





Chair:  
**Prof. Chiara Castiglioni**

## DOCTORAL PROGRAM IN MATERIALS ENGINEERING

The courses of the Doctoral Program provide Ph.D students in Materials Engineering with a common, basic knowledge on Materials Science and Technology, followed by a specialized training in specific fields. The objective is to combine the theoretical knowledge with the skills required by technology in order to form qualified researchers who can manage the design, manufacturing and use of traditional and/or new materials.

### Contents of the Doctoral Program

The Doctoral Course covers the following areas:

- Polymers and composites*
- Cements and ceramics*
- Metals*
- Biomaterials and materials for biomedical applications*
- Processing and characterization of advanced metallic alloys*
- Corrosion and durability of materials*
- Innovative materials for civil and industrial engineering*
- Materials Characterization (Microscopies, Scattering, Spectroscopy)*
- Modelling and theoretical approaches to the study of materials structure and properties*
- Micro and nanostructured materials*
- Functional materials for applications in photonic, electronic and sensors*
- Surface engineering and advanced coatings*
- Materials for industrial design*
- Meta-materials*
- Transformation of materials*
- Material for Cultural Heritage*

The courses face immediately advanced issues both in the main and elective courses. Different curricula are offered, which will be activated on the basis of the decisions of the faculty. The Doctoral program is characterised by high flexibility, in order to satisfy the needs of students that have to develop their research activity in different thematic areas. For this reason each student submit to the Faculty a "Curriculum" to be approved. The Courses offered deal with theoretical, experimental and modelling aspects. Several Courses comprise workshops and seminars, with the participation of invited internationally celebrated speakers.

Students can use the most modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories.

The research activities related to the Ph.D. theses develop, full time, along the three years of the Ph.D. courses. Stages in industries or in national laboratories in Italy or abroad are offered. Each Ph.D. student are supervised by a professor of the faculty: the faculty evaluates the progress of his research activity and at the end of each year expresses a judgement on the continuation of the work for the subsequent year. At the end of the third year the Ph.D. student presents and defends, in a public hearing, his thesis work with a jury formed by three experts.

The Ph.D. student is strongly encouraged to attend at national and international meetings and present papers in his specific field. The Ph.D. student is also assigned to give seminars on topical issues and/or to lecture on the specific fields of his research or on the cultural aspects related to his thesis.

The PhD Program in Materials Engineering requires the acquisition of 25 credits through attendance at Doctoral Courses (with positive evaluation in the examinations); in addition, attendance at National and International Schools are strongly encouraged.

- the remaining credits will be assigned on the basis of the research activity necessary to the development of the Thesis project.

### Faculty:

The faculty is constituted by Professors from two Departments of Politecnico di Milano:

DIPARTIMENTO DI CHIMICA, MATERIALI E INGEGNERIA CHIMICA "GIULIO NATTA"		
Chiara Castiglioni (coordinator)	Francesco Briatico Vangosa (vice-coordinator)	Chiara Bertarelli
Fabio Bolzoni	Massimiliano Bestetti	Fabio Ganazzoli
Luigi De Nardo	Giovanni Dotelli	MariaPia Pedeferra
Marinella Levi	Valdo Meille	Stefano Turri
Guido Raos	Lucia Toniolo	Claudia Marano
Pasquale Vena	Elena Redaelli	
DIPARTIMENTO DI ENERGIA		
Marco Beghi	Andrea Li Bassi	Paolo Ossi

### Professional skills achieved by PhD in Material Engineering:

The industrial world depends necessarily on a great variety of materials. Nowadays, it is easy to outline two industrial needs: i) development and innovation in the production, processing, application and conservation of traditional materials; ii) development of innovative materials for the production of new manufactured goods or devices to cope with the growing demands of modern technologies. Since these two kinds of industrial needs require specialized people a few specialized curricula

are offered. On the other hand, the capabilities acquired through the courses, the research work and the teaching activity assure an adequate preparation to the academic career.

#### REFEREES (COMITATO DI RIFERIMENTO)

Edoardo Bemporad, Dip. di Ingegneria Meccanica e Industriale, Università Roma Tre	Marco Bernasconi, Dip. di Scienza dei Materiali, Università Milano Bicocca
Marco Ferrera, ST Microelectronics	Stefano Gialanella, Dip. di Ingegneria Industriale, Università di Trento
Alessandro Martucci, Dip. Ingegneria Meccanica, Università di Padova	Laura Montanaro, Dip. Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino
Stefano Radice, Solvay Specialty Polymers SpA	Riccardo Po', eni SpA
Fiorella Pozzobon, ST Microelectronics	Mario Sobacchi, eni SpA.
Francesco Stellacci, Dept. of Materials Science and Engineering, EPFL, Lausanne	

#### GRANTING AGENCIES

ST Microelectronics s.r.l.	RSE Ricerca Sistema Energetico
Fondazione Istituto Italiano di Tecnologia IIT	Istituto Nazionale di Astrofisica
SOLVAY SOLEXIS SpA	INSTM
eni SpA	Electrolux SpA
Faber SpA	InnovHub

# MATERIALS DURABILITY IN HARSH ENVIRONMENTS FOR PROFESSIONAL APPLIANCES

**Margherita Basso - Supervisor: Prof. Luigi De Nardo**

The wide range of materials nowadays available posed new challenges, directed at improving their performances or synthesize new materials for specific applications. The increased performances and the high complexity of new materials, led to the need of evaluating their behavior in tailor-made environments, determined from the final product needs and use. For this, materials durability is nowadays increasingly studied to optimize their use and guarantee the needed performances over time.

This work has the aim of developing the investigation of materials durability in the professional appliances industry. The materials applied in such applications face every day harsh environments, with presence of thermal and mechanical stresses, but also the interaction with aggressive chemicals. In particular, washing and cleaning environments see the presence of strong acid and alkaline chemicals, which are commonly available in the market and used to maintain the hygienic status of professional appliances. Aiming at implementing the knowledge of such working environments and improve materials durability tests related to this issue, a structured methodology is proposed.

In order to satisfy customers and business needs, many appliances in professional kitchens are provided of automatic washing and cleaning systems. These systems are accurately designed to maintain the high productive work flow in the working environment, ensuring high hygiene standards, and food safety. For this reason, materials are subjected to more complex and harsher working conditions, characterized by a combination of thermal, chemical and mechanical stresses. The study of washing and cleaning environments is reported as a fundamental base of this work, allowing the development of testing protocols and set ups able to manage the big differences among chemical environments. Therefore, the motivations for the development of such testing protocols are exposed and related to the crucial role of failure analysis and materials selection in the company. The materials-centered validation process is then schematized and explained, in order to highlight the advantages of such approach and how it can be integrated into the different phases of a project, from idea generation to product series testing. From previous considerations, MatILDE (MATerials Intensive Life-tests for Durability Enhancement) testing

protocols have been developed and exposed as tunable, flexible and widely applicable set of testing methodologies able to simulate and reproduce the working environments present in professional food processing and dishwashers appliances. The application of the developed testing protocol on one industrial case study, and its correlation with the sensorial perception of aged materials, has been used to highlight their real applications and the beneficial results that this kind of approach is able to bring. The further improvement and next step in the development of materials durability evaluation is given by the integration of materials testing into the life-testing process, with furthermore implementation of the reliability concept. Materials exposed to harsh environments are subjected not only to possible degradation mechanisms, but also to change in materials properties which are not direct consequences of their usage. These characteristics of materials have to be taken into account in every phase of product development and testing. Ensuring and assessing materials durability is not an easy task, especially for industrial applications where products are high complex and induce materials to face highly stressed

working conditions. For this, the connection between the different testing protocols and phases is reported using one case study about the mechanical properties change of glass fibers reinforced polyamides in contact with foods at relatively high temperatures. Results showed that reliability curves are a representative and comprehensive tools to assess mechanical properties changes and materials durability. To furthermore develop the topic and integrate its application in industrial contexts, the testing pyramid proposed in the Building Block Approach (BBA) is used to optimize life-tests procedures and integrate materials durability testing protocols.

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such working environments and improve materials durability tests related to this issue, a structured methodology is proposed. The study of washing and cleaning environments is reported as a fundamental base of this work, allowing the development of testing protocols and set ups able to manage the big differences among chemical environments. The application of BBA is discussed in detail, together with a case study with the aim of finding the correlation between full appliances life-testing and the scaled one on single components exploiting the acceleration factors. In the last chapter, time-dependent properties and failure mechanisms are discussed, considering their connection with materials durability. The role of materials properties modeling is then discussed, with the aim of integrate it in the reliability and life-testing process already in the early stage of the projects. The study of creep and its modeling is then developed as example of generation of analytical models which can be applied in the further pre-study computational engineering phases. This study provides a complete and original insight into the integration of materials durability and the development of related testing approaches useful to

move a further step towards its integration in life-tests and reliability testing processes. Moreover, this thesis opens new scenarios in industrial contexts with the aim of implementing flexible and repeatable approaches able to integrate also materials selection and failure analysis in the validation process of projects at different TRL levels.

