MECHANICAL ENGINEERING | PHYSICS | PRESERVATION OF THE ARCHITECTURAL HERITAGE | SPATIAL PLANNING AND URBAN DEVELOPMENT | STRUCTURAL SEISMIC AND GEOTECHNICAL ENGINEERING | TECHNOLOGY AND DESIGN FOR ENVIRONMENT AND BUILDING | TERRITORIAL DESIGN AND GOVERNMENT | AEROSPACE ENGINEERING | ARCHITECTURAL AND URBAN DESIGN | ARCHITECTURAL COMPOSITION | ARCHITECTURE, URBAN DESIGN, CONSERVATION OF HOUSING AND LANDSCAPE | BIOENGINEERING | BUILDING ENGINEERING | DESIGN | DESIGN AND TECHNOLOGIES FOR CULTURAL HERITAGE | ELECTRICAL ENGINEERING | ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY | ENVIRONMENTAL AND INFRASTRUCTURES ENGINEERING | INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING | INFORMATION TECHNOLOGY | INTERIOR ARCHITECTURE AND EXHIBITION DESIGN | MANAGEMENT, ECONOMICS AND INDUSTRIAL ENGINEERING | **MATERIALS ENGINEERING** | MATHEMATICAL MODELS AND METHODS IN ENGINEERING

PhD Yearbook | 2016

DOCTORAL PROGRAM IN MATERIALS ENGINEERING

Chair:
Prof. Chiara Castiglioni

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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SOLUTION-PROCESSED METAL OXIDE LAYERS FOR PHOTOVOLTAIC AND PHOTONIC APPLICATIONS

Eduardo Aluicio Sarduy

Supervisors: Prof. Francesco Scotognella, Dr. Mario Caironi, Prof. Panagiotis E. Keivanidis

The use of metal oxides in optoelectronic and photonics has been rapidly growing during the last decades due to their appealing electronic structures, optical and electrical properties. In the particular case of organic photovoltaics (OPVs) its use as carrier-collecting layers or electrodes has improved the device performances and the stability issues due to moisture and oxygen interaction, making this technology a good candidate for large scale solar energy harvesting. In addition, the achieved reduction of the electric power demand of small electronics has opened to OPVs a wide range of low-power electronics niche applications (indoor applications) such as remote sensors, powered radio-frequency identification (RFID) systems, remote displays or portable consumer smart devices that may operate from a battery charged from an OPV cell. Besides their potentialities as carrier transport layers, they can be also used for light management like in the case of photonic crystals. The engineering of the different metal oxides layers of the photonic crystals makes possible the control of their properties allowing its use for OPVs applications and many others fields such as sensors, lasing, and optical switches. However, in all of these cases, the real commercial applicability of these new technologies will be determined, among others, by the materials price and the scalability of the production to the industrial fabrication lines that can allow large area deposition of flexible and light-weight modules. In order to overcome these problems, the development of these metal oxides as carrier-collecting layers or for photonic crystal fabrication must be based on solution-processed protocols of earth-abundant materials, compatible with the large scale sheet-to-sheet (S2S) or roll-to-roll (R2R) deposition lines that is already available in the industrial sector. For this reason, we have used the sol-gel technique for the synthesis of metal nanoparticles as precursor materials for the fabrication of metal oxides interlayers in OPV devices and one-dimensional photonic crystals (1DPCs). Materials such as ZnO, TiOx, WO3, MoO3 and V2O5 were synthesized. Subsequently, the corresponding thin films were realized by different deposition techniques and by using different processing conditions. These sol-gel based metal oxides were investigated for three main applications. First, for the fabrication of OPV devices using low cost non-fullerene electron-acceptor materials such as perylene-diimide (PDI) derivatives. The use of ZnO as electron collecting layer has allowed the elucidation of the role of the device architecture on the performance of these fullerene-free solar cells, resulting in a significant improvement of the power conversion efficiency up to 3.7%. Secondly, for the fabrication of scalable OPV architectures that can be integrated in modules. The inkjet printing compatibility of these solution-based metal oxides has allowed the fabrication of easily interconnected modules with higher geometrical fill factor that can be used for outdoor and indoor uses. Lastly, for the fabrication and tuning of the optical properties of 1DPCs with potential uses as back reflectors in OPV, electro-optical switches, sensing and photoluminescence applications. A bias induced tuning of the photonic band gap was demonstrated by using metal nanoparticle/metal oxide bilayers as building blocks for the photonic crystal fabrication.

NEW FORMULATIONS AND PROCESSES FOR CERAMIC LAYERS DEPOSITION ON COMPLEX GEOMETRY SUBSTRATES

Riccardo Balzarotti - Supervisor: Prof. Cinzia Cristiani
Tutor: Prof. Marta Rink

In this thesis work, new formulations and processes for structured catalyst production have been developed. A structured catalyst is a multifunctional object which allows to reach the target of process intensification. Its structure can be divided into three main components: the catalytic active phase, which is directly responsible of reduction in process activation energy, the morphologic support, which increases active phase content per unit volume, and the geometric support, which provides three-dimensional structure to the object.

In literature, many methods are available in order to deposit active phases on structured supports. The active phase can be directly deposited either onto support surface (i.e. incorporation) or onto a high surface area carrier (i.e. coating). The latter, is a very popular solution that allows to enhance catalytic properties. A variety of procedures are available in order to produce a catalytically active powder. Among others, incipient wetness method allows to easily manage active phase quantity and to produce highly dispersed metal phases.

In order to obtain good catalytic performances, a thin catalyst layer (tens of microns) have to be deposited onto structured supports surface. In order to that, dip-coating process from a slurry is widely considered as the best compromise among cost, time and effectiveness. Usually, support surface is pretreated, both thermally or chemically, in order to enhance coating to surface interactions. After slurry deposition, a sequence of subsequent thermal treatment steps is necessary in order to obtain the final product.

Many parameters needs to be carefully tuned to properly manage washcoating process. Slurry rheology plays a key role in order to produce thin and well adherent washcoat layers on support surface. As a matter of fact, low viscosity slurries usually lead to low loads and high adhesion, while high viscosity formulations promote high washcoat load but poor adhesion. Rheological properties can be modified by acting on formulation components, such as binder, dispersant, solvent and a properly sized powder.

Usually, acidic solution are used in order to obtain stable dispersions. Powder surface is covered by H$^+$ ions and, thus, stability is achieved by surface charging. Unfortunately, this method is not effective both in case of low surface area and chemically inert powders. Moreover, some active phases or supports may be altered in case of acidic solution. For these reasons, many organic compounds have been tested in order to properly stabilize catalyst powder dispersions.

The purpose of this work is to develop an acid-free liquid medium in order to avoid acidic solutions issues and to obtain a stable powder dispersion. The latter will be used for washcoat deposition onto complex geometry substrates, such as open cell foams and monoliths.

After a comprehensive introduction regarding structured catalysts and depositions techniques, in the first part of the research activity, a formulation study has been carried out, in order to stabilize carrier powder dispersions (i.e. cerium oxide and zirconium oxide). Resulting slurries have been used in order to perform preliminary washcoat depositions on ceramic open cell foams and monoliths, by means of a self-assembled dip-coating device. The influence of slurry viscosity, support morphology and procedural parameters (i.e. withdrawal speed and thermal treatments) has been investigated and good results have been obtained in terms of washcoat homogeneity. Then, model catalytic powders have been produced using nickel oxide and cobalt oxide, as active phase precursors, and zirconium oxide, as carrier. An attempt to correlate powder properties, rheological behavior and washcoat properties was made.

The same formulation and procedure was validated from the catalytic point of view, by depositing nickel and nickel/rhodium-based catalysts on ceramic open cell foams and monoliths. In all cases, good washcoat properties have been demonstrated, as well as satisfactory results in terms of catalytic activity.

Although dip-coating has been proved to be an easy-to-use technique for catalyst production, some limitations have been found. In particular, pore clogging and low adhesion have been recorded, in some cases. In order to overcome these problems, spin-coating has been evaluated as alternative deposition technique. The latter was studied using model water/glycerol solutions at various viscosities. Moreover, the influence of operative parameters (i.e. rotation speed, time, support morphology and size) has been investigated. Finally, cerium oxide was deposited onto 20, 30 and 40 PPI metallic open cell foams; excellent results have been obtained, both from the load management and washcoat adhesion points of view. For these reasons, spin-coating has been identified as a candidate for dip-coating substitution in washcoat deposition procedures.

