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 Doctoral School requires the acquisition of 180 credits (in 3 years) :

- at least 30 credits must be obtained 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
Luca Bertolini	Fabio Bolzoni	Massimiliano Bestetti
Alberto Cigada	Luigi De Nardo	Giovanni Dotelli
Fabio Ganazzoli	Luciano Lazzari	Marinella Levi
Valdo Meille	MariaPia Pedeferri	Guido Raos
Marta Rink	Lucia Toniolo	Stefano Turri
Pasquale Vena		
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	

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PROPERTIES OF CELLULAR POLYMERIC MATERIALS IN RELATION TO THEIR STRUCTURE

Michele Benanti Supervisor: **Prof. Francesco Briatico Vagosa**

Cellular materials are an important class of engineering materials, yet the knowledge and the understanding of their behaviour is far from being complete. The aim of this study is to investigate different aspects of the mechanical and acoustical behaviour of cellular polymeric materials in relation to their three dimensional structure. The first part of the work is devoted to the development of a method for predicting the mechanical response of honeycomb panels made by polymeric material via a continuous process, in the context of "Progetto Alveoplast", a funded project in the framework of "Industria 2015" initiative. After experimental validation of the predictive ability of the three dimensional finite element model, the mechanical response of several geometries was analysed in order to optimize the honeycomb structure for the use as acoustic barrier for traffic noise control, taking into account both the mechanical and acoustical requirements.

Besides honeycomb structure, also polymeric foams were studied. These materials find application, amongst many others, as sandwich panels cores, as shock absorbers and as acoustic liners for sound absorption purpose. Regardless the application they are used for, their mechanical and acoustical performances depend both on the nature of the constituent material and on the structure of the cells and its change under load. The possibility to use polymeric foams to enhance acoustic performances of panel led to the study of the influence of static deformation on the properties of the foam subject to cyclical stimuli. Indeed the static deformation may affect the microstructure and the constituent material properties, thus modifying significantly the foam behaviour. This study is of practical interest since foams, and in particular those used for noise control, are frequently subject to static deformation superimposed to cyclical one.

It was shown that the time-temperature equivalence is applicable to predict the dynamic mechanical (DMA) response at frequencies not directly accessible, and that the effect of static pre-strain and of temperature are decoupled. The obtained data were used to simulate the acoustic behaviour of a car part made by a layer of polyurethane foam sandwiched between two steel sheets. The prediction was in accordance with the measured acoustic performances over a wide range of frequencies, significantly wider than that directly accessible in DMA experiments, and gave better results than the prediction carried out using material properties measured at a single frequency only.

The acoustical and mechanical behaviour of foams is also affected by the presence of open porosity. This was investigated in a study on a novel open-cell polyethylene foam (PEOC) produced at CellMat laboratory (Universidad de Valladolid, Spain) through a well-controlled production route. This material displays a peculiar structure characterized by almost closed cell connected by small holes. Crushing the foam up to 90% of its original thickness allows to obtain a material with different structure and mechanical response (PEOC90). Results suggested that changing the microstructure can be a very effective way to control, and enhance, its sound absorption characteristic. The very same foams showed interesting response to quasi-static and cyclical mechanical stimuli. In fact, unlike other open cell foams, such as PU flexible foam, PEOC compression behaviour is significantly affected by the rate of the applied compressive strain. Extending the observations of the studies performed on liquid-filled polyurethane foams present in the literature, this peculiar behaviour was attributed to the stress contribution arising from gas flow through the holes interconnecting cells, and a simple model based on Darcy's law (flow through a porous medium) was able to describe the evolution of stress with strain at different strain rates. DMA characterization performed at fixed frequency (1Hz) and several static strains evidences the differences among the studied materials, which can be related to their structure. The comparison between PEOC and PEOC90 seems to confirm that the changes in the structure have an effect not only on the modulus, as expected, but also on the loss factor, which decreases with increasing holes size in cells walls, while static deformation does not seem to affect significantly the loss factor. In the case of closed cell foams, the observed reduction of loss factor with increasing static strain might be attributed to the contribution of air pressure to E'.

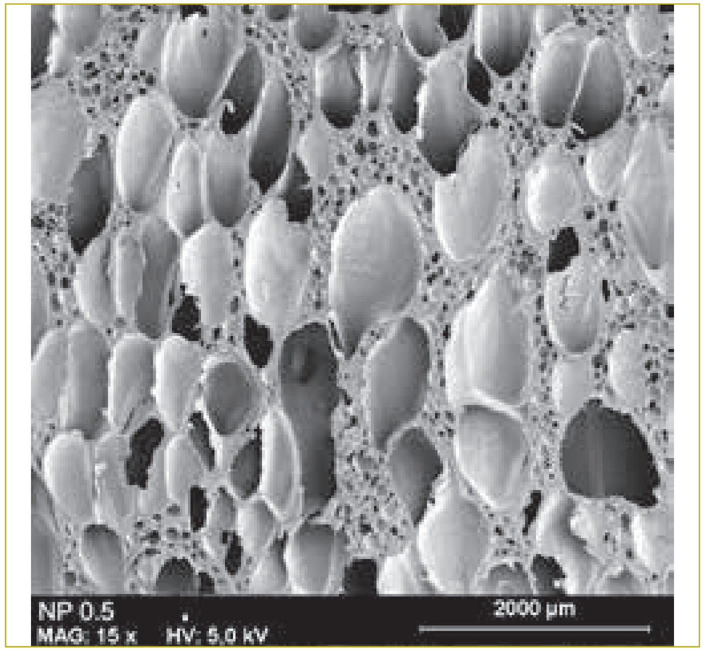
Finally, the mechanical properties in relation to anisotropic microstructure of polypropylene– based medium density (180 kg/m^3) foams were studied. A non-standard compression moulding technology, called improved compression moulding (ICM), was used to achieve anisotropy of cellular structure and a fine control on the final foam density. Four different processing pressures (0.5; 1.5; 4; 8 MPa) and two different formulations (pure PP and PP+nanoclays) were employed to prepare a total of eight different foams. The influence of processing condition and of the addition of nanoclays on the foaming process was studied by means of microstructure and mechanical characterisations. Changing the process parameters allowed obtaining different morphologies, while maintaining constant foam density.