# STRUCTURE/PROPERTIES RELATIONSHIPS IN NOVEL CARBON BASED MATERIALS: AN INVESTIGATION AT THE MOLECULAR SCALE

Luigi Brambilla - Supervisor: Prof. Chiara Castiglioni

In this work, the IR and Raman vibrational spectroscopy was applied to study three different materials based on carbon atoms in  $sp^2$  hybridization, namely i) graphite, ii) few layer nanostructured graphite and iii) organic polyconjugated polymers (polythiophenes). The aim of this work was to find new correlations between the vibrational properties of these materials and their chemical/electronic properties. We focused on the electrochemical production of graphene, on the functionalization of nanosized graphites aimed at improving the compatibility with polymers of biological interest, and on the structural/morphological characterization of oligo and poly-thiophenes, with controlled chemical structure. Theoretical prediction of the IR and Raman spectra by means of Density Functional Theory on molecular models has been used for the interpretation of the experimental data. Anions intercalation into graphene layers, structural disordering of the graphite surface and charge transfer phenomena between anions and graphene layers have been studied in function of the EC parameters and electrolytic solutions adopted. IR and Raman spectroscopy

was used to characterize i) the formation of graphene adducts with functionalized molecules prepared using ecofriendly procedure, ii) the interaction of these materials with polymers of biological interest for the production of carbon paper and carbon aero-gels. IR and Raman spectra of newly synthesized P3HT molecular models namely i) selectively deuterated polymers, and ii) polymers with controlled degree of regioregularity, have been used to identify domains of material where chains possess two slightly different molecular conformation, identified as

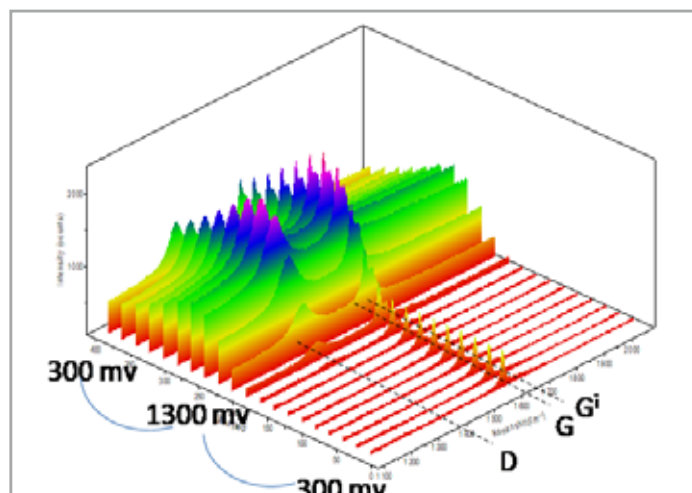


Fig.1 - Raman spectra (excitation at 632.8nm) of HOPG working electrode during cycle-voltammetry (potential sweep rate 10 mV/s) in  $H_2SO_4$  1M solution. Spectra are recorded in subsequent time intervals, during the potential sweep. Marker bands of pristine, disordered and intercalated graphite, namely G, D, and  $G'$ , and are labelled.

hairy-A and hairy-B, and the amorphous phase. A new simple method to quantify the relative content of these domains in solid material based on off resonance Raman measurements is proposed.

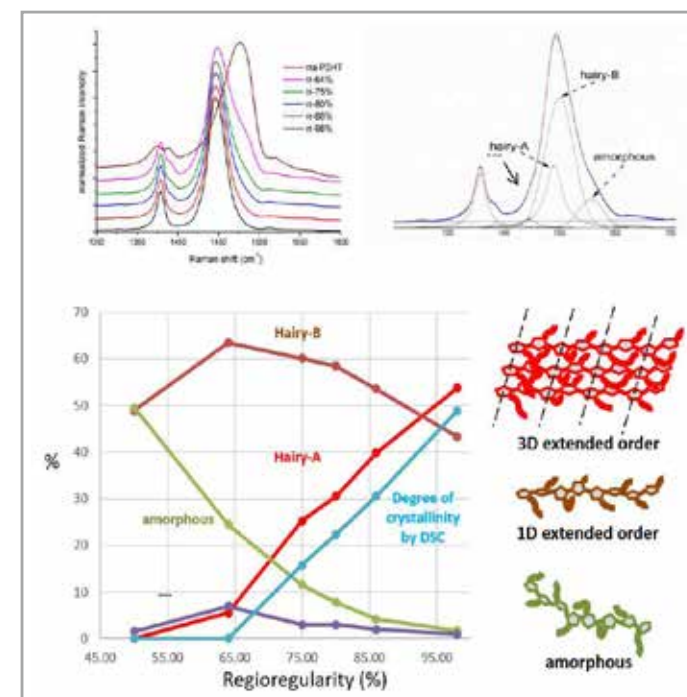


Fig.2 - FT-Raman spectra of P3HT samples with different degree of regioregularity. Spectral deconvolution for rr-75% sample. Relative amount of hairy-A, hairy-B and amorphous chains conformation as function of regioregularity obtained from deconvoluted integrated areas.



# BIOPOLYMER FIBROUS NETWORKS FOR TISSUE ENGINEERING APPLICATIONS

Chiara Emma Campiglio - Advisor: Dr. Lorenza Draghi

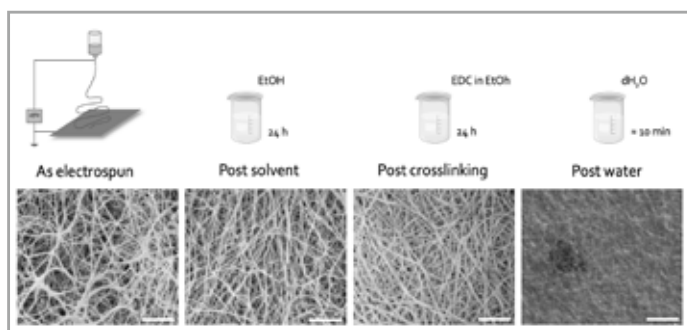
Tutor: Prof. Luigi De Nardo

The development of 3D fibrous networks from natural occurring polymers have always attracted considerable attention as platform for tissue engineering applications. Opportunely arranged micro/nano-scaled fibers, in fact, are an attractive architecture per se, for offering an intrinsically porous structure and a high surface to volume ratio. The combination of three-dimensional networks with natural polymers allows the production of matrices that can not only mimic the architecture of the native extra-cellular matrix (ECM), but also present specific chemical cues. Several studies have demonstrated that a fibrous structure can actively regulate cellular activities, offering anchor points for cell spreading, which in turn directs cell proliferation and differentiation, and allowing a homogeneous diffusion of nutrients and oxygen as well as removal of metabolic waste during tissue regeneration.

In this scenario, the research activity presented in this thesis is focused on the development of biopolymer fibrous networks using different approaches: the first one consisted in using protein fiber networks as scaffolding material for cell seeding; in the second approach alginate-based microfibers were used for cell

encapsulation. Accordingly, two different fabrication methods, electrospinning and wet-spinning respectively, were used to prepare fibrous hydrogel structures. More specifically, the first section is focused on the electrospinning technique involving natural polymers. This simple method allows to obtain interconnected nanofibrous scaffold with great potential as support for tissue engineering. Among natural polymers, gelatin is considered excellent biopolymer for this aim, due to its biocompatibility and biomimicry properties. Despite all its advantages, gelatin is a soluble polymer in physiological-like environment and cross-linking is generally required to achieve the necessary stability

and adjust scaffold degradation rate. When electrospun substrates are involved, cross-linking procedure should not only increase stability but also preserve nanofiber morphology and interconnected porous structure. Several protocols are proposed in scientific literature, but they resulted unsuitable under our conditions in preserving the advantageous fibrous topography of electrospun substrates. Thus, an innovative crosslinking protocol was developed using carbodiimide chemistry. The introduction of a different solvent (acetonitrile) together with the application of a controlled mechanical tensioning during the crosslinking process allowed to define a new EDC/NHS crosslinking protocol. Moreover,



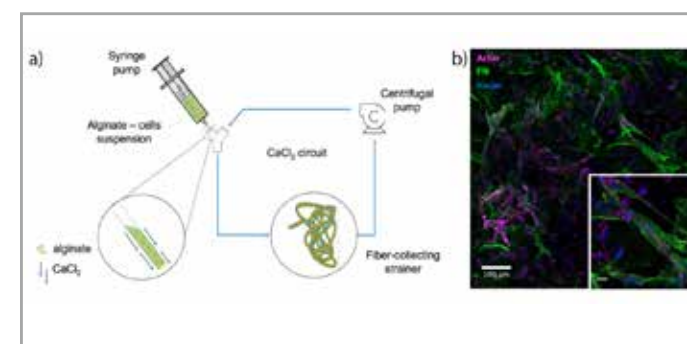
**Fig. 1 - SEM micrographs of gelatin nanofibers crosslinked with the optimized protocol (50 mM EDC, 20 mM NHS, 8 h, acetonitrile, radial-longitudinal tension and controlled evaporation with silice salts). From left to right, SEM images after electrospinning, immersion in acetonitrile, crosslinking process and immersion in distilled water. Scale bars represent 10 µm.**

a controlled evaporation of the crosslinking solution resulted an efficient strategy in maintaining the nanofibrous morphology. The crosslinking protocol was validated by means of morphological characterization, degradation test, mechanical and biological test on crosslinked fibrous mats (Figure 1). In the second part, wet-spinning technique was described to produce micro-fibrous 3D networks from ionically crosslinked hydrogel. In this section, to pursue a cell embedding strategy, the development of a purpose-designed simple circuit for cell encapsulation in hydrogel microfibrillar scaffolds is presented and its effectiveness for cell delivery using fast degradable,

alginate-based materials is validated. Due to its rapid gelation mechanism under mild conditions, alginate resulted an optimal candidate material to test the developed flow circuit. To fabricate the scaffold, cells suspended in hydrogel-precursor are injected in a closed-loop circuit, where a centrifugal pump circulates the cross-linking solution. The flow stretches and solidifies a continuous micro-scaled, cell-loaded fiber that whips, bends and is collected in a strainer as a self-standing fibrous scaffold. The versatility of this system represents a practical alternative to more refined (but significantly more complex) methods available for encapsulation in hydrogel

fibers. As different material formulations can be processed to create homogeneously cell-populated structures, this system appears as a valuable, widespread available platform, not only for cell delivery, but also, more in general, for 3D cell culturing *in vitro*. Both these applications were investigated using alginate, blend-modified alginate and chemical-modified alginate solutions in order to increase the ability of the scaffold to resemble ECM features. After an initial validation with cell line, an investigation on ECM-derived proteins production inside microfibers was carried out using mesenchymal stem cells, in order to demonstrate the suitability of the system proposed for the development of tissue engineering constructs (Figure 2).