SYNTHESIS AND CHARACTERIZATION OF HYBRID AND POLYMER BASED COATINGS WITH ACTIVE BARRIER PROPERTIES

Elisabetta Bossi - Relatore: Luigi De Nardo

The packaging industry has always been a fundamental support for most production fields. This thesis deals with barriers for food packaging and for electronics device encapsulation. Firstly, an overview about the studied different applicative fields is supplied, where basic degradation phenomena and possible solutions for each application were introduced and discussed. One of the main causes of food spoilage is oxygen, involved, for example, in oxidative stress or in proliferation of some aerobic bacteria. Thus, among active packages, those with antioxidant properties raise great interest for elongation of food shelf-life. In this work, the sol-gel process was employed for the preparation of coatings, which can release natural antioxidants, vitamin E (α-tocopherol) and vitamin C (ascorbic acid). The formulated sols were hybridized using organic-inorganic hybrid precursors. The organic component in the system made it possible to prepare flexible coatings on polyamide/polyethylene laminates and enabled the encapsulation of liposoluble molecules, like vitamin E. The use of aggressive acids or toxic solvents was avoided. Three formulations based on the precursor tetraethoxysilane (TEOS) were optimized with phenyl and methyl silicates, in aqueous solution. PA/PE laminates were dip-coated and the coatings thickness, roughness, composition, and antioxidant capacity were characterized. The latter was studied by FRAP test, an essay exploiting the reducing activity of antioxidant as promoter of reduction of a ferric complex to a coloured ferrous complex. The coatings showed efficacy, especially the one containing both the antioxidants. The antioxidant efficacy was verified after months of storage in the dark. The research concerning electronics device encapsulation was mainly performed by SAES Getters S.p.A. Corporate Labs. Two different adhesive formulations were optimized for use in multilayerd ultra-high barrier. This technology is enabling for organic devices encapsulation. Indeed, a limit for commercialization of organic electronics devices is their sensitivity to oxidizing agents, mainly water. Therefore, the adhesives must contain active components addressing water scavenging. Taking into account the polymer organic chemistry of the substrates, mild curing conditions, transparency, flexibility, and good adhesion are needed. The adhesives matched the requirements laid down by device process preparation and encapsulation, a roll-to-roll process. The process requires tuneable viscosity and fast curing. The optimized adhesives were an epoxy-based nanocomposite and an acrylic adhesive with active properties, addressing moisture sorption. The epoxy nanocomposite and the acrylic adhesive preparation and characterization were described. Nano-zeolites were characterized and used in epoxy-based nanocomposite. Functionalized nano-zeolite dispersion was achieved by a high-pressure homogenizer. Because of the complexity of obtaining an optimal dispersion in the epoxy/zeolite system, a deepening about the processes used for dispersion achievement and characterization is supplied. The importance of this topic is due to the growing employment of the nanocomposites: nanoparticles dispersion is a hot topic, indeed, the traditional mixing methods for micro-composites must be adapted or overcome in nano-dispersed systems. The experimental validation protocol of the nano-dispersion consisted of electroscopic analysis (SEM), rheological analysis, and size analysis based on the laser obscuration method. The techniques agreed, showing improved dispersion by employing the homogenizer. The acrylic adhesive active component is a hygroscopic salt. The acrylic resins are particularly suited for the intended application, thanks to their flexibility and transparency, but the adhesive properties and the viscosity must be optimized. Firstly, an initiator was selected. Secondly, a co-polymer was used to tune the viscosity and to increase adhesive properties. The adhesion properties were verified by peel test. An adhesion promoter and a catalyst contributed to the adhesion improvement. The sorption capacity of the hybrid adhesives was studied, in different configurations, by gravimetric measurements. Other features of the modified organic adhesives were analysed, for instance the wettability on polymer substrates.

NOVEL NANOMATERIALS TO TREAT GLOMERULAR DISEASES OF THE KIDNEY

Riccardo Bruni - Supervisor/Relatore: Francesco Cellesi

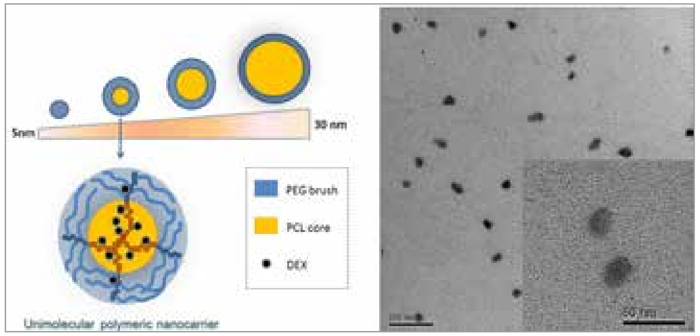
This PhD Thesis work aimed to develop novel nanomaterials directed to treat glomerular diseases of the kidney, which represent a major health problem worldwide. The project explored the use of new drug-loaded polymeric nanocarriers and their targeted delivery to the kidney glomerulus and in particular to podocytes, in order to overcome the failure of current therapeutic regimens in patients with proteinuric diseases. The most significant challenge was to develop colloidal nanomaterials which are able to cross the glomerular filtration barrier (GFB) in order to target podocytes. The barrier, a three-layer structure composed by fenestrated endothelial cells, podocytes and a basement membrane in between, possesses in healthy conditions an effective size cutoff of 6-10 nm, i.e a size which is generally too small for the permeation of many proteins and biomedical nanoparticles. Our synthetic approach focused on the design of ultrasmall polymeric nanocarriers (<30nm) to assess whether such carriers are able to permeate through the glomerular barrier, which is also expected to increase its size cut-off under pathological conditions. Ultrasmall colloidal nanomaterials were successfully synthesized from biodegradable hydrophobic multi-arm polyesters (i.e. poly(ε-caprolactone)) copolymerised with comb-like poly(ethylene glycol) (PEG), which serve as a dense hydrophilic corona. The main outcomes of this work can be summarised as follow:

a) A library of multiarm amphiphilic polymers were synthesized by Atom Transfer Radical Polymerisation of PEG-methacrylate, starting from commercial 4-Arm ATRP initiator as well as custom-made multiarm poly(ε-caprolactone) (PCL) macroinitiators. When needed, a fluorescent monomer (rhodamine methacrylate) was also copolymerized to obtain traceable materials for biological tests. ATRP kinetics and molecular weight distributions of the synthesized polymers were investigated in order to identify optimal reaction conditions (solvent, catalyst, ligand, concentrations, temperature) for the controlled polymerisation, in order to obtain nearly monodisperse polymers.

b) These polymers were characterized by NMR, IR and GPC analysis in order to identify composition, molecular weight and polydispersity. Dispersions in water and physiological buffers were analyzed by Dynamic Light Scattering (DLS) to assess average size and size distribution. A subset of polymers which present optimal physicochemical properties was identified and further used for biological tests. In particular, unimolecular carriers of target size <30nm (i.e. compatible with kidney filtration) were selected.

c) In vitro tests on podocytes were carried out to assess polymer cytotoxicity, damage on cell cytoskeleton with consequent morphological changes, and uptake. In vivo tests on healthy and proteinuria-induced mice were carried out to analyse material biodistribution following intravenous administration. The selected polymers showed a biocompatible profile, and the ability to cross the kidney glomerular barrier, depending on the extent of kidney damage.

d) A hydrophobic drug, dexamethasone, was successfully encapsulated in the nanoparticle core and release profiles were analysed under sink condition.

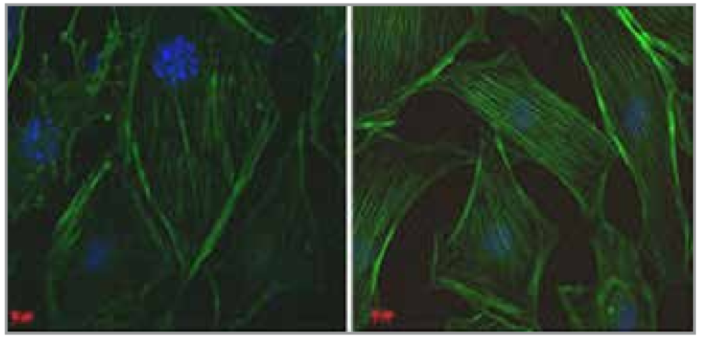


1. Left) Four-arm star-shaped polymers, with/without a hydrophobic PCL core and a brush-like PEG hydrophilic shell, form stable ultrasmall colloidal nanomaterials which are able to encapsulate and release dexamethasone and to cross the glomerular filtration barrier. Right) TEM image of a polymeric nanocarrier (A4CL10PEG20, scale bar 100nm). Inset: details of the nanocarriers at higher magnification (scale bar 50 nm).

Damaged podocytes were successfully repaired by controlled nanodelivery of dexamethasone, in view of developing new kidney-specific nanotherapeutics.

The marked efficacy of these drug-loaded nanocarriers in repairing damaged podocytes, together with their capacity to cross GFB may pave the way for developing a cell-targeted administration of new and traditional drugs in chronic kidney diseases, increasing efficacy and limiting side effects.

Furthermore, we attempted to increase the number of arms and branching in the macromolecular architecture, in order to enhance drug loading and release, while maintaining a ultrasmall particle size. A new class of hyperbranched block copolymers, composed of a hydrophobic brush of poly(ε-caprolactone) and a hydrophilic brush-like shell of poly(ethylene glycol) was successfully synthesized. These macromolecules form stable ultrasmall nanocarriers in aqueous suspensions. According to DLS analysis, a set of polymers with a hydrodynamic diameter between 18 and 30 nm (in PBS buffer at 37 °C) were obtained, and we expect that these nanomaterials would be able to encapsulate a relatively large amount of hydrophobic drug, such as dexamethasone, while maintaining a small hydrodynamic diameter.



2. A) Podocytes were treated with adriamycin to mimic cell damage in vitro. B) 48hr treatment with A4CL10PEG20 nanomaterial (20 µg/mL) loaded with dexamethasone (7%wt); cells partially recovered the normal orientation of actin stress fibers.

Finally, we explored an active targeting approach, by designing engineered polymeric nanoparticles conjugated with a cyclic RGD peptide, in order to target the endothelium of the kidney, accumulate into the glomerulus, and therefore release drug in close proximity to podocytes. Nanoparticle-peptide conjugation was successfully carried out by using a Michael-type addition. RGD-conjugated nanoparticles were able to interact with endothelial cells in vitro.

Future studies will be directed towards the functionalization of ultrasmall polymeric nanocarriers with ligands (peptides) which are highly selective in targeting glomerular endothelial cells and/or podocytes. A variety of different drugs, such as immunomodulators (Cyclosporin A) and ACE inhibitor, could potentially be investigated as payloads and used as alternative to dexamethasone for podocyte treatment.

IN-SITU MECHANICAL CHARACTERIZATION OF DEFORMABLE METAL/POLYMER ELECTRICAL INTERCONNECTS

Emanuele Cattarinuzzi - Supervisor: Prof. Pasquale Vena

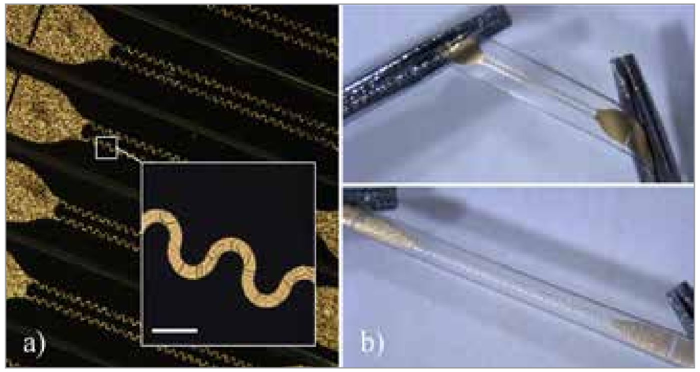
A stretchable metal interconnect is a key ingredient to ensure electrical continuity in a matrix of rigid sensors spread onto a deformable substrate. Enabling distributed measurements over complex and moving surfaces, this technology is attractive for many application fields, namely wearable energy storage devices and continuous healthcare monitoring.

