URBAN AND ARCHITECTURAL DESIGN | VIRTUAL PROTOTYPES AND REAL PRODUCTS | WATER ENGINEERING | AEROSPACE ENGINEERING | ARCHITECTURAL COMPOSITION | ARCHITECTURE, URBAN DESIGN, CONSERVATION OF HOUSING AND LANDSCAPE | BIOENGINEERING | BUILDING ENGINEERING | DESIGN AND TECHNOLOGIES FOR CULTURAL HERITAGES | ELECTRICAL ENGINEERING | ENERGY | GEOMATICS AND INFRASTRUCTURES | INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING | INDUSTRIAL DESIGN AND MULTIMEDIA COMMUNICATION | INFORMATION TECHNOLOGY | INTERIOR DESIGN | MANAGEMENT, ECONOMICS AND INDUSTRIAL ENGINEERING | MANUFACTURING AND PRODUCTION SYSTEMS | **MATERIALS ENGINEERING** | MATHEMATICAL MODELS AND METHODS IN ENGINEERING | MECHANICAL SYSTEMS ENGINEERING | PHYSICS | PRESERVATION OF ARCHITECTURAL HERITAGE | PROGRAMMING, MAINTENANCE, REHABILITATION OF THE BUILDING AND URBAN SYSTEMS | RADIATION SCIENCE AND TECHNOLOGY | ROTARY WING AIRCRAFT | SANITARY - ENVIRONMENTAL ENGINEERING | STRUCTURAL SEISMIC AND GEOTECHNICAL ENGINEERING | TECHNOLOGY AND DESIGN FOR ENVIRONMENTAL QUALITY IN BUILDINGS AND URBAN CONTEXT | TERRITORIAL DESIGN AND GOVERNEMENT |

PhD Yearbook | 2010

DOCTORAL PROGRAM IN MATERIALS ENGINEERING

Chair:
Prof. Chiara Castiglioni

Purpose of the courses of the Doctoral Program is to provide PhD students in materials engineering first with a common and basic knowledge followed by a specialized training in specific fields. The objective is to combine the theoretical knowledge with the requirements by technology in order to prepare a qualified researcher who can guide the design, manufacturing and use of traditional and/or new materials.

Contents of the Doctoral Program

The Doctoral Course covers the following areas:
Biomaterials
Polymers and composites
Cements and ceramics
Corrosion and durability of materials
Metals
Structure, properties and microscopic theories of materials
Materials for electronics, photonics and sensors
Nano-structured materials
Surfaces and coatings
Materials for industrial design
Transformation of materials

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 chooses the Introductory and Elective courses and submit to the Faculty a "Curriculum" to be approved. The Courses offered deal with both theoretical and experimental or numerical aspects. Workshops and seminars are organised with the participation of invited internationally well-known speakers. Great attention is paid to the fact that students are able to use the most modern facilities available at the Politecnico or in other research laboratories. The research activities for 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 planned. The Ph.D. student are supervised by a professor who reports to the faculty. The faculty evaluates the progress of the research at least twice a year 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 discusses, in a public hearing, his work in front of a committee of five experts appointed according to the rules of the Politecnico di Milano.
The Ph.D. student is asked to attend and present papers at national and international meetings 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):

- 60 credits must be obtained through attendance at Courses (with positive evaluation in the examinations, when required), attendance at Conferences and International Schools;
- the other 120 credits will be assigned on the basis of the research activity necessary to the development of the Thesis project.

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, necessarily, specialized people it has been decided to offer a few specialized curricula.
On the other hand, the capabilities acquired through the courses, the research work and the teaching assure an adequate preparation to the academic career.

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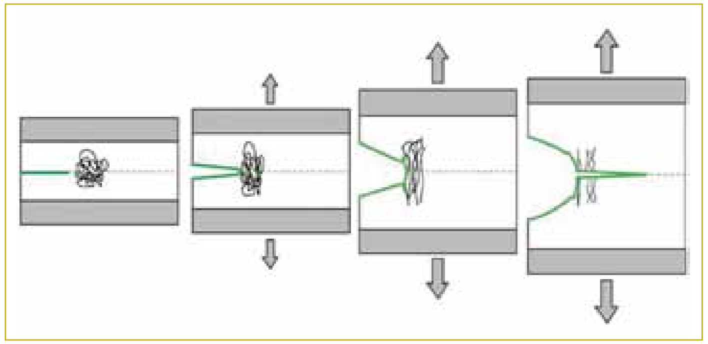
FRACTURE BEHAVIOUR OF CARBON BLACK FILLED NATURAL RUBBER

Manuela Boggio

An unexpected phenomenology of crack propagation in rubber compounds has been frequently reported in literature. In mode I fracture, in notched specimens, the crack propagates in the loading direction deviating from the expected path along the initial notch plane. This macroscopic observation is correlated with the molecular orientation and/or strain crystallization occurring during the test near the crack tip. When strained, macromolecules tend to assume a preferential orientation in the loading direction. In vulcanized rubber, since flow is avoided by intermolecular covalent crosslinks, the structure of the deformed material becomes anisotropic with a higher strength along the polymer chains direction and anisotropy increases as deformation increases. Further, being natural rubber macromolecules highly stereoregular, alignment between stressed polymer chains can result in strain induced crystallization, then when stress is removed, the crystallites melt. If anisotropy at the crack tip is high, crack deviation is observed. In this research, a suitable pure shear test was set up using a specimen geometry which allowed to study this particular fracture phenomenology and to analyze the relevant fracture toughness applying fracture mechanics.

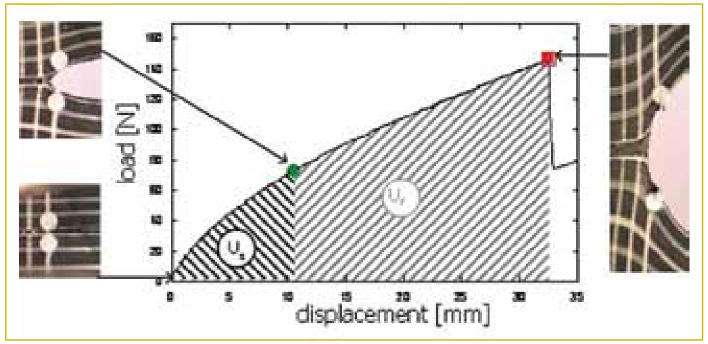


1. Schematic of a pure shear test on grooved specimens: as strain increases, the crack tip blunt, then when the macromolecules at the crack tip reach a certain orientation the sideways cracks onset, at larger strains the forward crack onset.

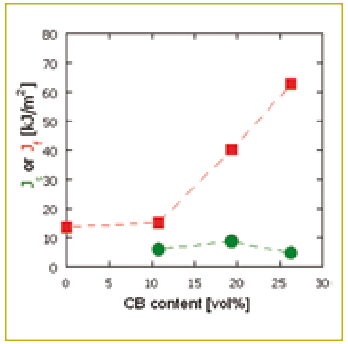
As schematically shown in Fig. 1, the adopted geometry well separates the onset of sideways cracks (in the loading direction) from that of a forward crack (perpendicular to the loading direction) which takes place at larger deformations. The material toughness was evaluated using an energy based fracture mechanics approach, in particular the J-integral was considered, and was calculated, at sideways and forward cracks onset, as input energy per unit of resistant area, as shown in Fig. 2. The effect of carbon black content and strain rate on the compounds ultimate behaviour was then studied. As for the effect of carbon black content (see Fig. 3) it was found that:

- sideways cracks initiate at a fairly constant value of J irrespective of CB content. The onset of sideways cracks is linked to chain orientability and carbon black aggregates, acting as a physical crosslinks, amplify molecular orientation for a given strain, in fact natural rubber does not show crack deviation and as carbon black content increases, crack deviation occurs at lower strain. X-ray scattering analysis on strained specimens was also performed in order to analyze the effect of carbon black on strain induced crystallization and molecular orientation and to correlate it to fracture phenomenology;
- toughness at forward crack onset increases as carbon black content increases.

