





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	Alberto Cigada
Luigi De Nardo	Giovanni Dotelli	Fabio Ganazzoli
Marinella Levi	Valdo Meille	MariaPia Pedeferra
Guido Raos	Lucia Toniolo	Stefano Turri
Pasquale Vena	Elena Redaelli	Claudia Marano
Luca Magagnin		
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

## HOW SUSTAINABLE IS STABILISED RAMMED EARTH? THE USE OF NATURAL MATERIALS AND OTHER STRATEGIES TO REDUCE THE LIFE-CYCLE ENVIRONMENTAL IMPACT OF BUILDINGS

**Alessandro Arrigoni Marocco** - Supervisor: Giovanni Dotelli

According to the last Intergovernmental Panel on Climate Change report, buildings account for a dramatic share of global environmental impacts. Indirect emissions related to the energy consumed during a buildings' operational stage are mainly responsible for these impacts; however, as the energy efficiency of construction is optimised, the contribution of materials-related impacts, such as raw materials extraction (ca. 45% globally) and waste generation (ca. 33% in Europe), emerges. In recent years, different strategies have been promoted to reduce the environmental burdens related to the pre-use and the after-demolition stages of a building life-cycle. In the present thesis, some of these strategies were analysed using the life-cycle assessment (LCA) tool and innovative methods were proposed to further improve the sustainability of buildings. The research encompassed different levels of the building's scale: from the microstructure of a construction material to the macrostructure of a whole edifice. The first strategy investigated was the use of natural materials, both in non-load-bearing components (e.g. insulation, plaster) and as base components for load-bearing structures. Raw earth, and in particular modern

rammed earth (RE), was taken as a representative case study. RE enjoyed a revival in recent decades due to its appealing environmental features and hygrothermal properties. However, contrary to the traditional technique, in modern RE construction the earthen mixture is stabilised with chemical binders to enhance strength and to reduce erosion and the tendency to crack. The LCA analysis highlighted the crucial role of the stabilising agent used, typically Portland cement, on the overall impact of modern RE buildings. Waste materials (i.e. fly ash, calcium carbide residue and recycled concrete aggregate) were here proposed as alternative stabilising agents and base mixtures for RE construction. The resulting mixtures were evaluated not only in terms of environmental impacts but also in terms of mechanical resistance, durability and hygrothermal properties. A thorough investigation of the microstructure was conducted to understand the short and long term interactions between the stabiliser and the soil. The results of the experimental campaign demonstrated that it is possible to have durable stabilised RE mixes without paying the cost of using environmentally-expensive stabilisers. On the other hand, all kinds of chemical stabilisation

seemed to reduce the moisture buffer ability typical of untreated earthen surfaces. Another natural building material investigated was hempcrete. Hempcrete is a non-load bearing insulation material that has known an increased popularity in recent years. It is made from a mixture of the inner woody core of the hemp plant (hemp shives) and a lime-based binder. In addition to the LCA of the material, an extensive sensitivity analysis was performed to highlight possible improvements in the mixture. Moreover, the carbonation of the binder was monitored through XRD analysis on hempcrete blocks and the resulting experimental findings were included in the sustainability analysis for the first time. In light of laboratory experimental evidence, although carbonation improved the global warming potential of the product, the generic assumption of a complete carbonation of the material during the building's lifetime proved to be unrealistic. Nevertheless, hempcrete blocks can be considered as a carbon sink, since the CO<sub>2</sub> stocked in the material was higher than the overall emissions during production. Design for disassembly and recovery of building materials and components after demolition are

other viable alternatives to reduce the life-cycle environmental impacts of buildings. In the present thesis, the importance of materials' selection and their recycling potential were investigated at the building scale by performing an LCA analysis on a temporary pavilion built for the EXPO 2015 event held in Milan. Environmental impacts of temporary structures can be considered a proxy indicator for low-energy buildings due to the shared minor importance of the use-phase in the overall sustainability. Data for the LCA were collected directly on site and the related difficulties were brought to light. Results confirmed the importance of the design phase and demonstrated that foreseeing a second use for the building components could significantly reduce the impacts of a building. LCA is an acknowledged tool aimed at uncovering the real impacts of a product and at highlighting the environmental "hotspots" of a production process. In the present work, the LCA tool was used as a starting point for further investigations: once the hotspots were identified, alternative solutions in terms of material selection were proposed and detailed experimental campaigns were

performed to prove their feasibility and performance. Finally, the assessment was not limited to an attributional approach, but the implications on the market of the alternative solutions were included via a tool known as consequential LCA. In conclusion, the strategies examined and the improvements proposed in this research study proved to be effective solutions in the framework of the buildings' impacts reduction challenge.