Both the approaches pursued in this thesis through the development of biopolymer-based fibrous networks resulted efficient in producing cell-free and cell-laden scaffold with advantageous features for tissue engineering applications.



**Fig. 2 - (a) Schematic representation of microfibrillar fabrication system. (b) After 14 days of culture, the production of ECM components was evaluated by different stainings. MSCs embedded in modified-alginate microfibers produced fibronectin as a 3D network (FN in green, actin in pink and nuclei in blue). Scale bar of insert images represents 20 µm.**

# LONG TERM FRACTURE BEHAVIOUR OF HDPE FOR HOUSEHOLD DETERGENT CONTAINERS: A STUDY ON ENVIRONMENTAL STRESS CRACKING

Marco Contino - Supervisor: Dr. Luca Andena

Tutors: Prof. Claudia Marano; Prof. Marta Rink

High-density polyethylene (HDPE) is widely used for the production of containers for cleaning products which, interacting chemically and physically with the polymer, can alter its mechanical properties and can lead to premature failure. In some cases, household detergents are complex chemical solutions whose ingredients can have different effects on the polymer mechanical behaviour. Commercial bleaches as considered in this work, in fact, contain substances like sodium hypochlorite which can cause chemical oxidation of polyethylene; surfactants can in turn be absorbed by the material in proximity of material defects, thus favouring a physical phenomenon called Environmental Stress Cracking (ESC). Since these two mechanisms have a different nature and require a different amount of time to occur, it is not straightforward to predict which of the two could be active under given conditions. For these reasons, in this study, the two phenomena were analysed separately on two blow moulding HDPE grades. The occurrence of polymer oxidation was investigated exposing HDPE samples to several solutions containing various combinations of bleach

ingredients. The evolution of several properties was monitored at regular time intervals up to a maximum of six months, corresponding to the service life of the container: at the end of this characterization only a negligible increase of the sample mass, related to the absorption of the solution, was measured, while no effect on tensile and scratch properties was detected. It was hence concluded that negligible chemical degradation phenomena occurred during the considered time range. Environmental Stress Cracking, instead, was studied using methods based on Fracture Mechanics. At first, 10 mm thick Single Edge Notch Bending samples were machined from compression moulded plates to study the fracture behaviour in air and when exposing the material to the aggressive environments, to evaluate the influence of the various bleach ingredients on the two HDPE grades. The sample thickness, significantly larger than that of typical household detergent containers, was selected to perform tests under plane strain conditions: plastic deformations ahead of the crack tip were thus constrained and the Linear Elastic Fracture Mechanics approach was found to be adequate for the

description of both crack initiation and propagation. Tests were conducted at 60°C to hasten the fracture process and the obtained results were expressed relating relevant fracture parameters (i.e. the stress intensity factor and the energy release rate) to the crack initiation time and to the crack propagation rate. It was observed that in presence of environments containing surfactants, after a critical interaction time and below a critical propagation speed, the crack initiated earlier and propagated faster with respect to what observed in air; it was also found that the other bleach ingredients have a negligible effect on material fracture resistance. To obtain a tool for the long term prediction of the ESC resistance of the two materials, tests were repeated at temperatures between 23°C and 60°C and the applicability of a time-temperature superposition reduction scheme was verified. The obtained curves turned out to be self-similar also in the presence of the active environment, demonstrating that temperature acts only indirectly on ESC via the material intrinsic viscoelastic behaviour. The initiation and propagation master curves shown in Figure 1 and Figure 2 were thus built and the available experimental window

was considerably extended also in the presence of the active environment.

Knowing the effect of the various bleach ingredients on the fracture resistance of HDPE, the behaviour of compression moulded samples having a thickness comparable to that of the container was analysed at 60°C. Due to the reduced thickness, Double Edge Notched Tension specimens, used for these fracture tests, experienced a different stress state with predominant plane stress conditions. Since extensive plastic deformations occurred ahead of the crack tip during the test, the -integral approach was used to characterize the initiation behaviour. As already observed with thick samples in the presence of solutions containing surfactants, after a critical interaction time, ESC occurred.

Finally, to study the effect of the production process on fracture and ESC resistance of HDPE, tests were conducted also on Double Edge Notch Tension samples obtained directly from blow moulded containers. As shown in Figure 3, compression moulded samples (CM), having a higher degree of crystallinity, show a higher fracture resistance in air if compared to blow moulded specimens (BM). For what concerns the behaviour in presence of the active environment, instead, it can be observed that data obtained from compression moulded and blow moulded specimens fall on the same curve. This result can be explained considering that, as reported in the relevant scientific literature, the active environment mainly acts by favouring the disentanglement of the amorphous polymeric chains connecting the different crystalline domains. Since in this case the starting material is the same, the length of the polymeric chains should be identical irrespective of the production process employed during sample manufacturing and, therefore, it is reasonable to expect that the same amount of energy would be required to disentangle them and promote Environmental Stress Cracking. These findings constitute an important result since they could lead to a time and cost saving laboratory testing procedure during the material ranking and selection phase, as there is no need to manufacture containers of a given material to obtain information on their expected lifetime.

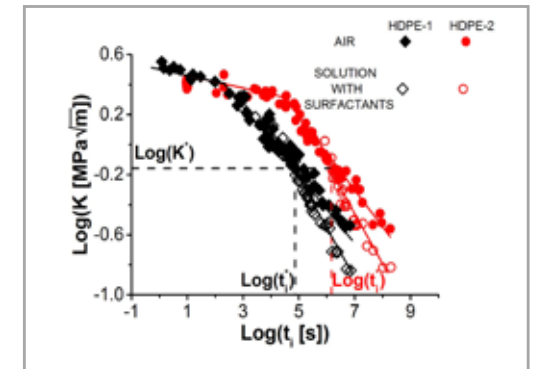


Fig. 1 - Initiation master curves of the two materials under plane strain conditions. Reference temperature: 23°C.

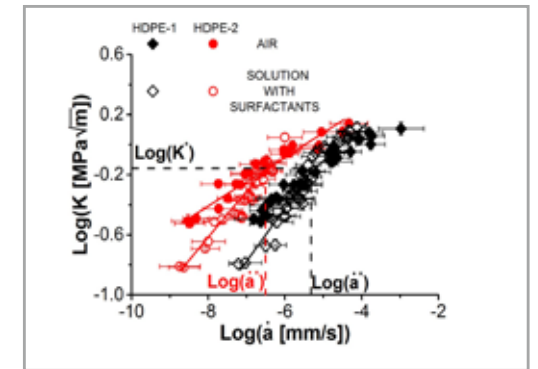


Fig. 2 - Propagation master curves of the two materials under plane strain conditions. Reference temperature: 23°C.

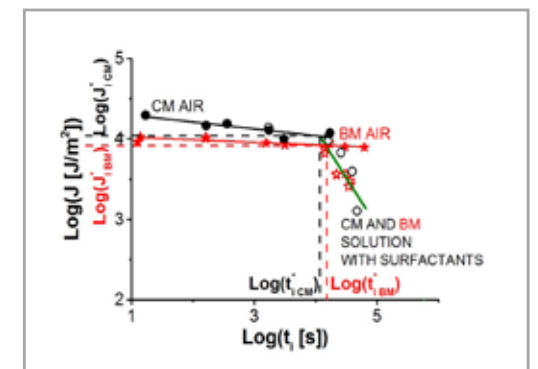


Fig. 3 - Initiation curves of Compression Moulded (CM) and Blow Moulded (BM) samples under plane stress conditions at 60°C. Green line is the concatenate fitting of BM and CM data obtained in presence of solutions containing surfactants.

# DEVELOPMENT AND LIFE CYCLE ASSESSMENT OF POLYMERIC MATERIALS FROM RENEWABLE SOURCES

M. Nelly García González

Supervisor: Prof. Stefano Turri, Prof.ssa Marinella Levi

The general aim of the present thesis was focused on the study of different polymer systems obtained from renewable sources and its manufacturing through various technologies related to the coating industry. This concept was based on the principles of green engineering, green chemistry and sustainability (especially LCA studies) for materials such as lignin, polyurethanes and polyesters.

One of the emerging topics in modern polyurethane (PU) technology is the exploitation of monomers and macromers from renewable resources to improve the environmental sustainability while preserving their excellent technical performances. Based on this concept, the main objective of the first part of the present thesis was related to a new class of polyester binder based on FDCA suitable as precursor of PU coating materials. The new 100% bio-based structure was re-designed and obtained through the selection and copolymerization of four different monomers, all available from modern biorefinery downstreams such as glycerine (Gly), 1,3-propanediol (1,3-PD), 2,5-furandicarboxylic acid (FDCA) and succinic acid (SA). The selection of all monomers was according to their functional

role and available data from literature for the environmental study. Moreover, this new structure was benchmarked against a partially bio-based (75% renewable carbon) and two fossil-based polyester binders. Successively, the corresponding four PU coatings were obtained by crosslinking of a conventional polyisocyanate and the polyesters synthesized on lab-scale. Their technological performances were evaluated, especially for the new precursor of PU coating. The results obtained in the technological evaluation showed a stiffer PU1 coating (based on FDCA) and a more hydrophilic character leading not only to a better adhesion but also to a more moisture-sensitive surface compared to the other coatings. With these characteristics, a possible application is in the field of coil coating and automotive as intermediate layers or primers where a high adhesion of the material and recoatability are required.

