



Chair:
Prof. Chiara Bertarelli

DOCTORAL PROGRAM IN MATERIALS ENGINEERING

The Ph.D. Programme in Materials Engineering provides high educational opportunities to young talents and executives who intend to become proactive professionals and researchers skilled in the design, production and application of both traditional and innovative materials, their optimization for specific applications, the prediction and assessment of their performance, and in developing new concepts and technologies in any materials-related fields.

Highlights of the Ph.D. Programme in Materials Engineering are:

- a rigorous scientific approach to address outstanding research
- an effective interdisciplinary approach
- connection with international leading scientific and technical communities
- a strong integration with the Doctorate School of Politecnico di Milano to increase knowledge with transversal courses, to gain soft skill and to join stimulating activities.

PHD CONTENTS and PROGRAM STRUCTURE

Materials Engineering involves the investigation of correlation among materials structure, processing and functional and structural properties, and the knowledge management from materials design to final applications.

The Programme includes advanced research and training on:

- Research and development in traditional materials (*polymers metals, ceramics, concretes, composites*) and related technologies.
- Specific application areas: *materials for energy, materials for environment, materials for electronics, optoelectronics and photonics, materials for cultural heritage, materials for product design, materials for packaging, biomaterials.*
- *Smart, responsive and self-healing materials, nanostructured materials.*
- *Materials corrosion and durability, life cycle assessment, coating and surface functionalization*

The achievement of the Ph.D. title in Materials Engineering requires a full-time study and research activity of at least three years which is completed by the development and defense of the Ph.D. thesis.

The PhD. students give an original contribution to increase knowledge in a material-related research field, and they acquire a problem-solving capability in complex contexts, including the ability of performing deep problem analysis, identifying original solutions, and evaluating their applicability in practical contexts. Students can use modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research

laboratories.

The Ph.D. Programmes and the Ph.D. School activate courses, seminars, project workshops and laboratories. Teaching activities cover both basic research topics (problems, theories, methods) and specialistic topics related to the subjects developed in the theses. Ph.D. students are also encouraged to attend national and international Conferences Workshops and Schools and to plan a research period abroad.

PROFESSIONAL OPPORTUNITIES AND THE JOB MARKET

The Ph.D. Programme in Materials Engineering aims at training Ph.D. laureates having a common background and specialized qualifications in advanced research areas. The knowledge and skills of a Ph.D. in Materials Engineering enable graduates to pursue their career in the Manufacturing industry, given its quest for innovation in the production, processing, application and conservation of traditional materials, and for the development of innovative materials allowing radically new, currently unforeseeable applications.

Moreover, the background deriving from full-time activity both in research and in education also qualifies the Ph.D. graduates for an academic career. Several graduates from the Materials Engineering Programme have been able to secure post-doctoral research positions at high-ranking universities and research Institutes.

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CHEMICALLY CROSSLINKED METHYLCELLULOSE HYDROGEL PLATFORMS: FROM DESIGN TO SMART APPLICATIONS

Lorenzo Bonetti – Supervisors: Prof. Silvia Farè, Prof. Luigi De Nardo

Stimuli-responsive biopolymers have attracted significant attention over the last decades as platforms for tissue engineering and regenerative medicine (TERM). In addition to their similarity with the native extracellular environment, stimuli-responsive biopolymers are also capable of responding to environmental changes in a tunable and determined way, supporting the development of innovative solutions. Among them, thermo-responsive biopolymers are the most studied for TERM purposes, since temperature can be regarded as the most available stimulus in the human body. In this PhD thesis work, methylcellulose (MC) is presented as a noteworthy cellulose derivative for the preparation of hydrogels with thermo-responsive behavior. Specifically, the transition of MC hydrogels from the sol, hydrophilic state, to the gel,

hydrophobic state (Fig.1), makes it interesting for different applications. A thorough literature review revealed that the main application areas of MC hydrogels are related to i) *in situ* gelling systems, ii) 3D (bio)printing, and iii) cell sheet engineering (CSE). In this regard, an optimal design of MC hydrogels was here disclosed as the fundamental stage to correctly tune their properties (e.g., thermal, mechanical, biological), first and foremost the lower critical solution temperature (LCST). For the scope of this thesis, MC hydrogels (8% w/v in 50 mM Na₂SO₄) were optimally formulated to exhibit a LCST around 37 °C, to exploit physiological temperature as a trigger to activate their thermal transition. A new tool for the LCST quantification was then developed. On this topic, *in situ* Raman Spectroscopy was disclosed for the first time as an

innovative technique for the precise identification of the LCST of MC hydrogels (Fig.2). *In situ* Raman Spectroscopy offered the distinctive advantage of being non-destructive compared to other well-established techniques (e.g., rheology, DSC) for LCST identification, also providing supplementary insights about the chemical make-up of MC during the thermal transition.