Microstructure characterization, through image analysis, revealed an overall cell orientation in the expansion direction and a dependence of structure morphology on the process conditions and formulations. Nanoclay charged foams prepared at the lowest pressure conditions displayed high structure anisotropy and bimodal cell size distribution (see Figure 1).

More homogeneous cell size distribution was obtained in pure PP foams and in foams produced at higher pressure.

A correlation between cell anisotropy and cell size was observed and a different trend for each material was observed. In particular, it was noted that smaller cells of nanocomposite PP foams tend to have rounded shape (see Figure 1). Structure anisotropy was reflected by mechanical properties: all materials displayed higher stiffness in the expansion direction with a ratio between the modulus measured in the expansion to transversal direction ranging from 1.5 to 3.

A part of the study was devoted to assess the applicability of existing models in order to predict the dependence of mechanical behaviour on the anisotropy ratio of the foams microstructure. The simple model based on rectangular cell proposed by Gibson and Ashby, in spite of the complexity of the structure of the studied foams, can describe their behaviour in acceptable way.



1. Cross section of nanoclay-reinforced polypropylene foam prepared at 0.5 MPa. Elongated cells give the material anisotropic mechanical properties; small rounded cell formation is favoured by the nucleating effect of nanoclay.

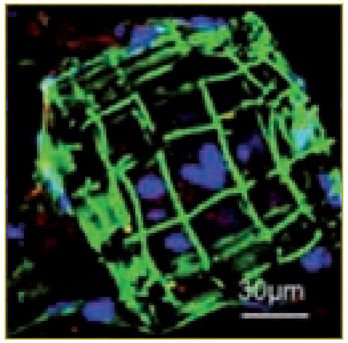
POLYMERIC MATERIALS FOR ADVANCED HUMAN HEALTH APPLICATIONS

Caterina Credi - Relatore: **Prof. Stefano Turri**

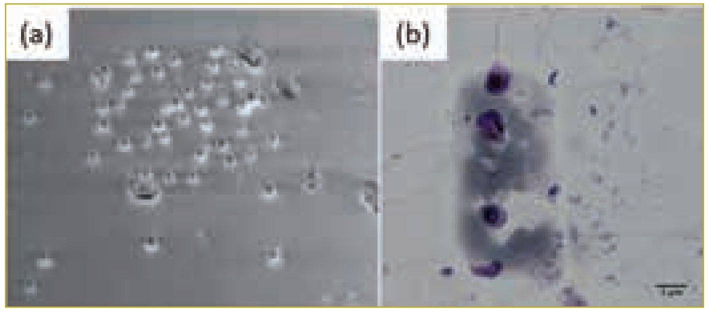
The research work of the present thesis can be divided in two main parts both related to the development and functionalization of polymeric materials for advanced human health applications. One deals with stem cells-based therapies for tissue engineering applications whereas the other deals with the development of patterned functional biomaterial surfaces for rare cells capture and isolation. The goal of tissue engineering is to replace or to repair a damaged tissue or organ with autologous-engineered artificial substitutes made by seeding living autologous "organ specific" cells on a biomaterial, a *scaffold*, acting as an extra-cellular matrix and culturing them giving proper cues until maturation in a functional tissue ready to be transplanted. One promising strategy consists in addressing stem cells fate by fine-regulating their interactions within 3D artificial microenvironments, "synthetic niches" engineered to mimic individual biochemical and biophysical factors. To this end, our first objective was to fabricate and functionalize 3D synthetic matrices which are engineered to enable independently tuning their physical-mechanical properties, in terms of geometry and stiffness, thus allowing investigating the specific role that each stimulus have on stem cells response. 3D freestanding niches with tailored geometry were fabricated by two-photon polymerization (2PP), which allows rapid prototyping of 3D complex polymer structures. In order to widen the range of 2PP structures mechanical properties, hydrogels were considered as biomimetic materials suitably for 2PP scaffold coatings.

Immobilization strategies based on physical, chemical and photochemical interactions were explored to functionalized 2PP structures with thin layers of hyaluronan- and gelatin-based hydrogels, which were developed to have tailored stiffness encompassing the range of physiological values. Hydrogel mechanical properties were evaluated validating a reliable methodology based on three independent experimental techniques. Rheological results obtained on macroscopic samples were successively benchmarked with swelling experiments following Flory-Rehner theory and by Atomic Force Microscopy (AFM) nanoindentation, the latters considered more suitable techniques for the characterization of small-scale hydrogel samples as those grafted onto niches. Finally, biological tests were performed on hydrogel-coated structures to study aspects of biocompatibility and differentiation. All the hydrogel coatings resulted high biocompatible with enhanced proliferation and higher metabolic activity compared to uncoated scaffold. Preliminary results assessed that HA-coatings induced the formation of cells agglomerates, which maintain their plurypotency thus suggesting their potential application to produce therapeutic MSCs in large, pharmaceutically relevant scales. Conversely, commitment towards the osteo-chondral lineage was observed for softer gelatin-coated niches, highlighting the main role that the chemistry of the surface coating, combined with the geometry of the micro architectures, has respect to the mechanical properties of the coating in addressing stem cells differentiation while cultured in

