



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. 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 submits to the Faculty a "Curriculum" for its approval. 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 has a tutor, who is a member of the faculty. At the end of each year, the faculty evaluates the progress of the research activity, expresses an assessment, and establish the admission of the Ph.D. student to 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 national and international meetings and to present papers in his specific field. The Ph.D. student can be 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 obtained 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)	Luigi De Nardo	MariaPia Pedferri
Francesco Briatico Vangosa (vice-coordinator)	Giovanni Dotelli	Guido Raos
Chiara Bertarelli	Fabio Ganazzoli	Lucia Toniolo
Luca Bertolini	Luciano Lazzari	Stefano Turri
Fabio Bolzoni	Marinella Levi	Pasquale Vena
Massimiliano Bestetti	Claudia Marano	
Alberto Cigada	Valdo Meille	

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 courses 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
Emanuele Carpanzano, Dipartimento tecnologie innovative, SUPSI (CH)	Stefano Gialanella, Dip. di Ingegneria Industriale, Università di Trento
Alessandro Martucci, Dip. Ingegneria Meccanica, Università di Padova	Laura Montanaro, Dip. Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino
Stefano Radice, Solvay Specialty Polymers SpA	Riccardo Po', eni SpA
Fiorella Pozzobon, ST Microelectronics	Mario Sobacchi, eni SpA.
Francesco Stellacci, Dept. of Materials Science and Engineering, EPFL, Lausanne	

GRANTING AGENCIES:

ST Microelectronics s.r.l.	Media Lario Technologies
Fondazione Istituto Italiano di Tecnologia IIT	Istituto Nazionale di Astrofisica
SOLVAY SOLEXIS SpA	INSTM
eni SpA	Electrolux SpA
Faber SpA	

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

Arrigoni Marocco Alessandro – Supervisor: Prof. Giovanni Dotelli

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

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

all kinds of chemical stabilisation seemed to reduce the moisture buffer ability typical of untreated earthen surfaces. Another natural building material investigated was hempcrete. Hempcrete is a non-load bearing insulation material that has known an increased popularity in recent years. It is made from a mixture of the inner woody core of the hemp plant (hemp shives) and a lime-based binder. In addition to the LCA of the material, an extensive sensitivity analysis was performed to highlight possible improvements in the mixture. Moreover, the carbonation of the binder was monitored through XRD analysis on hempcrete blocks and the resulting experimental findings were included in the sustainability analysis for the first time. In light of laboratory experimental evidence, although carbonation improved the global warming potential of the product, the generic assumption of a complete carbonation of the material during the building's lifetime proved to be unrealistic. Nevertheless, hempcrete blocks can be considered as a carbon sink, since the CO₂ stocked in the material was higher than the overall emissions during production. Design for disassembly and recovery of building materials and

components after demolition are other viable alternatives to reduce the life-cycle environmental impacts of buildings. In the present thesis, the importance of materials' selection and their recycling potential were investigated at the building scale by performing an LCA analysis on a temporary pavilion built for the EXPO 2015 event held in Milan. Environmental impacts of temporary structures can be considered a proxy indicator for low-energy buildings due to the shared minor importance of the use-phase in the overall sustainability. Data for the

LCA were collected directly on site and the related difficulties were brought to light. Results confirmed the importance of the design phase and demonstrated that foreseeing a second use for the building components could significantly reduce the impacts of a building. LCA is an acknowledged tool aimed at uncovering the real impacts of a product and at highlighting the environmental "hotspots" of a production process. In the present work, the LCA tool was used as a starting point for further investigations: once the hotspots were identified,