The evaluation of the total impact of greenhouse gas emissions (GHG) and the total non-renewable energy use (NREU) of all polyesters by the Life Cycle Assessment (LCA) were included on the basis of a cradle-to-gate approach separating the contributions

due to the monomer mixture composition and those related to the copolymerization process, and considering an FDCA production process starting from sugar beet (primary data). Specifically, a finer analysis of the impact of marine eutrophication and freshwater eutrophication was developed, providing relevant information about the environmental implication of the production of a chemical derived by biomass (sugar beet). The latter part was developed at Lund University during my PhD internship. The results obtained in this environmental impact assessment showed that the introduction of bio-monomers may significantly reduce the total GHG emissions and the total NREU.

The second objective of the research was related to the improvement of filler/matrix compatibility by introducing nanometer/sized particles of lignin, expecting to obtain a more efficient interaction with the polymer matrix (polyurethane and epoxidized natural rubber, ENR). The preparation of nanolignin (NL) particles was carried out by ultrasonication treatment and after 6h of treatment, 10 nm – 50 nm dimensions were obtained. An excellent water-dispersion stability of the ultrasonically

treated NL-based system for over 15 months was observed and an increase of polarity on NL compared to pristine lignin was obtained. Successively, the obtained NL particles were initially incorporated at varying concentrations into an epoxidized rubber matrix (10 and 40%) and the vulcanization process parameters and mechanical properties of the resulting (nano) compound materials were evaluated. The results testified that the reduction of the micro-particles to nano-particles in the lignin was not enough to reduce the big polarity existing between the filler and the rubber matrix. In particular, the use of nanosized lignin particles allowed to improve the stiffness of the rubber matrix material without affecting its elongation at break, especially for ENR/NL-10. Nevertheless, a decrease of toughness was observed at increasing filler loading. The vulcanization process indicated that the retardant vulcanization effect with the introduction of pristine lignin (IND) was weaker than the effect found with the incorporation of NL. Finally, the obtained NL particles were also incorporated at varying concentrations into a thermoplastic PU matrix (5, 10 and 20%) and the morphological, thermal and mechanical

properties of the resulting (nano)composite materials were assessed. The results attested that there was an excellent level of dispersion and distribution of NL particles into the PU matrix and an ability of NL to establish effective non-covalent interactions with the polymer matrix. In the case of tensile tests on the (nano)composites at increasing filler loading, there was a remarkable development in the mechanical properties of the systems incorporating NL particles compared to pristine lignin in terms of elastic modulus, ultimate tensile strength and elongation at break, especially for 20% of filler.



# ELECTROPHORETIC DEPOSITION FOR BOTTOM-UP DESIGN OF CELLULAR SOLIDS IN BIOMEDICAL APPLICATIONS

Arash Ghalayani Esfahani - Supervisor: Prof. Luigi De Nardo

Tutor: Prof. Alberto Cigada

Electrophoretic Deposition (EPD) has been proposed as a fabrication technology for self-standing structures based on biopolymers. Thin or thick films, deposited in an ordered fashion under suitable conditions, can be easily peeled-off the substrate replicating the working electrode morphology. By coupling EPD with replica-approach, structures with controlled three-dimensional morphology can be obtained. EPD is a convenient, cost effective, and efficient bottom-up technology, recently proposed as a novel method for the fabrication of scaffolds and coatings. In this thesis, we present the first successful effort to fabricate cellular solids via a combination of EPD, replica technique. The prospective of such approach by using chitosan as a model polymer, further functionalized for specific applications, has been demonstrated. In this thesis EPD has been exploited to generate different combinations of bio polymer/ bioactive agent on metallic substrates with the aim of enhancing bioactive characters, drug delivery abilities and minimizing infection. To begin with, hierarchic micro-patterned porous scaffolds via electrochemical replica-deposition,

fabricated to fulfill bio-applications. In the following, to support the bioactive character of the coating for bone tissue regeneration, EPD bioactive composite was obtained. Furthermore, passive and active drug delivery systems for oral application and orthopaedic antibacterial implants designed, respectively.

### **Biopolymer micro-structuring**

Hierarchic micro-patterned porous scaffolds which are produced by electrochemical replica-deposition, designed to enhance neo-vascularization. Furthermore, biopolymer micro-structured patches for dermal regeneration was evaluated.

This study supports the general idea that patterns of micro-channels enhance intra-scaffold neo-vascularization and promote tissue regeneration. At *in vitro* tests, endothelial cells firmly adhered to the highly cytocompatible substrates during migration, with a cell density that was modulated by the scaffold micropattern. It was particularly favored by precisely-designed micro-channels. When such micro-patterned scaffolds were implanted *in vivo*, neo-vascularization resulted enhanced, in comparison to random-pore scaffolds. In continue, a novel approach to design

patterned-chitosan (CS) scaffolds by electrophoretic deposition (EPD) which can effectively induce the regeneration of dermis in an animal model of skin loss was developed. To evaluate the effect of patterned scaffolds on dermal regeneration, single layer chitosan porous scaffolds of flat (no pattern), circular pattern with  $\Phi = 500 \mu\text{m}$  and 1 mm were fabricated and used to treat full-thickness wounds in a one-stage grafting procedure in a rat model. Taken together, this animal test may represent an alternative pre-clinical screening tool to evaluate novel *in vivo* therapeutic strategies. Furthermore, the CS scaffolds evaluated in this study was clinically effective, suggesting the potential for this strategy as a therapeutic intervention to reconstruct the skin.

### **Bioactive composites**

Bioactive ceramics, e.g. 45S5 bioactive glass (BG) was applied in this study. It is promising bone substitute material which was investigated to support the bioactive character of the coating for bone tissue regeneration, an enhanced bone-to-implant interaction as well. The polymer component considered in this PhD thesis, e.g. chitosan, will not only strengthen the bonding of bioceramics coating to the surface

of the implant, but also offer the possibility to control the *in-situ* release of dissolution products and can accelerate the attachment of biomolecules and cells by the presence of functional groups. A multilayer coating, considered to impart the osteoconductivity and other intended biomedical properties, was successfully fabricated via a combination of EPD and thin sheet lamination additive manufacturing. The aim of this project, which focused on exploiting the EPD technique to fabricate biomedical coatings with specific functions, oriented porous structures and self-standing membranes for emerging biomedical applications, was achieved and a series of new coating systems, well characterized and exhibiting combination of favorable properties, are thus available for further applications and dedicated *in vivo* evaluations.

### **Drug Delivery Systems**

A series of coatings with different combination of inorganic agents and biopolymer matrix were successfully fabricated by EPD from aqueous based and ethanol-based suspensions at room temperature. The co-deposition systems produced and characterized in this thesis were CS/Clobetasol Propionate (CP) and CS/ Gallium (Ga). The co-deposition mechanisms were experimentally investigated, and the coating properties were comprehensively assessed by means of relevant material characterizations and cell biology and microbiology tests. The coating properties, including degradation, adhesion and drug (or inhibitor agent) release profiles, which are key

factors for an effective and sustained antibacterial effect, were optimized and validated. In this thesis, a novel class of biopolymer-based patches in which anti-inflammatory steroidal agent (CP) is loaded via electrophoretic deposition has been developed. Ethanol-based deposition bath was used to allow one pot deposition process of the hydrophobic CP drug, together by modulating the amount of CP in order to design a platform of drug delivery systems. Despite notable success of metallic orthopaedic prosthesis in clinical, their long-term survivability remains a major challenge due to the lack of osteoconductivity and risks associated with post-surgery infections and surface corrosion. Modification of implant surfaces with bioactive materials and antimicrobial agents is being intensively investigated to prevent these negative effects. Last but not certainly least, in this thesis, EPD as a convenient coating technique has been developed to generate different combinations

of biopolymer-inorganic coatings (CS/Ga) on metallic substrates with the aim of enhancing bioactive characters and minimizing infections. Keywords: Electrophoretic deposition (EPD); chitosan (CS); physical hydrogel; skin regeneration; scaffolds; neo-vascularization; electrochemical deposition; tissue engineering; Bioactive glass 45S5; cortical bone reconstruction; hybrid scaffold; Hierarchical scaffolds; Clobetasol propionate; topical oral drug delivery; gallium (Ga); *Staphylococcus epidermidis*; *Staphylococcus aureus*; post-arthroplasty infection; PEMF; biofilm.