This toughness increase is mainly linked to energy dissipation mechanisms occurring at large deformations. While straining, part of the energy is stored in the chains and part is dissipated. The energy dissipating mechanisms are favored by heterogeneity in the molecular weight between junctions distribution and the presence of carbon black develops this heterogeneity. Forward crack initiates when a sufficient number of chains in the process zone, at the crack tip, store sufficient energy. Ad hoc "loading-unloading" experiments were performed to separate the stored and dissipated energies during fracture tests and correlated with the carbon black content.



2. Typical load displacement curve with the frames corresponding to the unloaded specimen, to sideways cracks onset and to forward crack onset



3. Fracture toughness at sideways and forward cracks onset as a function of carbon black content

As for the effect of strain rate on fracture toughness, which was studied only for one carbon black content:

- toughness at sideways cracks onset does not depend on strain rate as could be expected since orientation of a rubber should not be time dependent unless loading times become comparable to relaxation times of a material well above the glass transition.
- toughness at forward crack increases as strain rate increases indicating that probably the dissipation mechanisms occurring at large deformations are time dependent. This result could be related to the behaviour of the material linked to the carbon black which may have a much lower mobility than the overall macromolecule. This hypothesis is still under verification by performing test on compounds with different carbon black content and "loading-unloading" test.

STUDY OF AC-CORROSION ON MILD STEEL UNDER CATHODIC PROTECTION

Characterization of oxide films by electrochemical and surface analytical methods

Veronica Bueno

It has been reported that the corrosion of underground power cables is caused, or at least greatly enhanced, by ac leakage from the cable to the ground. Even the corrosion of underground pipelines in close proximity to overhead power lines has been attributed to the leakage of ac to the surrounding soils. For the study of such an effect, some workers have carried out current-potential measurements with a superimposed sinusoidal modulation, and indications of high corrosion current densities were reported.

The presence of alternating current (ac) causes serious corrosion damages on metallic structures, even when they are under cathodic protection (cp). i.e., on the places where a "cathodically protected structure", like a metallic pipe, runs parallel to High Voltage Lines (HVL), an inductance effect is produced (if the pipe is sufficiently isolated by an organic coating), causing the circulation of the ac from the HVL to the structure. These ac passes through the metal and, on its exit place, the metal corrodes. Cathodic protection decreases ac-corrosion, but the magnitude of dc-currents required is high and until now difficult to predict.

With this research it is intended to obtain an insight into the nature and mechanism of the electrode reactions during ac-corrosion processes, through both the production and the characterization of oxide films at applying electrochemical and surface analytical methods. Special attention is given to processes occurring in the range of dc potential considered in cathodic protection systems.

Mild steel samples and a solution of 1M NaOH has been employed in order to reproduce the high pH levels than can be locally reached in the metal surface when high cathodic protection currents are applied.

A state of the art based in previous studies about reaction mechanisms and mathematical models of ac-corrosion process, is presented.

This study has for objectives: to identify the reactions, to characterize the oxides and to evaluate the surface damages that occur in mild steel samples when disturbed simultaneously with continuous and sinusoidal potentials.

In the Laboratory, the electrochemical technique that applies such a combined potential to solid working electrodes is the "Ac-voltammetry" (ACV).

With this technique, samples are disturbed with a sinusoidal potential that is superimposed to the steps of a direct potential. Ac-voltammetry, applied at small potential amplitudes (5-10mV), serves to identify reactions occurring at the metal surface in a determined solution. When applied at higher amplitudes it intensifies the effects of sinusoidal voltages on the metal surface. For single amplitudes, scans at predetermined frequencies of the sinusoidal potential were even performed.

In another set of experiments, after the application of ac-voltammetry, and with the oxidized species accumulated in front of the surface, a galvanostatic chrono-potentiommetry (GCP) was applied, with a negative current in one step, in order to reduce, identify and quantify the oxidized species. This combined technique brought additional benefits in obtaining information about the surface reactions, the formed oxides and the diffusion phenomena.

After the application of "ACV" or "ACV plus GCP" to mild steel samples in NaOH 1M solution, the surface films were evaluated through selected physical and/or chemical techniques for surface characterization, like optical microscopy (OM), stereoscopic microscopy (SM), X-ray diffractommetry (XRD), scanning electron microscopy (SEM), environmental SEM (ESEM), focused ion beam (FIB) and X-ray photoelectron spectroscopy (XPS). Surface analysis was performed selectively to mirror-polished, oxidized and pickled samples.

In addition, experiments with dc-Voltammetry were conducted for comparative purposes.

Finally, the amplitude of the first harmonic component of the current, obtained experimentally with ACV, was mathematically simulated, in order to better identify the reactions occurring at the metal surface. From the simulation, some electrochemical and kinetical information was obtained.

Between the main conclusions, were:

AC-Voltammetry is useful for:

- The simulation of polarization due to ac currents (or voltage signals)
- The identification of reactions occurring at the surface of a reacting working electrode, when small amplitudes are applied.
- The study of ac-corrosion damages.
- In 1M NaOH solution, and in the cathodic region of potential for mild steel, there are reactions not reversible to dc nor to ac perturbations, corresponding to ac-corrosion and the formation of porous oxides.

Forward scans of ACV present three peaks, between -1.3 and -0.7 (V) vs. SCE, associated to the following proposed reactions:

Peak 1: $Fe \leftrightarrow Fe(OH)_2$;
$Fe \leftrightarrow Fe_3O_4$; $Fe(OH)_2 \leftrightarrow Fe_3O_4$
Between Peak 1 and Peak 2 and part of Peak 3: FeOOH
Peak 3: $FeOOH^- \leftrightarrow Fe(OH)_3$;
$FeOOH^- \leftrightarrow Fe_3O_4$

According to the applied amplitude and frequency of the sinusoidal signal there is a cyclic passage between one peak reaction and another. This phenomenon is responsible for the formation of porous oxides which do not protect the underlying metal from corrosion.

In cathodically protected system, it is suggested to maintain the dc potential in the minimum points of ac voltammetric curves. In those regions, the concentration of reactants are minimum and selecting this potential, the damaging reactions if not avoided, can at least be minimized.

But, it has to be taken into account that maximum and minimum points move to more positive or negative potentials according to the related rectification current that is produced by asymmetrical reactions when sinusoidal signals are applied. This rectification current increases with the amplitude; for this reason unexpected reactions occur at potentials at which they are not expected. In other words, the rectification current modifies the potential at which reactions occur.

ACV is a useful technique to estimate how much the reaction potential is shifted from the natural standard potential and, then, knowing the amplitude of an interference current, the new potential at which the reaction will occur can be known. Thus, the range of cathodic potential shall be moved to avoid unwanted reactions.

From XPS results, after a forward scan with ACV, $Fe(OH)_3$ was found. The appearance of this species coincides with the increase in current of Peak 3 in AC voltammograms. On the other hand, after a background ACV scan, $Fe(OH)_3$ was consumed whilst FeO is formed.

SM, ESEM and FIB surface analysis, after ACV application, has shown that the color, concentration and thickness of the oxides intensify/increase with the amplitude of the applied sinusoidal signal and with the scan number. On the other hand, those characteristics vary less markedly with the frequency of the applied sinusoidal signal. The porosity of the oxide film was a common characteristic in metal surfaces and did not change with the amplitude, frequency or scan number.