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

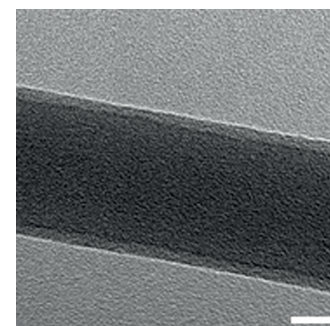
ELECTROSPINNING OF BIOPOLYMERS FOR REGENERATIVE MEDICINE

Marcolin Chiara – Supervisor: Ing. Lorenza Draghi

Extra-cellular matrix (ECM) is a three-dimensional structure constituted by interconnected nanofibers, which serves as scaffold for cell proliferation and plays also an important role in tissue function. ECM is composed of several types of proteins, polysaccharides and glycoproteins. In tissue engineering field, a scaffold with adequate composition and properties is fundamental to favor physiological healing process and successful outcome. In this regard, electrospinning (ES) represents a valuable fabrication technique, as it allows the production of nanofibers in a simple and convenient way; moreover, natural polymers, and in particular ECM biopolymers, can be processed by ES, thus allowing the fabrication of membranes whose chemical composition and morphology closely resemble those of physiological ECM. Several studies in literature have focused their attention on ES of biopolymers; however, some limitations remain, as solvents commonly used for ES are not necessary good solvent for natural polymers and they can be toxic or cause extensive molecule denaturation, biopolymer solutions usually lack viscoelastic properties essential for a stable ES, and finally, a crosslinking post-treatment, which is necessary to improve

matrix stability, may introduce cytotoxic residues. Therefore, more detailed comprehension and study on biopolymer ES are necessary in order to elucidate possible solutions, thus leading to production of membranes with a tremendous potential as scaffold for tissue engineering. In Chapter 1, ECM composition and function were reviewed, and the most studied strategies for ECM mimicry were presented. Then, ES process was described, and the influence of several parameters on the process outcome was discussed. Particular attention was dedicated to ES of natural polymers and the relative characterization techniques commonly used in literature. In the second Chapter, the most abundant ECM macromolecules (i.e. collagen/gelatin, elastin and hyaluronic acid) were used to obtain different composition blends, and their ES process was optimized in order to produce electrospun matrices with tunable composition that closely mimics ECM of different tissues. The use of a non-fluorinated solvent, namely formic acid, for solution preparation was advantageous in reducing both toxicity and cost of the process with respect to the solvents commonly used in literature for biopolymer ES (i.e. hexafluoroisopropanol, HFIP, and

trifluoroethanol, TFE). Influence of collagen batch variability on ES process was also evaluated. Finally, the efficacy of the most common crosslinking methods for natural polymers was compared by evaluating matrix morphology and membrane stability. The third Chapter is dedicated to the ES of fibrinogen, which has a major role in clot formation and physiological tissue repair, and of fibrinogen/gelatin blend. For the first time fibrinogen was successfully electrospun by means of an acidic solvent system composed of formic and acetic acids, instead of the commonly used HFIP. However, fibrinogen solution gelification at the tip of the spinneret occurred, thus hindering process continuity. As it was not possible to solve this problem, an alternative solution consisted in electrospinning a blend of fibrinogen/gelatin (1/1). Moreover, solution gelification phenomenon was investigated in details, and in particular the effect of acidic pH on fibrinogen molecular structure was examined by means of experimental and computational studies, which elucidated the denaturing effects of the solvent used for ES on the biomolecule. In Chapter 4 a variation of traditional ES technique, namely co-axial ES, was used to obtain



1. TEM image of core-shell fibers obtained by co-axial ES of gelatin 10% w/v in formic acid as core solution and hyaluronic acid 2% w/v in formic acid as shell solution. Scale bar: 20 nm.

core-shell fibers with application in wound healing. In particular, gelatin and hyaluronic acid were used as core and shell materials, respectively (**Fig. 1**); moreover, CCG-203971 drug to prevent myofibroblast differentiation, which is responsible for excessive scar formation during wound healing, was loaded within the fiber core. The membranes were crosslinked by glutaraldehyde vapor, and influence of different process durations on electrospun matrix chemical structure were investigated. Finally, *in vitro* drug release and cell tests were carried out in order to evaluate the feasibility of drug-loaded bicomponent fibrous membrane for the application intended.