# AN ALTERNATIVE METALLIZATION PROCESS OF ADVANCED POLYMERS: DEVELOPMENT AND APPLICATIONS

Andrea Oriani - Supervisor: Luca Magagnin

The production of adherent metal coatings on polymers, especially fluoropolymers, is still an open issue for many applications. Many pre-treatment and metallization processes have been proposed, which are either time/money consuming or limited to few specific polymers. In order to propose a versatile and simple process to face this issue, this thesis work is focused on the combination of open-air atmospheric-pressure plasma treatment and electrochemical processes for the metallization of advanced polymers. Plasma treatment, in particular, was performed to graft nitrogen-bearing functionalities that are known to coordinate with ionic palladium species in the activation bath. After plasma and activation with palladium, electroless copper metallization was usually performed. Also silver deposition was considered for specific applications.

The manuscript is organized in four chapters: the first proposes a literature review regarding atmospheric plasma, electrochemical metallization and plasma treatment applied to electrochemical metallization of polymers. In the second chapter, the basic principles of the characterization techniques, used during this research activity, are

described. In the third chapter the experimental procedures are defined and in the fourth chapter results are discussed. In particular, the text is organized according to the polymeric materials studied during experimentation. The same pattern is followed for each polymer, namely KETASPIRE® KT-820 PEEK, HALAR® 350LC ECTFE and SOLEF® 60512 (plaques) or 80000 (foams) PVDF. At first, parameters and characterization results of plasma treatment are discussed, afterwards outcomes of electrochemical metallization are described and finally the performances of the metallized polymer for the selected application are studied by means of specific tests.

Looking at the big picture, it is possible to say that atmospheric plasma treatment is a suitable process to pre-treat polymeric materials with different chemical structures, e.g. aromatics (PEEK) and fluorinated (ECTFE and PVDF), in order to promote electroless metallization. Plasma treatment, especially if performed in the suitable conditions, was found to increase the surface tension of the polymeric substrates, mainly due to a marked increase of its polar component. The process of hydrophobic recovery was studied and was found to be temperature dependent. A

model was proposed that implied the building of master curves and the determination of the activation energy for the process of hydrophobic recovery. Chemical analysis of the surface revealed that plasma treatment leads to the grafting of nitrogenated and oxygenated functional groups. The presence of such functional groups after plasma treatment is in agreement with the literature and justifies the increase of the polar component of surface tension. At the same time morphological characterization pointed out that the surface roughness of the polymers is not affected by the preferred plasma conditions; this is an advantage with respect to wet chemical etching, especially when low surface roughness is desired for the final application. It was found that plasma parameters need to be optimized depending on the chemical structure and on the form of the polymeric substrate, therefore allowing to obtain continuous and homogeneous copper deposits with good adhesion levels. Nucleation of copper was found to occur with no induction time on all the studied plasma-treated polymers; this means that the palladium nuclei, adsorbed during the activation process, are in the catalytic state before dipping the sample in the

deposition solution.

Moving to the specific applications, metal-coated ECTFE was proposed as flexible concentrator mirror. Spectral reflectance studies, performed on simplified samples, revealed that good reflection properties can be obtained. Moreover the deposition of silver layers allowed improving the performances with respect to copper coated ECTFE samples. Two different applications were considered for copper coated PEEK films, depending on their thickness. Thermal and mechanical properties of thin, 6  $\mu\text{m}$  thick, films were determined to quantify the effect of copper layers on thermal conduction/dissipation and apparent elastic modulus. This information was needed to validate the applicability of these samples as oscillating diaphragms for micro-speakers. Results revealed that thermal conduction/dissipation is highly increased by metallization and the effect on the mechanical properties can be tailored to obtain a good compromise. Secondly the applicability of thicker copper coated PEEK stripes as switches for circuit breakers was studied. In this case electrical and thermal responses of polymer-metal switches were studied, revealing that, modulating sample geometry, it is possible to control with remarkable precision the actuation current and the thermal deflection of the polymer-metal stripes. Finally the whole-surface plating of PVDF foams with copper was studied for aerospace applications. It was indeed verified that pristine PVDF foams didn't