The main objective of the second part of the present research was the design and realization of patterned functional surfaces for rare cells capture and isolation. Currently, biomolecular patterning is considered one of the key technologies for the realization of living-cell arrays and for the study of specific individual cellular processes instead of analyzing the behavior of a whole cell population, as for conventional cell-based assays. Among all the different kinds of proper chemicals, derivatives of hyaluronic acid and heparin were first chosen as baits due to their preferential interactions with cancer cells and malaria-infected red blood cells (pRBCs) respectively. Particularly, HA is involved in tumor growth and metastasis, while heparin is able to bind to the protein domain expressed by malaria-infected erythrocytes and their availability in well-defined positions offer the possibility to immobilize cancer cells and pRBCs and to make these cells available for specific tests and experiments thus encouraging the discovery and formulation of new drugs and therapies. A fundamental issue was the selection of the substrate material that deeply affects the final performance of the array. Best performing materials should avoid non-specific cells binding, thus perfluoropolyethers (PFPEs) were considered due to their wide range of properties including very low surface tension, which enhances PFPEs anti-fouling/fouling release properties. Different photocurable PFPEs were compared and deeply characterized to understand the possible relationship between their main structural parameters and their protein resistance behavior. PFPE-dimethacrylathes were selected as the most valuable candidates as substrate for HA and heparin selective patterning. To this end, photo-lithography and soft-lithography were developed and optimized as technologies to selectively functionalize PFPEs surfaces following different strategies. Particularly, free radical polymerization was exploited for glycidyl methacrylate modified HA grafting onto partially cross-linked PFPE surfaces by photo-lithography through photomask. Whereas, biomolecular recognition and strong specificity between avidin and other biotin-binding proteins was used for patterning. A photo-activable biotin was preprinted by μ–contact printing and UV-grafted onto partially cured PFPE substrate, then biotinylated-heparin was immobilized using avidin as intermediate linker. Preliminary cellular tests performed with cancer cells and malaria-infected red blood cells assess the capability of HA and heparin patterned PFPEs surfaces in selectively capturing individual population cells.



1. Confocal images acquired on GEL-SH-coated niche substrates seeded with MSCs and cultured for 14 days. Nuclei stained blue, collagen type-I stained red and actin stained green.



2. SEM image showing cancer cells adhering selectively on GMHA spot (a); optical microscope image showing malaria-infected red blood cells (staining violet) adhering on heparin (b).

CARBON NANOSTRUCTURES FOR ELECTROCHEMICAL ENERGY CONVERSION AND STORAGE APPLICATIONS

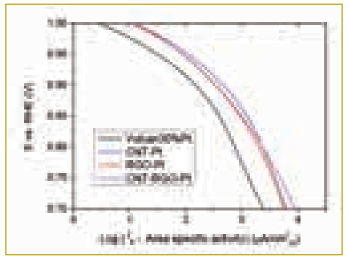
Mazdak Hashempour Igderi - Supervisor: **Antonello Vicenzo**

Tutor: **Massimiliano Bestetti**

In the current dissertation, under the general framework of "Carbon nanostructures for electrochemical energy conversion and storage applications", a range of activities with main focus on synthesis and electrochemical characterization of carbon nanostructured materials have been carried out. Accordingly, the thesis has been divided into three chapters and a summary of each activity will be presented in the following as the objective and results of a chapter.

(i) Chemical vapor deposition (CVD) direct growth of carbon nanotubes (CNTs) on stainless steel (SS) and their application for the bipolar plates of proton exchange membrane fuel cells (PEMFCs): in this part, a systematic study of the parameters affecting the direct growth of CNTs on SS was carried out and the suitability of the resulting material for working in electrochemical environments was investigated. CNTs were successfully grown on SS via a simple CVD method and without application of any external catalyst after fine tuning all the surface characteristics of SS as well as the growth parameters. It was found out that during the controlled atmosphere heating of SS up to CNT growth temperature, its surface undergoes nano–scale modifications and the type of the subsequently grown filamentous carbon shows a direct relation to the size of surface nano–features formed on SS substrate. CNTs were the dominant growth products where the average size of SS surface nano–features was below 60 nm. Due to the surface modifications of SS during the high temperature carbon–rich CVD treatment, a reduced corrosion resistance of the SS was found to occur. In particular, chromium depletion of SS due to chromium carbide formation and sensitization caused an infirm behavior of the material in electrochemical media, appearing in the form of intergranular corrosion. Accordingly, although problems such as high electrical contact resistance of bare SS in corrosive media (mainly due to passive oxide layer) were addressed, the CNT coating provided by this method was evaluated insufficient as a corrosion barrier in the electrochemical media such as bipolar plates of PEMFCs.

(ii) Investigation on different carbon nanostructures as the catalyst support of the PEMFCs: in this part, fabrication of Pt electrocatalyst supported on different carbon materials, namely, CNT, reduced graphene oxide (RGO) and hybrid CNT–RGO was demonstrated using a rapid and single step microwave–assisted polyol process, and the activity of Pt towards the oxygen reduction reaction (ORR) was studied on different supports. Due to direct relation of the abundance of defects on the support and Pt concentration and dispersion, a Pt nanoparticle (NP) size trend as follows was found on different supports: RGO–Pt < CNT–RGO–Pt < CNT–Pt. XPS studies, demonstrated a C/O ratio trend of the supports in the following order: RGO–Pt (7.26) < CNT–RGO–Pt (17.49) < CNT–Pt (21.32). The content of sp^2 carbon was also following the same trend. Area specific activity evaluation of the samples towards ORR showed a clear outperformance of all the lab-made samples compared to the commercial Vulcan XC72–30%Pt over the entire kinetic region. In particular, the specific activities of RGO–Pt, CNT–RGO–Pt and CNT–Pt samples at E = 0.90 V_{RHE}, were 2.25, 2.3 and 3.13 times higher than the commercial sample, respectively. Fig. 1 shows the Tafel plot of the specific activity in the kinetic region.