AN ALTERNATIVE METALLIZATION PROCESS OF ADVANCED POLYMERS: DEVELOPMENT AND APPLICATIONS

Oriani Andrea – Supervisor: Prof. Luca Magagnin

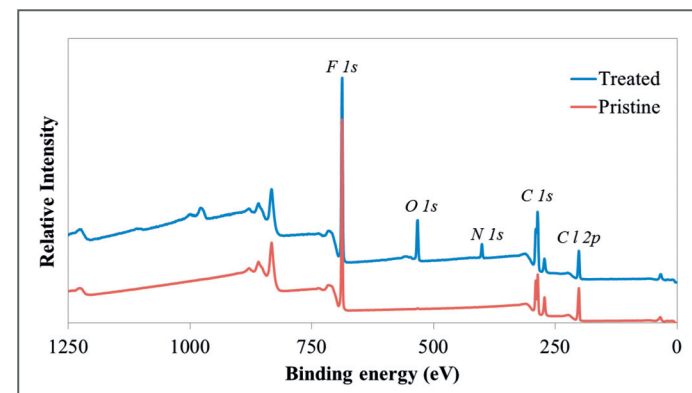
The production of adherent metal coatings on polymers, especially fluoropolymers, is still an open issue for many applications. Many pre-treatment and metallization processes have been proposed, which are either time/money consuming or limited to few specific polymers. In order to propose a versatile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

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

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

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

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

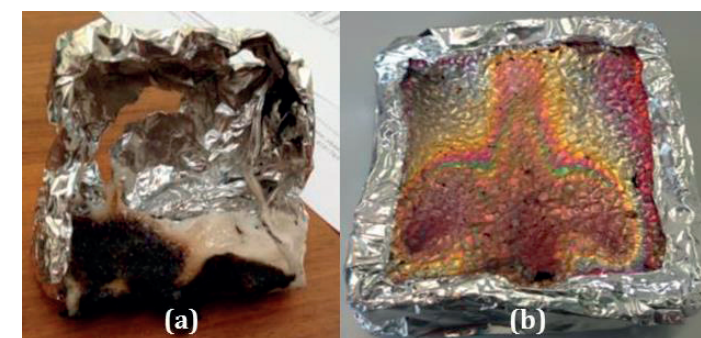


1. XPS spectra for pristine and plasma treated ECTFE.

Moving to the specific applications, metal-coated ECTFE was proposed as flexible concentrator mirror. Spectral reflectance studies, performed on simplified samples, revealed that good reflection properties can be obtained. Moreover the deposition of silver layers allowed improving the performances with respect to copper coated ECTFE samples. Two different applications were considered for copper coated PEEK films, depending on their thickness. Thermal and mechanical properties of thin, 6 μm thick, films were determined to quantify the effect of copper layers on thermal conduction/dissipation and apparent elastic modulus. This information was needed to validate the applicability of these samples as oscillating diaphragms for micro-speakers. Results revealed that

thermal conduction/dissipation is highly increased by metallization and the effect on the mechanical properties can be tailored to obtain a good compromise. Secondly the applicability of thicker copper coated PEEK stripes as switches for circuit breakers was studied. In this case electrical and thermal responses of polymer-metal

switches were studied, revealing that, modulating sample geometry, it is possible to control with remarkable precision the actuation current and the thermal deflection of the polymer-metal stripes. Finally the whole-surface plating of PVDF foams with copper was studied for aerospace applications. It was indeed verified that pristine PVDF foams didn't meet smoke toxicity requirements due to generation of HF during flame resistance tests. The flame resistance test is part of the set of characterizations that are required, for new materials, from the aerospace industry. Copper coated PVDF foams, on the other end, were found to pass the flame resistance test without generation of HF. This work is part of a research project within Solvay Specialty Polymers with perspectives of commercialization.



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

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

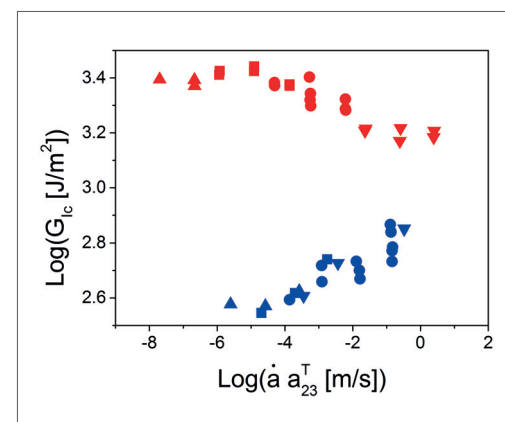
Pini Tommaso – Supervisor: Prof. Roberto Frassine