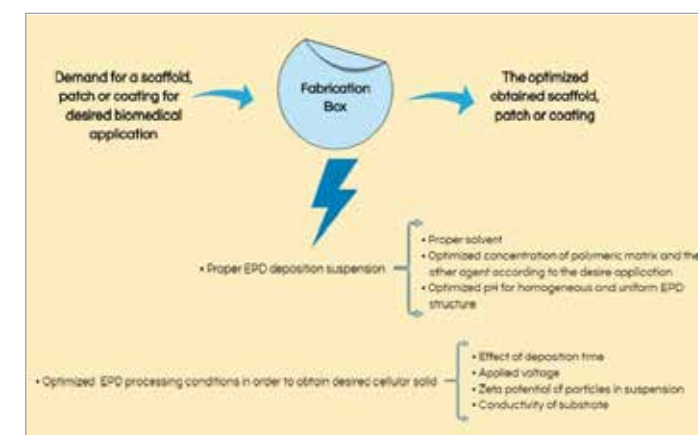


Fig. 1 - Schematic illustration of the fabrication approach designed for the present PhD

# ADVANCED POLYMERS AND POLYMER COMPOSITES FOR ADDITIVE MANUFACTURING

**Marta Invernizzi - Supervisor: Marinella Levi**

Additive manufacturing (AM), generally known as 3D printing, is one of the technologies foreseen to replace conventional product processes, as part of the predicted fourth industrial revolution "Industry 4.0". AM fabrication allows the manufacturing of parts in a faster and cheaper way than conventional manufacturing processes, thus gained a lot of attention and its use is still established in several processes such as aerospace, automotive, biomedical and electronics. In addition, AM enabled high degrees of flexibility also in product design, as a result of using smart computer-aided-design (CAD) systems. In particular, AM technologies based on polymers as feedstock are the most widespread thanks to their low glass transition temperature (thus lower processing temperature), cheapness and high permeability to air.

The main drawbacks in using plastics instead of metals regards the poor mechanical properties, the chemical degradation and oxidation over time, distortion and delamination phenomena. The research described in this PhD thesis aim to address specific solutions to some of these drawbacks, by tailoring both the material properties (i.e. designing new polymers

and polymer composites) and process parameters. Moreover, a new material never 3D printed before was developed, to confirm the feasibility of AM in replacing the traditional manufacturing processes by simply adapting both the material features and the AM technique. This established the flexibility of AM, able to change with and for the materials. The followed pathway involved the synergistic development of the materials with the used technologies, passing from a low resolution and low cost 3D printer capable to print large objects to the design of micrometric parts printed with one of the most advanced 3D printing technology. Only UV-assisted AM technologies were considered, due to the high potential given by photoinitiated polymerization, often coupled with sequential thermal curing to obtain enhanced performances. This type of polymerization presents some advantages such as the use of low toxicity monomers, the possibility to fine tune the molecular architecture of such monomers and the processability at room temperature. The first part of the thesis dealt with the development of thermosetting composites based on glass and carbon short fibres. These were 3D printed by means of a low-cost

technique, the liquid deposition modeling (LDM), belonging to the class of material extrusion technology. The polymeric matrix comprised a photocurable acrylate monomer and an epoxy resin. First, the acrylate part was polymerized during the 3D printing process by means of UV light, then a subsequent thermal curing was necessary to activate and complete the epoxy resin polymerization. The formation of an interpenetrated polymer network (IPN) was demonstrated, leading to enhanced properties respect to the single components. In fact, to demonstrate the possibility to use these composites in the aerospace and automotive fields propellers and air foils were printed (fig.1). Preliminary studies on a physical sizing for short carbon fibres were also performed, introducing the



**Fig. 1 - 3D printed propeller with the formulation at 5% of short glass fibres**

possibility to improve the physical adhesion and therefore the stress transfer from the fibre to the matrix. To further enhance the mechanical effect provided by the fibres, a continuous glass reinforcement was also taken into account. In this case, a dual curable cationic formulation was considered evaluating also different type of functionalized silica filler (i.e. hydrophobic and hydrophilic). In particular, a covalent interaction between the epoxy resin and the hydrophilic silica promoted by the cationic mechanism was proved. In fact, an enhancement of the mechanical properties was observed thanks to an optimized stress transfer. Then, the focus moved on the design of a material with new features printable with digital light projection (DLP) technique, included in the class of vat photopolymerization technology. The material was a thermally activated shape memory polymer, capable to fix a temporary shape by means of a thermomechanical programming cycle. The "memory" functionality resided in the ability to restore the original shape by entropic elasticity. Thanks to its elasticity and capability to perform this effect, PCL could be used as raw material for soft robotics, in particular as actuator. To make it more attractive for this field, a self-healing feature was introduced to enhance the durability of the material. The shape memory matrix selected was a polycaprolactone (PCL), properly chosen in function of its molecular weight and chemically modified to make it light reactive; the self-healing property was

given by ureidopyrimidinone (UPy) monomer, capable to form four hydrogen bonds with itself, favoured by temperature. As common solvent chloroform was selected.

The DLP printer was modified because of the solid state of PCL at room temperature, by adding a heating plate and modifying the reservoir to optimize the requested formulation volume. This new material was thus 3D printed for the first time. UPy monomer did not altered the properties of PCL, and printed samples maintained the chemical and mechanical properties of cast samples. The shape memory effect was maintained also after the healing of bulk scratches, enabling this new material as raw material for a new generation of soft robotic actuators. The last part of the research was dedicated to the stereolithographic (SL) technique. A dual curable cationic resin was developed and successfully printed at 405 nm by means of a photosensitizer. The formulation was based on two epoxy monomers and a tetrafunctional acrylate resin, to reduce the fragile behaviour at break typical of pure epoxy resins. The use of a particular photoinitiator (i.e. an onium salt) allowed to ignite both a free radical and a cationic polymerization without the need of a dedicated radical initiator. In this case, the formation of a phase separated IPN was demonstrated both with an experimental and a theoretical evaluation. In fact, an immiscibility between two components was predicted by means of the Hoftzyer and Van

Krevelen method, confirmed by the presence of two  $T_g$ s by DSC analysis, detecting the presence of two distinct domains. The dark curing process was improved coupling it with a thermal treatment, and the addition of stabilizers slowed the photoinitiator deactivation process. Mechanical and tensile properties were found to be enhanced respect to commercial high-performance resins. To further improve these properties, nanosilica was added and the resulting nanocomposite showed a marked toughening effect. To demonstrate the feasibility in using this high-performance resin for the micro robotic field, micro screws, nuts, gears were 3D printed with high fidelity and resolution with respect to the digital model. Moreover, scaffolds and capacitors were printed with the nanocomposite with a shrinkage level one order of magnitude lower than commercial resins.

# PHOTOCHROMIC MATERIALS FOR SMART OPTICAL APPLICATIONS

Luca Oggioni - Tutor: Chiara Bertarelli

## Supervisor: Andrea Bianco

Photochromic materials have been attracted the interest of the scientific community in the last decades, thanks to their ability to reversibly change their properties with a light stimulus. Such systems are based on photochromic moieties that have the ability to switch between two isomers with different structures and colours. Consequently, they show a modulation of many other properties such as polarizability, dipole moment, luminescence, vibrational structure, etc. The research activity behind my thesis aimed at carry on the progress of smart materials based on photochromic systems and test their capabilities as real devices. In particular, we focused the attention to the development of rewritable optical components, mainly for astronomical applications. Indeed most of the research work was carried on at the Astronomical Observatory of Brera. Here, the approach considered the light-induced chromatic variation of photochromic layers as a transparency modulation, which can be exploited in devices that act as light filters in a target spectral region. Interestingly, the photoreaction also shows difference in mobility of the two isomers and such difference can be used in promoting the

formation of Surface Relief Gratings (SRGs) and 2D structures. Among the different photochromic materials, we selected two classes: diarylethenes and spirooxazines. Thin films of photochromic material, onto glass substrates, were produced by spin coating, following three different strategies: polymer blends, polyurethanes and pure molecular amorphous films. The optical and physical properties of the films have been optimized in order to meet the requirements of our technological applications. An important parameter that characterizes the photochromic materials is the fatigue resistance. We performed a study on a set of diarylethene molecules finding a linear dependence of the fraction of degraded molecules with the specific absorbed UV dose by the closed-ring isomer is observed. From this consideration, the ratio at the UV wavelength used to convert the molecules, is proposed as an important indicator of the degree of degradation. A higher ratio turns into lower fatigue resistance. A computational tool to predict the absorption properties of photochromic films have been developed. Knowing the film thickness, the concentration of the photochromic dye and the illumination conditions, the model provides the

conversion profile through the film thickness. By means of this tool, it is possible to design a material with reversible transparency in a specific wavelength range and with a defined contrast, according to the device requirements. Three application were selected for the test of our photochromic materials: Focal Plane Masks (FPMs) for multiobject spectroscopy (MOS), Computer Generated Holograms (SGHs) and Amplitude modulation optical lithography (AMOL). The first step in the FPM production was the development of a simple “end to end” model of an astronomical spectrograph, able of simulating the CCD image collected by the instrumentation parameters (telescope and spectrograph), the astronomical objects to be observed and the mask contrast. Thanks to this tool, we were able to select the minimum contrast necessary to collect spectra with suitable S/N ratio. The contrast requirement was then translated into a requirement on the film absorbance. The films were produced with the blend strategy dispersing a mix of two different photochromic dyes in the CAB matrix. Two FPMs were written and tested at the 1.8 m Copernicus telescope