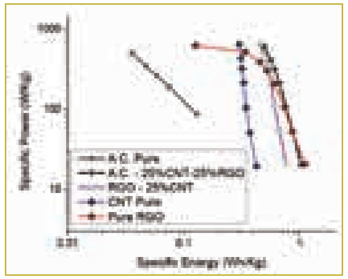


1. Tafel plot of the specific activity of Pt on different carbon supports in the kinetic region.

Regarding the mass specific activity, CNT–RGO–Pt support showed particularly high activity due to simultaneous benefitting from the conductivity of CNTs, and wettability and surface area factors of RGO. It was finally concluded that hybridizing the 1D and 2D support families (CNT– RGO), shared the features of individual components, so as to result at the same time in high area and mass specific activities.

(iii) Investigation on different carbon nanostructures as the active materials for the supercapacitors: the main focus of this part was on the electrochemical behavior of CNT, RGO and their composites as the active materials for supercapacitors, compared to activated carbon (AC) as the conventional material for this application. Supercapacitor electrodes were prepared in three main classes including AC–CNT, AC–RGO and AC–CNT–RGO. Using techniques such as cyclic voltammetry (CV), cyclic charge–discharge (CD) and electrochemical impedance spectroscopy (EIS), different characteristics of the supercapacitor such as specific capacitance (C_s), internal resistance (R_i), energy density (E_s), power density (P_s), relaxation time (τ_0) and lifetime were evaluated. C_s and E_s studies showed that the addition of conductive species (i.e., CNT and RGO) can improve a part of the deficiency of poorly conductive AC electrodes. Increased CNT contents could however, suppress the capacitance again due to the low specific surface area of CNTs. In AC–RGO class however, both C_s and E_s continuously increased by RGO content due to simultaneous improvement of conductivity and surface area. AC–CNT– RGO class, borrowing the conductivity from CNT and surface area from RGO, presented steadily high C_s and E_s. Studies on the rate capability, power performance, frequency response and internal resistance of the electrodes showed a superior behavior of pure CNT electrodes (a $\tau_0 = 0.19$ s, $R_i = 0.83\ \Omega$ and a $P_{s,\ max} = 22$ kWkg^{-1} at matched impedance condition) or those containing a high content of CNTs. Pure RGO (with a $\tau_0 = 6.31$ s, $R_i = 6.38\ \Omega$ and a $P_{s,\ max} = 5.6$ kWkg^{-1}) was behaving better that pure AC (a $\tau_0 > 100$ s and a $P_{s,\ max} = 4.1$ kWkg^{-1}) in this respect, but still more sensitive to rate compared to CNTs. Composite three component electrodes of AC–CNT–RGO class benefited from low ionic diffusivity resistance of mesoporous CNTs along with high surface area of RGO, presenting high rate capability and energy density at the same time ($\tau_0 \approx 1$ s, $R_i \approx 1.4\ \Omega$ and a $P_{s,\ max} \approx 10$ kWkg^{-1} steadily all over the range composition).

Fig. 2 shows the Ragone plot of different active materials, projecting the power densities available at certain energy densities.



2. Ragone plot of different carbonaceous active materials for supercapacitors.

FABRICATION OF CZTS/CZTSE THIN FILM SOLAR CELLS FROM ELECTRODEPOSITED METALLIC PRECURSOR LAYERS

Md Ibrahim Khalil - Supervisor: **Prof. Luca Magagnin**

Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) are promising absorber material for thin film photovoltaic devices due to their abundant constituent materials, suitable direct band gap ranging from ~1.0 eV (CZTSe) to ~1.5 eV (CZTS), large absorption coefficient over 10^4 cm^{-1} as well as theoretical conversion efficiency of 32%. Current commercial absorber material for thin film photovoltaic devices are CdTe and $Cu(In,Ga)Se_2$(CIGS) which contain earth rare and toxic materials. In this work, CZTS/CZTSe thin films were successfully prepared using an electrodeposition – annealing route, in which Cu-Zn-Sn metal precursors (co-electrodeposited/stacked layers) were deposited by a novel approach on Mo substrate, followed by annealing in elemental sulfur/selenium environment in quartz tube furnace with N_2 atmosphere. Different characterization techniques like XRD, SEM (EDS), Raman spectroscopy, GDOES, Photoluminescence spectroscopy and cross-sectional image have ensured the well formed Kesterite (CZTS/CZTSe) after sulfurization/selenization of the precursor. As investigation of the phase diagram of these materials show that only a small region (in terms of composition) is possible to make single phase CZTS/CZTSe. As a result, different precursor compositions of Cu-Zn-Sn ranging from Cu-poor, Zn-rich to Cu-rich, Zn-poor have been investigated. Results showed that Cu-poor, Zn-rich precursor (here, Cu/(Zn+Sn)≈0.91, Zn/Sn≈1.21) is best for getting single phase CZTS. It is well known by literatures that Cu_2ZnSnS_4 forms with solid state reaction of Cu_2SnS_3 and ZnS at high temperature. For this reason, it is very important to have homogeneous compositions of Cu, Zn and Sn on precursor before sulfurization. By using rotating horizontal working electrode, we have got almost mirror like surface (Ra ≈ 0.094 μm) with homogenous distribution of Cu, Zn and Sn from single electrolyte. In case of co-electrodeposited precursors, two different ramping rates (20°C/min. and 2°C/min.) during sulfurization at 550°C have been applied and it has been observed by XRD and SEM (EDS) that low ramping rate does not necessarily increase the grain size of the film rather create some secondary phases in the film as Kesterite is metastable. Moreover, formation of undesired MoS_2 was also observed in the XRD in case of 2°C/min ramping rate. Effects of different sulfurization periods (10 min, 30 min, 60 min and 120 min) at 550°C have been investigated. It was observed and confirmed by XRD, SEM (EDS) and Raman spectroscopy that in order to get good crystalline form of CZTS, longer sulfurization time (here, 120 min) at high temperature is needed. Raman spectroscopy is employed here as diffraction peak of Cu_2ZnSnS_4, Cu_3SnS_4 and ZnS are very close to each other. SEM (EDS) analysis show that composition of CZTS are very near to the stoichiometric ratio Cu, Zn, Sn and S. Cross-sectional SEM image show that CZTS possess bimodal distribution of grains: smaller grains are located near the interface of Mo and larger grains at the top of the CZTS which use to reported in literature. In order to make sure that the CZTS compound are intended for photonic application (i. e. solar cell) samples were characterized by Photoluminescence (PL) spectroscopy at low temperature (15K). A broad and sharp PL was observed at 1.21 eV in our studies, which has matched up with the existing literatures, as a broad PL band from CZTS compound at around 1.2 to 1.3 eV are found in many studies. GDOES analysis shows that the composition of Cu, Zn, Sn and S were not changed along the film thickness which confirms the formation of CZTS along the film thickness also. Moreover, the effect of intermediate annealing step (soft annealing) at comparatively low temperature (350°C) before sulfurization was also explored. It has been observed that by using soft annealing step, sulfurization time could be minimized to 10 min.