Since MC hydrogels usually show reduced water stability and low mechanical properties, chemical crosslinking is required to enable the use of MC hydrogels for different TERM applications. A citric acid (CA)-based method for MC hydrogels crosslinking was thus designed and developed. Following a design of experiment (DOE) approach, three crosslinking parameters (CA concentration, crosslinking time, crosslinking temperature) were studied. Through this approach, three optimized crosslinked MC hydrogels (MC-L, MC-M, MC-H) were obtained and characterized. Particular consideration was given to the preservation of MC thermo-responsive character after crosslinking. In this regard, MC-M samples were shown to preserve their responsive behavior, while displaying superior properties (i.e., water stability and rheological) compared to MC control. Higher crosslinking (i.e., MC-H) was instead demonstrated to impair MC thermo-responsiveness.

The optimized crosslinked MC hydrogels were then tested as substrates for CSE. First, CA was disclosed as a non-cytotoxic crosslinking agent for MC. Confluent

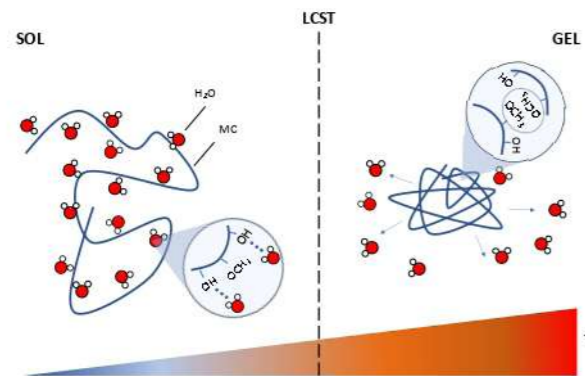


Fig. 1 Thermo-responsive behavior of MC aqueous solutions: for $T < LCST$, H bonds between water and the -OH groups of MC dominate (i.e., sol state). For $T > LCST$, H bonds are disrupted and CH₃-CH₃ hydrophobic interactions occur, leading to the formation of a physically crosslinked gel (i.e., gel state).

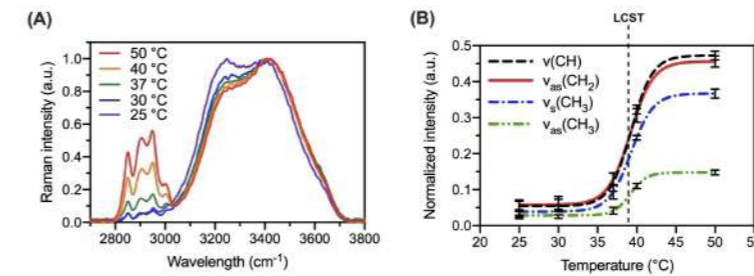


Fig. 2 A) Representative Raman spectra of MC hydrogels (8% w/v) in the 2700 - 3800 cm⁻¹ region in the 25 - 50 °C range. B) 4PL curve fitting applied to the intensities of C-H_x bands as a function of temperature.

cell sheets (CSs) were harvested from crosslinked MC hydrogels (MC-L, MC-M) without the need for any proteolytic enzyme (e.g., trypsin), simply by lowering the external

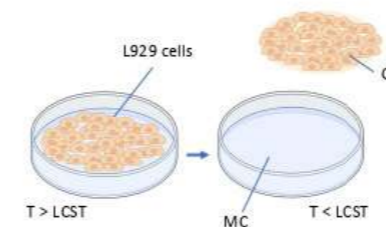


Fig. 3 Scheme of CS detachment: at 37 °C (i.e., LCST), L929 cells adhere and proliferate on the MC surface, due to its moderately hydrophobic nature. At $T < 37$ °C, MC change to hydrophilic, allowing the spontaneous detachment of an intact CS.

temperature below the LCST (Fig.3). The harvested CSs displayed adhesive and proliferative activity after their transfer to a new culture surface, indicating their high regenerative potential. MC-H surfaces did not allow the detachment of any CSs, due to the loss of their thermo-responsive character caused by over-crosslinking.

In conclusion, this thesis describes, for the first time, the use of chemically crosslinked MC hydrogels for CSE. The crosslinking approach and the tool developed for LCST assessment (i.e., *in situ* Raman Spectroscopy) synergistically contributed to the development of crosslinked MC hydrogels with superior properties (compared to pristine MC) and preserved thermo-responsiveness. Crosslinked MC hydrogels have been demonstrated as suitable substrates for CSE, but lend themselves well for a wide range of innovative applications. For instance, these systems could be used in the field of soft robotics or as smart sensors. Furthermore, such systems could be used as innovative

thermo-responsive platforms for the development of smart water harvesting systems.