(Asiago, Italy), collecting the spectra during two nights of observation. One of the mask was erased and printed again with another pattern to demonstrate the device rewritability. CGHs are optical components able to reproduce a desired optical wavefront. This project was carried on in collaboration with LAM (Laboratoire D'astrophysique De Marseille, France) in the framework of the OPTICON European Project (FP-7). One set of polyurethanes and two set of blend polymers have been produced. Two writing strategies have been tested: a mask projection via a DMD (Digital Micromirror Device) assembled in Marseille by our colleagues of LAM, and a direct laser writing machine, designed and built in our laboratory at the Astronomical Observatory of Brera. The DMD projection, allows transferring at once the entire CGH pattern, enabling also the realization of gray scale amplitude holograms, with the same technology. However, the technique is limited by the size of the DMD chip (27 mm x 13 mm) and its resolution (pixel size of 13.64  $\mu\text{m}$ ). Concerning the direct laser writing technique, the mechanical and optical designs were done in our group, as well as the control software. It enables to write binary hologram up to 50x50  $\text{mm}^2$  with a pixel resolution of 3-4  $\mu\text{m}$ . The writing system is fed by a 4-Channel Fiber Coupled Laser Source equipped with four laser at different wavelengths (406 nm, 520 nm, 638 nm and 685 nm). Some photochromic Fourier and Fresnel CGHs have been recorded

with the DMD machine, both binary and grayscale. The point by point laser writing machine, was tested writing a 1D grating, two Fresnel lenses and two binary CGHs for image reconstruction. A set of photochromic polyurethanes based on a specific diarylethene molecule, have been exploited as tunable filters for Amplitude Modulation Optical Lithography (AMOL). In this technique a photoresist material is covered with a photochromic film, then it is exposed to both visible (modulated) and UV (constant) light. The photochromic film acts as a tunable filter and depending on the relative intensity of the UV radiations and the visible modulation, the photoresist is consequently exposed. Finally, it follows a development of the resist, obtaining 1D or 2D surface morphology patterns. In this framework we developed: i) a kinetic model of the photochromic layer in order to simulate the Vis/UV combined illumination and to predict the transmitted UV profile; ii) a diffractive model based on the Fresnel diffraction theory to predict the propagation of UV light through the photoresist layers. The results showed that the size and the quality of the written pattern is strongly dependent to the ratio between the visible and UV intensities and to the photoresist thickness. Several tests were performed producing 1D and 2D patterns with period of 1.5  $\mu\text{m}$ , confirming our theoretical observations. Light induced mass transfer used to obtain SRG, is

another strategy that can be used to obtain directly 1D and 2D patterns. In this way, we can obtain a change in surface morphology without any chemical development, taking out one critical step from the process with respect to the AMOL case. In our research, we explored the possibility to apply the same AMOL illumination strategy to SRGs, controlling the final geometry by modifying the illumination conditions. Spirooxazines have been chosen as candidates for these tests, since they show absorption properties similar to diarylethenes, one isomer absorbs in the UV, the other is characterized by a strong absorption in the visible. The switch between the two forms is prompt by UV/visible light and by thermal relaxation. We produced and characterized some amorphous films of spirooxazines and we were successful in SRGs production using the AMOL illumination strategy, using a modulated visible light and a uniform UV, obtaining 1D and 2D surface patterns. In my research, I tried to push further the possibility to develop real technological applications based on photochromic materials. The effort was to build a bridge between the chemists, who provide the basic units for the material production, and the engineers, who exploit these materials for specific applications. I hope my work could be useful for both these communities and such fruitful collaborations will increase in the future.

# DEVELOPMENT OF SURFACE TREATMENT FOR INCREASING CORROSION RESISTANCE OF COMMERCIAL PURE TITANIUM

**Davide Prando** - Supervisor: Prof. Marco Ormellese

The thesis work started with a comprehensive literature review about corrosion mechanisms on titanium in different aggressive environments and about the possible treatments to increase its resistance. Among them, three were chosen for their application easiness, cost effectiveness and improvability: anodizing, chemical oxidation and thermal treatment. A preliminary but exhaustive research was conducted to identify the proper testing environment to assess titanium corrosion resistance. As localized corrosion is more dangerous compared to uniform one, a species able to cause oxide breakdown at relatively low anodic potential on titanium was found and its concentration tuned taking into account reagent consumption during the next tests. Thus, bromides 0.5 M solution was chosen to represent the ideal aggressive environment for titanium, and it was used for all the corrosion resistance assessing tests.

Starting from anodic oxidation, treatments were applied to commercially pure titanium grade 2 to enhance its corrosion resistance. Anodizing treatments were performed from 10 V to 200 V with DC current using both galvanostatic and constant

voltage ramp anodizing regimes. A full sample characterization was performed after each treatment, resulting in the identification of two main treatments: low voltage or standard anodizing, and anodic spark deposition anodizing. In fact, contrarily to what expected, corrosion resistance does not increase with increasing anodizing voltage, but shows an abrupt increase when passing from standard to ASD anodizing. The small advantage of samples anodized at 80 V respect to the ones anodized at 20 V in terms of oxide breakdown potential and oxide breakdown current does not justify the higher energy consumption of the first treatment. Thus, anodic oxidation at 20 V is suggested as corrosion enhancing treatment for non-critical samples or samples too big to be effectively treated at higher voltages. On the other hand, if superior corrosion resistance is required, it is suggested to go above 150 V, keeping treatment duration around two minutes to obtain the best result. To further optimize these anodizing treatments, a study on anodizing efficiency was conducted in collaboration with the National Center for Metallurgical Research CENIM (Centro Nacional de

Investigaciones Metalúrgicas) in Madrid, where it was possible to monitor in real-time the amount of oxygen developed at the anode during anodic polarization. Thus, the charge responsible to water oxidation was subtracted to the total charge supplied during galvanostatic oxidation to calculate the real amount of charge required for film growth. The results of this study indicate that, in the range from 1 mA/cm<sup>2</sup> to 20 mA/cm<sup>2</sup>, lower anodizing current densities lead to higher efficiency. After anodic oxidation, chemical one was taken into account. NaOH and H<sub>2</sub>O<sub>2</sub> were chosen as representative of alkali and peroxides oxidizing species. The effects of solution concentration, solution quantity, treatment duration and treatment temperature were studied. Treatments in NaOH 10 M for 24 h at 25°C and H<sub>2</sub>O<sub>2</sub> 10 M for 6 h at 25°C were selected as the best compromise between treatment cost, easiness, effectiveness. These procedures stimulate the growth of a film that shows corrosion resistance comparable with the one obtained using low voltage anodic oxidation. As chemical oxidation proved to be a valid substitute to anodic oxidation, able to solve some problems affecting the latter, it

was tested as possible treatment to perform in-situ recovery of damaged anodized treatments. In fact, although anodic oxide is particularly corrosion resistant, it is very thin and a mild abrasion during transport or installation might result in oxide removal, with consequent decreasing in corrosion resistance. While a further re-anodization requires a power supply, anodizing bath and controlled conditions, chemical oxidation only requires the exposure to the oxidizing reagent. Results indicate that both NaOH and H<sub>2</sub>O<sub>2</sub> are suitable for recovery treatment, however, being the latter less stable and easy to store, a treatment based on NaOH 10 M performed for 72 h at room temperature was suggested in case of low voltage anodic coating recovery. Moreover, thermal treatment was studied in combination with chemical oxidation to find an alternative treatment to anodic oxidation at high voltage, which produces higher corrosion resistance. In this case sodium hydroxide treated samples show no improvement after annealing at any temperature, while samples treated in hydrogen peroxide increase their oxide breakdown potential in bromides 0.5 M from about 4 V vs SSC to 6.5 V vs SSC. A mechanism based on cracks sealing was proposed to explain this behavior. Chemical oxidation shows to be more sensitive to titanium morphology, with the reproduction of grain boundaries on the top of some chemically treated samples. For this reason, a better comprehension of sample

morphology was considered necessary to reproduce tests result and to allow further studies about the influence of grain size on chemical oxidation treatment effectiveness. Sample morphology, in terms of average grain size, was acquired through classic titanium metallography, using mechanical polishing up to mirror surface followed by etching in Kroll's solution. However, to allow this analysis in laboratories where the usage of hydrofluoric acid is not permitted, and to increase researcher safety, a new metallography procedure HF-free was developed. This research was conducted in collaboration with Monash University in Melbourne (Australia) and extended from titanium grade 2, to the more common titanium alloy Ti-6Al-4V, known as grade 5. Results indicate that it is possible to substitute Kroll's solution exposure of 1 minutes with 24 hours exposure in a mix of sulfuric acid 2 M and hydrochloric acid 2 M, without any significant difference in mean grain size. However, this new procedure does not produce the same kind of contrast between grains. In fact, while the Kroll's solution highlight grain boundaries, the new solution changes the apparent brightness of each grains, depending on its orientation. This cause the need of a slightly different image analysis procedure to obtain the final results. After the development of a suitable and industrially applicable anodizing treatment, an alternative based on chemical oxidation able to treat small parts or complex geometries, and a procedure

to recover accidentally abraded titanium treated pieces, a further optimization was pursued using discontinuous anodic oxidation. Starting from previous knowledge on other light metals, monopolar pulsed anodization was applied to titanium using different duty cycles (25% and 75%) at different frequencies (20 Hz and 1000 Hz) up to 120 V, 160 V and 220 V. The obtained samples were compared to their analogous obtained with DC anodizing in terms of energy consumption, oxide crystallinity, porosity and corrosion resistance. Results indicate that it is possible to fine tune these properties by acting on pulsed anodizing parameters. For example, the same results of corrosion resistance can be obtained with more than 70% of energy saving passing from DC anodizing to duty cycle 25% at 20 Hz in case of anodic oxidation carried out up to 120 V. It is also possible to reduce porosity by 60% using the same technique, or decrease oxide crystallinity for applications in which amorphous oxide is desired. It is even possible to pass from oxides obtained at 220 V containing almost only rutile crystalline phase to oxides with the same corrosion resistance and porosity but composed principally by anatase crystalline phase. In conclusion, several treatments were found to fulfill titanium corrosion resistance enhancement requirements in different conditions, based on the desired resistance, the extension of the piece to treat, the power available and the possibility to treat the piece without industrial plants.



