



## DOCTORAL PROGRAM IN MATERIALS ENGINEERING

Chair:  
**Prof. Chiara Castiglioni**

The courses of the Doctoral Program provide Ph.D students in Materials Engineering with a common, basic knowledge on Materials Science and Technology, followed by a specialized training in specific fields. The objective is to combine the theoretical knowledge with the skills required by technology in order to form qualified researchers who can manage the design, manufacturing and use of traditional and/or new materials.

### Contents of the Doctoral Program

The Doctoral Course covers the following areas:

- Polymers and composites*
- Cements and ceramics*
- Metals*
- Biomaterials and materials for biomedical applications*
- Processing and characterization of advanced metallic alloys*
- Corrosion and durability of materials*
- Innovative materials for civil and industrial engineering*
- Materials Characterization (Microscopies, Scattering, Spectroscopy)*
- Modelling and theoretical approaches to the study of materials structure and properties*
- Micro and nanostructured materials*
- Functional materials for applications in photonic, electronic and sensors*
- Surface engineering and advanced coatings*
- Materials for industrial design*
- Meta-materials*
- Transformation of materials*
- Material for Cultural Heritage*

The courses face immediately advanced issues both in the main and elective courses. Different curricula are offered, which will be activated on the basis of the decisions of the faculty. The Doctoral program is characterised by high flexibility, in order to satisfy the needs of students that have to develop their research activity in different thematic areas. For this reason each student submit to the Faculty a "Curriculum" to be approved. The Courses offered deal with theoretical, experimental and modelling aspects. Several Courses comprise workshops and seminars, with the participation of invited internationally celebrated speakers. Students can use the most modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories.

The research activities related to the Ph.D. theses develop, full time, along the three years of the Ph.D. courses. Stages in industries or in national laboratories in Italy or abroad are offered. Each Ph.D. student are supervised by a professor of the faculty: the faculty evaluates the progress of his research activity and at the end of each year expresses a judgement on the continuation of the work for the subsequent year. At the end of the third year the Ph.D. student presents and defends, in a public hearing, his thesis work with a jury formed by three experts. The Ph.D. student is strongly encouraged to attend at national and international meetings and present papers in his specific field. The Ph.D. student is also assigned to give seminars on topical issues and/or to lecture on the specific fields of his research or on

the cultural aspects related to his thesis.

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

- at least 30 credits must be obtained through attendance at Doctoral Courses (with positive evaluation in the examinations); in addition, attendance at National and International Schools are strongly encouraged.
- the remaining credits will be assigned on the basis of the research activity necessary to the development of the Thesis project.

### Faculty:

The faculty is constituted by Professors from several Departments of Politecnico di Milano:

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#### Professional skills achieved by PhD in Material Engineering:

The industrial world depends necessarily on a great variety of materials. Nowadays, it is easy to outline two industrial needs: i) development and innovation in the production, processing, application and conservation of traditional materials; ii) development of innovative materials for the production of new manufactured goods or devices to cope with the growing demands of modern technologies. Since these two kinds of industrial needs require specialized people a few specialized curricula are offered. On the other hand, the capabilities acquired through the courses, the research work and the teaching activity assure an adequate preparation to the academic career.

## A PROPOSAL OF AC CORROSION MECHANISM OF CARBON STEEL IN CATHODIC PROTECTION CONDITION

Andrea Brenna

Buried pipelines used to transport hydrocarbons and dangerous fluids are provided with corrosion prevention systems, consisting of an insulating coating and a cathodic protection (CP) system. CP reduces (or halts) corrosion rate, so that corrosion damage cannot occur during the designed lifetime of the structure. The presence of AC interference may cause serious corrosion damages on metallic structures, even in CP condition. When a metallic pipe is parallel to an high voltage transmission line (HVTL), AC interference can take place by a conduction or an induction mechanism causing corrosion corresponding to coating defects, even if the  $-0.850$  V CSE criterion is matched. Uncertainties still exist on CP criteria in the presence of AC and on the mechanism by which AC corrosion occurs. In this research, a mechanism of AC-induced corrosion of carbon steel in CP condition is proposed. Electrochemical tests were carried out on carbon steel in soil simulating environment varying protection and interference conditions. Laboratory tests showed that AC causes the increase of both protection potential and current, due to an effect on steel polarization curves. An experimental corrosion risk diagram is proposed:

overprotection (potential lower than  $-1.1$  V CSE) is the most dangerous condition. A two-steps corrosion mechanism is proposed:

- Step 1: AC causes the electro-mechanical breakdown of the passive film formed on carbon steel in CP condition;
- Step 2: corrosion occurs if the pH at the metal-to-electrolyte interface is close to 14.