Most frequently, stretchable interconnects consist in thin metal films deposited on compliant polymeric substrates and patterned in a meandering fashion (Figure 1.a): as a consequence, large strains can be accommodated by in-plane and out-plane distortions of the serpentine structure, while the underlying compliant substrate prevents strain localization and related ductile metal failure.

Functional reliability of stretchable interconnects, then, dramatically relies on the mechanics at the characteristic length scale of the meander (~100μm) and the metal film (~100nm). This project was devoted to the identification of suitable combinations of mechanical testing and imaging techniques to gain insights on the local mechanics of stretchable interconnects.

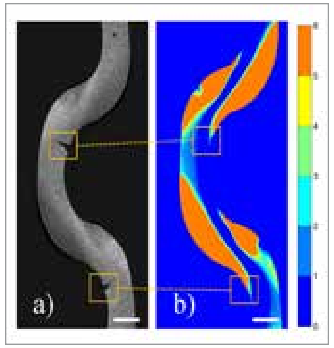
Stretchable interconnect samples were fabricated by the Microsystems Technology unit (MST, Fondazione Bruno Kessler, Trento, IT). Two different metal/polymer systems were addressed: 1μm-thick Aluminum (Al) film evaporated onto 10μm-thick spin coated Polyimide (PI) and 100nm-thick Gold (Au) film evaporated onto 100μm-thick spin coated Polydimethylsiloxane (PDMS). In both cases, the polymeric surface was activated by O$_2$-plasma treatment at 80°C and 200W (exposure time: PI, 80s; PDMS, 15s) right before metal deposition, in order to enhance the metal/polymer adhesion. The meandering pattern was defined by lift-off for the Al/PI samples and wet-etching for Au/PDMS. Different shapes were obtained varying the width (W=[10-50μm]), the inner radius (R=[10-40] μm) and the amplitude (A=[60-270] μm) of the metal track, so as to investigate the influence of the meander shape on the local mechanics. The overall in-plane dimensions of each sample were in the range of 2x15mm (Figure 1.b).

Three laboratories were involved in the experimental activities: the Laboratory of Biological Structure Mechanics (LaBS) and the Service for Microstructural Analysis of Materials (SAMM) at Politecnico di Milano (PoliMI, IT) and the Multiscale Lab at the Eindhoven University of Technology (TU/e, NL). Micro-tensile testing was combined with in-situ optical microscopy (OM), scanning electron microscopy (SEM) and confocal laser scanning microscopy (CSLM) to investigate the behavior of samples upon uniaxial stretch.



1. (a) example of meandering metal/polymer interconnect for stretchable electronics. In the inset, the length of the scale bar is 100μm; (b) deformable interconnect sample upon stretch.

Electromechanical testing of Al/PI interconnects did show that the Al film remained conductive (although free-standing, as testified by in-situ OM) even after polymer failure, suggesting the mechanical reliability issues of Al/PI interconnects to be mainly related to metal/polymer delamination. Indeed, a relatively poor toughness was measured for the Al/PI interface (~100 J/m^2) by means of 90° peel tests combined with in-situ SEM imaging. Interestingly, in-situ CLSM analysis revealed an interplay between delamination, buckling and fracture (Figure 2.a), enabling to quantify the extent of delamination based on the measured out-plane lift of the metal film. According to the delamination maps (Figure 2.b), metal fracture develops where delamination meets a stretched metal film region, suggesting that fracture is triggered by strain localization in the metal film, made free-standing by delamination.



2. (a) reflected intensity image of an Al/PI interconnect at 50% strain; (b) corresponding delamination map, where blue to orange indicates ascending chance of delamination. Orange boxes highlight the correspondence between the region of fracture and the delamination front. The length of scale bars is 50μm.

Matching results by functional- (i.e., electrical) and mechanical reliability- (i.e., in-situ CLSM) tests, a comprehensive comparison and rating of different meandering geometries was enabled.

In-situ CLSM of Au/PDMS samples upon uniaxial stretch revealed extensive cracking of the PDMS surface at moderate applied strains (5%), which involved the metal track causing functional failure. The observed embrittlement was attributed to the harshness of the O$_2$ plasma treatment, which can cause the PDMS surface to turn into a porous silica. The latter phenomena was investigated exploring three different combinations of two significant plasma treatment parameters, namely, radio-frequency power and exposure time. Uniaxial stretch with in-situ CLSM of PDMS samples (i.e., no Au film was deposited) revealed that the embrittled PDMS layer featured an alternation of two different bands: (a) transverse cracks, exposing the underlying compliant PDMS and (b) embrittled regions, undergoing well ordered buckling instabilities. Having recognized the periodic nature of both phenomena, the use of spectral analysis of topographic images was proposed in order to monitor the evolution of both (a) the crack density and (b) the wavelength and amplitude of the buckling patterns. When modeling the embrittled PDMS skin as a stiff film on a compliant substrate by means of existing analytical models, results by the spectral analysis provided the opportunity to cast arguments on the rate of thickening and stiffening of the embrittled PDMS layer in relation to the plasma treatment parameters. The observed trend was consistent with the literature.

To conclude, the combination of mechanical testing and in-situ imaging has been proposed as a relevant method to assess and characterize the reliability of deformable metal/polymer interconnects. Addressing two specific case studies, it was shown that both (i) the interconnect design and (ii) the fabrication process can be reviewed based on the local mechanics, to which the sole functional (i.e., electromechanical) characterization has no access.

FIRST PRINCIPLE MODELLING FOR THE PREDICTION OF THE STRUCTURE AND THE SPECTROSCOPIC RESPONSE OF MOLECULAR MATERIALS

Daria Ruth Galimberti - Relatore: Alberto Milani

Molecular and polymeric materials are now an unavoidable ingredient of the everyday life, playing a major role in building the world as we know it. Despite their well-assessed employments, pure and applied research and technology are still focusing deeply on polymers, providing innovative applications in several fields, ranging from nanotechnology to design, from physics to biomedicine. The development of novel systems is indeed very active, as continuously demonstrated by the scientific literature and by new relevant industrial outcomes.

The molecular nature is of this wide family of materials determines a close correlation between the properties of the materials - at the macroscopic scale - and the material structure at the atomic, mesoscopic and microscopic scale. The close dependence of the properties from the phenomena occurring at the molecular scale allows, in principle, to tune the macroscopic behaviour through a rational design of the nano, micro and mesoscopic structure. Acting on these scales requires a deep knowledge of the molecular and supramolecular architecture of the material and how this architecture can affect the physicochemical properties.

Therefore, an investigation at the molecular scale becomes crucial in the development of new nanostructured molecular materials (such as for example polymeric nanofibers, nanocomposites, hybrid organic-inorganic or biomaterials) and requires appropriate characterization techniques.

In this thesis, we explored the potentialities and the reliability of different state-of-the-art computational techniques for the investigation of the structural and vibrational properties of complex macromolecular materials. In particular we wanted to verify if some powerful computational tools, seldom adopted in polymer science, could be employed to make a further step in quantum chemical modelling of polymeric materials, also in connection with practical, technological issue. In this context, the work focused on three interconnected topics i) the application of periodic Density Functional Theory (DFT) calculations through the CRYSTAL code to crystalline polymers for investigation of their structural and spectroscopic properties; ii) the development of theoretical models to investigate the molecular charge distribution by means of Equilibrium Charges and Charge Fluxes; iii) the application of First-Principles Molecular Dynamics (FPMD) simulations for the computation of the spectroscopic response of both small molecular systems and polymers in condensed phase. In particular we adopted Born-Oppenheimer MD as implemented in the CP2K code. An unambiguous and very accurate description of the molecular properties of these materials has been obtained, showing, in particular, that DFT calculations can be applied confidently to support, complement and interpret the experimental data and to characterize in details complex molecular phenomena.

The understanding of the structure-properties correlations, the behavior of the material also in terms of its macroscopic properties and the rationalization of physicochemical effects, require a molecular perspective which is completely fulfilled by our computational approach.

In such a perspective intra- and intermolecular effects can be analyzed in details and connected to macroscopic properties, such as for example the polymorphism of even nylon or the mechanical-induced transitions in Poly(butylene terephthalate).

As a first outcome, our work demonstrated that DFT periodic calculations are a mature, well establish and reliable technique, whose importance extends also to technological applications.

On the other hand, a dynamical approach by means of FPMD simulations would pave the way to a countless number of applications in the field of polymer science and characterization.

Our investigation moved the first step in this direction, even if in the case of FPMD there are still many open issues to be solved. However our results show that FPMD start to be an intriguing choice for material scientists. In particular the possibility of taking into account external variables (e.g. temperature, pressure...) is promising for future applications.

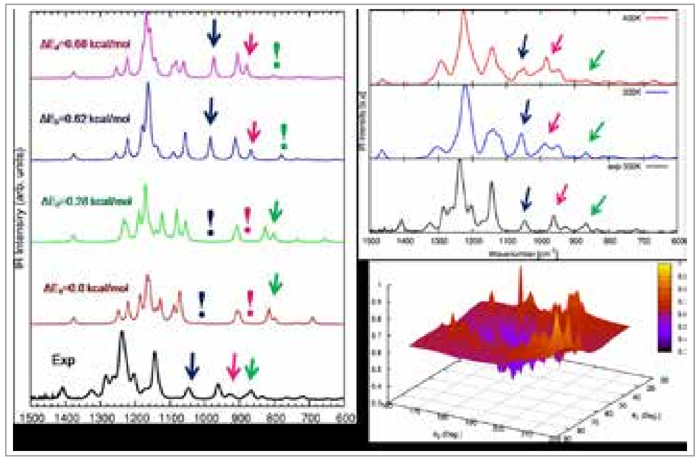
In this context, we explored the application of this technique to molecular systems almost never approached before with FPMD, proposing some strategies to overcome the current limitations.

The significance and the outcomes of this thesis are two-fold. In the context of fundamental research we verified the potentialities of new methods and simulations tools never applied in some fields of material science, such as polymer science and characterization. These tools allow the description of some molecular properties (e.g. solid state packing, environmental effects...) which are mandatory to understand the behaviour of materials and which cannot be investigated by usual computational approaches.