# ORGANIC THERMOELECTRICS: DEVELOPMENT OF NEW DOPANTS FOR N-TYPE NAPHTHALENE DICARBOXIMIDE COPOLYMERS

Beatrice Saglio - Supervisor: Prof. Chiara Bertarelli

In the last years conducting polymers have found application into various electronic devices, including transistors, solar cells, OLEDs and, more recently thermoelectric generators. The thermoelectric effect is the direct conversion of thermal energy, triggered by thermal gradients, into electric energy and viceversa. The efficiency of a TE material is determined by a dimensionless figure of merit  $ZT = (\sigma S^2 T) / \kappa$  where T is the temperature,  $\sigma$  is the electrical conductivity, S is the Seebeck coefficient or thermopower and  $\kappa$  is the thermal conductivity of the material.

For thermoelectric devices, high values of conductivities are required. The generation of localized defective sites in the pristine polymer chains (i.e. polarons and bipolarons) by doping are accounted for the increase in the number of charge carriers, hence of conductivity. A huge variety of conducting p-type polymers and related dopants have been deeply investigated, and impressive conductivity values have been recently achieved. However, both p-type and n-type semiconductors are required to implement thermoelectric devices. The uneven development of n-type polymers and dopants is still a key issue.

Recently, new n-type polymers showing good electron mobility and stability to the environment have been developed. The first high performance n-type polymer was the poly([N,N'-bis(2-octyldodecyl)-11-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'(2,2'-bithiophene)) P(NDI2OD-T2).

Using this class of polymers, we show that a tailored modification of the dopant chemical structure is highly effective in avoiding phase segregation and increasing doping ratio of n-type polymers. Specifically, we present a new series of N-alkyl 1H-benzimidazoles in order to study the doping of the P(NDI2OD-T2) (Fig. 1). Moreover, we do not limit the discussion to 1H benzimidazoles, but a new class of n-type dopants belonging to the class of tetrazafulvalenes

are developed. Their thermal behavior and crystalline structure were analyzed by means of DSC and structural modeling with Avogadro, which revealed that the isopropyl-benzimidazole derivative show a greater tendency with respect to the other dopants to be solubilized and not to segregate. The different alkyl chains demonstrated a strong effect on the doping of P(NDI2OD-T2) (Fig. 2), where longer alkyl chains result in higher electrical conductivity; effect that is highly enhanced with hindered isopropyl-substituents, which give the highest electrical conductivity so far reported for this polymer. AFM tomographies, differential scanning calorimetry and x-ray structural analysis, leads to the conclusion that increasing the length of the alkyl substituents the miscibility between dopants and polymer increase, increasing the electrical conductivity. So, the

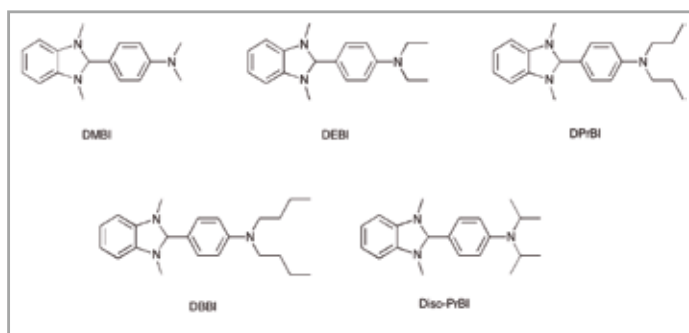


Fig.1

alkyl chain in 1H-benzimidazole could have a relevant role in the intercalation of small molecules as dopants in these conjugated polymers rather than affect the electron transfer from dopant to polymer. As a side project, the same n-type polymer is investigated in the pristine state while it is confined in nanofibers. This study has a twofold aim: first nanostructures allow for a miniaturization of the electronic devices (OFETs); moreover, the confinement of the polymer chains in anisotropic 1-D nanostructures opens to fundamental study concerning electron transport in organic semiconductors. Here, we show that electrospun P(NDI2OD-T2) nanofibers exhibit electron mobility strongly dependent on the solvent used for the process and, even more important, values higher than those obtained in thin films can be achieved. The role on the charge transport ability of

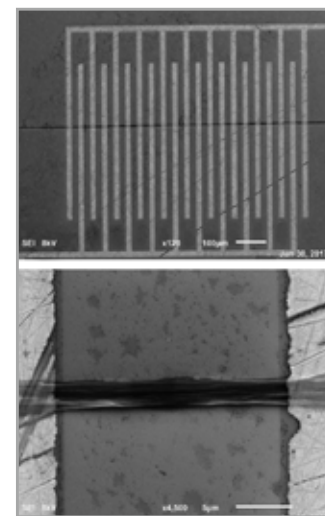


Fig.2

polymer preaggregates in specific solvents, to form domains with long range order at the solid state, is investigated. Specifically, we highlight that chain orientation, which is driven by the high electric field applied in electrospinning, does not favor charge transport in the P(NDI2OD-T2). Fibers were characterized by infrared spectroscopy with light polarized in two perpendicular direction to i) investigate dichroism aimed at study differences in chain orientation, induced from different processing conditions, and ii) relate the results to electron mobility. Finally, GIWAXS analyses are performed to define the role of crystalline structure on the resulting electrical characteristics. Finally, P(NDI2OD-T2) is electrospun with a p-type polymer (i.e. P3HT) to realize for the first time ambipolar nanofibers, which are highly desired in electronics for the development of logic circuits and inverters. A solution made by a blend of

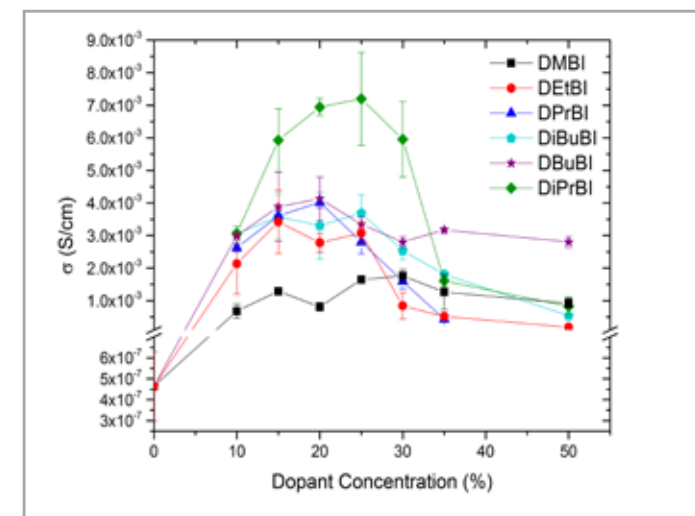


Fig.3

two complementary conjugated polymers, P(NDI2OD-T2) and poly(3-hexylthiophene-2,5-diyl) (P3HT) was electrospun obtaining defect free semiconducting fibers. (Fig. 3)

The electrical characterization of the fibers revealed that a balanced ambipolar behavior can be demonstrated. This result underlines that two different channels of conduction, for both electrons and holes, were present. Moreover, an in-deep analysis of the balanced ambipolar fibers shown that each fiber was composed by a large number of nanometric fibers. X-ray diffraction analysis confirmed that blend fibers contain the crystalline phases of both p and n-type polymers, demonstrating that segregation of the two components occurred, permitting the formation of the two distinct conduction channels.



# SYNTHESIS AND MODIFICATION OF TiO<sub>2</sub> NANOSTRUCTURES FOR THE DEGRADATION OF POLLUTANTS BY HETEROGENEOUS PHOTOCATALYSIS

Beatriz Eugenia Sanabria Arenas - Supervisor: Prof. Maria Pia Pedferri

Tutor: Prof. Fabio Bolzoni

Environmental pollution is one of the biggest challenges to overcome after the industrial revolution, in which the release of several hazardous substances (e.g. chemical compounds) in water bodies and in the atmosphere is constantly taking place. During the last years, the nocive effects of these pollutants have become more evident, affecting not only humankind but also different ecosystems and the weather. New technologies are therefore crucial to avoid clean water shortages and to mitigate the negative effects associated with air pollution. Advanced oxidation processes (AOPs) are a set of chemical reactions that use radicals to destroy a wide variety of compounds by oxidation reactions. Among AOPs, heterogeneous photocatalysis is a promising technology because it can be used at ambient conditions without adding additional reagents, allowing the complete mineralization of several organic and inorganic compounds. Particularly, TiO<sub>2</sub> has demonstrated to have excellent photocatalytic properties, good stability to photocorrosion, and it is a low-cost material. Some industries have already demonstrated the economic viability of this material as

photocatalyst, but for large-scale environmental applications, there are still two main limitations to overcome: the low efficiency of the reaction and the need of using ultraviolet (UV) light to trigger the process, which makes it power consuming and expensive. During my Ph.D. studies, different approaches were tested in order to increase the photocatalytic efficiency of anodically grown TiO<sub>2</sub> nanotubes for the degradation of pollutants by heterogeneous photocatalysis. First, different synthesis parameters and the morphology/crystalline structure of the photocatalyst were correlated, and their impact in the material photoactivity was evaluated in liquid phase and gas phase. Rhodamine B (textile dye) was used as model pollutant for the liquid phase, while toluene (volatile organic compound -VOC) was used as a model pollutant in the gas phase. The electrolyte composition (i.e. organic s/n (O-NT), acidic aqueous s/n (ASD) and buffered aqueous s/n (A-NT)) has strong impact not only in the morphology of the nanostructures but also on the crystal phase composition as observed in Fig.1. The organic electrolyte showed the best photocatalytic activity in both, liquid and gas phase. Second, the functionalization

of TiO<sub>2</sub> nanotubes with noble metals nanoparticles (i.e. Au and/or Pt) was done in order to reduce the rate of charge recombination and increase the efficiency of the photocatalytic degradation reactions. Two different methodologies were tested (i) sputtering/dewetting of a thin film of noble metal on the NTs top section (*extrinsic decoration*), and (ii) anodic oxidation of the titanium alloy containing the noble metal (*intrinsic decoration*). The intrinsic decoration showed homogeneous distribution of the noble metals nanoparticles along the nanotube walls, while the extrinsic decoration presented a limitation in the penetration depth of the nanoparticles of some hundreds of nanometers and the formation of Pt oxides were only

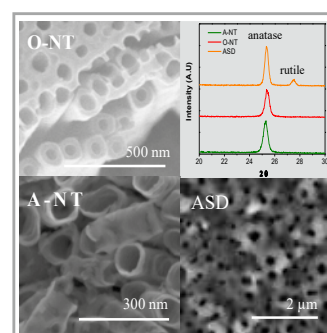


Fig.1 - SEM images top view of O-NT, A-NT and ASD nanostructures; and XRD analysis.