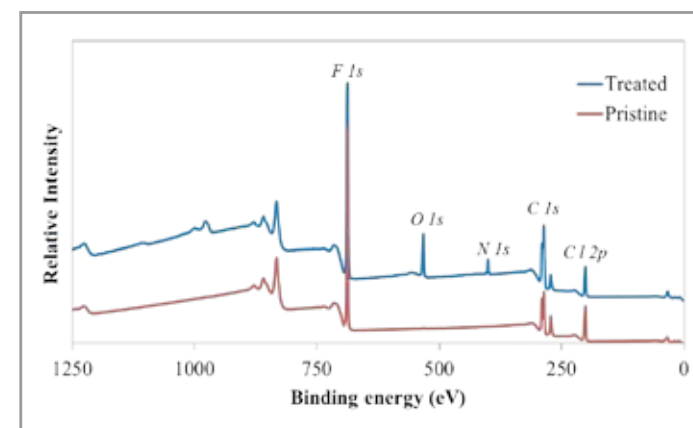


Fig. 1 - XPS spectra for pristine and plasma treated ECTFE

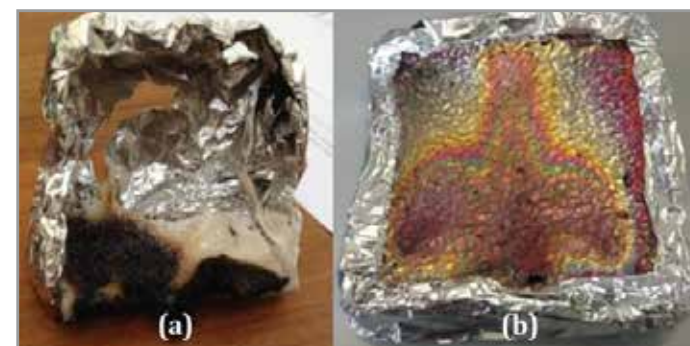


Fig. 2 - Comparison of pristine (a) and copper-plated (b) PVDF foams after flame resistance test.

meet smoke toxicity requirements due to generation of HF during flame resistance tests. The flame resistance test is part of the set of characterizations that are required, for new materials, from the aerospace industry. Copper coated PVDF foams, on the other end, were found to pass the flame resistance test without generation of HF.

This work is part of a research project within Solvay Specialty Polymers with perspectives of commercialization.

# FRACTURE BEHAVIOUR OF THERMOPLASTIC ACRYLIC RESINS AND THEIR UNIDIRECTIONAL CARBON FIBRE COMPOSITES: RATE AND TEMPERATURE EFFECTS

Tommaso Pini

Fracture behaviour of novel acrylic thermoplastic resins to be used as matrices for composite materials was studied. These resins, one plain and one toughened with rubber, are suitable to prepare composite materials adopting a reactive processing technique such as infusion moulding, overcoming in this way the issues typical of thermoplastic composites production. The matrices were investigated at small strains, yield and fracture, taking into account the influence of displacement rate and temperature on the mechanical response. Small strain behaviour was investigated with Dynamic Mechanical Analysis in a three-point bending configuration, adopting the time temperature equivalence postulate to reduce data obtained from tests conducted at different temperatures to one single reference temperature. Uniaxial tensile tests were performed to investigate yielding behaviour while fracture was studied with Double Torsion and Double Cantilever Beam techniques for matrices and composites respectively. In all cases, tests were conducted at different displacement rates and temperatures and the time temperature was applied so as to obtain fracture toughness vs. crack propagation speed and yield stress

vs. time to yield master curves. The results from fracture tests showed that Williams' viscoelastic fracture theory was suitable to predict fracture toughness dependence on crack propagation speed in the case of the plain resin, while in the case of the toughened resin a dependence opposite to that expected was found. This trend was attributed to different deformation mechanisms occurring at the crack tip at different conditions of strain rate and temperature. The process zone ahead the crack tip was then studied more in depth adopting Single Edge Notched Bending configuration and performing Digital Image Correlation analysis. Results showed that, concerning the plain resin, the size of the process zone was approximately constant with respect to the temperature. The results obtained for the toughened resin on the other hand, confirmed that the size of the process zone was actually different at different temperatures. The damage mechanisms in the toughened resin were investigated studying the changes in volume occurring during tensile tests at different conditions of temperature and displacement rate. A change of mechanism at different testing conditions was found. Fracture behaviour of the toughened

resin was also studied in double notched four-point bending configuration from which a fully developed yet intact process zone at the crack tip can be obtained. The optical observation of the process zone at the crack tip obtained in different conditions of temperature and displacement rate confirmed the change in the damage mechanisms. This was associated with different amounts of energy dissipated thus explaining the trend observed in the fracture toughness vs. crack propagation speed curve for the toughened resin. Concerning the fracture behaviour of the composites, in order to better understand the transfer of toughness from matrix to composites, both the crack initiation and propagation stages were analysed. At crack initiation the toughening contribution of the fibres is limited, compared to that during crack propagation, and therefore the main fracture toughness contribution is given by the matrix. It was found that in the case of the plain matrix based composites the fracture toughness was higher than that of the matrix, while in the case of the toughened matrix based composites it was smaller. This result can reasonably be explained with the physical constraint induced by the presence of the fibres on the