The GCP in combination with SIB allowed the identification of reduction reactions, calculation of oxide thickness and yielded important information for the simulation of ACV curves that allows of the characterization of reactions from the electrochemical point of view.

Further developments shall measure the rectification current (that is expected to be produced due to non-linearities of the electrode reactions in the presence of sinusoidal perturbations).

This rectification current is related to unwanted changes of the electrode potential. Preliminary tests of this kind have been performed in this research (not reported), but the measurement circuit and the equation that calculates the amplitude present at the metal surface, shall both be improved.

SYNTHESIS AND CHARACTERIZATION OF PHENYL OLIGO- AND POLYTHIOPHENES

Molecular structure *versus* electrical bistability and phototransduction properties

Eleonora Canesi

Conjugated molecules are a promising alternative to the traditional inorganic semiconducting materials in electronics and optoelectronics applications, thanks to the peculiar optical and electrical properties strictly related to their chemical structure.

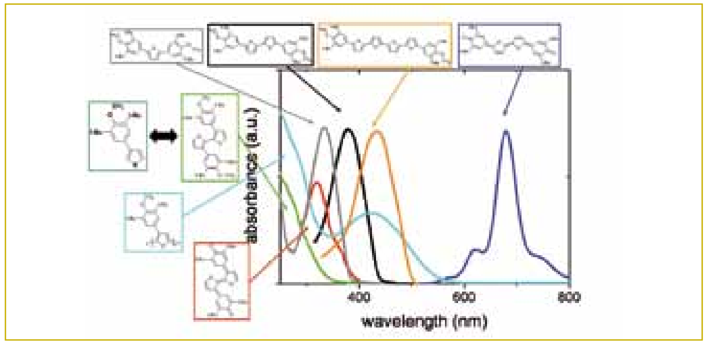
Organic devices can be ideally scaled down to molecular dimensions; moreover, they can be developed as low cost, flexible, large area systems.

Being the optical and electrical properties of conjugated functional materials intrinsic of their structure at the molecular level, the development of such compounds rests with the study of the molecular design.

The comprehension of the structure-property relationships comes out to be the essential step in order to develop devices with optimized performances.

In this framework, my research activity has been mainly focused on the class of molecules of phenyl thiophenes (PTs), which have been recently applied in such technological area with promising results.

The work involved the synthesis, the characterization and the processing of phenyl oligo- and polythiophenes for the development of memory cells and photodetectors. Molecules with controlled variations in the chemical structure have been designed and synthesized,



1. Molecular structures and UV-visible spectra of phenyl thiophenes

with the aim of highlighting the relationship between structure and physical (optical and electrical) properties.

An example of the wide tunability of the optical features obtained is shown in figure 1, where the UV-visible absorption spectra of some of the phenyl thiophenes studied is reported.

Syntheses of the targeted molecules have been optimized by defining new experimental routes.

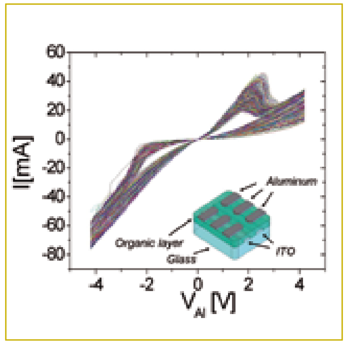
As it is well known that, going from molecules to materials, morphology and intermolecular interactions play a relevant role, processing has been considered with great attention: indeed, uniform thin films with monitored characteristics have been produced in order to control the device performance. Good homogeneity and repeatability of the films have been obtained thanks to a standardization of the deposition procedure.

A model, which has been reported in the literature for polymers, has been fitted to predict the thickness of spin-coated films of conjugated oligomers, and it has been applied to predetermine the setup conditions to obtain PTs films with desired thickness.

Based on these films, electrical and optoelectronics devices have been realized. Several experiments and a deep spectroscopic characterization have been carried out for understanding the molecular processes at the basis of their operation.

Regarding photosensitive devices, attention has been focused on the detection of red and near-infrared radiation, that is of interest for many applications, such as optical communications, chemical and biological sensors, remote control and medical instrumentations. Transient electronic spectroscopy has been applied to clarify the excitation and relaxation processes triggered by device irradiation. For heterojunctions made of a quinoid species and a conjugated polymer, an efficient unidirectional charge generation has been identified.

The use of these findings in the field of organic photovoltaics is currently under study.



2. I-V curves recorded with a PTs based memory cell, whose device architecture is shown in the inset

Phenyl thiophenes showing electrical bistability have been exploited for the development of memory cells. With two terminal devices, whose architecture is sketched in figure 2 (inset), results of relevance have been obtained, with significant improvement of performance when a polymer matrix has been introduced: more than one thousand write&erase operations have been recorded, as shown in figure 2. A key point in the field of orgainc based information storage is the demonstration of the molecular origin of the observed bistable behavior: indeed, in the literature such peculiar finding is under debate and it is often related to extrinsic processes rather than to intrinsic properties of the organic material.

For PTs, the development and characterization of memory cells with controlled variations in the device composition, both regarding the organic layer and the electrodes, gave significant indications on the molecular origin of the electrical switching observed. Moreover, an expressly designed experimental setup made possible the *in-situ* optical characterization of an operating device, revealing small but repeatable variations of the molecular properties during the switching process.

To go further in the control of the organic layer morphology and properties down to molecular dimensions, phenyl thiophenes able to self-assemble have been designed and synthesized: such species allow the realization of monolayer-based devices, aimed at verifying if the electrical switching behavior of memory cells is maintained also at the molecular scale.

CALCIUM OXALATE: CHEMICAL STABILITY, CONSERVATIVE TREATMENT BASED ON AMMONIUM OXALATE, HISTORICAL FILMS.

Claudia Conti

This thesis wishes to combine new scientific knowledge with applied science in the field of conservation of works of art. One of the most controversial issue still under discussion among conservation scientists is about the oxalate films detected on the surfaces of several ancient monuments of the Mediterranean Basin, observed for the first time at the end of 19th century on the stone surfaces of Parthenon. They are constituted by the presence of calcium oxalate in the most common forms, whewellite ($CaC_2O_4 \cdot H_2O$) and weddellite ($CaC_2O_4 \cdot (2 + x)\, H_2O$), which chemically differ only on the amount of water molecules, while the mineralogical structure is completely different, monoclinic for whewellite and tetragonal for weddellite. They have been detected both on natural stone materials as marble, calcarenite, sandstone, granite and on artificial stone materials as plasters or terracotta.
Whewellite is stable at environmental conditions, while weddellite, under the same conditions, quickly changes into whewellite. Several problems still need to be solved namely why have whewellite and weddellite been often detected both within the same film? What makes the formation of whewellite and weddellite easier, together or separately? And finally, is there a recurrent stratigraphy of the two calcium oxalates from the surface to the inner portions of the substrate? The undiscussed peculiarity of these films is their chemical stability, proved by their persistence during the centuries on surfaces exposed to the atmospheric conditions, in spite of the strong increase of atmospheric acidity in all urban sites. The stability of calcium oxalate is easily explained by its water solubility; indeed this value is very low (0.05 mmole/l at pH between 5 and 11) still at acid pH (0.37 mmole/l at pH 2.5). Stratigraphic studies showed that, below the calcium oxalate film, the substrate is in a good conservation state, it is then possible to state that this film slowed down the decay process of the material. The chemical stability and the "protective" action of the calcium oxalate film induced some scientists working in the field of conservation of stone surfaces to suggest a protective treatment able to induce the formation of calcium oxalate on decayed carbonatic surfaces. In the '90s Mauro Matteini suggested a conservative treatment based on ammonium oxalate, then rather employed by restorers, in order to preserve limestones, marbles or plasters. The ammonium oxalate water solution induces the transformation of calcium carbonate into the less soluble calcium oxalate. Compatibility, durability, absence of colour and hydrophilicity are necessary conditions for a good protective treatment and they are satisfied in the case of "artificial" calcium oxalate. The application of oxalic acid is too aggressive for the surfaces, while ammonium oxalate is a more bland source of oxalic ion. Indeed its aqueous solution is neutral and most of all the secondary by-product is decomposable:

$$CaCO_3 + (NH_4)_2C_2O_4 + H_2O$$

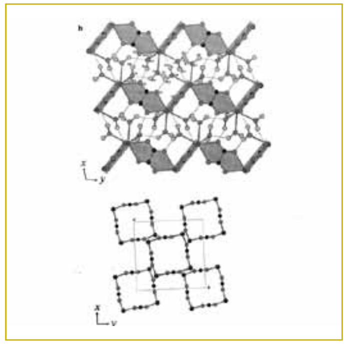
$$\downarrow$$

$$CaC_2O_4 \cdot H_2O + (NH_4)_2CO_3$$

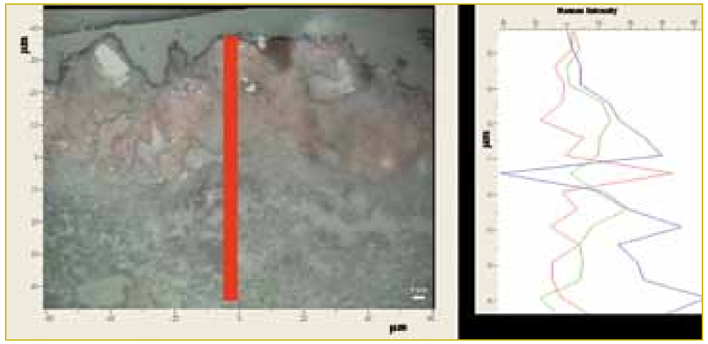
If the reaction is done properly, there should be no residual amount of $(NH_4)_2CO_3$ since NH_3 and CO_2 are developed.
Although ammonium oxalate treatment showed some disadvantages, as discoloration of a limited number of stone surfaces by iron mobilization and alteration of some Cu-based pigments, at present it becomes apparent that the ammonium oxalate treatment is to be preferred to organic compounds because of the good durability and high compatibility with the carbonatic surface of calcium oxalate.
To find methods for evaluating the penetration depth of a consolidation treatment is a hot issue in the conservation of work of art: the penetration of a product inside the porous matrix of materials as stone, plaster, mortar, terracotta and brick, is important to evaluate the effectiveness and durability of a treatment. The analytical techniques employed so far showed ambiguous results, thus highlighting the complexity of the problem; indeed many variables may act simultaneously such as the physico-chemical properties of the substrate, the characteristics of the products used and the method of their application. Another important and often neglected aspect is the distribution of the products within the substrate at the microscopic level and their physico-chemical interactions with the treated matrix.

This study aims at contributing to the solution of some of these problems:

- Understand the mechanisms of formation and transformation of calcium oxalate phases.
  Part of the work of this research has been devoted to the study of the stability of whewellite and weddellite, by laboratory synthesis and monitoring of the transformations in different experimental conditions.
- Find a method able to probe in a direct way the inner portions of the materials treated with protective or consolidant substances. Micro-Raman mapping on polished cross sections has been proposed as an effective analytical direct technique able to map the penetration depth of a product and the distribution of the various chemical components in the treated domains of the sample. The method proposed is innovative in the field of conservation science and the transfer to the conservation sites of the results obtained will allow the optimization of the treatments.
- Apply the described method in order to map the stratigraphy of whewellite and weddellite also in the calcium oxalate films occurring on the monument surfaces over centuries. The analyses carried out by micro-Raman mapping on polished cross sections allowed to unquestionably identify the presence of calcium oxalates and, most of all, to obtain direct information and with an high spatial resolution of their distribution with respect to the material surface.



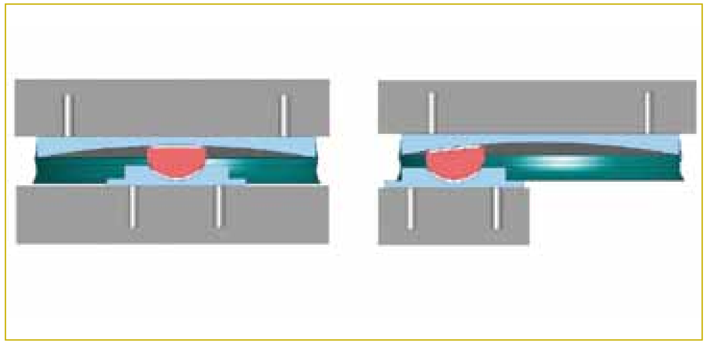
1. The tetragonal structure of weddellite



2. Linear map obtained on a plaster polished cross section treated with ammonium oxalate solution: (left) microscopic image of the specimen, the map has been carried out along the red line; (right) distribution of the three mapped phases; calcite (blue), whewellite (green) and weddellite (red)

EXPERIMENTAL INVESTIGATION AND DEVELOPMENT OF SLIDING MATERIALS FOR SEISMIC ISOLATION DEVICES

Paolo Dubini



1. Curved Sliding Isolator

The protection of transport infrastructures, industrial plants and strategic buildings from earthquake damage is vitally important. With relevance to developed countries, seismic risk involves particularly the southern areas of Europe, including Italy, the west coast of North America, China, Japan and New Zealand.

Seismic isolation is a strategy for protection of buildings and structures from earthquake, consisting of isolating the structure from the supporting ground in order to reduce the transmission of the seismic motion to the superstructure itself. Among the devices recently developed to the scope are sliding isolation bearings, which include one or more pairs of partner surfaces, either flat or curved (Figure 1), that slide one upon the other to reduce the transmission of horizontal forces and accommodate the large horizontal displacements induced by seismic actions.

Friction between the partner surfaces is crucial for the performance of the isolation system, since low friction reduces the transmitted forces, but high friction promotes the dissipation of the seismic energy and reduces the total displacement. The design of sliding isolation bearings has been developed in the last years and at present their performance is affected by the lack of knowledge about the friction behavior of the materials currently used, and its dependence on typical earthquake conditions like extreme velocities.

The target of the thesis work is therefore to investigate the frictional behavior of candidate materials for the sliding surfaces and to develop and validate a tool for the selection of suitable materials to be employed in sliding isolation bearings. In the first part of the work, thermoplastic polymers currently used in the technology of mechanical bearings are chosen and tested in order to assess their friction properties under conditions typical of seismic excitation. The experiments are carried out using a small scale model of a flat sliding bearing installed on a custom testing machine (Figure 2) available at Politecnico di Milano, and specimens of the various polymers are tested in combination with a partner surface made of stainless steel, like in current isolation bearings.

The effects of contact pressure, velocity of sliding, environmental temperature and local temperature rise due to frictional heating, and roughness of the partner surface on the static and dynamic coefficients of friction of each polymer are determined. A physical interpretation of the experimental behaviors is given and the friction properties are related to physical and mechanical properties of the polymers like the melting temperature, the elastic modulus and the plastic flow stress.

The results are finally collected in a database of friction properties which allows to rank the different materials according to various functional characteristics.

The second part of the work is devoted to the selection and validation of a proper sliding material for a particular project, the isolation of the Golden Ears Bridge at Vancouver, Canada (Figure 3).