PHOTOACTIVE TITANIUM DIOXIDE FILMS OBTAINED BY PLASMA ELECTROLYTIC OXIDATION FOR ENVIRONMENTAL APPLICATIONS

Arab Hamed – Supervisors: Prof. Silvia Franz, Prof. Massimiliano Bestetti

Photoactive-based applications of titanium dioxide (TiO_2) are well known in the areas of environmental applications. Among proposed techniques to obtain photoactive TiO_2 , this thesis focuses on Plasma Electrolytic Oxidation (PEO) which operates in a configuration similar to conventional anodic oxidation but at higher potential (i.e., 100 V >). PEO is capable to produce photoactive TiO_2 but has not received much attention in the literature. Considering this scarcity, the aim of this PhD thesis was to synthesize photoactive TiO_2 catalysts by PEO and exploit them in environmental applications such as photo-electro-catalytic water splitting and waste-water treatment. This thesis is divided into two parts namely synthesis and characterization of photoactive titanium dioxide films and exploit them as photo anodes. As for synthesis, the effect of different parameters such as PEO potential and type (DC and Pulsed DC), processing time, dopant, and electrolyte temperature on morphology, TiO_2 film thickness growth, elemental characterization, electrochemical surface area (ECSA), crystalline phase composition (Real time/ ex-situ), band gap, and photocatalytic properties were studied. Overall, SEM images showed a 3-D sponge-like morphology where pore diameter varies depending on PEO potential and time. The growth of TiO_2 film oxide depended mostly on PEO potential where PEO time became important at higher potentials (above 160 V). Overall, it changed from ca. 500 nm (at 100 V) to 11 μm (at 200 V and 400

Hz). All the TiO_2 films were crystalline in structure as pure anatase and rutile (in lower and higher PEO potential, respectively) and a mixture of anatase and rutile in other conditions. The instantaneous investigation of crystalline phase transformation by Real-time Raman spectroscopy (Fig.1) showed that at lower voltages (100 V and 120 V), the crystalline phase composition was stable within the processing time (5 minutes) and consisted in 75 wt.% and 90 wt.% anatase respectively. At intermediate voltage (150 V), a phase transition was observed from 90 wt.% to 35 wt.% anatase within 150 s, and at higher cell voltages (180 V), the anatase content decreased from 74% to 15% just in 90

s. Based on the reflectance UV-VIS spectra, the band gap of the films decreased from about 3.2 eV to 2.94 eV which were in agreement with the crystalline phase contents.

The photoelectrochemical activity of the TiO_2 coatings was assessed by means of linear sweep voltammetry carried out in dark and under poly/mono chromatic source of light. Three main different parameters namely crystalline phase content (optimum: 60-70 Anatase, 40-30 Rutile), TiO_2 film thickness (Optimum 2-3 μm), and ECSA determined photoelectrochemical activity, and incident photon to current efficiency (IPCE) of specimens met the aforementioned optimum conditions

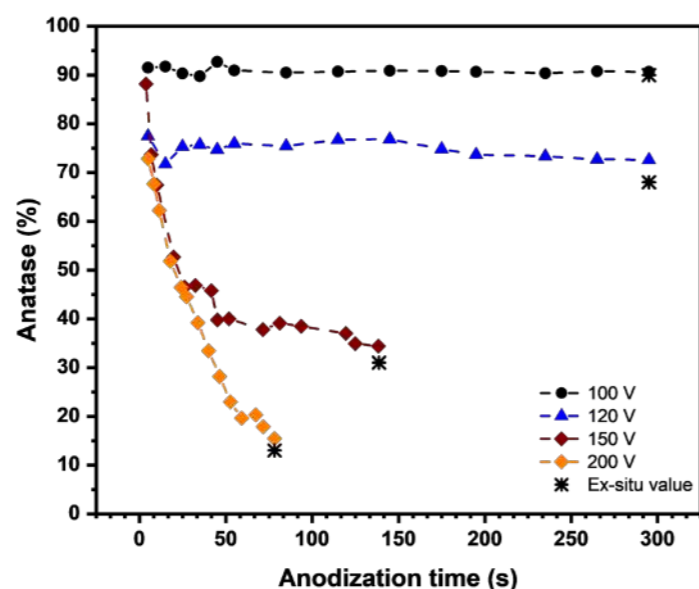


Fig. 1 Instantaneous weight fraction of anatase based on real-time Raman spectroscopy as a function PEO time at different cell voltages.