development of the process zone ahead the crack tip in the case of the toughened composites. In the case of the plain matrix, in which the dimensions of the process zone are smaller, the matrix toughness seems to be fully transferred to the composite. During the propagation stage, it was found that the fracture toughness was higher than that of the relevant matrix, for both matrices. The additional toughening effect given by the fibres was found to be dependent on crack propagation speed, probably due to time dependent matrix-fibre interfacial strength.

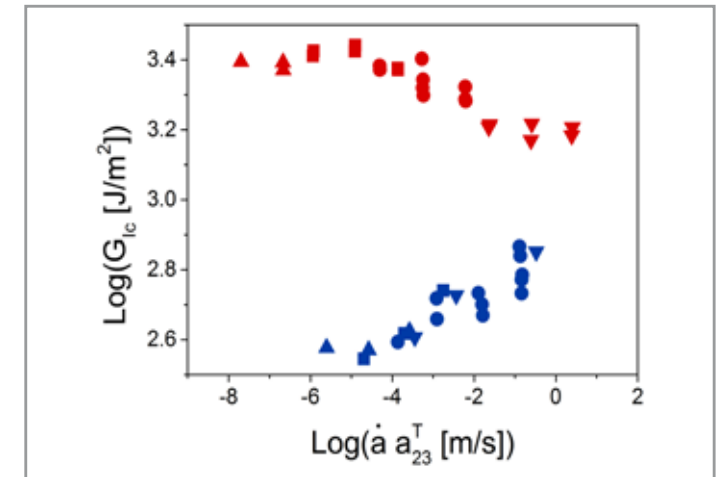


Fig. 1 - Fracture toughness vs. crack propagation speed master curves for plain (blue symbols) and toughened resin (red symbols)

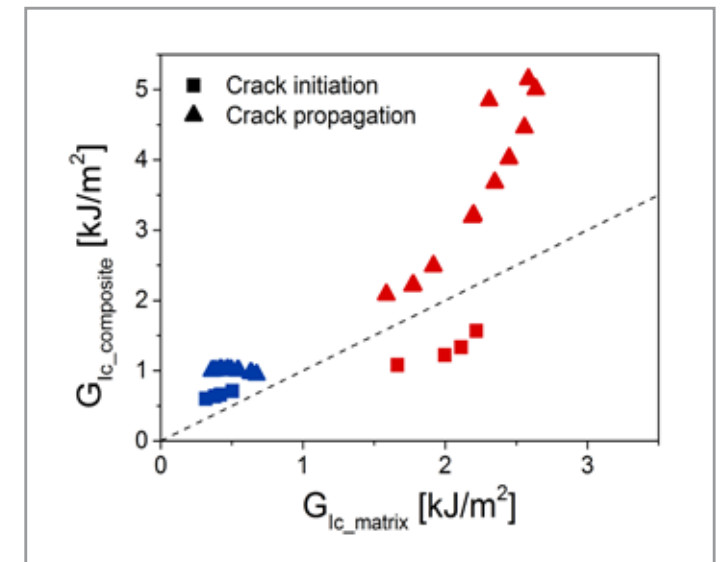


Fig. 2 - Fracture toughness of composites vs. fracture toughness of relevant matrices at crack initiation (squares) and during crack propagation (triangles) for plain (blue symbols) and toughened matrices (red symbols)

Giovanni Postiglione - Supervisor: Prof. Stefano Turri

The interest of the scientific community in smart materials is constantly growing mainly because of their huge potential in several technological applications, including coatings, structural components and electrical sensors. The strategy for the designing of such systems is correlated to the observation of the natural world where countless examples of stimuli-responsive behaviour can be found. In recent years, the development of novel polymeric smart formulations was encouraged by concurrent advances in the field of additive manufacturing. Additive technologies, initially adopted for rapid prototyping of digital product renderings, have become an established method for manufacturing objects suitable for end use. Their continuous development, especially in term of processable materials, is now allowing the fabrication of cutting-edge devices with unconventional performances.

In the work presented in this PhD thesis, new polymeric smart materials and additive manufacturing technologies were examined independently, at first, and then focusing on the relationship between innovative processing and advanced functionality. The final aim of the research project was

developing new smart polymers and composites suitable to be realized by additive manufacturing technologies.