2. Custom servohydraulic testing machine (Politecnico di Milano)

3. Golden Ears Bridge at Vancouver, Canada

The particular requirements for the sliding material are derived from the project specifications, and a candidate material is selected according to the ranking given by the database developed in the first part of the Thesis. Further tests are then carried out on the candidate material in order to characterize its friction behavior under the seismic conditions at the particular site of the bridge. Finally, two full scale prototypes of the isolation bearings incorporating the candidate sliding material are built and tested in a Bearing Testing System reproducing the actual seismic conditionsin terms of loads and velocities.

The isolation characteristics of the two prototypes well match the design specifications, so validating the use of the proposed sliding material.

The main outcomes of the thesis can be summarized in the following points :

1. the experimental characterization of the friction behavior of various polymers under typical seismic conditions;
2. the creation of a database of friction properties which can be used as a selection tool depending on the particular requirements;
3. the selection and validation of a proper sliding polymer to be used in a particular isolation project.

The research carried out in this Thesis provides new chances for the development of more efficient, more reliable and more environmentally adapted devices for seismic isolation.

The goal and importance lay in the improvement of seismic isolation technologies and of earthquake-protective techniques, in particular the main impacts can be summarized as follow:

1. the use of high performance sliding materials with properties tailored for seismic isolation systems, will increase the safety of civil engineering works against seismic actions;
2. the development of sliding materials that overcome the limits of polymers today in use will allow the design of more performing devices, with technical and economical benefits; in particular the use of smaller devices will facilitate the operation of seismic adjustment of existing structures (retrofit).

INTERACTIONS BETWEEN NEW DISPERSING POLYMER AND CEMENTITOUS MATRIX: SYNTHESIS AND STRUCTURAL MODEL

Lidia Giuseppina Eusebio

The PhD research has been focused on the study of the interactions between polycarboxylate-based superplasticizer and cementitious matrix. Superplasticizers are considered the most important admixtures for concrete production to avoid rapid flocculation and to allow convenient workability time. Despite their relevance, the way they act and the interactions with the particle surface during hydration are not yet completely clear. The interaction between mineral components of cement and admixtures at the surface of the hydrating material are very complex. To investigate these aspects it is necessary to simplify the system studying suitable model matrixes. The selected model materials are: I. tricalcium aluminate (C3A), the most reactive of the Portland clinker phases, II. tricalcium silicate (C3S), responsible for setting and development of cement "early" strength (I. and II. synthesized "ad hoc"), III. Ettringite, the more prominent representative of AFt phases (synthesized by reaction of $Al_2(SO_4)_3*16H_2O$ and $Ca(OH)_2$) IV. $CaCO_3$ (inert mineral) used for studying the interactions at hydration reaction time equal zero. V. Two cements type CEM I 52.5R having different concentration of sulphate ions, in order to investigate the effect of the polymer on the dispersing behaviour. In fact SO_4^{2-} ion competes with the polymer carboxylic group as regards bonding Ca^{2+} ions. Cruas and Gargenville cements satisfy the request with low and high SO_4^{2-} concentration respectively in the aqueous solution after contact with them (Table 1).

CEM I (52.5R)V	[CA^{2+}] MMOL/L	[K^{+}] MMOL/L	[NA^{+}] MMOL/L	[SO$_4^{2-}$] MMOL/L
Cruas	44,74	10,86	4,65	12,74
Gargenville	24,12	182,75	56,45	83,25

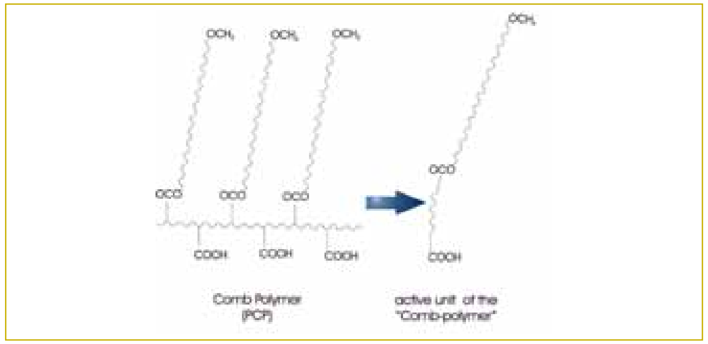
Table 1: Ions in the aqueous solution after contact with the cements

The investigation was directed towards the study of the influence by the polymer structure on the hydration products, their morphology / surface modifications at different times and the dispersing capability. In particular we examined the role of the link site between the dispersing polymer and the matrix.
For these purpose we synthesised a set of linear polymers as models composed of a negative link site (carboxylic group), able to be adsorbed on the matrix by ionic interaction with its Ca ions, and a long ethylene oxide chain $O\text{-}CH_3$ terminated (MPEG having M_w =1000 or M_w=4000). The model polymer have been tailored in order to represent the active unit of a typical commercial comb-polymer (PCP) (Figure 1).

Depending on the chain structure supporting the carboxylic group the model polymer can be divided into two families:
A. "Flexible polymer" having a non-rigid joint between the link site and the dispersing chain,
B. "Rigid polymer" having a rigid joint between the link site and the dispersing chain, such as aromatic ring or double bond.
We evaluated the adsorption ability of the dispersing polymer (PCP and linear polymer) on cement matrix and $CaCO_3$ surface by using the COD technique. We have observed that the PCP polymer adsorbs differently on the two selected cement because of the different concentration of sulphate ions, while the linear one shows the same behaviour for the two substrates. This remark could be take into account for designing new polymers having tailored adsorption behaviour and better performance with targeted cement.

We also evaluated the dispersing capability of the polymer too (PCP and linear polymer) by means of rheological test carried on the cementitious matrix.
We have observed that the model polymer with a rigid structure present a better dispersing ability. Moreover with SEM, TG/DTG analysis and conduction calorimetry, we investigated the surface modifications induced by the organic compounds on the hydrated cement phase of cement and on $CaCO_3$.
We observed that the polymer acts on the surface of the matrix causing relevant modifications of the morphology and/or of the entity of the inorganic species (Calcite, Ettringite and Portlandite). The great effect has been shown by the PCP polymer (Figure 2).

The results of this study are not only useful to a better understanding of the microscopic effects of the dispersing polymer but also to have valuable information for designing new polymers.



1. Structure scheme of superplasticizer and its active unit

2. Portlandite growth in absence and in presence of superplasticizer

MODELING OF CHARGE TRANSPORT PROPERTIES AND PHOTOINDUCED PROCESSES IN ORGANIC CONJUGATED MATERIALS

Daniele Fazzi

Organic opto-electronic applications have emerged, in the last decades, as a vibrant and hot field of research, spanning from chemistry, physics, materials science and technology. Organic opto-electronic devices (i.e. field effect transistors, heterojunction solar cells, memories and single molecular junctions) share a common feature: the fine interplay between the π-conjugated electronic structure and the molecular architecture (in terms of both single molecule structure or supramolecular organization). This relationship is peculiar for organic compounds and characterize them with respect to the classical inorganic silicon-based materials for opto-electronic applications.

The device performances of organic solar cells, transistors or photodetectors and sensors (i.e. the *I- V* characteristic, the charge carrier mobility, the quantum yield, etc) indeed critically depend on the efficiency in which charge carriers (electrons or holes) move within the π-conjugated materials. From these general considerations emerge that the study and the deep comprehension of the molecular properties of organic materials are fundamental for the design and the optimization of the device performances.

In this framework, theoretical approaches as quantum chemical simulations (*ab-initio* methods) are one of the main tools used for the investigation and rationalization of the organic materials properties.