In case of CZTSe thin films also, different precursors of Cu-Zn-Sn with same compositions have been selenized at 550°C with different selenization periods (10 min, 30 min, 60 min and 120 min). XRD, SEM (EDS), Raman and Photoluminescence (PL) spectroscopy results showed that 60 min selenization is enough for the well formation of CZTSe without having any secondary phases. In case of CZTSe, a broad PL peak was observed at 0.94 eV at low temperature (15K) which is in good agreement with existing literatures.

After fabrication of CZTS/CZTSe, n-type CdS buffer layer was deposited by chemical bath deposition using cadmium acetate. Before depositing of CdS, CZTS/CZTSe films were etched by 3.5% KCN solution for 30s. A 80 nm intrinsic i-ZnO buffer layer, which acts as to prevent any shunts, was then deposited by RF sputtering. The TCO layer consisting of 350 nm Al-doped ZnO (AZO) was grown by DC pulsed (2 kHz) sputtering. Finaly, cells were completed by evaporating an Al grid contact on it.

A 0.6% efficient CZTS solar cell was fabricated on Mo foil substrate which is the first of this kind of solar cell on Mo foil (fig.1)

Fig.1: External quantum efficiency (EQE) of CZTS solar cell prepared from co-electrodeposited Cu-Zn-Sn precursor

Besides from co-electrodeposited Cu-Zn-Sn precursor, Kesterite-Cu_2ZnSnS_4 (CZTS) films were also successfully synthesized by using electrodeposition-annealing by using novel stacked layer approach. Adherent and homogeneous Cu-poor, Zn-rich stacked metallic Cu-Zn-Sn precursors with different compositions were sequentially electrodeposited, in Cu-Sn/Zn order onto Mo foils substrate. Subsequently, stacked layers were soft annealed at 350^{o}C for 20 min in flowing N_2 atmosphere in order to improve intermixing of the elements. Then, sulfurization was completed at 585^{o}C for 15 min in elemental sulfur environment in a quartz tube furnace with N_2 atmosphere. Here also different characterization techniques such as XRD, SEM (EDS), Raman spectroscopy, GDOES, Photoluminescence spectroscopy have confirmed the well formation of CZTS.

In addition to this, a sulfurized CZTS film was again selenized in order to form CZTSSe as record efficiency of this kind of solar cell are coming from CZTSSe thin film solar cell. The major XRD diffraction peak of CZTSSe was observed at 27.35°, 45.35° and 53.77° which are in good agreement with the literatures.

CATIONIC POLYMERS FOR THE DESIGN OF MULTIFUNCTIONAL GENE DELIVERY VECTORS

Chiara Diletta Malloggi - Supervisor: **Prof. Gabriele Candiani**

Gene therapy can be broadly defined as the introduction of genetic material, either DNA or RNA, into target cells in order to modify and control their protein expression. Offering new treatment possibilities for both inherited and acquired human diseases, in the last two decades, gene therapy has become one of the most intensively developing strategies for current clinical research. Direct administration of free oligonucleotides and DNA to cells is rather ineffective because of their large dimensions and their anionic charge that does induce repulsion with the negatively charged biological cell surfaces. Therefore, it is necessary to develop efficient and safe gene delivery systems able to protect DNA against degradation by nucleases and transfer the genetic materials to target cells. To date, the two main approaches for the delivery of genetic materials into cells are based on viral and non-viral vectors. Viral vectors are reported to be highly effective but they all share many critical disadvantages which strongly limit their clinical application, such as immunogenic and mutagenic issues, and the limited extent of the DNA they can carry. In light of these drawbacks and due to their high standards in terms of safety, versatility and easiness of use, non-viral vectors have been proposed as promising and safer alternatives.

Non-viral vectors for gene delivery are natural or synthetic materials which are positively charged at physiological pH. They spontaneously interact with the anionic nucleic acids and condense them into micro-and nano-scale particles, which protect the genetic material from degradation until they reach their targets. Unfortunately, despite the development of an extensive number of reagents, several issues still need to be solved, hindering efficient non-viral gene delivery.

In this scenario, the aim of my Ph.D. thesis was to address some of the unsolved issues in the gene delivery field, by developing, characterizing and/or optimizing some newly synthesized and commercially available cationic polymers.