The first part dealt with the study of smart systems designed to give an intelligent response to damage events. One approach consisted in providing a material with the ability to display a visual change as a result of a local deformation due to impacts or scratches. To this end a polymeric coating was functionalized with microcapsules containing an UV-fluorescent dye so that the resulting composite was capable of showing a visual signal upon capsules breakage. This damage sensing material allows to easily detect external damages and its implementation facilitates maintenance operations.

The analysis of smart systems was extended to self-healing

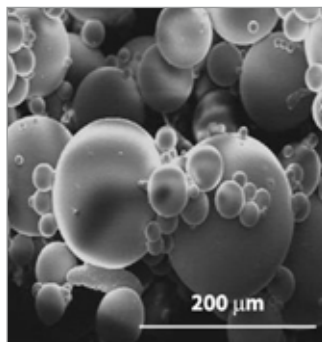


Fig. 1 - Sem image of microcapsules containing an UV-fluorescent dye

materials, that, in term of material functionality, represent the logical evolution of damage sensing. Their ability to counteract degradation and damages with automatic repair mechanisms was assessed by formulating a polymeric coating based on the Diels-Alder reaction. The resulting polymer, upon application of a simple thermal treatment, reduced or eliminated small defects or microcracks, potential points of weakness that could otherwise lead to structural failure.

The second part focused on the development of polymeric nanocomposites for different extrusion-based additive manufacturing technologies. The proposed processes, termed liquid deposition modeling (LDM) and UV-assisted 3D printing (UV-3DP), consisted in the layer-by-layer deposition of fluid material that solidified after flowing out of a computer-controlled moving nozzle. Using LDM it was possible to fabricate conductive microstructures with resolution down to 100 μm from a solvent based formulation containing carbon nanotubes. Conversely, through UV-3DP, nanocomposites composed by different combinations of photocurable matrix and inorganic fillers were successfully processed. A systematic investigation on the

rheological properties of different formulations allowed to achieve a deeper understanding of the processes related criticalities, and hence the best printability conditions. In the attempt to expand the use of UV-3DP to the fabrication of reinforced composites, a sequential interpenetrated polymer network, loaded with short carbon fibers, was especially devised. The outstanding mechanical properties showed by the resulting prints have significant implications for the future manufacturing techniques of composites. Finally, self-healing materials based on microvascular networks were designed exploiting the additive process ability in



Fig. 2 - optical photograph of a ldm-based 3d printed conductive filament deposited in a freeform manner (a 1 cent euro coin is reported in the image for dimensional reference)

generating controlled geometric patterns. In practice a specific procedure allowed to convert a 3D printed microarchitecture into a system of microchannels. The healing function, comparable to that of human skin, could be performed upon release of liquid healing agents accurately stored into the microchannels embedded within the matrix. This ability favorably affected the durability and mechanical performance of the tested polymeric materials. The innovative approaches based on additive manufacturing, such as those proposed in this work, will open the way towards the implementation of smart functions, commonly associated with the biological world, into novel polymeric and composite materials.

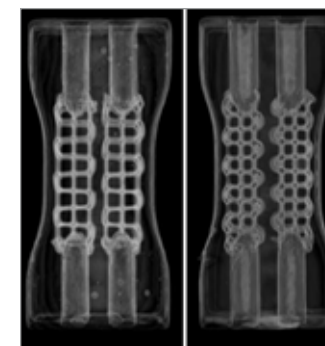


Fig. 3 - Micro-CT images of self-healing samples based on microvascular networks having different microchannel density

# INVESTIGATION OF COLLIMATOR MATERIALS FOR THE HIGH LUMINOSITY LARGE HADRON COLLIDER

**Elena Quaranta - Supervisor: Stefano Redaelli**

**Advisor: Prof. A. Cammi**

Beam intercepting devices, such as collimators, are essential components for machines handling high-energy and high-intensity particle beams. Despite the improvement in techniques to control the beams, particle accelerators are continuously exposed to leakage of beam particles, which can be highly dangerous for the machine equipment if not tightly controlled by collimators.

The CERN Large Hadron Collider (LHC) was designed to accelerate proton and ion beams to provide collisions with centre-of-mass energies of 14 TeV. In the future, the High-Luminosity LHC project (HL-LHC) aims at an upgraded accelerator with smaller beam emittance and doubled beam current, i.e., double the actual stored beam energy.