On the other hand, our results open many perspectives in applied research and technology: quantum chemical calculations are finding more and more importance in the industrial environment for their ability to give a detailed interpretation of the experimental data, but also for possible design purposes. Indeed, the use of computational techniques to give a *priori* information for the design of new materials, is not only a future hope but a reality.

Due to the importance of a correct characterization of the material for practical purpose, we clearly demonstrated that only though the computational methods here adopted we have been able to give unambiguous and complete investigations of the response of the materials, showing that proper molecular simulations are mandatory to investigate complex or new materials. Moreover, the high accuracy and reliability obtained, surely make these quantum chemical methods a possible design techniques of pilot studies of new materials, avoiding more cost time expensive experimental explorations.

We believe that this thesis will have outcomes extending to many practical applications in current technology, paving the way to the daily employment of quantum chemical modeling in chemical and materials engineering.



1. Conformational effects on the IR spectrum of $ClCF_2CF(CF_3)OCF_2CH_3$ molecule: Static vs Dynamic DFT modelling

NANO-STRUCTURED COATINGS FOR STONE AND PAINT SURFACES OF CULTURAL HERITAGE

Francesca Gherardi - Supervisor: Prof. Lucia Toniolo

Soiling of Cultural Heritage in urban areas is mainly due to the accumulation of pollutants, which can contribute to the formation of thick deposition and black crusts, affecting the buildings from both aesthetical and chemical point of view. In the last decade, considerable scientific efforts have been devoted to the preparation of innovative self-cleaning treatments, based on dispersion of photoactive TiO_2 nanoparticles, able to decompose organic and inorganic pollutants deposited on the surfaces. The use of photocatalytic materials can lower maintenance costs for restoration and cleaning, by reducing soiling accumulation. However, the efficiency of these systems is limited, due to their poor light absorption in the VIS range and to nanoparticles aggregation and/or precipitation phenomena, which lead to non-homogeneous and whitish films. Thus, the development of solar-light activated treatments containing homogeneously dispersed TiO_2 nanocrystals, which at the same time are able to maintain their peculiar photocatalytic properties when deposited and to preserve the original aesthetic of the surfaces, remains an open challenge.

The general aim of this project was the set-up of formulations of protective treatments for stone and paint materials of Cultural Heritage, modified by appropriate photocatalytic TiO_2 nanoparticles.

The selected TiO_2 nanoparticles have been prepared following the synthesis proposed by Niederberger to produce highly transparent nanostructured pure phase anatase, covered by residuals of benzyl alcohol, anchored on the surface. Thanks to this surface capping, the obtained dispersions are photo-active not only under UV-light but also under solar light irradiation. Moreover, the proposed nanoparticles allow to obtain highly stable dispersions in aqueous systems, both respecting important safety and green chemistry requirements and preserving the aesthetical compatibility with the substrates on which they are applied.

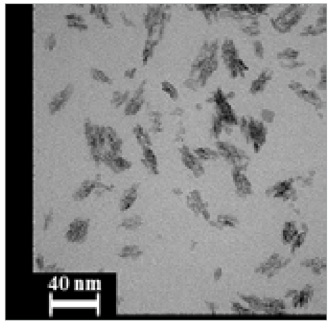
The good results in terms of optical properties, transparency and nanoparticles dispersion in aqueous solvent of nanocomposites based on dispersions of nano-TiO_2 and hydrophilic poly(2-ethyl-2-oxazoline) (commercially available Aquazol 200®) for the consolidation of matte painting layers for contemporary artifacts, allowed us to deepen their possible application for the development of photocatalytic treatments for stone surfaces.

Initially, water and ethylene glycol nano-TiO_2 dispersions with different nanoparticles concentration were studied and their effectiveness after the application on two lithotypes (Noto stone and Carrara marble) was evaluated. The efficacy of new treatments was compared with that of water dispersions of commercial TiO_2 nanoparticles (TiO_2 P25, Evonik AEROXIDE®). Compared to commercial nano-TiO_2, the proposed new dispersions showed better optical properties, more homogeneous nanoparticles distributions on the stone surfaces and higher photocatalytic activity thanks to the physical properties of the treatments and to the presence of benzyl alcohol molecules anchored on the anatase surface, which provides solar light absorption and improves the charge trapping effect, thus increasing the photoefficiency.

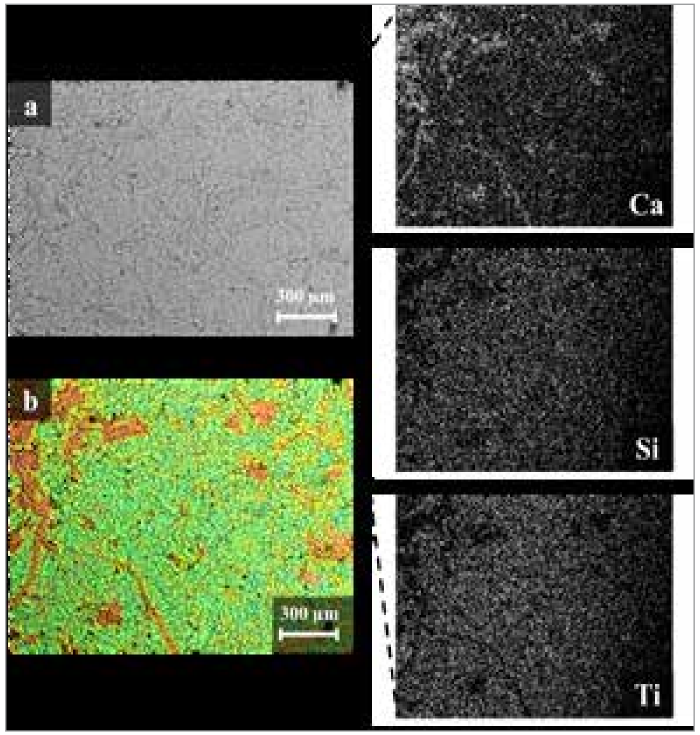
Moreover, in order to improve the treatment performances by preventing the penetration of nanoparticles into the porous substrate or their release in the environment, the development of hydrophilic SiO_2-TiO_2 treatments realized by applying nano-TiO_2 dispersions after a pre-treatment with tetraethyl orthosilicate (TEOS) to the surface was proposed. Such treatment resulted well distributed on the stone surface with the presence of nano-TiO_2 incorporated in the silica gel. Moreover, the photocatalytic activity is increased compared to the same nano-TiO_2 treatments applied without TEOS.

Then, in order to provide water repellent properties to the stone surfaces, the set-up of formulations of photocatalytic water repellent nanocomposites obtained by mixing different ratios of TiO_2 nanoparticles dispersions in commercial polymeric emulsions and alcoholic solution of SiO_2 and silicon alcoxides was developed. The obtained nanocomposites showed better aesthetic compatibility, higher contact angle, higher reduction of water absorption by capillarity compared to the pure coatings. Moreover they show a photocatalytic activity, thus providing a barrier against soiling.

Finally, the best formulations of treatments developed during the PhD research were applied on two marble blocks (Candoglia and Crevola marble) in a pilot-area on the façade of *Duomo di Monza* and the good results of the laboratory tests were confirmed by a protocol of non-destructive tests carried out onsite.



1. TEM image of water dispersion of TiO_2 nanoparticles with concentration of 3 % by weight.



2. a) ESEM-EDX characterization of Carrara marble surface treated with SiO_2 - nano-TiO_2 treatment; b) the corresponding false color image (b) indicating the distribution of titanium (green), silicon (yellow) and calcium (orange) and the maps of distribution of Ti, Si and Ca.

NOVEL MATERIALS AND TECHNOLOGIES FOR POLYMER SOLAR CELLS

Giovanni Iannaccone - Supervisor: Prof. Marinella Levi

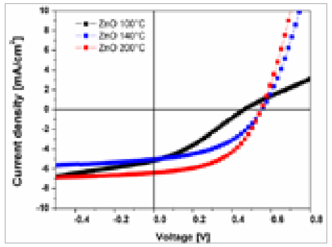
The driving force that has significantly encouraged progress in polymer solar cells (PSCs) over the past 25 years in the scientific community is correlated with their potential as a low-cost, lightweight, and flexible renewable energy source by means of all solution-based and large-scale roll-to-roll (R2R) processing. However the low efficiency and poor operational stability have limited a widespread diffusion and commercialization of this technology.

PSC technology was explored in the research work presented in this PhD thesis, taking into account different aspects related to processing, efficiency and environmental stability.

A preliminary study was carried-out in order to produce and test inverted PSCs based on standard materials such as ITO-coated glass substrate, ZnO as electron-transporting layer prepared from high-temperature sol-gel process, P3HT:PCBM as photoactive layer and PEDOT:PSS as hole-transporting layer. It is known that thermal evaporation, usually employed for the deposition of the metal back-electrode in lab scale devices is not suitable for roll-to-roll fabrication and therefore for large-scale production.

In the attempt to replace the thermal evaporation process the produced devices were completed using a conductive silver paste deposited in air by a screen printing equipment, designed and assembled in our laboratories. The photovoltaic tests performed on the produced PSCs demonstrated the possibility of producing working and reproducible PSC devices with efficiency comparable with those obtained with reference cells, produced by thermal-vacuum evaporation of an 80-nm-thick silver back-electrode.

In order to produce flexible devices, a systematic study was conducted on low-temperature solution-processable ZnO thin films, obtained *via* the sol-gel technology, incorporated in the solar cell structure as electron transporting layer (ETL). The annealing temperatures was found to strongly influence the photovoltaic performance of the devices (Figure 1), playing an important role in the charge extraction due to the modification of the surface morphology as well as to the chemical composition of the ZnO-based ETL.



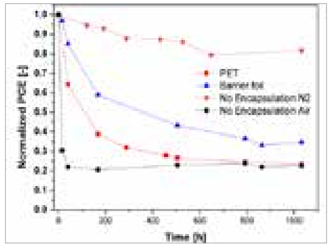
1. *J-V* characteristics of inverted PSCs with sol-gel based ZnO thin film as ETL annealed at 100°C, 140°C and 200°C.