Pt was present, which resulted in deactivation of the material. The formation of alloyed nanoparticles during the anodic oxidation of the alloy containing both noble metals (i.e. AuPtTi), conferred synergism in its properties as co-catalysts and resulted in an increase on the photocatalytic activity of the material up to 34 % with respect to the pristine TiO<sub>2</sub> nanotubes, in order to destroy acid orange 7 (textile dye) in liquid phase.

Finally, doping and codoping strategies with nitrogen and transition metals (i.e. Ta or Nb) were tested in order to increase the light absorption properties of the nanotubes under the visible light (i.e.  $\lambda > 400$  nm). For the doping with the transition metals (TMs), the anodic oxidation was done using as substrate the alloy that contain both the Ti and the TMs, while the introduction of the N was done in a thermal treatment under NH<sub>3</sub> atmosphere after the anodization. An algicide/herbicide called *diuron* was used as model pollutant for this set of experiments. An increase in the photocatalytic activity under visible light was observed when TiO<sub>2</sub> was doped with Nb, while a detrimental effect was observed in the codoped samples (i.e. N,Nb-TiO<sub>2</sub> and N,Ta-TiO<sub>2</sub>). After

XPS analysis, it was possible to determine the presence of diuron in the codoped samples suggesting a poisonous effect from the pollutant with the consequent deactivation of the photocatalyst. Further studies are necessary to investigate the influence of the different interfacial interactions that can exist between the photocatalyst and the pollutant. Moreover, the determination of OH groups and hydro-phobic/philic properties of the semiconductor can provide useful information related to the substrate specificity of the reaction.

# DEVELOPMENT OF A COMBINED CHARACTERIZATION METHOD FOR NANOSTRUCTURED MATERIALS USING TRANSMISSION ELECTRON MICROSCOPY

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The enormous scientific and industrial interest nowadays surrounding the material properties and characteristics at the nanoscale is pushing every structural characterization technique to work on small objects, either individually or as large assemblies. Structure determination or refinement, phase identification and contents (amorphous or crystalline, mixtures, etc.), microstructure (isotropic/anisotropic crystallite sizes, shapes, microstrain, defects, etc.), preferred orientation (crystallographic texture) are some of the desired targets for the quantitative characterization of a material. These kind of analysis are routinely performed using X-ray and neutron diffraction (XRD and ND, respectively) with excellent results on bulk materials. However, in the case of nanostructured materials this classical characterization approach can face some difficulties. Strong line broadenings and overlaps in the diffraction spectra can determine complications in the phase identification and quantification analysis, structure and microstructure determination, which become less quantitative or even unreliable. Furthermore, with concern to not homogeneous nanostructured

crystalline materials, local quantitative information on the phase and microstructure may not be easily reachable using bulk analysis methods like XRD and ND. Additionally, in order to achieve reliable results with the mentioned techniques they require the analysis of a not negligible quantity of material, that is not ever available in case of nanomaterials. In these circumstances the Transmission Electron Microscope (TEM) is one of the few characterization tool able to provide quantitative results on nanomaterials. Phase, structure and shape and size of nano-crystalline object can be determined inside a TEM combining imaging, diffraction and spectroscopies techniques at

the nanoscale level. The present thesis investigates the information attainable from the quantitative Rietveld analysis of SAED (selected area electron diffraction) pattern of nanoparticles assemblies and, generally speaking, of nanostructured materials. For this purpose a dedicated routine procedure for the Rietveld analysis of SAED pattern was developed within the MAUD (Material Analysis Using Diffraction) software for determining the constituting phases and their various microstructural and crystalline structural characteristics. Additionally, the SAED analysis was combined with the EDXS (Energy Dispersive X-rays Spectroscopy) complementary technique in order to fulfill the lack of the diffraction

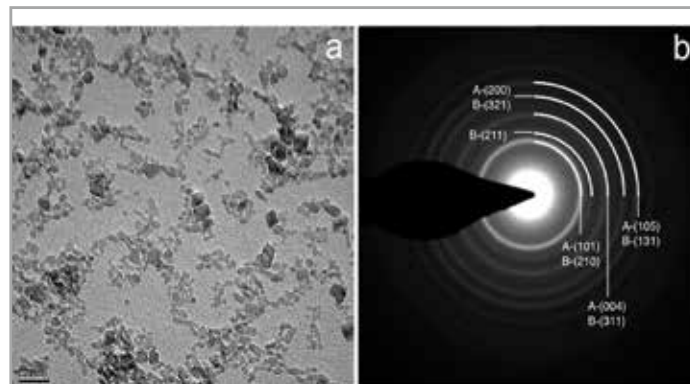


Fig.1 - Bright Field TEM micrograph of the nanocrystalline powders (a); indexed SAED ring pattern (b) of the nanopowder aggregates showing the presence of two TiO<sub>2</sub> polymorphs: anatase (A) and brookite (B).

analysis in case of complex systems where the chemical composition is determinant in the phase identification and structural characterization of the nanomaterials. As case of studies for testing the advantages, limitations and possible employments of the proposed method the following nanocrystallites ensemble were chosen: nanocrystalline polymorphs of TiO<sub>2</sub>; nanograined powders composed by ZnS and ZnO nanocrystals; tetragonal and monoclinic ZrO<sub>2</sub> nanocrystals; zirconia coatings doped with gallium atoms; polycrystalline thin films composed by Mn/Co mixed oxides. On the mixtures of titania polymorphs nanocrystals a preliminary comparative study between the usage of the Rietveld analysis with SAED data and conventional X-ray diffraction (XRD) was made. The present phases (anatase and brookite), their structural parameters (cell

parameters, atomic positions, etc.) and microstructure (anisotropic crystallites shape and size) were successfully determined through the analysis of electron diffraction pattern and all these parameters are in excellent agreement with the XRD analysis results. The same procedure using the SAED pattern Rietveld analysis was profitably employed on the ZnS/ZnO nanostructured system allowing the phase identification and the correct microstructural characterization of both phases. Interestingly, in this system the bulk XRD method fails in the phase identification and characterization of the ZnO phase presents in the system as an undesired impurity. Additionally, the phase and microstructure evolution of various mixtures of ZrO<sub>2</sub> nanocrystals, synthesized under different time and precursor concentration, were successfully followed using the developed SAED analysis approach. In this

study the electron diffraction results were also combined and critically compared with the XRD and Raman characterization. Moreover, the combined SAED/EDXS method was used for the characterization of ceramic Zirconia thin film doped with Gallium atoms and subjected to various thermal treatments. On this samples, the developed technique allows to determine not trivial material characteristics, such as the phase, the microstructure and the degree of substitution of the gallium atoms in the nanostructured Zirconia based coatings. Lastly, this combined approach was also able to correctly determine the phase, structural and microstructural characteristics of complex not stoichiometric polycrystalline Mn/Co mixed oxides. So, with its application on the various study cases mentioned above the proposed method we demonstrate the possibility of this technique to achieve a full and quantitative structural and microstructural characterization of nanomaterials. Moreover, the combination with the complementary EDXS techniques allows to study the chemical composition of the systems and conduct fast and reliable phase identification at the nanoscale level.

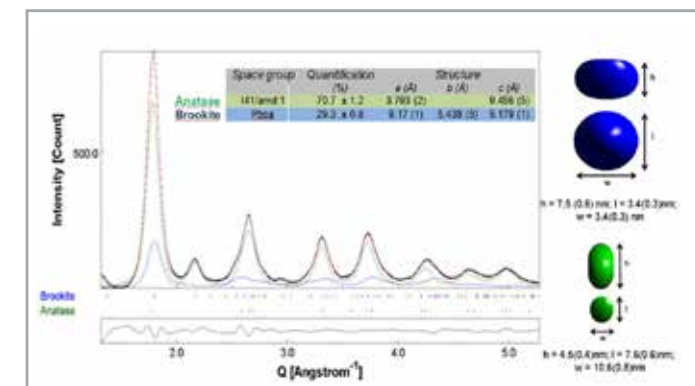


Fig.2 - SAED pattern of TiO<sub>2</sub> nanopowders, analyzed by the Rietveld method. The black dots represent the experimental data, while the red line is the computed profile. The blue and green line represent the contribution to the intensity profile of the identified brookite and anatase phase, respectively. In the table the results of electron Rietveld analysis are reported. The numbers in parentheses denotes the estimated standard deviation in the last digit. The h,w,l crystallite size lay respectively on the following crystallographic directions: [0,0,1]; [0,1,0]; [1,0,0].