The present LHC machine works extremely well. On the other hand, the challenging parameters of the HL-LHC beams are beyond the values foreseen by the original design of the accelerator. Therefore, an upgrade of the collimator system is also required. Materials of future collimators must ideally optimise different thermo-mechanical properties:

- Density, to guarantee beam cleaning efficiency
- Electrical conductivity, to

reduce beam coupling impedance

- Mechanical strength, to withstand shock impacts from beam losses
- Thermal expansion and diffusivity, to withstand thermal loads, preserving geometrical stability of the device
- Radiation hardness, to withstand high cumulated doses due to radiation exposure before property degradation occurs.

The objective of this PhD work is to propose, based on the results of experimental activities and numerical simulations, optimum materials for the HL-LHC collimators.

A material that fulfils all the requirements for the HL-LHC collimators does not exist. An ambitious material R&D program

has been launched at CERN in the last 10 years, which foresees a strong collaboration with external industrial companies, to develop novel composite materials to face the High-Luminosity challenges. The main purpose was to explore composite materials ideally combining the properties of graphite or diamond (low density, high thermal properties) with those of metals and transition metal-based ceramics (low resistivity and high mechanical strength).

To date, Molybdenum-Graphite composite (MoGr) and Copper-Diamond composite (CuCD) are the most promising candidates for the HL-LHC collimators (Fig.1). MoGr is produced by Pulsed Electric Current Sintering technique from a cold pressed mixture of molybdenum powder, graphite flakes and carbon



**Fig. 1 - Left: plate of Mo-Gr (Brevetti Bizz, Italy). Right: bar samples of Cu-CD (RHP Technology, Austria)**

fibers. It features a factor of 5 higher electrical conductivity than the present carbon-based composite (CFC) currently used in the LHC primary and secondary collimators. Therefore, the use of MoGr for the collimator jaw would strongly reduce the single-collimator contribution to the machine impedance. Moreover, the addition of a thin coating layer of pure Mo or TiN on top of the bulk material can further improve the electrical conductivity, with a reduction of the impedance. CuCD is produced by conventional Hot Pressing using cold pressed powders, including diamond particles, copper powder and a small addition of boron that overcome the low chemical affinity of the main components. Copper provides excellent thermal and electrical conductivity, along with its good ductility, while diamond is added to reduce the density and the coefficient of thermal expansion, while contributing to the thermal conductivity. Collimators are the most exposed



**Fig. 2 - aw of the low impedance secondary collimator prototype for HL-LHC, delivered at CERN in November 2016. It features a Mo-Gr bulk in 3 configurations: without coating, with Mo layer and with TiN layer**

components to beam losses, therefore modifications of the material properties are expected as a consequence of high radiation doses. Several irradiation campaigns have been performed in partner laboratories, such as BNL (USA) and GSI (Germany), to study the consequences of proton, neutron and ion irradiation at different energies on collimator materials. The results of the irradiation campaigns, analysed in this thesis work, demonstrate that recent and more optimised MoGr grades possess good radiation resistance to both proton and ion beams, with a threshold of structural degradation not far from that of graphitic materials. CuCD also showed high resistance to radiation damage at macroscopic and microscopic level.

Simulation studies have been carried out to validate the choice of materials and layout of the HL-LHC collimation system. The simulations were performed with SixTrack code, the standard tool for collimation performance studies at the LHC. A new collimator material implementation has been developed, which includes a model for composite materials, while the existing routing only treats mono-element materials. The implementation was successfully benchmarked with other simulation codes and found to be fully adequate for the scope of this work. A new method to reliably calculate the onset of beam-induced damage to material of accelerator components was also presented. It consists of a three-step approach: particle

tracking studies (largely covered by this thesis) to determine beam impact conditions for design failure cases, energy deposition studies and thermo-mechanical analysis of the dynamic response of the material to the impact. The results showed that, in HL-LHC operation, large losses are expected on tertiary collimators with the risk for the tungsten jaws to experience permanent deformation. CuCD jaws to replace those in IT-180 are proposed as a viable solution to mitigate the robustness constraints for these collimators. Based on the outcome of recent impact tests on CuCD jaws, preliminary estimates would indicate that a collimator with CuCD jaws is about 15 times more robust than a tungsten-based tertiary collimator.

The studies carried out in this PhD thesis pose a solid basis for the choice of materials for the collimation baseline layout in the HL-LHC collimation upgrade. A prototype of a new low-impedance collimator, featuring MoGr jaws with two coating options (Fig. 2) has been recently produced and installed in the LHC. It will be tested in operation during the next machine runs.