In addition, a systematic study on the ZnO precursor formulation was carried-out, particularly aiming at the optimization of the hydrolysis step in the sol-gel process and responsible for the formation of the ZnO precursors. The photovoltaic tests of the investigated devices evidenced a clear efficiency improvement using a modified sol-gel formulation that allows to promote the initial hydrolysis step and facilitate the subsequent release of residual organic compounds during low-temperature (140°C) annealing, thus resulting in better electron extraction. A thorough chemical, physical and morphological characterization of the obtained ZnO films corroborated these findings.

With the prospective of exploring novel silver inks for the production of the back-electrode by means of R2R compatible processing techniques, a further experimental work was conducted on a solution-processable reactive silver ink that required mild annealing temperatures (<100 °C) to achieve high conductivity, thus limiting the morphological and thermal degradation of the underlying PSC layers and potentially lowering the costs of PSC fabrication. The reactive silver ink was opportunely modified in order to be suitable for flexographic printing and then used as precursor for the metallic back-electrode in flexible inverted PSCs entirely fabricated by means of R2R-compatible processes (Figure 2). In order to evaluate the effect of the ink printing on the underlying PSC layers, different back-electrode configurations and different thicknesses of the PEDOT:PSS buffer layer were investigated. An optimized combination of back-electrode architecture and PEDOT:PSS thickness was found that also allowed to achieve functioning semi-transparent PSC devices. Moreover, the optimized processing conditions found on the flexographic printed PSC devices, were extended to another deposition technique, namely spray coating, in order to demonstrate the clear versatility of such reactive silver ink.

2. PSC devices produced on flexible substrate by all solution R2R-compatible processes.

A final study on the lifetime of PSCs was conducted by monitoring the photovoltaic properties of rigid and flexible PSCs over a period of more than two months in different conditions (air and nitrogen). In addition, the effect of device encapsulation was also examined, after the development and optimization of an encapsulation process suitable for flexible devices. The tests confirmed the importance of the encapsulation procedure by using appropriate barrier films in order to guarantee improved device lifetime (Figure 3).



3. Power conversion efficiencies (PCE) recorded as a function of storing time and normalized to their initial value for flexible PSCs stored in air and encapsulated using both polyethylene terephthalate (PET) and a commercially available barrier foil as barrier films. Devices without encapsulation stored in air and nitrogen were also monitored as a comparison.

METAL-MEDIATED PHENOMENA FOR ENHANCED PERFORMANCE - IN SENSING AND OPTOELECTRONIC DEVICES

Lohith Karnam - Tutor and supervisor: Prof. Chiara Bertarelli

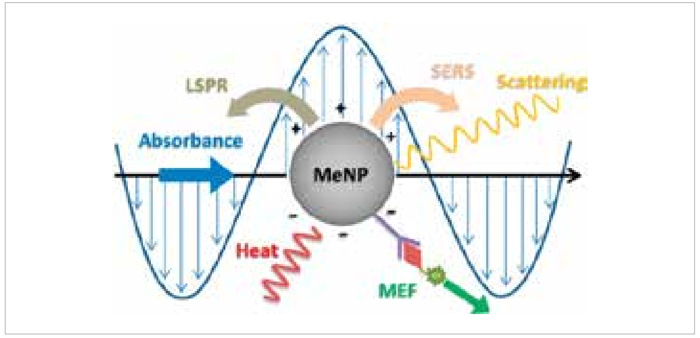
Co-supervisor: Prof. Mirella Del Zoppo

Nanotechnology has grown tremendously during the past few decades and it deals with materials, systems and devices on the nanometer length scale (1–100 nanometer). Metal nanoparticles have interesting chemical and physical properties which make them attractive for applications such as in optics, electronics, catalysis, and biology.

Metal nanoparticles have the ability to produce enhanced electromagnetic near field which basically arises from the resonant coupling between the collective metal free electron oscillation and an incident light.

This localized plasmon of metal nanoparticles allows confining the electromagnetic field creating high-field regions “hot spots”, most useful for a variety of applications. The focus of this thesis is to investigate plasmonic nanoparticles composed of gold or silver and optimize their performance in sensing and optoelectronic devices.

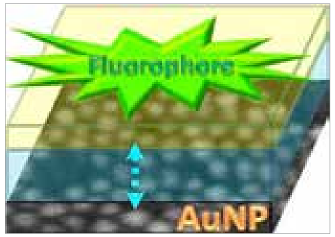
In this work, different sizes and shapes of metal nanoparticles have been synthesized in aqueous medium and further characterization has been done by means of UV-Vis and SEM measurements. It is known in the literature that the phase transfer of nanoparticles to organic layers is critical above a threshold dimension. Here we have employed an ethanol mediated protocol to effectively transfer nanoparticles and nanorods in an organic phase, which make use of dodecanethiol (DT) to stabilize the colloidal dispersion, achieving good quality spherical nanoparticles and nanorods dispersed in organic phase. Further, three important phenomena are studied to see effect of the metal nanoparticles namely, Fluorescence, Foster resonance energy transfer (FRET) and Surface Enhanced Raman Spectroscopy (SERS).



1. Schematic illustration of localized surface plasmon induced by an external electrical field and its possible applications.

In the first case, Metal-enhanced fluorescence (MEF) is demonstrated with two different approaches. The main problem which must be faced when trying to observe MEF is that of optimizing the distance between the emitting molecule and the metal nanoparticle. In fact, a close contact between the two leads to an effective quenching of the fluorescence, whereas long distance produces no effect.

Two different approaches have been described in this work in order to control such a distance namely, a multilayer strategy and a blend strategy. In both cases the active materials were completely obtained via spin coating differently from the methods published in the literature where complex, multistep deposition techniques are reported. In the multilayer strategy, an all-solution based multilayered structure, which was obtained via spin-coating, has been applied to two organic systems, namely, a molecular dye (Lumogen F Red305) and a polyconjugated polymer (P3HT) where the distance between the fluorophore and the metal nanostructure can be controlled by using a polymer spacer.



2. Schematic illustration of Multilayer structure for the generation of MEF.

In the blend strategy, NP-Fluorophore distance is modulated by changing the relative concentrations of the two components in a blend.

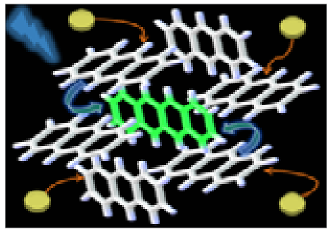
Moreover, nanoparticles with controlled size and shape are synthesized to study size and shape dependent Metal-Enhanced Fluorescence (MEF) along with distance dependency. A maximum enhancement of 8 fold intensification was obtained in the case of gold nanoparticles with 10 nm diameter (Au10).

In the framework of emitting materials, organic co-crystals have been extensively studied due to their high fluorescence quantum yield and thermal stability. Specifically, in the case of Anthracene/Tetracene co- crystals, Foster resonance energy transfer (FRET) occurs efficiently from host to guest molecules and they have been successfully used in Luminescent solar concentrators (LSCs). One possible approach to improve the efficiency of the system, is Metal Enhanced-FRET obtained by incorporating metal nanoparticles in the system.

Here, the preparation and optical characterization of thin films where dodecanethiol capped Silver and Gold nanoparticles are co-deposited with Anthracene/Tetracene Co-crystal (ATC) in a PMMA matrix is reported. The best enhancement (7-fold) has been obtained with silver NPs whose plasmon is in resonance with the donor emission (Antarcene, Ac).

A smaller enhancement has been obtained with gold NPs where the plasmon frequency is in resonance with the acceptor emission (Tetracene, Tc). These observations suggest that the increase of Tc emission is chiefly due to a more efficient FRET rather than an increased radiative emission rate. We also discuss possible morphological effects induced by the presence of the metal NPs.

Finally, we present the wavelength dependence of ATC fluorescence emission which further elucidates the predominance of the ME-FRET.



3. Schematic illustration of Metal-Enhanced FRET phenomena.

Lastly, metal nanostructures have been used in sensing application in the field of SERS. SERS was used to detect Apomorphine, which is a well- known short-acting dopamine agonist typically used in the treatment of patients with advanced Parkinson’s disease.

A novel fiber optic SERS sensor has been assembled that can be re-used simply changing the SERS agarose substrate containing silver nanoparticles. We have tested this particular SERS set-up for the detection of apomorphine and we are able to detect concentrations which is close to the typical therapeutic values. These results open the way to promising opportunities in medicine where the detection of this drug in the blood is of great interest. Moreover, this technique is more user friendly, easy to handle, cost effective and can be easily coupled with portable raman for in-situ/on-field measurements compared to the micro-raman and could be of great interest in the medical field.

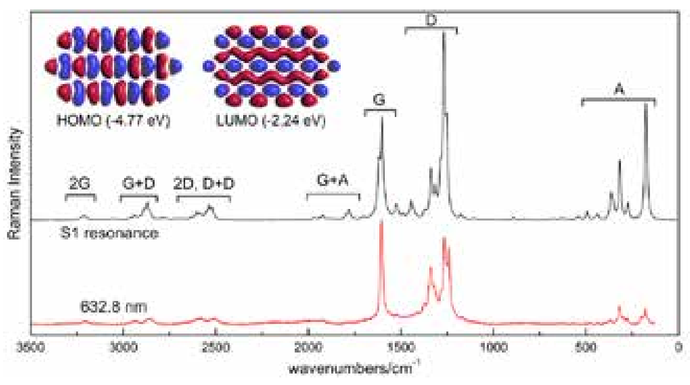
RAMAN AND IR SPECTROSCOPY FOR APPLICATIONS IN MOLECULAR ELECTRONICS

Ali Maghsoumi - Supervisor: Prof. Matteo Tommasini

Tutor: Prof. Chiara Castiglioni

This dissertation focused on the use of vibrational spectroscopy for the characterization of advanced molecular materials appealing for applications in molecular electronics due to the electronic and optical properties imparted by the presence of π-conjugated electrons. Several molecular systems have been considered, belonging to two broad classes, namely (i) graphene molecules (synthesized in Prof. K. Müllen group – Max Planck Institute for Polymer Research, Mainz, Germany) and (ii) thiophene derivatives (synthesized in Prof. C. Bertarelli group – Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Italy).