reached 96%. Ni-doped TiO_2 showed a higher photocurrent values under monochromatic irradiation in the UV-Vis range, outperforming pure TiO_2 . In agreement with photocurrent measurements, photoluminescence (PL) spectra confirmed that less intense PL emission, i.e. lower electron-hole recombination rate, was observed for Ni-doped samples, though over-doping was detrimental. As for application of TiO_2 photoanodes, water splitting measurements was conducted under simulated solar light irradiation, and the highest H_2 production rate was obtained for the electrode prepared at 150 V and 300 s

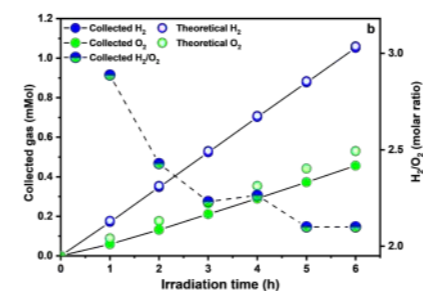


Fig. 2 H_2 (blue) and O_2 (green) gases effectively collected under irradiation (full symbols) together with their theoretical values (empty symbols; right ordinate: experimental H_2/O_2 molar ratio (blue-green symbols)).

which showed a H_2 production rate of 0.17 mmol/h (Fig.2). In the case of waste-water degradation, an immobilized photoactive TiO_2 catalysts having a surface area of ca. 400 cm^2 was

grown directly on titanium meshes based on the optimum condition investigated above. The TiO_2 mesh was placed in a photoelectrochemical reactor where the reactor was capable to be operated in four different configurations namely Photoelectrocatalysis (immobilized TiO_2 +UV+bias), Photocatalysis (Immobilized TiO_2 +UV), Electrochemical oxidation (Immobilized TiO_2 +bias), Photolysis (only UV). Different sources of wastewater (MilliQ and secondary water spiked with Carbamazepine, pharmaceutical waste-water, etc.) were successfully treated and when applicable, the result was compared with suspended TiO_2 powder (Degussa P25). Results (Fig.3) showed that carbamazepine degradation rate follows the order UV/supported TiO_2 +bias = UV/ TiO_2 Degussa P25 > UV/supported TiO_2 > UV. In the case of decolorization of pharmaceutical wastewaters, an intense recalcitrant color was treated by photoelectrocatalytic (PEC) and H_2O_2 -assisted PEC. H_2O_2 -assisted PEC showed the highest decolorization efficiency.

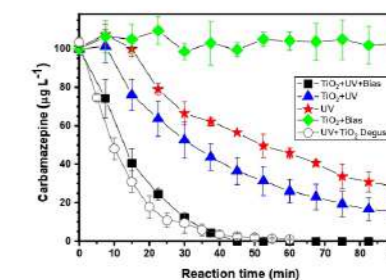


Fig. 3 Degradation of carbamazepine by photoelectrocatalysis and conventional photocatalysis (Degussa P25) performed in real secondary effluent wastewater. Error bars represent the standard deviation obtained for three replicates.

IMAGE-BASED ALGORITHM FOR STRUCTURE INVESTIGATION AND MECHANICAL MODELLING OF EXPANDED POLYMERIC MATERIALS

Stefano Tagliabue – Supervisor: Prof. Luca Andena

Expanded polymeric materials are of great importance in many engineering applications. Despite this, as of today the development of models able to describe their macroscopic mechanical behaviour considering their actual microstructure is still an open challenge.

In the following study different image-based algorithms were developed, validated and optimized for microstructure characterization and subsequent three-dimensional numerical mechanical simulations, both linear and non-linear.

Microstructure was investigated through different algorithms, scalar and tensorial, to identify key parameters able to describe the internal structure. Finite element simulations were performed considering the real microstructure obtained from high-resolution X-Ray computed tomography images through the application of two different image-based approaches: a classical algorithm based on Representative Volume Elements, aimed at modelling the linear elastic behaviour of the material; a second novel approach aimed at providing an efficient and powerful numerical tool to perform non-linear simulations. The application of algorithms for structure analysis and the image-based approaches for mechanical finite element simulations led to the identification of general relationships between expanded material microstructure and relevant macroscopic physical and mechanical properties, resulting in the formulation of a closed system of analytical

equations. This framework can serve as a tool to optimize foam morphology and product final properties for widely different engineering applications, simplifying and speeding up all the prototyping phase, which usually turns out to be, from an industrial point of view, the most expensive one in terms of time and cost.

Finally, the efficiency of the numerical tool designed for non-linear mechanical simulations was analysed, opening new paths to simulations and to the extension of analytical relationships between macroscopic mechanical parameters and microstructure quantities in the non-linear mechanical regime.