# NANOSTRUCTURED ZIRCONIA: SYNTHESIS OF ZERO AND TWO DIMENSIONAL STRUCTURES FOR ADVANCED APPLICATIONS

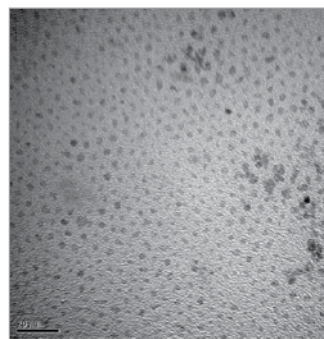
Francesca Tana - Supervisor: Luigi De Nardo

This thesis deals with the development of zirconia nanostructures exploiting two different synthetic routes grouped in the family of sol-gel process investigating zirconium oxide properties at scales ranging in submicron dimensions, from few nanometers to larger nanostructured systems. Indeed, the first part focuses on the synthesis of crystalline nanoparticles through non-aqueous sol-gel route while the second one presents the synthesis of mesostructured zirconia coating exploiting the conventional sol-gel route in presence of a soft template agent. The obtained zirconia nanostructures were following employed for the preparation of hybrid coatings for different applications. Zirconia nanoparticles were used as nanofiller for anti-scratch organic-inorganic transparent coatings for commodity polymers (in details, polymethylmethacrylate, PMMA, and polycarbonate, PC), while mesoporous zirconia coatings were tested as nanopatterned substrates to promote osteoblastic cells adhesion and proliferation. Zirconia nanoparticles were synthesized taking advantage from the so called non-aqueous sol-gel route. This method allows obtaining crystalline oxide particles in one-step reaction.

The chemical reaction took place in the absence of water heating a precursor (*i.e.* metal salts or alkoxide) in appropriate organic solvent, under continuous stirring. Moreover this synthetic procedure allows obtaining ready to use crystalline nanoparticles, often composed by pure crystal phases dispersed in organic media without requiring functionalization procedure or calcination passage. For the purpose,  $ZrCl_4$  was chosen as zirconium oxide precursor and reacted in benzyl alcohol. By this synthetic route, the involved chemical reactions occur slowly in comparison to the standard hydrolytic sol-gel route permitting a controlled growth of a crystalline structure. The obtained zirconia powders were characterized by thermogravimetric analysis, XRD, TEM and Raman analysis in order to elucidate the thermal stability, nanoparticles dimension, phase and morphology. The developed synthetic procedure was further studied applying different experimental conditions, modifying precursor concentration (0.16 M-0.39 M-0.5 M) and reaction time (2.5-7-24 hours). At lower precursor concentration pseudo-spherical tetragonal particles of 2 nm were obtained. Higher amount of zirconium precursor and long reaction time caused increasing amount of monoclinic

phase to growth. Moreover, TEM and HRTEM analyses showed an increase in zirconia nanoparticle size and changes in particles shape. Interestingly, increasing of reaction time and concentration of precursor solution caused anisotropic particles to growth from the starting pseudo-spherical crystallites to rice-shaped particles (preferential growth along c axis).

This phenomenon could be attributed to a specific oriented attachment growth process in solution. Size, shape and phase of zirconia nanoparticles can therefore be tuned changing experimental conditions. The employed non-hydrolytic sol gel process facilitates the introduction of nanoparticles inside a matrix to create nanocomposites bringing down mixing problems and

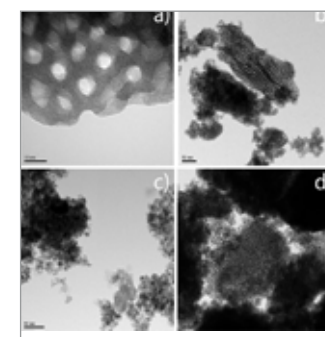


**Fig. 1 - Representative TEM image of zirconia nanoparticles synthesized heating  $ZrCl_4$  (0.16 M) at 200 °C for 2.5 hours in benzyl alcohol**

macroscopic phase separation, resulting in homogeneous nanoparticles dispersion. Anti-scratch coatings were successfully obtained mixing 5 and 10% wt. particles in a commercial epoxy resin on PC and PMMA slices increasing polymer scratch resistance in the absence of delamination phenomena. Taking advantage of the results of my research activity, the synthesis of mesoporous zirconia coatings was carried out alongside. On the base of the self-assembly procedure from liquid precursor, a soft template agent was introduced in the mixture and subsequently thermally removed (calcining at 400-500-600 °C), in order to obtain the mesoporous structure. Zirconia has different biomedical application since it is a non-toxic material with excellent mechanical properties and high chemical stability. For instance, it is especially appreciate in dentistry as a replacement for titanium dental implants due to its similarity with natural teeth. The surface modification through mesoporous coating formation was carried out to increase implants osseointegration process due to the intrinsic porosity and the increase of surface area. Pure ad CaO doped (11 and 25 % mol.) zirconia structures showing 5-10

nm pore size were tested.