With the aim to combine the high transfection efficiency of branched polyethylenimine (bPEI) with the biodegradability of chitosan, 2 kDa bPEI was grafted to the chitosan backbone, obtaining a series of seven chitosan-*graft*-bPEI copolymers with different degrees of grafting (Chi-*g*-bPEIx). Along the Chi-*g*-bPEIx series, the higher the degree of grafting, the greater the ζ-potential and the cytotoxicity of the resulting polyplexes. Among the copolymer series, chitosan-graft-bPEI with an intermediate grafting degree of 2.7% was the most effective transfectant and allowed for increased transfection efficiency and lower cytotoxicity than the gold standard polymeric transfectant 25 kDa bPEI. Most important, we demonstrated how the degree of grafting directly affects the surface charge, the transfection efficiency and the cytotoxicity of copolymer-based polyplexes. Moreover, in order to expand the understanding of the processes of gene delivery, a Chi-*g*-bPEIx copolymer was further characterized for its complexation behavior with time-resolved fluorescence spectroscopy in combination with SYBR Green I. Fluorescence amplitude and lifetime measurements during DNA-condensation by a Chi-g-bPEI copolymer, the building block 2 kDa bPEI and the gold standard 25 kDa bPEI highlighted polymer-specific DNA arrangements within the polyplexes. Dynamic time-resolved fluorescence measurements provided better insights into the process of polyplex formation and disassembly in the presence of anionic competitors. Some relationships existing among the optical behavior, the physicochemical properties and the transfection activity of Chi-*g*-bPEI-based polyplexes shed light on their superior transfection properties.

A family of three aminoglycoside-rich dendrimers, based on polyamidoamine dendrimer generation 4 (dPAMAM G4) linked to neamine, paromomycin and neomycin, was developed. Conjugation of dPAMAM with paromomycin and neomycin led to products with increased transfection efficiencies and lower cytotoxicities compared to the unconjugated dPAMAM. Moreover, dPAMAM G4-paromomycin and G4-neomycin, at their optimum N/P, displayed enhanced transgene expression also compared to the gold standard 25 kDa bPEI. Moreover, given the well-known antibiotic properties of aminoglycosides, dPAMAM G4-conjugates were tested whether they still possessed antibacterial activity, either alone or in combination with the plasmid DNA (pDNA). The conjugation of dPAMAM G4 to aminoglycosides greatly enhanced its antimicrobial activity. Moreover, the antibacterial properties of dPAMAM G4 derivatives were not influenced by their complexation with DNA.

Of note, dPAMAM G4-paromomycin and G4-neomycin were shown to efficiently transfect mammalian cells and to inhibit bacterial growth at once. Importantly, dPAMAM G4-paromomycin displayed the highest transfection effectiveness and prominent antibacterial activities, disclosing this polymer as very suitable for future *in vivo* applications.

Finally, aiming to study the correlation among the intrinsic properties of cationic polymers, the experimental conditions and the *in vitro* transfection outcomes, a systematic comparison of the most used commercially sourced polymers for gene delivery was carried out and the role of several important parameters affecting the transfection efficiency was evaluated. lPEIs, bPEIs, lPLLs, and dPAMAMs, differing in *Mw*, were characterized after complexation in terms of physicochemical properties and transfection behavior as a function of N/P and complexation buffer. Of note, 25 kDa lPEI complexed at N/P 40 in 150 mM NaCl was by far the most effective transfectant. Moreover, factors such as the composition of the culture medium, the order of mixing of the reagents, the transfection time, the dose of polyplexes delivered to cells, the cell seeding density, and the volume of culture medium were evaluated experimentally. Of note, the cytotoxicity was mainly influenced by the variation of the experimental conditions, and the pDNA concentration was revealed to be a key parameter in gene delivery. By optimizing the transfection parameters, we provided useful information on testing conditions for the *in vitro* screening of non-viral gene vectors.

In conclusion, my thesis shows that the integration of different moieties into a single transfectant is a promising approach to design new and more effective multifunctional systems, which join the advantages of their building blocks. The structure-activity relationship studies have established the correlations among the chemical structure of newly synthesized and commercially sourced polymeric gene vectors, the physicochemical properties of vector/DNA complexes and their biological activity, providing useful information for the rational design of more and more effective transfectants. Further advances in this area would require interdisciplinary approaches to understand the role of the vector chemistry, and the physicochemical properties of the vector/DNA complex, combined with mathematical modeling and fundamental studies of cellular processes.

YIELD AND POST-YIELD BEHAVIOUR OF SEMICRYSTALLINE POLYMERS: OPEN ISSUES OF PRACTICAL INTEREST

Nadia Perillo - Supervisor: **Prof. Claudia Marano**

This PhD thesis covers three different research topics in the field of science and technology of polymeric materials. They all have in common the fact that the knowledge of the yield and/or the post yield behavior is necessary for their analysis. Further, they all deal with semicrystalline polyolefins. In some cases a correlation between the macroscopic mechanical behavior of the semicrystalline polyolefins investigated and semicrystalline polymers main deformation mechanisms was attempted.

A study of the yield and post-yield behavior of syndiotactic polypropylene

The research activity aimed to the study of the mechanical behaviour of syndiotactic polypropylene (s-PP) started within a collaboration with the research group of Prof. De Rosa of the Chemical Science Department of Università degli Studi di Napoli "Federico II" which has performed a wide characterization of polyolefins structure since the '80s and more recently has focused on the study of the strain-induced crystal form transitions of s-PP. Considering the high strain recovery of s-PP when strained after being plastically deformed (i.e. strained above its yield point), they proposed the use of s-PP as a thermoplastic "elastomer". Within the collaboration with De Rosa's group the possibility to produce s-PP fibers or films with an "elastomeric behaviour" through the extrusion and cold drawing processes was considered. Indeed s-PP processing has not been faced in the research activity of this PhD thesis, which is mainly aimed to study the mechanical behaviour of s-PP in relation to the strain-induced microstructural transformations suggested by literature. A suitable experimental method was set up to overcome the necking effect which causes strain localization in a s-PP specimen during a tensile test: considering different zones of a single specimen as different specimens strained up to different strains, a larger amount of data from few tests was obtained and it was possible to investigate a wider strain range than that explored in literature. The effect of configuration regularity of s-PP on its yield and post-yield behaviour was examined considering three commercial syndiotactic polypropylenes having different stereoregularity index.