In order to investigate the AC effect on passive condition (Step 1), tests were carried out on passive metals, as stainless steels in neutral solution and carbon steel in alkaline environment. AC has an harmful effect on passive condition, reducing the critical chlorides threshold and pitting potential and causing the film breakdown over a critical AC interference level. A mechanical breakdown mechanism is proposed: high alternating electric fields (in the order of  $10^6$  V/cm) within the passive film could cause the breakdown of the film itself. Electrostriction stresses are a possible explanation. After film breakdown, corrosion can occur if the pH inside the crack is close to 14; this strong alkalization can be reached in overprotection condition (high cathodic current density) and in the presence of AC. AC corrosion morphology is localized and corrosion propagation was evaluated by

means of penetration depth measurements on carbon steel specimens cathodically protected in soil through a magnesium alloy anode. Even if a service life prediction could be too hazardous by experimental data, the use of extreme value statistics provides a safe approach and is recommended in order to assess AC corrosion risk. AC has a harmful effect on magnesium anode consumption, due to the protection current increase and to the strong anodic efficiency decrease. The second effect plays the main role to increase anodic consumption.

# STABILITY AND EFFICIENCY OF ORGANIC MATERIALS AND DEVICES FOR THE PHOTOVOLTAIC TECHNOLOGY

Gianmarco Griffini

New materials and technologies have been explored in the past decades in the attempt to meet the demand of energy production from clean, renewable sources.

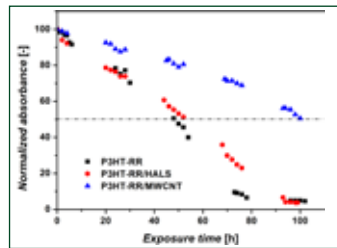
In particular, organic materials and conjugated polymers have been investigated for use in polymer-based solar cells (PSCs) and in organic luminescent solar concentrators (OLSC).

Long-term stability of materials and devices together with power conversion efficiency (PCE) have been recognized as central research areas, both in academia and industry.

In the work presented in this PhD thesis, PSC and OLSC technologies were examined and aspects related to their environmental stability and efficiency were studied, with the aim of achieving a greater understanding of the criticalities characteristic of these two research fields.

A first study was carried out on the photo-chemical stability of a model PSC polymer (regioregular poly(3-hexyl-thiophene) - P3HT-RR) in the solid state.

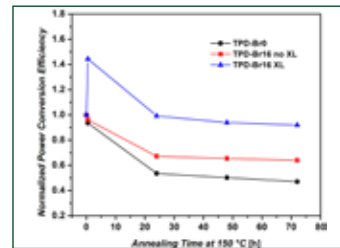
The results obtained from this study underlined a substantial instability of P3HT-RR to photo-oxidation following exposure to simulated sunlight. In particular a degradation mechanism for the polymer was proposed and strategies for lengthening its photo-stability were examined,



**1. Variation of normalized absorption intensity of the alkyl group FTIR signals as a function of irradiation time for pure P3HT-RR, P3HT-RR/HALS system and P3HT-RR/MWCNT system.**

including the use of hindered amine light stabilizers (HALS) and multi-walled carbon nanotubes (MWCNT) (Figure 1).

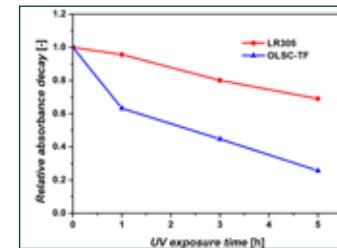
Together with photo-chemical stability, morphological stability of PSC polymers and devices was also examined. To this end, a series of photocrosslinkable low band-gap polymers was prepared and tested in PSC devices during long-term high-temperature annealing. Photocrosslinking allowed the formation and preservation of an optimal bulk-heterojunction (BHJ) morphology, and highly efficient PSC devices could be fabricated (Figure 2). Atomic force microscopy (AFM) studies on the photoactive layer of devices evidenced a good correlation between surface morphology of the photoactive



**2. Normalized power conversion efficiencies of control (TPD-Br0), non-photocrosslinked (TPD-Br16) and photocrosslinked (TPD-Br16) devices during long-term thermal annealing at 150 °C with PC<sub>61</sub>BM as n-type material. The efficiency of each device was normalized to its initial efficiency (at annealing time 0 h).**

layer and photovoltaic behavior of devices.