(i) Graphene molecules constitute effective models of graphene confined over a limited region. Due to confinement, the electronic and vibrational properties of graphene molecules can be modulated, leading to functional molecules optimized for specific applications. Polycyclic Aromatic Hydrocarbons (PAHs) are well defined cutouts or model compounds of graphene and graphene nanoribbons (GNRs). They inspired scientific research for several reasons and have provided models to develop and test elementary π-bond theory. Their extended π-conjugation and self-organizing properties are important for molecular electronics. They are of high interest not only in organic chemistry but also for various applications, including sensing, (opto-)electronics and catalysis. When chemically functionalized with aliphatic chains at their edges they form π-stacked discotic liquid crystals that may yield useful electron transport properties. Resonance Raman (RR) spectroscopy of π-conjugated materials is an effective probe of both the electronic and the vibrational properties, due to the strong electron-vibration coupling typical of π-electrons. Hence the experimental pre-resonance/resonance Raman response of a representative graphene molecule (C78) has been investigated in details and rationalized based on Peticolas-Nafie-Stein theory (see Fig. 1). For selected wavelengths, which better match resonance condition, it is possible to observe clear Raman signals ascribed to the first overtone of the characteristic Raman markers of graphitic materials (G, D). Interestingly, G+D combinations are also evident in the Raman spectra. This feature is a specific signature of confinement and it is usually absent in graphene. The multi-wavelength Raman spectra of C78 also display important features at lower wavenumber than D and G. Some of these features can be associated to in-plane acoustic-like vibrations that depend on the molecular size and can be used as a further marker of confinement. The outcomes of this analysis can be extrapolated to graphene, for which Raman spectroscopy is one of the more commonly used characterization techniques. These RR spectroscopy results have been extended to other molecular graphenes. This allowed testing the RR theory for molecular graphenes, which was developed for C78, and confirming it in terms of observed lines, relative intensities, and resonance behavior.



1. Comparison between calculated S1 perfect resonance spectrum (black line) with experimental spectrum recorded with 632.8nm laser excitation (red line). Also HOMO and LUMO levels of C78 calculated by DFT at the B3LYP/6-31(d,p) level have been shown.

Hexa-peri-hexabenzocoronene (HBC) is one the most important examples of the fully benzenoid PAHs: it is very stable and it can form columnar structures through self-assembly promoted by the strong π-stacking interactions. HBCs are characterized by their unique opto-electronic behavior, which can be tuned by suitable chemical modification at the molecular edge. PAHs with K-regions or zigzag periphery are more unstable, but demonstrate interesting properties such as lower bandgaps. Raman and IR spectroscopies have been used to characterize and prove the chemical structure of tetra-zigzag-HBC, selected graphene nanoribbons (GNRs) and their monomers, chlorinated molecular graphenes (HBC-Cl and C96-Cl) and a model molecule of a "hole" in graphene (C216). In the case of tetra-zigzag-HBC, Clar's annellation theory was successfully used to rationalize the electronic structure, which implies a sizable (179 nm) redshift of the para-absorption band in the UV-Vis spectrum of tetra-zigzag-HBC compared to that of HBC.

Furthermore, IR spectroscopy was used to investigate and find different edge markers (zigzag vs. armchair) or functionalisation markers (phenyl caps, iodination, chlorination, hole). From this point of view, IR spectroscopy is complementary to Raman spectroscopy for which the signals are mostly due to the collective motions involving the molecular π-conjugated core and usually carry less information on functional groups.

(ii) Two different thiophene derivatives (QBT and QDTT phenoquinones) have been also investigated with vibrational spectroscopy. These molecules present an interesting radicaloid character; when used as third components in bulk-heterojunction solar cells, they improve the performance of the cell. Raman spectroscopy confirmed the radicaloid character of both QBT and QDTT, while IR spectroscopy and DFT calculations revealed a very strong C=O stretching at the phenoquinones moiety. By comparison with DFT calculations on isolated phenoquinone, it was possible to relate the strong enhancement of the C=O stretching vibration with the peculiar electronic structure of QBT and QDTT.

Finally, vibrational spectroscopy was used to investigate orientational properties and intermolecular interactions in selected molecular materials.

In particular, IR spectroscopy was used to analyze strain induced crystallization and orientation in different types of rubbers. Crystallization is important for rubbers because it highly affects their mechanical properties (tensile strength, fracture and fatigue resistance). IR spectroscopy, compared with results from X-ray diffraction, revealed several markers of strain induced crystallization. The X-ray diffraction and mechanical characterization parts of this work were done in collaboration with the group of Prof. C. Marano (Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Italy). On the other hand, Resonance Raman spectroscopy was used for monitoring aggregation of AmB (a π-conjugated polyene macrocycle widely used as antibiotic) in solution state. It turned out that Raman intensity is a useful marker of aggregation processes in solution state as a function of concentration. Since AmB aggregates by π-stacking (similarly to many advanced π-conjugated materials), these results may find application in characterizing the experimental conditions leading to the controlled production of films for applications in molecular electronics.

THE MATERIAL ROLE ON BONE AND ARTICULAR IMPLANTS

Virginia Melli - Advisor: Luigi De Nardo

The need for bone implant concerns different clinical issues, such as bone defects derived from trauma or bone pathologies, treatment of congenital imperfections, tumor resections, joints arthroplasties, joint revisions surgery and fracture fixations. Due to this variety of implant functions required, implant materials come from different classes. Nowadays, articular joints are mainly made of biocompatible metal alloys and polymeric inserts, while bone defects filling material belong to the class of bioceramics that includes ceramic materials, glass ceramics and bioglasses. Since the ageing population and the requirement of better living standards raise the healthcare national systems expenses, it become important to evaluate different low cost strategies to manufacture implant devices and ways to increase their service life.

In the main introduction of this thesis work the step of the osseointegration process are reviewed (Figure 1).

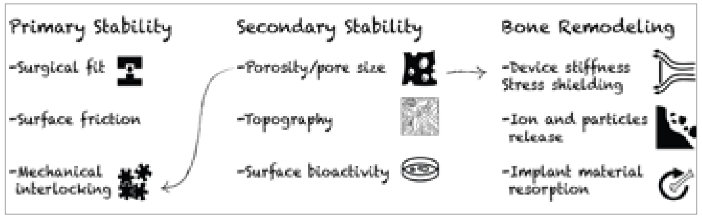
Osseointegration appeared to be dependent on several material properties and devices design features. In the case of metal alloys the ion release has shown to cause delayed implant loosening, moreover new bone tissue formation could be impaired by the presence of particulate developed from material wear.

The First Part, therefore, is devoted to the characterization of electrochemical and in vitro behavior of bioinert metallic implant materials. The problems of short term and, above all, long term osseointegration of these materials are discussed. Aseptic loosening complications are mostly responsible for long term implant failure and they are attributed to ions and debris release. The electrochemical behavior of three different metallic materials have been elucidated applying simulating body conditions.

In the first case the CoCrMo implant alloy used for the production of tibial trays for total knee prosthesis was compared to the same alloy processed through Metal Injection Molding. This manufacturing process allows to save raw materials and to reduce the production cycle steps and consequently to reduce costs.

The electrochemical behavior and in vitro cyto-compatibility of the traditional and the MIM material was not significantly different while a slight worsening of the tribological behavior and a small decrease in the fatigue limit of the final device has been observed.

Secondly, the CoCrMo implant alloy coated with a PVD monolayer and a novel multilayer both exposing TiNbN has been characterized. These layers proved to be good barrier against ion release and to have no cytotoxic behavior. The effectiveness of the coating was strongly related to its thickness homogeneity and absence of defects. Moreover, no galvanic coupling was observed between the CoCrMo substrate and the TiNbN coating. This aspect is very important in the case of unwanted coating wear during service and substrate exposition, in fact, the substrate corrosion rate would not increase due to the presence of the conductive coating.



1. sketch of the three main stages individuated for the osseointegration process.

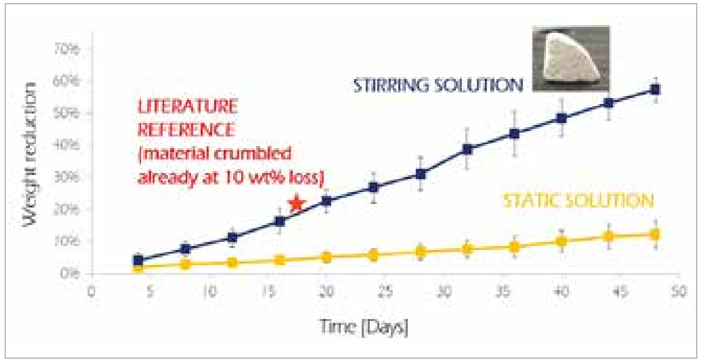
Thirdly, the increase of ion release in a titanium grade 2 foam has been evaluated. The material, produced at Canada NRC-CNRC, demonstrated to have a surface oxide with a higher passivating character than the polished bulk material. This allowed to measure a limited increase in ion release compared to the increase of surface area facing body fluids. From the cyto-compatibility test of the foam a prolonged proliferation phase for osteoblast cells in vitro has been also highlighted.

In the Second Part the focus is shifted to bioactive and bioresorbable "bioceramics" with particular attention to 45S5 Bioglass®, the most promising synthetic material able to directly bond with both bone and soft tissues. The reasons that, until nowadays, impaired its use in the production of scaffolds for bone defects filling and regeneration are extensively discussed.

The main issues, declared in literature, refer to the low processability of this material, which devitrify during thermal treatment and the instability of the interface between crystalline phase and amorphous phase during its resorption.

It has been observed that, optimizing the process parameters for the production of porous structures, well-sintered scaffolds can be produced with different techniques. Among them a powder metallurgy inspired technique, developed at Canada NRC-CNRC, could produce scaffolds with porosity values (60-70 %) and pore size distribution (average pore size 200-300 μm with macropores of 500-600 μm) theoretically able to guide the formation of new vascularized tissue without decreasing too much the mechanical properties (as sintered compressive strength lower value 5 MPa).

The resorption ability and resorption mechanism of the 45S5 Bioglass®-based glass-ceramic scaffold produced with the powder metallurgy technology, has been evaluated, correlating the observations with a deep investigation of the material microstructure and microstructural changes in different environments, using different characterization techniques. The experimental evidences suggest that the glass ceramic material constituting the porous scaffold is completely resorbable in water environment and no instability of the interface between crystalline and residual amorphous phase has been observed.