During my PhD project I explored from a quantum chemical point of view, the *structure-property* relationships for some organic compound developed and used in various opto-electronic applications; in particular I was involved in the study of:

- the *electrical bistability* process, used to developed organic non-volatile memory applications;
- some *photo-induced mechanism* in organic materials employed in photocromic, photovoltaic, sensor and optical applications.

I was interested in finding those molecular parameters able to control the mechanisms governing the device performances as:

1. the *charge transfer processes* to rationalize electrical bistability in organic non volatile memories
2. the *photoinduced processes* to study those organic materials employed in photocromic, photovoltaic and optical applications.

Electrical bistable materials show two different electrical conductive states, by varying the bias applied to the device electrodes. This properties is used to develop memories in which the OFF state is the low conductive state while the ON state is the high conductive one (see Figure 1).

I proposed a model able to rationalize the electrical bistability behavior from a molecular point of view. The model is based on molecular parameters used in the electron transfer theory, namely the *reorganization energy* λ *and the charge transfer integrals* V_{ij}.

Good candidates for organic memory applications are those organic molecules which display high reorganization energies and moderate charge transfer integrals.

In my thesis work the model is successfully applied and tested on many organic systems, giving active materials for resistive organic memories as thiophene based molecules (DPBT), benzoquinone derivatives (DDQ and TCNQ) and xanthene compounds (Rose Bengal), well known active materials for memory applications (see Figure 2).

Based on the study of specific molecular properties, I rationalized the light induced property variations in photocromic materials (i.e. diarylethenes and spirooxazine).

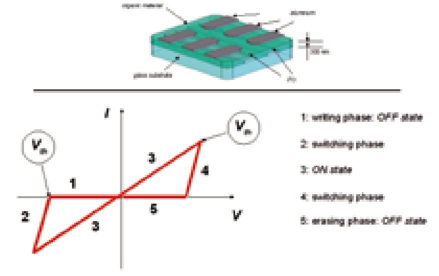
In particular the refractive index modulation (Δn) has been rationalized by studying the relationship between the bulky optical property (Δn) and the molecular polarizability α (single molecule), before and after the photochromic reaction.

A molecular model has been proposed in order to optimize the modulation of the refractive index by changing only a molecular parameter.

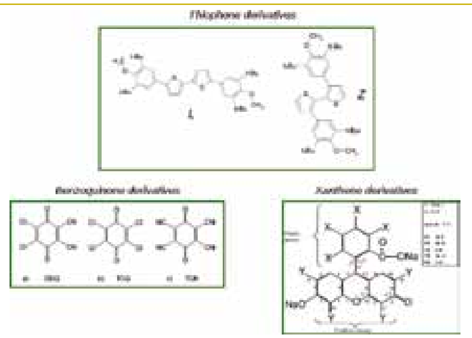
In the field of photovoltaic applications I studied the excited state properties of organic molecules in terms of i) exciton formation (by using post Hartree Fock and time dependent DFT approaches) and ii) exciton diffusion, by calculating those *intra-* and *inter*-molecular quantities (exciton site energy ω_0 and exciton coupling integrals J_{ij}) between pairs of molecules.

In this framework (Frenkel exciton theory) I explored the exciton properties of some organic materials used in opto-electronic applications; the aim is the simulation of the absorption spectra (UV-Vis) of solid state (crystalline) organic compounds.

I found that the absorption spectra is proportional to the density of exciton states (DOS) of the organic material; a systematic procedure has been proposed in order to apply the model on other crystalline organic compounds.



1. Upper: sketch of an organic resistive memory device (Al/material/ITO); bottom: *I-V* hysteresis cycle



2. Molecules studied in this Ph. D. thesis concerning the electrical bistability effect

IN SITU SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY OF PD SUPPORTED CLUSTERS

Stefano Foglio

In heterogeneous catalysis, a complete knowledge of the catalytic processes at the atomic level is today forbidden because of the chemical complexity of the catalyst materials and the intricacy of the steps involved even in the simplest oxidation-reduction reactions.

Surface science and surface chemistry have developed a simplified approach towards the study of these systems based on the so-called *model catalysts*, i.e. isolated nanoparticles or clusters of the active species dispersed on atomically flat surfaces where *in situ* structural investigations can be carried out, and model reactions can be studied down to the atomic level.

Great efforts are aimed to reduce the discrepancy between model systems that can be addressed with instruments typical of surface science, and real systems. This distance, known as *material gap* and *pressure gap*, is due to the differences between structural properties and working conditions of the studied systems with respect to the real ones. Therefore the production and the analysis of model catalyst with characteristics similar to real catalytic systems is of primary importance.

This PhD thesis deals with an *in situ* Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) study of Pd nanoparticles supported on Au(111) and Al_2O_3/NiAl(001) substrates: our interest in this materials combination arises from the multiple catalytic applications that can be understood and optimized thanks to the knowledge gained by these model investigations.

The main goal of this work is to give an atomic-level understanding of the basic mechanisms underlying Pd clusters nucleation and their interaction with the Au(111) and Al_2O_3/NiAl(001) surfaces: a detailed characterization is of fundamental importance in order to provide a deeper comprehension of various aspects of heterogeneous catalysis such as the sample morphology/activity relationships. In these sense the capabilities offered by STM and STS to determine both the geometric and the electronic structure of the surface with atomic resolution, are ideally suited.

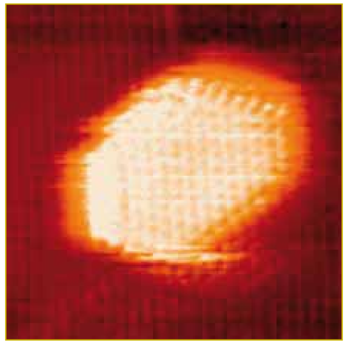
Meanwhile in the perspective to bridge the *material gap* we have explored the possibility to deposit both the Pd nanoparticles and the Al_2O_3 support by an unconventional method in the production of model catalysts, namely the Pulsed Laser Deposition (PLD).

We proposed PLD believing that this technique provides all the necessary attributes to produce model catalyst more similar to real systems characterizable both on atomic scale and macroscopically.

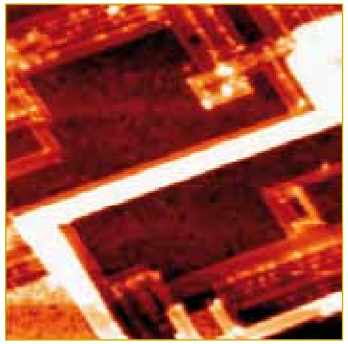
Pd was deposited also by thermal evaporation, to have a direct term of comparison with a standard and widely employed technique.

Our results pointed out a common nucleation mechanism for Pd deposited with both techniques on the Au(111) substrate: depositions resulted in the well know ordered aggregation of Pd islands in correspondence of the elbows of the 22 x √3 Au(111) surface reconstruction (Fig.1), according to a growing regime already observed in literature but still lacking of unanimous interpretation.

Thanks to atomically resolved STM images it was possible to clear up that the island nucleation occurs via atomic place exchange, a mechanism strongly dependent on the energy deposition regime and the size of the deposited species. By varying properly some parameters involved in the PLD process it was possible to control the evolution of Pd islands growth and islands size distribution decoupling it from the coverage, a possibility that is precluded for depositions by evaporation.



1. STM image (8x8 nm^2) at atomic resolution of a Pd island evaporated on Au(111) in correspondence of an elbow of the surface reconstruction



2. STM image (50x50 nm^2) showing the crystalline Al_2O_3 stripes grown on the NiAl(001) surface after the exposure to a controlled O_2 atmosphere and subsequent annealing.