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

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

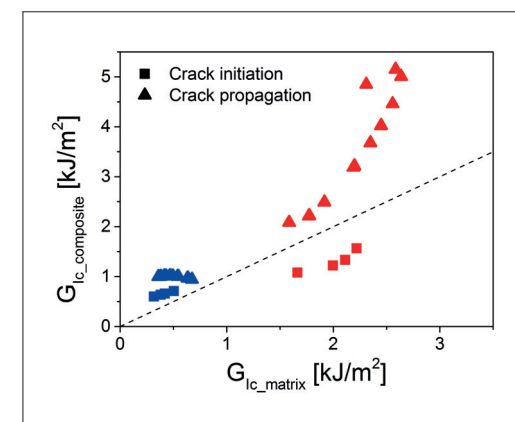
tip can be obtained. The optical observation of the process zone at the crack tip obtained in different conditions of temperature and displacement rate confirmed the change in the damage mechanisms. This was associated with different amounts of energy dissipated thus explaining the trend observed in the fracture toughness vs. crack propagation speed curve for the toughened resin.

Concerning the fracture behaviour of the composites, in order to better understand the transfer of toughness from matrix to composites, both the crack initiation and propagation stages were analysed. At crack initiation the toughening contribution of the fibres is limited, compared to that during crack propagation, and therefore the main fracture toughness contribution is given by the matrix. It was found that in the case of the plain matrix based composites the fracture toughness was higher than that of the matrix, while in the case of the toughened matrix based composites it was smaller. This result can reasonably be explained with the physical constraint induced by the presence of the fibres on the development of the process zone ahead the crack tip in the case of the toughened composites. In the case of the plain matrix, in which the dimensions of the process zone are smaller,



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

the matrix toughness seems to be fully transferred to the composite. During the propagation stage, it was found that the fracture toughness was higher than that of the relevant matrix, for both matrices. The additional toughening effect given by the fibres was found to be dependent on crack propagation speed, probably due to time dependent matrix-fibre interfacial strength.



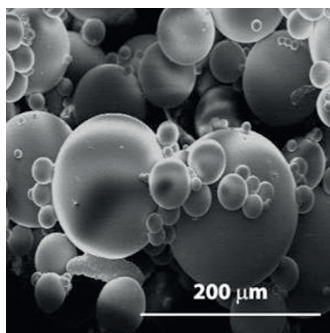
2. Fracture toughness of composites vs. fracture toughness of relevant matrices at crack initiation (squares) and during crack propagation (triangles) for plain (blue symbols) and toughened matrices (red symbols)

SMART MATERIALS AND ADDITIVE MANUFACTURING

Postiglione Giovanni – Supervisor: Prof. Stefano Turri

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

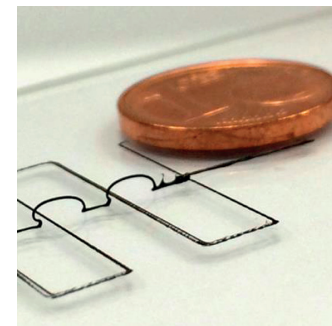
developing new smart polymers and composites suitable to be realized by additive manufacturing technologies. The first part dealt with the study of smart systems designed to give an intelligent response to damage events. One approach consisted in providing a material with the ability to display a visual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



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

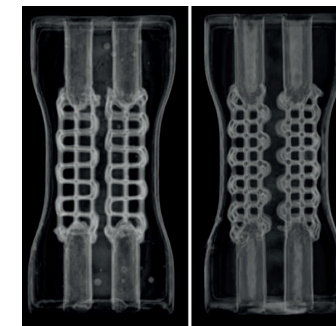
functionality, represent the logical evolution of damage sensing. Their ability to counteract degradation and damages with automatic repair mechanisms was assessed by formulating a polymeric coating based on the Diels-Alder reaction. The resulting polymer, upon application of a simple thermal treatment, reduced or eliminated small defects or microcracks, potential points of weakness that could otherwise lead to structural failure. The second part focused on the development of polymeric nanocomposites for different extrusion-based additive manufacturing technologies. The proposed processes, termed liquid deposition modeling (LDM) and UV-assisted 3D printing (UV-3DP), consisted in the layer-by-layer deposition of fluid material that solidified after flowing out of a computer-controlled moving nozzle. Using LDM it was possible to fabricate conductive microstructures with resolution down to 100 μm from a solvent based formulation containing carbon nanotubes. Conversely, through UV-3DP, nanocomposites composed by different combinations of photocurable matrix and inorganic fillers were successfully processed. A systematic investigation on the rheological properties of different

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



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

The healing function, comparable to that of human skin, could be performed upon release of liquid healing agents accurately stored into the microchannels embedded within the matrix. This ability favorably affected the durability and mechanical performance of



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

the tested polymeric materials. The innovative approaches based on additive manufacturing, such as those proposed in this work, will open the way towards the implementation of smart functions, commonly associated with the biological world, into novel polymeric and composite materials.