2. Weight reduction in water in the case of static and stirring environment. The inset shows a specimen at the end of the experiment maintaining mechanical integrity. The overall trend is compared with the only literature record existing (red star).

Finally, the in vivo performance of this porous material has been assessed with a subcutaneous mice model. The material showed great affinity with host tissue and no inflammatory infiltrate was present in the implant vicinity. New vascularized tissue colonized the scaffold already after 3 weeks and mechanical consistency was maintained also after 6 weeks of implantation. The glass-ceramic material highlighted progressive amorphization and the development of a bioactive CaP surface layer. Initial struts hollow-out appeared at 6 weeks.

FUNCTIONAL MATERIALS FOR ACTIVE OPTICAL ELEMENTS

Martino Quintavalla – Supervisor: Andrea Bianco

Tutor: Prof. Chiara Bertarelli

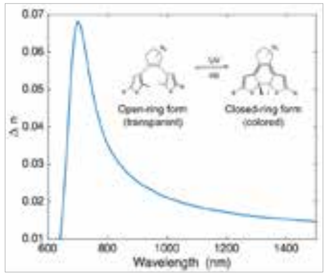
This PhD research work deals with some possibilities to use functional materials, i.e. those materials whose properties undergo a reversible change as a consequence of external stimuli, to modify the properties of optical systems and, in particular, with the modulation of the optical path (OP) that is defined as the product of the refractive index and the geometric distance through which light travels. Being light propagation governed by interference and diffraction, this quantity is extremely important in any optical system because a difference in the OP between different electromagnetic waves means a phase shift that can lead to significant differences in the behavior and optical quality of the whole system. The modulation of the OP is exploited in many optical systems and the opportunity to induce it in a controlled fashion by light or electric stimuli is of great interest. In this framework, the capabilities of two different functional materials, photochromic materials and photoconductors, and their relative technologies were investigated.

A study on the application of photochromic materials for optical waveguides

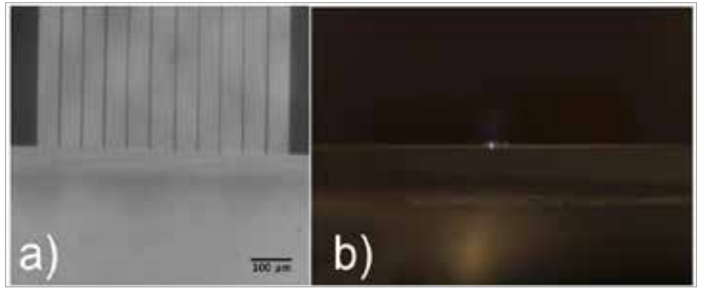
The possibility to use photochromic materials to realize reconfigurable waveguide platforms for quantum optics experiments was considered. The refractive index modulation induced by the photoisomerization reaction of photochromic diarylethenes can in fact be deployed to guide light using the total internal reflection as for optical fibers. In addition, the reversible nature of the photochromic reaction can be exploited to make reconfigurable devices where waveguides are optically written on a thin photochromic film. Photochromic polyurethane films based on diarylethene monomers with different chemical structure were realized and their refractive index modulation was evaluated using different techniques and discussed in relation to the structure. Values of the order of 10^{-2} were obtained at the wavelength of 1.5 µm indicating that these materials are suitable for this application.

Characterization of the photo fatigue resistance of some diarylethene-derivatives

Since the reversibility is a fundamental property of photochromic materials, especially when these are used to realize active devices, the phenomenon of photo fatigue, i.e. the number of cycles that these materials can undergo without a consistent degradation of their properties, was studied. A versatile setup allowing to automatically perform photochromic cycles was designed and built. Moreover, a theoretical approach was developed to analyze the UV-vis spectra of photochromic materials during the cycling procedures and determine the fraction of active molecules and the amount of degraded byproduct. Using this apparatus and the developed approach, the photo fatigue resistance of different diarylethenes derivatives was evaluated. A fundamental outcome of this study is that the photo fatigue resistance in diarylethenes strongly depends on the wavelength of the UV light used to perform the photochromic conversion from the open- to the closed-ring form of these compounds. In particular, the photo fatigue resistance decreases with the increase of the UV light dose absorbed by the closed-ring (colored) isomer. This evidence is of fundamental interest for the practical application of these materials since a change in the wavelength of the UV light used, translates into a large change in their photo fatigue resistance.



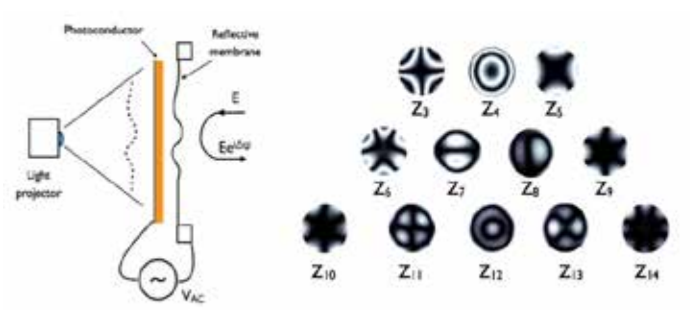
1.- Refractive index modulation for a photochromic polyurethane film with 30% of active units. Inset: photo induced isomerization of diarylethenes.



2. Photochromic waveguides: a) image of waveguides on a 5 um thick polyurethane film; b) light spot escaping from a photochromic waveguide.

Materials choice and development for Photo Controlled Deformable Mirrors

A second line of research was the development of photo controlled de- formable mirrors (PCDMs), a particular type of active optical elements whose shape is determined by the illumination pattern sent on a photoconductive substrate, that are used in adaptive optics. A complete electric model of these devices was developed to cover the lacks of previous studies and determine the correlation between the photoconductive material properties and the static and dynamic response of these devices. The outcome of this analysis is that a large photoconductor thickness and a low dielectric constant are required to have a high dynamic range (corresponding to a large deformation), while a high charge carrier mobility is required to have a fast response. An electro-opto-mechanical model was developed to determine the useful working range of PCDMs in terms of key parameters that contribute to its functioning and response. The possibility to develop these devices from a material point of view was investigated, considering the importance of scalability together with the other requirements in terms of response time and dynamic range. Both inorganic and organic materials were considered for this purpose. Zinc selenide was identified as a good candidate for the realization of large aperture PCDMs and was characterized and employed to build a 2” aperture PCDM, that is the biggest state of the art device of this type. This PCDM was tested in an adaptive optics set up to demonstrate its capabilities to induce wavefront modifications. Organic materials were also considered, starting from chemical systems developed in photovoltaics and xerography fields, such as P3HT:PCBM bulk heterojunction, as charge generating system, and molecularly doped polymers as charge transport materials. Organic photoconductors were developed starting from a multilayer configuration where charge generation and charge transport were optimized separately. These structures were electrically tested, simulating the real working conditions and this approach evidenced that the main limitation of these materials regards the realization of thick photoconductors with sufficient charge carrier mobility. Starting from this evidence, single layer organic photoconductors were realized and proposed as possible candidate for quasi-static active elements such as active mirrors.



3. Working principle of a PCDM and interferograms of Zernike polynomials generated with a 2” aperture ZnSe PCDM.

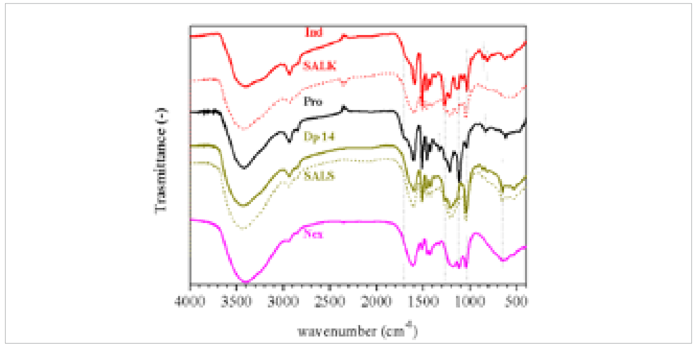
LIGNIN AS RENEWABLE MATERIAL FOR INDUSTRIAL APPLICATIONS

Carmela Scarica - Supervisor: Stefano Turri

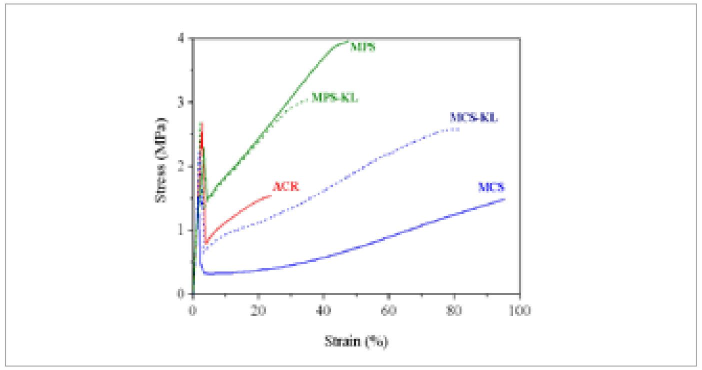
Renewable resources present unique features that can contribute to the development of a novel generation of high performance materials offering economical/environmental advantages over its petroleum-based counterparts. The conjunction of all these factors constitutes, undoubtedly, a driving force to consolidate the utilization of renewable materials in the development of new products. The concept of biorefinery falls within the approach of green chemistry and "integrated" process, avoiding the production of waste low value-products and recycling solvents used to extract all the components of biomass feedstock (closed loop systems). Lignin, the main natural source of aromatics, has been considered for a long time as a waste from pulp and paper industry and commonly used as fuel. However, it is a highly aromatic polymer with a variety of functional groups that make it a potential building-block for the formulation of dispersants, adhesives, coatings and surfactants or as antioxidant in plastics and rubbers. Because lignin composition and content in lignocellulose feedstock are influenced by the plant type and by the delignification process, the development of lignin-based materials is challenging and relatively limited.

In this contest, the research described in this PhD thesis aims to study and explore the potential of this renewable resource, analysing at first the raw material structure and then investigating the incorporation of lignin into polymeric matrices, directly and after chemical modification. In the first part of this thesis, several lignin grades were evaluated considering aspects such as structure (Figure 1), thermal properties, solubility, molecular weight and reactivity.