Mesoporous zirconia coatings demonstrated improved cells viability in comparison with the non-porous surface even if the contribution to cell adhesion, growth and proliferation or the interaction between proteins and the structured has to be elucidated. Calcium oxide allowed maintaining the pseudo-ordered porous structures up to 600 °C in comparison with the pure zirconia coatings and higher cells viability was observed for 25 % mol. CaO-doped samples.



**Fig. 2 - Representative TEM images of a) pure zirconia mesoporous, b) CaO-doped coating calcined at 400 °C, c) pure zirconia coating calcined at 600 °C, d) CaO-doped coating calcined at 600 °C**

# DEVELOPMENT OF ORGANIC MATERIALS FOR INTERFACES IN PEROVSKITE SOLAR CELLS

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Due to the relatively high production costs of conventional solar cell devices there is a growing interest in alternative technologies with abundant materials and lower production costs. This development has led to several types of systems such as dye-sensitized solar cells (DSSCs) and more recently, perovskite solar cells. The initial research activity of this PhD. work was focused on DSSCs with the development of Lewis-base organic dyes with a pyridyl group as an alternative binding group as presented in appendix A. Nevertheless, further development of DSSCs with the replacement of the organic sensitizer by organic-inorganic halide perovskite has led to a new type of solar cells. With a state-of-the-art PCE of 22.1% perovskite solar cells are a very good competitor for conventional Si-based solar cells.

Despite the fact that organic-inorganic halide perovskite is a promising class of light absorbing material, one of the major drawbacks are hysteresis and long-term stability which can hinder the commercialization of perovskite solar cells. In solar cells interfaces play an important role in the degradation of the perovskite material. By careful modification of the interfaces in the device the long-term stability of the device

can be improved.

In this work, we present the modification of different interfaces in the perovskite solar cell to increase the PCE and improve the stability. Modification of the  $\text{TiO}_2$  layer with fullerene derivatives has proven to be effective to increase the PCE and improve the electrical stability of the device. In this framework we present the modification of the  $\text{TiO}_2$  by the introduction of a thermally cross-linkable [6,6]-phenyl- $\text{C}_{61}$ -butyric styryl dendron ester (PCBSD), which forms a thin solvent-resistant, robust electron-extracting layer (EEL). In addition we show that in the device with PCBSD, the  $V_{oc}$  is increased in comparison with devices having the commonly used [6,6]-phenyl- $\text{C}_{61}$ -butyric methyl ester (PCBM) as EEL.

Moreover, we present an alternative method to cross-link PCBSD by UV-curing, which allows for low temperature processing of perovskite solar cells and other optoelectronic devices. Low temperature processing turns into the reduction of production costs and applications on flexible substrates could also be possible. In addition, we show the synthesis and cross linking of [6,6]-phenyl- $\text{C}_{61}$ -butyric 1,4-pentadien dendron ester by UV-curing in the presence of a photoinitiator. Furthermore, it is known that defect sites in the perovskite structure formed during crystallization or degradation are one of the causes for electrical instability of the perovskite solar cell. Several methods have been reported for the passivation of defect sites on the surface of perovskite material. Here we

report on the passivation of the perovskite surface in the inverted architecture with different Lewis-base binding units functionalized with triphenylamine. The interaction between the passivation materials and the perovskite is analysed and the effect on the performance of the device is highlighted.

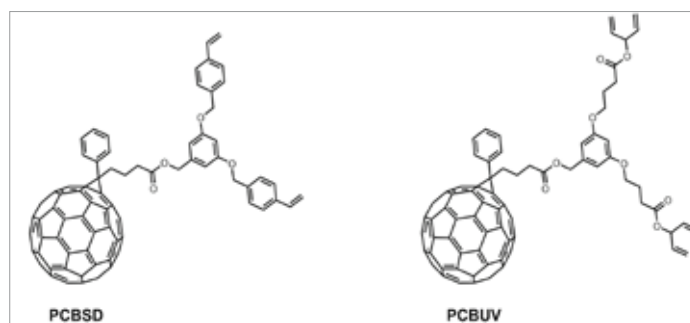


Fig. 1 - Figure 1 encaption: crosslinkable fullerene derivatives PCBSD and PCBUV