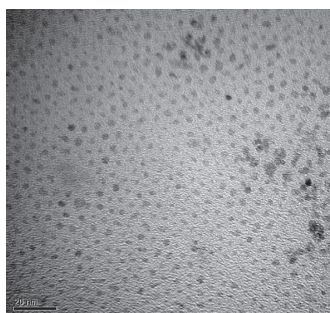
NANOSTRUCTURED ZIRCONIA: SYNTHESIS OF ZERO AND TWO DIMENSIONAL STRUCTURES FOR ADVANCED APPLICATIONS

Tana Francesca – Supervisor: Prof. Luigi De Nardo

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

Zirconia nanoparticles were synthesized taking advantage from the so called non-aqueous sol-gel route. This method allows

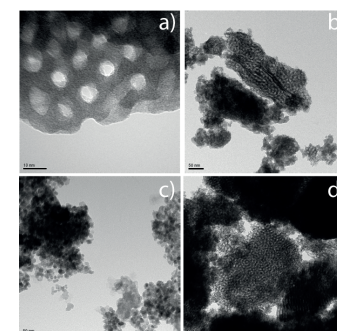
obtaining crystalline oxide particles in one-step reaction. The chemical reaction took place in the absence of water heating a precursor (i.e. metal salts or alkoxide) in appropriate organic solvent, under continuous stirring. Moreover this synthetic procedure allows obtaining ready to use crystalline nanoparticles, often composed by pure crystal phases dispersed in organic media without requiring functionalization procedure or calcination passage. For the purpose, $ZrCl_4$ was chosen as zirconium oxide precursor and reacted in benzyl alcohol. By this synthetic route, the involved chemical reactions occur slowly in comparison to the standard hydrolytic sol-gel route permitting a controlled growth of a crystalline



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

structure. The obtained zirconia powders were characterized by thermogravimetric analysis, XRD, TEM and Raman analysis in order to elucidate the thermal stability, nanoparticles dimension, phase and morphology. The developed synthetic procedure was further studied applying different experimental conditions, modifying precursor concentration (0.16 M-0.39 M-0.5 M) and reaction time (2.5-7-24 hours). At lower precursor concentration pseudo-spherical tetragonal particles of 2 nm were obtained. Higher amount of zirconium precursor and long reaction time caused increasing amount of monoclinic phase to growth. Moreover, TEM and HRTEM analyses showed an increase in zirconia nanoparticle size and changes in particles shape. Interestingly, increasing of reaction time and concentration of precursor solution caused anisotropic particles to growth from the starting pseudo-spherical crystallites to rice-shaped particles (preferential growth along c axis). This phenomenon could be attributed to a specific oriented attachment growth process in solution. Size, shape and phase of zirconia nanoparticles can therefore be tuned changing experimental conditions. The

employed non-hydrolytic sol gel process facilitates the introduction of nanoparticles inside a matrix to create nanocomposites bringing down mixing problems and macroscopic phase separation, resulting in homogeneous nanoparticles dispersion. Anti-scratch coatings were successfully obtained mixing 5 and 10% wt. particles in a commercial epoxy resin on PC and PMMA slices increasing polymer scratch resistance in the absence of delamination phenomena. Taking advantage of the results obtained by the starting part of my research activity, the synthesis of mesoporous zirconia coatings was carried out alongside. On the base of the self-assembly procedure from liquid precursor, a soft template agent was introduced in the mixture and subsequently thermally removed (calcining at 400-500-600 °C), in



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

order to obtain the mesoporous structure. Zirconia has different biomedical application since it is a non-toxic material with excellent mechanical properties and high chemical stability. For instance, it is especially appreciated in dentistry as a replacement for

titanium dental implants due to its similarity with natural teeth. The surface modification through mesoporous coating formation was carried out to increase implants osseointegration process due to the intrinsic porosity and the increase of surface area. Pure and CaO doped (11 and 25 % mol.) zirconia structures showing 5-10 nm pore size were tested. Mesoporous zirconia coatings demonstrated improved cells viability in comparison with the non-porous surface even if the contribution to cell adhesion, growth and proliferation or the interaction between proteins and the structured has to be elucidated. Calcium oxide allowed maintaining the pseudo-ordered porous structures up to 600 °C in comparison with the pure zirconia coatings and higher cells viability was observed for 25 % mol. CaO-doped samples.

