and hexanoic) and a surfactant (either cocamide DEA or GENAPOL X-80) for an overall COD level of roughly 2750 mg L^{-1}: such mixture was a good approximation of a synthetic, lab-scale sample of an industrial degreasing effluent. The results showed that anodic oxidation can deliver a non-negligible COD reduction (up to 40% in 2h) and most importantly a fivefold increase in the biodegradability, thus exceeding the threshold for easily biodegradable effluents. This enabled the coupling of AO with an activated sludge

bioreactor, which was able to achieve an overall COD reduction above 95% in just eight days; an electrochemical finishing (AO for 120 min at 25 mA cm^{-2}) allowed to push efficiency up to 99%. Consequently, degradation tests were conducted on real degreasing effluents coming from the washing of industrial tanks, featuring a mix of alcohols, glycols, acids and surfactants with adjusted COD of 2000 mg L^{-1}. The electrochemical pre-treatment of the effluent allowed to lower COD content of about 30% and to raise dramatically the biodegradability (moving BOD$_5$/COD from 0.07 to more than 0.5). The effectiveness of the electro-treatment was validated for different batches of industrial degreasing wastewaters,

always providing more than 30% COD abatement as well as a biodegradability index greater than 0.4 at the end of the electro-treatment (Fig.2). Under the optimal set of operating parameters (37.5 mA cm^{-2} for 120 min, 20 g L^{-1} Na$_2$SO$_4$), AO coupled with bioremediation was able to deliver more than 80% COD reduction. To further push the removal efficiency of the system, a finishing stage featuring a mild anodic oxidation was employed under similar conditions as for the pre-treatment (37.5 mA cm^{-2} for 240 min). It was found that the electrochemical post-treatment was able to raise both COD and surfactants abatement as much as to 95% reduction (Fig.3). These results confirmed

the feasibility of the coupling between electrochemical and biological processes, with limited power consumption of about 8-10 kWh kg$_{COD}$$^{-1}$. Hence, a scale-up of the process to the pilot scale (reactors with liters of solution) would be desirable to further investigate the industrial applicability of the process.
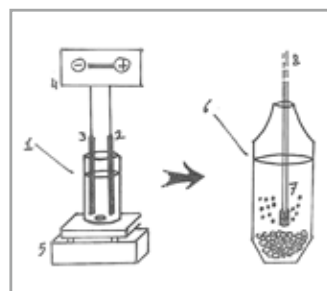

Fig.1 - Layout of the combined electrochemical and biological processes: 1) electrochemical cell for anodic oxidation; 2) BDD anode; 3) stainless-steel cathode; 4) DC power supply; 5) stirring plate; 6) activated sludge bioreactor; 7) air diffuser; 8) air supply.
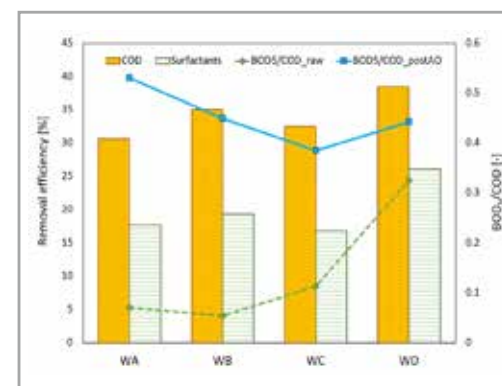

Fig.2 - Organics and surfactants removal and biodegradability increase of different degreasing wastewaters after anodic treatment; electrochemical processing was conducted at 37.5 mA cm^{-2} for 120 min using 20 g L^{-1} Na$_2$SO$_4$ as supporting electrolyte.
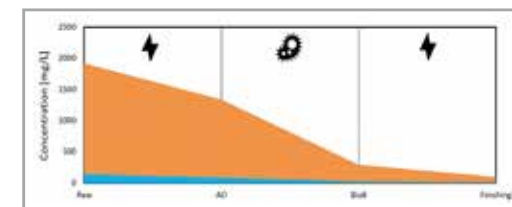

Fig.3 - COD (orange) and surfactants (blue) evolution of degreasing wastewaters along the electro-oxidation (AO), bioremediation (Bio8) and finishing (Finishing) stages; anodic oxidation was conducted at 37.5 mA cm^{-2} for either 120 min (AO) or 240 min (Finishing), and the effluent was treated in the bioreactor for 8 days.

DEVELOPMENT OF NOVEL SMART SENSING MATERIALS

Filippo Pinelli - Supervisor: Filippo Rossi

Functional polymers and responsive colloids are essential for several applications of the materials science. The possibility to modify their structure, through the introduction of specific functional groups not present in their initial structure, is an effective strategy to obtain the desired behaviour for smart devices. In this context, the work of my PhD thesis is focused on the design of polymeric gels to be employed in multiple fields for various applications. An illustration of this kind of polymeric gel systems in an aqueous environment is reported in Figure 1.

Our discussion started with polymeric nanogels, hydrogels systems characterized by nano dimensions, for drug delivery applications, investigating the influence of various functionalization strategies on their features such as dimensions, surface charges and selective drug loading and release ability.
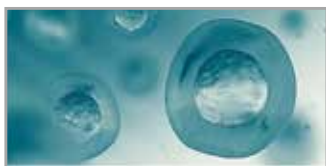
These systems were successfully employed in selective drug delivery for the cells of the central nervous system.
Alongside, working with similar gelation procedure, we focused on the synthesis of graphene – based aerogels, obtained from precursor hydrogels, and we studied their multiple and versatile characteristics. We designed graphene – conductive polymers aerogels for volatile organic compounds (VOCs) sensing, testing various polymers, and observing the best results working with graphene oxide (GO) – polyaniline composite gels and we assessed their performance improvement through the encapsulation of graphene nanoplatelets in their framework. Similarly, always working with this kind of systems, we designed graphene oxide (GO) – chitosan aerogels and we applied them in

the selective removal of anionic dyes from water, studying their mechanical characteristic, the dynamic of the adsorption process and the possibility of the regeneration of the materials. Successful results both in term of adsorption properties and in term of regeneration confirmed the potentialities of these structures. The materials studied in this thesis are summarized in the following Table 1.

The general aim of this work is to demonstrate how a multidisciplinary approach involving physical chemistry and engineering allows to identify common strategies of polymer functionalization and colloidal synthesis that can be employed in multiple fields to develop selective and sensitive materials.

Fig.1 - Schematic representation of gels structures in aqueous environment.

MATERIAL	SYNTHETIC STRATEGY	APPLICATION
Polymeric nanogels	Polymers crosslinking	Selective drug delivery
GO – polyaniline aerogels	Oxidative polymerization	VOCs sensing
GO – chitosan aerogels	Electrostatic interactions	Anionic dyes adsorption

Tab. 1 - Summary of the materials, applications and synthetic strategies used in the thesis.