Material yielding in relation to the applicability of the Essential Work of Fracture method

The essential work of fracture (EWF) method is widely used to characterize the fracture behaviour of thin polymeric films whose application is mainly in plane stress conditions. It allows to obtain a material's specific fracture energy by performing fracture tests on several notched specimens (for example Double Edge Notched Tension DEN(T) specimens) differing in the cross-section width. The method is valid if the plane stress conditions prevail and there is not edge effect: the low thickness of the specimen and a notch length higher than a minimum value allow to satisfy both the conditions. In addition the method can be applied only if the yielding of the whole cross-section has occurred before crack onset. In this PhD thesis the latter hypothesis was verified, considering a HDPE, performing fracture tests on DEN(T) specimens. To determine the yield onset (stress and strain at yielding) loading-unloading tensile tests were performed up to different strains: through the back extrapolation of the permanent strain versus the applied strain the yield strain was obtained and the corresponding yield stress determined. The tests were performed under uniaxial and plane strain conditions and using DEN(T) specimens as well. While the yield stress resulted to be dependent on the loading conditions, the yield strain turned out to be fairly constant. This result suggests that the strain at yield onset in DEN(T) specimen can be obtained by the uniaxial tensile test which, using a standard specimen geometry deforming homogeneously up to yield, is more simple to perform. The hypothesis of yielding of the whole cross-section was verified for the studied material.

Assessment of long-term performance of isotactic polypropylene using short term tests

The experimental work related to this topic was performed during the six-months term period at Technological University of Eindhoven (TU/e) in the Netherlands. In the last decades polymers have been increasingly employed in the production of loadbearing component to be used also at relatively high temperature. Pipes for hot water and gas transportation are an example. They are commonly subjected to a fairly constant pressure for most of their service life. For such applications it is necessary to predict the pipe lifetime. Generally temperature accelerated creep tests are performed to build the hoop stress vs. failure time curve and eventually to predict pipe time-to-failure in correspondence of the applied hoop stress. These tests are expensive because timeconsuming. A method based on short-term tests to predict failure in the plasticity controlled regime is reported in literature. This method is based on the hypothesis that failure occurs when the increase in the non elastic strain component, which is in literature commonly named as "plastic strain", reaches a critical value and on the fact that the relation between the yield stress and the strain rate in a constant strain rate test is equal to the relation between the stress applied in a creep test and the corresponding strain rate in the creep steady state. The stress-strain rate relation can be easily determined performing short term constant strain rate tests. Time to failure for a certain value of the applied stress can be predicted once that the critical value of the plastic strain has been determined through a preliminary characterization of the yield and the creep behaviour of the material. The method has been set up for the characterization of amorphous polymers. Recently it has been extended to semicrystalline polymers. In this thesis the plasticity controlled failure of isotactic polypropylene was studied and data from creep tests on pipes were used for prediction validation.

PRESERVATION OF PLASTIC ARTEFACTS: MULTI-ANALYTICAL ASSESSMENT OF MATERIALS DEGRADATION AND DEVELOPMENT OF CONSERVATION STRATEGIES

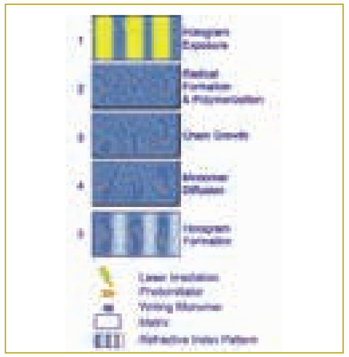
Daniela Saviello - Supervisor: **Prof. Lucia Toniolo**

Since their early production, plastics have been increasingly used to create artworks. Nowadays, a wide range of plastic objects is displayed in museums or private collections and artworks like sculptures or paintings, installations, toys, cinematographic and photographic films and collectable industrial design objects have become part of our cultural heritage. However, there is an increasing concern about the preservation of plastics in collections because such materials may have a short life expectancy, being much more susceptible to chemical degradation reactions.
Degradation mechanism can involve both thermal and oxidative processes, firstly during manufacture and then because of the usage, as objects are continually exposed to air, moisture, light and heat. Degradation does not entail only physical and chemical changes but may result also in loss in function, form or significance of the object, which can show deformation, shrinkage, cracking, surface deposits or discoloration.
For the preservation of plastic materials and artifacts, it is necessary to understand degradation patterns, assess condition and estimate risks. Therefore, there is a growing need for research activities that provide information on the chemical composition, the state of preservation and the effectiveness of conservation strategies.
This PhD project was designed in order to address some of these issues related to the conservation of plastic artefacts, which include the study of degradation processes of selected polymeric materials, the development of active conservation strategies and the improvement of a multi-analytical investigation protocol for the assessment of the conservation conditions. The study of degradation processes was carried out on five specific materials used in design objects and contemporary artworks of the 20th century, such as acrylonitrile butadiene styrene (ABS), poly(vinyl chloride) (PVC), polypropylene (PP), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). Accelerated photo-oxidative ageing was performed on specimens in order to simulate, in a suitably short time, the photo-oxidation of the materials in museum conditions.
A cutting-edge multi-analytical investigation, including spectroscopic techniques (with lab and Synchrotron equipment), optical and electronic microscopic observations and mechanical tests, was setup in order to fully investigate changes in the chemical and mechanical surface properties.
All the selected materials showed a surface degradation although with different extent and depths. Each aged polymer exhibited different products of oxidation due to the different pattern of ageing and in the same material different products of oxidation have been detected at different depths.
These chemical changes lead to surface cracking and strong yellowing of the specimen, mainly for ABS, PVC and PP.
Mechanical investigation was carried out with three different techniques such as scratch, micro- and nano-indentation tests that allowed the testing of materials to highlight the differences between unaged and aged samples at different depth scales.
The conservation strategies developed include cleaning treatments, to reduce the surface yellowing of aged materials and to remove surface deposits, and procedures for the introduction of specific additives in already manufactured objects, called “post-additivation techniques”. Agar gel was selected as cleaning agent while specific optical brighteners and plasticizer were selected for the post-additivation procedures.
The investigation protocol proposed in the PhD project provided the accomplishment of compositional analysis of the artworks and evaluation of the actual state of conservation.
The procedure included mainly microscopic observations and use of spectroscopic with the aims of identification of materials, surface morphology characterization and assessment of chemical, physical and mechanical properties of material surface and bulk.
Finally, a complete and extended portable FTIR spectroscopic campaig, was carried out on standard polymeric specimens and artworks from the collection of the Art Institute of Chicago; the obtained data allowed to build-up a very reliable database of total reflectance IR spectra, shared in the scientific community.