DEVELOPMENT OF ORGANIC MATERIALS FOR INTERFACES IN PEROVSKITE SOLAR CELLS

Van der Velden Jeroen – Supervisor: Prof. Chiara Bertarelli

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

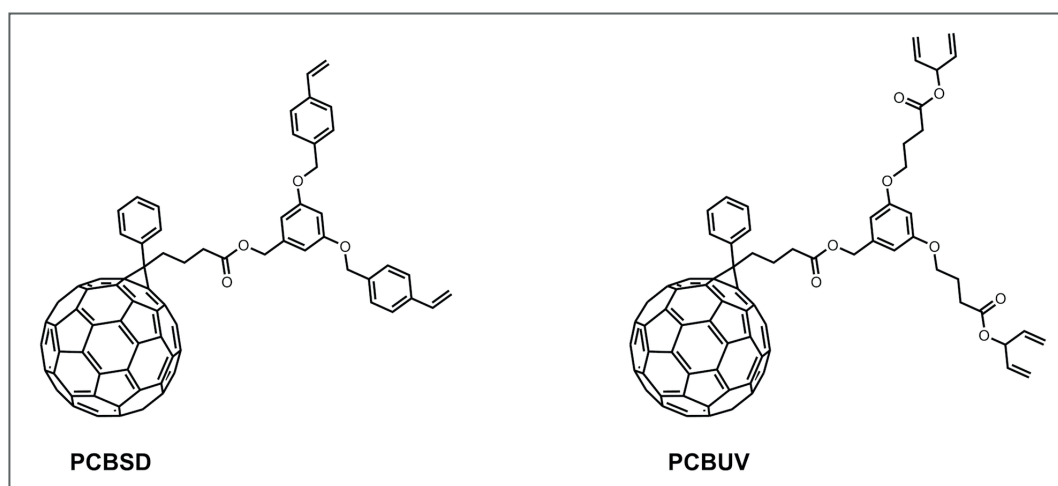
halide perovskite has led to a new type of solar cells. With a state-of-the-art PCE of 22.1% perovskite solar cells are a very good competitor for conventional Si-based solar cells. Despite the fact that organic-inorganic halide perovskite is a promising class of light absorbing material, one of the major drawbacks are hysteresis and long-term stability which can hinder the commercialization of perovskite solar cells. In solar cells interfaces play an important role in the degradation of the perovskite material. By careful modification of the interfaces in the device the long-term stability of the device can be improved. In this work, we present the

modification of different interfaces in the perovskite solar cell to increase the PCE and improve the stability. Modification of the TiO_2 layer with fullerene derivatives has proven to be effective to increase the PCE and improve the electrical stability of the device. In this framework we present the modification of the TiO_2 by the introduction of a thermally cross-linkable [6,6]-phenyl- C_{61} -butyric styryl dendron ester (PCBSD), which forms a thin solvent-resistant, robust electron-extracting layer (EEL). In addition we show that in the device with PCBSD, the V_{oc} is increased in comparison with devices having the commonly used [6,6]-phenyl- C_{61} -butyric

methyl ester (PCBM) as EEL. Moreover, we present an alternative method to cross-link PCBSD by UV-curing, which allows for low temperature processing of perovskite solar cells and other optoelectronic devices. Low temperature processing turns into the reduction of production costs and applications on flexible substrates could also be possible. In addition, we show the synthesis

and cross linking of [6,6]-phenyl- C_{61} -butyric 1,4-pentadien dendron ester by UV-curing in the presence of a photoinitiator. Furthermore, it is known that defect sites in the perovskite structure formed during crystallization or degradation are one the causes for electrical instability of the perovskite solar cell. Several methods have been reported for the passivation of

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



1. encaption: crosslinkable fullerene derivatives PCBSD and PCBUV