Since the majority of the industrial catalysts are composed by an active component dispersed on high surface area oxides, Pd nanoparticles were deposited and characterized on ultra-thin film of crystalline Al_2O_3/NiAl(001) (Fig.2). The analysis of the clean NiAl(001) and Al_2O_3 surfaces was carried out to better understand the NiAl oxidation dynamics and gain a control on the oxide growing process.

Pd deposited on Al_2O_3/NiAl(001) shows a better thermal stability with respect to more largely studied systems where metals are evaporated on Al_2O_3/NiAl(110) and TiO_2.

Pd depositions on Al_2O_3/NiAl(001) demonstrate the higher versatility of PLD with respect to thermal evaporation, offering the interesting possibility to control the characteristics (i.e. size, kinetic energy, structure) of the deposited species simply by varying the parameters involved in the deposition process.

This capability becomes essential since the electronic properties of clusters (which influence their catalytic activity) are dramatically size-dependent, as indicated by STS measurements.

Performing the ablation in a reactive atmosphere of O_2, PdO clusters were produced.

It was also explored the intriguing possibility to produce the whole model catalyst (i.e. both the ultra-thin Al_2O_3 support and the active species) by PLD. The samples complied with the limits imposed by the surface analysis technique and showed interesting aspects from a catalytic point of view. The Al_2O_3 created with PLD is characterized by an heterogeneous electronic structure with several sites that can potentially enhance the reactivity of the active species.

In fact the cluster properties are strongly influenced by the interaction with the substrate. Therefore the PLD gives the unexplored opportunity to control the catalytic activity of the produced system by tuning properly both the substrate and nanoparticles characteristics.

This work demonstrates that Pulsed Laser Deposition can be considered by valid reasons, a suitable technique to bridge the material gap between model catalyst and real systems: PLD allows the production with the same elevated control of both model catalyst that can be characterized at atomic scale by UHV surface techniques, and real catalyst testable in a reactor on laboratory scale.

The closer perspective is to gain a finest control on the morphologic/electronic characteristics of the samples produced by PLD; this would lead to the production of a new class of materials and systems with tailored properties for specific applications in the catalytic field. To this purpose it would be very interesting to test in a catalytic reactor the effective performance of the systems produced by PLD.

ELECTROCHEMICAL MODIFICATION OF NI-P ALLOYS FOR EUVL APPLICATIONS

Fabio Muscolino

The continuous drive to offer faster, smaller, and cheaper semiconductor ICs, requires advancements in lithography (a photography-like technique of using light to carve channels on silicon wafers), thermal treatments, and inspection in the wafer process line to enable printing narrower gates, smaller line-width, shallower S/D junctions, and a fail-safe inspection and metrology capability. This challenging set of requirements can only be realized through a paradigm shift to lower operating wavelength, enabled and supported by the deployment of more efficient, cost effective, and high-precision optics. As manifested with the lithography technology, these ambitions will continue in every aspect of the optically driven processing equipment technologies. Today, state of the art techniques use ultraviolet (UV) light, and experts believe that chips will continue to follow Moore's law for another 10 years as even shorter wavelengths are used. Current systems use refracted UV light with a wavelength of 0.248 micrometer, to image a master pattern through lenses onto a silicon wafer that is covered by a resist. This technology can produce features of just 0.25 micrometer. In less than 10 years, engineers plan to build chips with features measuring about 0.13 micrometer by using wavelengths of 0.193 micrometer. But beyond that point, a shorter radiation (13.5 nm) is strongly absorbed by all known materials. The lithography industry, defining its own development on wafer writing production capacity increasing, requires metallic optics that can work in critic reflection conditions for short wavelength (13 nm) and grazing angles. Therefore refractive optics can not be used. Optical systems can only be realized with reflecting mirrors. Called extreme ultraviolet lithography (EUVL), the technique bounces EUV photons off an elaborate setup of mirrors, including a mask made of reflective materials, that ultimately focuses the photons on a resist-coated silicon wafer. By doing so, an EUV system that can pattern features smaller than 0.05 micrometer. Three optical components are required for an EUV exposure tool, the collector which captures as much radiation from the source as possible, the illumination system which homogeneously illuminates the used field on the mask, and finally the projection optics which demagnifies the structures from the mask to the wafer. In addition EUV exposure tools must operate under high vacuum conditions to avoid absorption of EUV light by gases.

The industry demonstrated that electroforming allow production of lightweight mirror shells with optical surface areas up to 1.3 m^2, enabling the production of low cost, isotropic, precision optical shells like reflectors highlighting excellent performances. In principle, any reflector thickness can be electroformed with the desired curvature and surface characteristics which is close to the optical quality of the mandrel.

A technique for optics realizations is based on Ni electroforming using electroless nickel- phosphorus (Ni-P) coated Al nearly cylindrical masters as substrate, machined with diamond turning technique. Amorphous Ni-P alloys show high hardness, outstanding wear resistance, low friction coefficient, paramagnetic characteristics and high electrocatalytic activity. This unique combination of functional properties has resulted in widespread application of Ni-P. Protective coatings from Ni-P alloys are indispensable to withstand severe corrosive and mechanical burdens. They are widely applied in such optical applications, automotive, aerospace, oil and gas, computers, electronics, mining and military. Their uses in computer hard disk, electromagnetic shielding of cell phones, large scale valves, under sea drilling tools and catapults on aircraft carriers are spectacular examples of amorphous Ni-P versatility.

Being the reflective mirror surface an accurate replica of mandrel surface, polishing treatment on Ni-P and a perfect release system between mandrel and Ni mirrors become fundamental aspects of the optical system realization. Mandrels for optical electroforming range come from diamond turned metal (copper, brass, aluminum coated with Ni-P alloy). One unique advantage electroforming has to offer is the ability to precisely replicate in a hard and wear resistant metal a pattern (for instance, holographic) that can only be generated in a soft material such as photo resist. Then, the mandrel is cleaned and mounted in an electroforming fixture and a replica is created byelectrodeposition in a suitable electrolyte. Another benefit of this technology is the ability to replicate sequentially, thus producing generation of mirrors from only one master. This Ph.D. thesis have two different scopes, the develop of an anodic oxidation process of electroless Ni-P smooth surfaces (< 2 nm) in NaOH based alkaline bath as release agent for Ni mirror replicas and an ECMP process in acid solution with alumina particles for mandrel polishing after diamond turning mechanical machining.

It's basic that mirror surface roughness is less in one order magnitude respect incident wavelength in order to allow wafer writing with the spot energy. So, mandrel surface is submitted to a long mechanical polishing in order to have final surface roughness not over 5-6 Å. Ni-P mechanical polishing can be replaced with an electrochemical-mechanical polishing (ECMP), improving surface finishing more than limit allowed by only mechanical systems. Acid solutions based lactic acid were before used without particles to understand Ni-P behavior in only electrochemical polishing (ECP) terms. Electrochemical characterization was performed with rotating disk electrode (RDE) by potentiodynamic studies to identify polishing plateau conditions. ECP was performed for different times and rotating speed. In addition, an ECMP machine was used to check results with Al_2O_3 particles addition (40 nm size) in the solutions. Samples characterization was performed with precision balance, AFM, Nomarski optical microscope and laser profilometry to measure roughness improvements and thickness removal rate. An excellent polishing effect on surface was obtained. For only ECP tests not more of 10% roughness decreasing was measured, but measurements performed after ECMP show that roughness decrease more than 70%. Moreover, ECMP results are better than the only summary of ECP and CMP, proving the synergistic influence of combining the two effects. Ni-P removal rate of 200 nm/min approximately was measured after ECMP process. Therefore, an automatic brush based system for Ni-P ECMP was realized with a modified lathe and using an Ni-P coated cylinder machined by diamond turning. The results indicate that ECMP enables the polishing of amorphous Ni-P structures with minimal defect density, and that can be a true alternative surface process (respect mechanical polishing or CMP) for application in high-end optical systems.