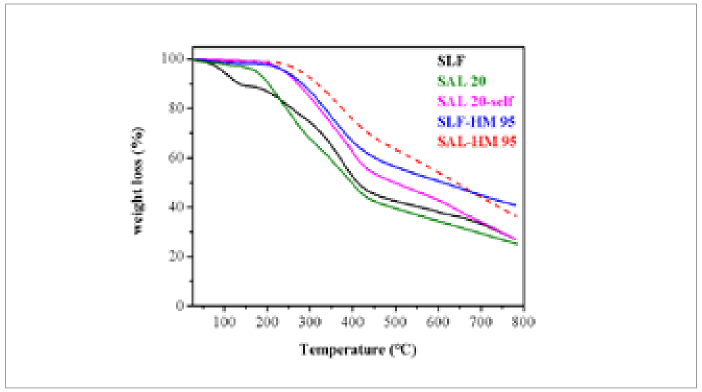
In addition, a strategy to improve lignin processability was evaluated, involving solvent fractionation. After the preliminary screening, unmodified lignins were tested as eco-friendly alternative to synthetic binders in a specific industrial application, namely the production of nonwovens (NW) made from recycled PET and used as roofing membranes. In this technology a key step is represented by the impregnation of the polyester fibers, nowadays performed with acrylic polymers crosslinked with melamine-formaldehyde resins, which are however toxic and suspect carcinogenic. The experimental work concerning the production of the impregnated NW was carried out an industrial pilot plant. The obtained prototypes were subjected to mechanical characterization at different temperatures and were shown to give good mechanical properties, in line with those achieved using conventional synthetic binders. Moreover, unmodified lignins were combined with polysaccharides such as starch and nanocellulose. In the first case, after a preliminary screening of different starch grades in terms of morphology, thermal and structural properties, a "green" crosslinking reaction with polycarboxylic acids was performed in order to give crosslinked starch materials. The addition of lignin allowed to overcome some of the main limitations related to the use of starch, namely its limited thermal stability and its highly hydrophilic nature. Also in this case, PET-based NWs were produced, impregnated with the lignin-starch based binder and characterized. In addition to improved thermal stability and resistance to water, these systems also exhibited good mechanical properties, thus providing a clear evidence of the possibility to partially replace formaldehyde in acrylic resins (Figure 2)



1. FTIR spectra of several grades of lignins: kraft-type (Ind, SALK), Soda-type (Pro) and lignosulphonate-type (Dp 14, SALS, Dp 31 and Nex).



2. Comparison of representative tensile curves of nonwovens impregnated with acrylic binder (ACR), starch-based binders (MCS and MPS) and starch-lignin-based binders (MCS-KL and MPS-KL).



3. TGA thermograms of unmodified lignin sample (SLF), modified sample (SAL 20) and lignin-based polyesters (SAL 20-self, SLF-HM 95, SAL-HM 95), recorded by TGA under nitrogen flux.

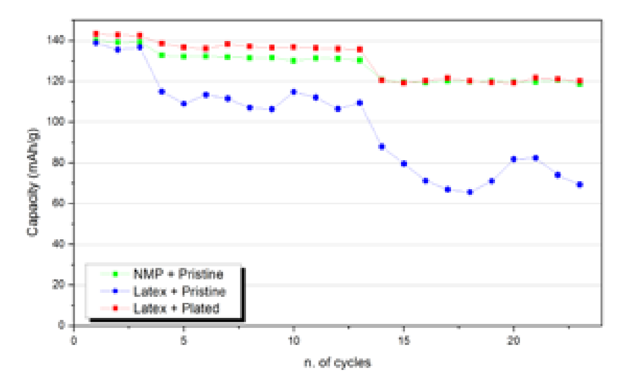
The second part of the project, spent at Aalto University (Helsinki, Finland), was focused on the crosslinking reaction between lignin and nanocellulose in order to combine the broad chemical modification capability of nanocellulose with lignin properties. Finally, the utilization of lignin as a filler in natural rubbers was investigated as a green alternative to the usual carbon black. The third part of the work was focused on the chemical modifications of lignin. In detail, an easy approach to introduce new materials properties to the base lignin was developed through an esterification reaction in which a carboxylic moiety was attached to the lignin backbone, thus resulting in the formation of lignin-based precursor for the preparation of lignin-based materials. The newly developed crosslinked materials based on this lignin precursor were fully characterized in terms of solvent resistance, thermal stability and adhesive properties on different substrates. The effect of co-curing agent and self-crosslinking reaction was evaluated in the attempt to obtain a highly performing lignin-based polyester coating to be used as a green alternative to the common employed oil-based systems (Figure 3).

ELECTROCHEMICAL SURFACE MODIFICATION OF ACTIVE MATERIAL FOR LI-ION BATTERIES

Marco Spreafico - Supervisor: Prof. Luca Magagnin
Co-Supervisor: Dr. Paula Cojocaru

In the industrial LiBs electrodes preparation process, the slurry containing the active material (source of Li ions in the battery), carbon additives (to increase electrode conductivity) and polymeric binder (to ensure mechanical stability) are mixed together in a volatile solvent to form a slurry, which is cast on a metallic current collector and then dried. The dominant solvent used to perform this process is N-Methyl-2-pyrrolidone (NMP), which has been classified by the European CHemicals Agency (ECHA) as "substance of high concern due to its carcinogenic, mutagenic and toxic for reproduction properties" (decision n. EC N 212-828-1).
The aim of this work is then to replace NMP by using water as solvent in the preparation of electrodes for LiBs, by using an aqueous binder, a latex of PVDF. In order to do so, it is necessary to "protect" the active materials (AMs) from the interaction with water as this class of undergoes chemical dissolution when in contact with water. The protection of the particles of AMs has been done by means of plating a coating on their surface by using electrochemical deposition techniques, such as electroless deposition (ELD) and galvanic displacement (GD). The idea is to deposit a coating capable of protecting the particles of active material from the interaction with water without hindering the Li ions flow during battery cycling. This concept has been tested on the mostly used cathodic AM in the LiBs market, lithium cobalt oxide (LCO), and then transferred to other innovative active materials used at LiBs cathode (lithium nickel manganese cobalt oxide, NMC) and anode (silicon).

In the case of LCO particles, a copper-based coating has been plated by means of electroless deposition: this technique is composed by two distinct steps, surface activation and deposition. The surface activation electrolyte is an aqueous Pd-based acid solution, while the deposition electrolyte contains ions of the metal to deposit, in this case copper, and a reducing agent to perform the deposition of such ions, in this case formaldehyde. The deposition process is performed by dipping the particles in the activation solution for a certain time to allow the adsorption of Pd atoms on the surface of the particles, then the particles are separated from the liquid phase by filtering. The same process is then repeated with the deposition electrolyte, the filtration takes place after the desired amount of copper ions have been reduced on the Pd-catalyzed particles surface. For LCO, activation and deposition times were of 1 minute and 30 minutes, respectively. After the deposition of the metal layer, an annealing step (1 h at 200°C) is performed to allow the oxidation of copper: this is done to ensure the necessary electrochemical stability during cycling. TEM and XPS analyses on plated LCO particles showed that the deposited layer is made of copper(II) oxide (i.e. CuO), with a thickness around 30 nanometers. The inner structure of LCO particles was unaltered after the coating process, thus not affecting the cycling properties of the material in operative conditions. Comparing electrodes prepared with PVDF latex, the ones containing plated LCO showed increased electrical conductivity, and superior cycling performance against electrodes containing pristine LCO, while it is at the same performance level than the reference sample made of pristine LCO using NMP as solvent, as shown in figure 1.



1. Cycling test for water-based electrodes containing pristine (blue curve) and plated (red curve) LCO, and NMP-based electrode with pristine LCO (green curve). Cycling schedule is as follows: 3 cycles at D/20, 10 cycles at D/10 and 10 cycles at D/5. Charge was always performed at a C/20 for the first three cycles and then at C/5. Cutoff voltages are 2.8-4.2 V

A Ni-based coating has been applied with electroless deposition to NMC particles for application at higher cut-off voltage (up to 4.6 V). The coating proved to stabilize NMC cycling behavior preparing electrodes containing plated NMC and PVDF latex at a cut-off voltage of 4.3 V. However, when increasing the cut-off voltage to 4.6 V a decrease in cycling performance is observed, probably due to the interaction of the deposited coating with the electrolyte present in the battery. Further tests are needed to validate this hypotheses that are supported by the analysis of the voltage profiles of the plated NMC electrode, obtained during battery cycling.

Metallization of silicon particles proved to be a very promising tool to enhance the performance of pristine Si. The presence of a copper layer on the particles determined an increase in conductivity in the negative electrodes. Cycling tests showed an initial enhancement in the delivered capacity, which is hindered by the typical Si pulverization effect upon cycling. In table 1 are summarized the 1st cycle capacity charge values obtained by the metallized and pristine Si electrodes.

	Charge Cap. (mAh/g)	Eff. (C_D/C_C)
Pristine Si	3444	33%
Plated Si GD	3765	45%
Plated Si ELD	4047	62%

Table 1: Values of charge capacity and first cycle efficiency calculated as ratio between discharge and charge capacity

It can be seen a marked increment on the delivered charge capacity together with an increase in the Li lithiation/delithiation efficiency defined as the ratio between discharge and charge capacity. However, after some battery cycles, this boost in the cycling performance is dominated by the pulverization effect typical of Si anodes. This negative effect should be counteracted by the binder action, which in our case (carboxymethyl cellulose, CMC) was not sufficient. The metallization technique proved to be able to increase the performance of the Si anodes, but a parallel development of the polymeric binder is needed to achieve long term cycling stability.

The last part of the work deals with the scale-up of the metallization process to a semi-industrial scale, in the framework of the LIFE+ GLEE EU funded project. A formaldehyde-free deposition electrolyte has been developed to be used in the plant. The main issues in the scale-up of the metallization process are due to the compliance to the metallization parameters used in the lab scale process, i.e.1 minute activation time. A screening of PP filters having different porosities has been done to comply with process parameters and process yield. Cycling tests assess that LCO plated using the GLEE plant has performance in line with lab scale LCO samples.