PHOTOACTIVE MATERIALS FOR ASTRONOMICAL HOLOGRAPHIC OPTICAL ELEMENTS

Alessio Zanutta - Supervisor: **Prof. Andrea Bianco -** Tutor: **Prof. Chiara Bertarelli**
Coordinator: **Prof. Chiara Castiglioni**

The progressive increase in telescope size and in complexity of the astronomical instrumentation has highlighted how the current technologies and traditional materials do not completely meet the present and future astronomical requirements. Therefore, new materials and solutions have to be developed not only to realise future astronomical facilities, but also to improve the performances of already available instrumentations. In this context, this research project deals mainly with the study of photoactive materials for the production of either refractive or diffractive holographic optical elements. In particular, attention has focused to Volume Phase Holographic Gratings (VPHGs) as reference diffractive optical elements, since they are considered nowadays the baseline for dispersing elements in modern astronomical spectrographs thanks to their high diffraction efficiency. Moreover, VPHGs can be used as a tool to determine the performances of holographic materials. Their working principle is based on the periodic modulation of the refractive index (Δn) in a thin film of photosensitive material having a uniform thickness (d). This modulation is usually induced by means of a holographic process. The light diffraction takes place through the thickness and the diffraction efficiency, which is one of the key properties in the astronomical field, directly depends on Δn and film thickness.



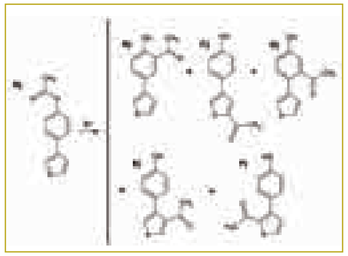
1. Mechanism of hologram formation in photopolymeric Volume Phase Holographic Gratings

The dichromated gelatin (DCG) is the common used holographic material, which provides high performances (especially in terms of Δn). However, it requires a complex developing process, its chemical composition is variable and it is highly sensitive to humidity. It turns out that there is a limited number of manufacturers of VPHGs for astronomy, which are located only in the US. Therefore, alternatives in term of holographic materials that overcome the drawbacks of DCGs while providing equal performances, are higlhy desired and the achievement provides a spin-off for economy in Europe.

We have found a good candidate in photopolymers, which is an important class of holographic materials that are becoming popular in visual art, anti-counterfeit and for displays. In the framework of a scientific collaboration for diffractive holographic elements for astronomy, Bayer MaterialScience and Polygrama Lynx provided solid and liquid acrylic-based photopolymers both green sensitive and panchromatic. Materials were characterised in terms of refractive index modulation as function of chemical composition, grating line density, and holographic writing conditions, i.e., light power density and exposure time. Moreover, transparency of the photopolymers before and after the exposure has been measured in the UV-Vis-NIR in order to determine the wavelengths range of use. The gratings based on photopolymers were tested at normal conditions and in cryogenic environment, and ageing resistance was also evaluated. Interestingly, the VPHGs based on the Bayer's materials showed constant performances at room and cryogenic temperatures for long time. VPHG dispersing elements for the AFOSC camera of the Asiago Telescope (1.82 m) and for the ALFOSC camera at the Nordic Optical Telescope (2.56 m) in La Palma (Canary Islands) were successfully designed and manufactured. All the elements were tested both at the laboratory level and on sky providing excellent results.

2. Astronomical dispersive elements designed and produced for the ALFOSC spectrograph at La Palma (ES)

Along with the main project on photopolymers, another important research activity concerned the study of a new class of materials that show a high refractive modulation upon exposure to UV light. Specifically, we focused our attention on the Photo-Fries rearrangement that occurs in aromatic esters. In literature, many polymers have been reported showing high Δn values. Nevertheless, a complete understanding of the mechanism leading to such a great variation still missed. By means of DFT calculations on reference molecules and applying a Lorentz-Lorenz model, polymers that undergo a photo-Fries rearrangement were studied to predict the refractive index modulation, which accompanies this light-induced process. The results demonstrated that a change in material density has to be considered the main source of the modulation of the refractive index. The change in material density was experimentally confirmed by measuring the spectral reflectance of thin films of polystyrene derivatives undergoing photo-Fries rearrangement. Such results provide useful guidelines to design polymers with enhanced refractive index modulation. Indeed, we recently designed new thiophene-based molecules that could be interesting candidates for a next generation of photo-Fries polymers.



3. Photo-Fries rearrangement scheme of one of the synthesized and studied molecules