A process for anodic growth of an oxide release layer on electroless Ni-P smooth surfaces (< 2 nm) was developed in NaOH based alkaline bath. Different cycles of electrochemical oxidation are tested. Atomic force microscope (AFM) and non coherent phase shift interference microscope are used to characterize roughness before and after anodic oxidation, revealing no significant variations after the oxidation process. X-ray photoelectron spectroscopy (XPS) was used to examine the passive film growth. Depending on the anodic oxidation process, an oxide thickness from 40 to 140 Å was measured compared with a 10 Å natural oxide thickness, and a dual layer structure was detected. Based on the XPS spectra of Ni 2p and P 2p, the oxide film is composed by nickel oxide, hydroxide, phosphate and phosphite. Ellipsometry and X-ray reflectivity (XRR) confirm thickness measurements and give results about oxide density. The oxide uniformity and morphology, together with the high repeatability process, suggest that Ni-P anodic oxidation is suitable for nickel mirrors replica.

NEW MATERIALS AND TECHNOLOGIES FOR LAB-ON-CHIP MICRODEVICES

Raffaella Suriano

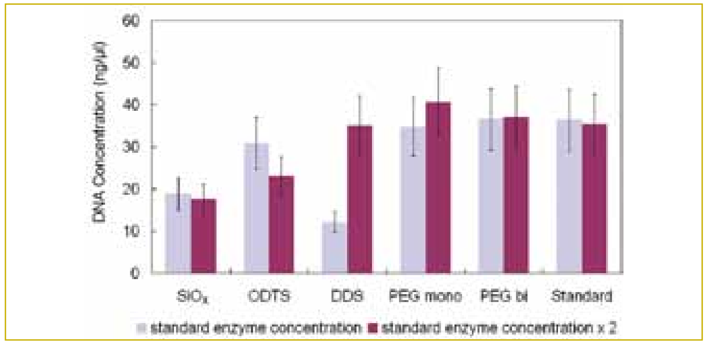
Lab-on-Chip (LoC) microdevices are expected to revolutionise the field of medicine, chemistry and biology in the near future: they will perform chemical analyses, biological samples treatment and detection, very close to the point of sampling, replacing slow and expensive traditional analytical instruments. These systems allow reducing reagents volumes and chemical wastes as well as analyses costs. They are based on fluids transportation inside microchannels and microchambers, where the entire analysis process can be carried out. Although silicon and glass are quite widespread materials for microdevices fabrication, polymers have a great potential as substrates in LoCs applications because of their low cost, disposability and available broad range of properties and production techniques.

Various prototypes have been recently developed but microfluidic devices have still some open technical issues, related to two aspects: compatibility with biological fluids and the need of rapid prototyping. To produce robust microsystems which perform reliably quantitative analysis, there is clearly a need to control phenomena of non-specific biomolecules adsorption at microchannels surfaces.

Moreover it would be very useful a versatile microfabrication technology which enables rapid testing of LoCs and optimization of new designs. This research work aims to address specific solutions to these problems.

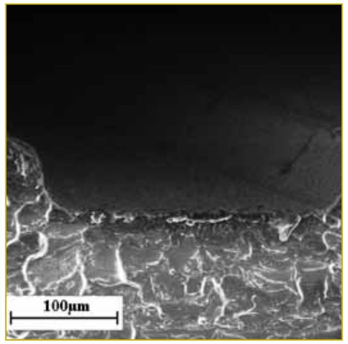
In the first part of work surface functionalisation of silicon oxide and polymeric materials were investigated to improve their bio-compatibility.

Surface modification techniques were applied both to silicon wafers coated with thermal oxide and to SiO_x surfaces of prototypal chip, specifically designed by STMicroelectronics, S.r.l., for realisation of a LoC for PCR (Polymerase Chain Reaction). PCR is a molecular biology technique which allows amplifying DNA specific portions in vitro by means of a series of thermal cycles and catalytic activity of an enzyme, called Taq polymerase.

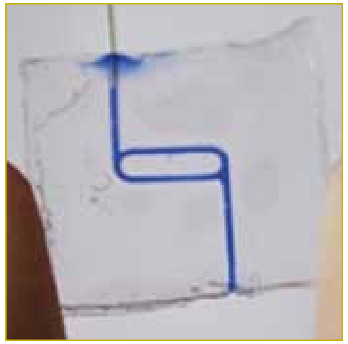


1. Average concentration of final DNA after PCR on each type of surface plus in the standard thermocycler for standard and doubled enzyme concentrations. Error bars are equal to ± 20% of average values.

Hydrophobic and hydrophilic surfaces were achieved, respectively, by treatment with silanes bearing alkylic chain (octadecyltrimethoxysilane, ODTS and dimethyldichlorosilane, DDS) and by “grafting to” technique of poly(ethylene glycol) (PEG), using two different types of PEG, mono and bifunctional polymer chains. These functionalisation techniques allowed tailoring the silicon oxide wettability characteristics: this wettability control is much desired because it can be used to manipulate the flow of biological aqueous solution in microdevices. PCR compatibility tests showed low DNA amplification reaction yields with bare SiO_x, partial inhibition with hydrophobic surfaces and best yields with PEG-modified surfaces, comparable to those obtained in a conventional thermocycler with standard procedure (Figure 1).



2. ESEM images of microchannels ablated in COP



3. Image of closed devices with good sealing. The liquid remains just inside the channels and clearly outlines the microchannels pattern.

For polymeric materials such as poly(methyl methacrylate) (PMMA), biomimetic coatings with phosphorylcholine groups were examined to reduce protein adsorption.

Two different copolymers bearing phosphorylcholine functionality and PEG chains were synthesised by free-radical polymerisation, varying the feed molar ratios. They were coated onto PMMA with spin-coating process by aqueous solutions.

The functionalised surfaces appeared to be more hydrophilic and protein-resistant than blank PMMA.

The second part of work is concerned with development and improvement of new microfabrication technologies for fast prototyping of polymeric LoCs.

Microchannels fabricated by femtosecond laser ablation in three polymeric materials, i.e. PMMA, polystyrene (PS) and cyclic olefin polymer (COP) were studied. Morphological characterisation, performed by Environmental Scanning Electron Microscopy (ESEM) and by optical profilometry, evidenced a trapezoidal cross-section (Figure 2) and bottom surface roughness values, comparable with those obtained by micromilling.

Chemical degradation induced by femtosecond laser processing was assessed: PS and COP showed evidence of strong oxidative degradation, whereas PMMA likely decomposed to monomer according to the degradation mechanism called unzipping.

Alternatively, LoC prototyping was evaluated through UV photopolymerisation of PEG-methacrylates. To design LoCs for PCR applications, PEG-methacrylates material formulation was optimised to fulfil the following requirements: anti-fouling properties, good hydrophilicity and proper thermal and mechanical stability, to withstand PCR thermal cycling. Optimisation of microfabrication process was achieved, resulting in microchannels with desired depth, vertical sidewalls and reproducible width. Optical profilometry showed that surface roughness inside channels, produced by this technology, is much lower than that obtained by laser ablation. Efficient sealing between polymerised layers via the same technique was demonstrated by leakage tests (Figure 3).

These capabilities were exemplified in different fluidic patterns that range from 3D fluidic channels with closed loop to a microchamber fabricated for PCR yield tests.