The analysis on PSC technology was extended to the evaluation of the power conversion efficiency (PCE) of devices, employing new isothianaphthene (ITN)-based low band-gap polymers with various electron-withdrawing substituents as active layer materials. BHJ PSC devices were fabricated with PCEs up to 3.0% and the electron-withdrawing character of functional groups was shown to strongly influence the polymer electronic behavior. In the attempt to explore novel processing techniques compatible with large-scale production of PSC devices, a preliminary study on inverted PSCs was carried-out. As alternative to thermal



**3. Normalized absorbance decay over light-exposure time of the ratio between FTIR absorption peaks associated with organic dye bond vibrations of lateral substituents (875 cm<sup>-1</sup>) and perylene core (1586 cm<sup>-1</sup>) for LR305 and OLSC-TF samples.**

evaporation, the metallic back-electrode was deposited onto the device by blade-coating an Ag paste. Both device fabrication and testing were completely performed in ambient air and PCEs in the order of 0.5% were achieved on large area (3.6 cm<sup>2</sup>) PSC devices. These results demonstrated the possibility of producing working PSC devices in air with no need of vacuum processing steps. The work carried out on OLSC technology firstly addressed the study of the photo-chemical stability of the materials constituting the thin-film luminescent concentrator, namely an organic luminescent dye (LR305) dissolved into a polymer matrix (PMMA). The behavior of each material constituting the OLSC device was monitored (PMMA alone,

luminescent dye alone and combination of the two – OLSC-TF) during exposure in air to high-energy UV-light and a degradation mechanism for the dye molecule was proposed. In addition, the role of the organic dye molecule in the degradation of PMMA was elucidated and the effect of the state of aggregation of the organic dye on its photo-stability was clarified (Figure 3).

The stability study on OLSC materials was followed by a parametric study on the efficiency of a working OLSC device coupled to a c-Si solar cell, tested under simulated sunlight. A number of device parameters were analyzed and successively optimized, including the organic dye concentration and the thickness of the thin-film OLSC. A maximum efficiency gain of over 40% was achieved after the integration of the c-Si solar cell with the OLSC thin-film. These results give important guidelines for the fabrication of efficient OLSC devices.

## ELECTROCHEMICAL CAPACITORS BASED ON CNTS

### Reza Kavian

Supercapacitors, also known as ultracapacitors, are electrical energy storage devices exploiting the charging and discharging of the electrochemical double layer for storage and release of energy. The mechanism of charge storage entails substantial advantages over conventional dielectric capacitors, such as a very high capacitance (up to 5000 F), energy density (30 Whkg<sup>-1</sup>) and longer cycle life. Consequently, supercapacitors have been intensively investigated for a wide range of applications from electric vehicle propulsion to power leveling and balancing.

In the first step multi-walled carbon nanotubes were grown by chemical vapour deposition on aluminium strips pre-plated with nickel thin films.

The preparation of hybrid materials, based on the combination of metal oxides and CNTs, improves on the properties of the two components. To achieve this goal, the thin films of manganese oxides were deposited on the CNTs layer by different techniques.

The CNT network was found to facilitate the dispersion of the oxide nanoparticles as a consequence of their large surface area and the ability to provide continuous conducting pathways for the transportation. These characteristics made CNTs and metal oxides composite a

promising hybrid material for applications in ECs. To achieve this aim CNT/MnO<sub>x</sub> electrode was fabricated by sol-gel process on nickel substrate.

Future applications for electrochemical energy storage will focus on both high gravimetric power and high energy. For this devices that can cover the performance gap between existing technologies are needed. The layer by layer (LbL) deposition is a thin-film fabrication technique (<300nm) based on alternatively charged layers onto a substrate at room temperature and in aqueous environments. The high surface area, chemical functionality and high porosity, combined with the absence of binder in these electrodes show that CNTs are one of the best promising materials for electrochemical capacitors.

## POLYMER NANOCOMPOSITES BASED ON CARBON NANOTUBES

**Diego Molina**

Carbon nanotubes (CNTs) have emerged as the most promising nanofiller for polymer nanocomposites due to their outstanding mechanical and electrical properties. Theoretical enhancement of properties are not easily accessible due to their strong tendency to form agglomerate and due to difficulties in processing their nanostructure in polymer systems. Despite the vast amount of data available in literature, a lot of controversial results are still present. The most effective way to stabilize dispersion is by CNTs' surface functionalization that could also efficiently transfer external stress to nanotubes increasing the mechanical properties of the nanocomposites. The first part of the thesis was directed in order to study the effectiveness and effects of CNTs' surface functionalization. Efficient functionalization methods were investigated to prepare MWCNT with carboxylic (COOH-CNT) and amine (NH<sub>2</sub>-CNT) functionalities. The procedures were carried out with high yield obtaining functionalized carbon nanotubes. A quantitative characterization of the functionalities present on the external wall were exploited. Moreover, the functionalization methods developed didn't reduce significantly the

peculiar aspect ratio of carbon nanotubes. As widely known, achieving an homogenous dispersion of carbon nanotubes inside polymer matrices is the main objective in order to enhance the different properties of nanocomposites. Besides all the published works, obtaining a good dispersion in nanocomposites is not trivial. Moreover, a great interest in imparting conductivity in highly insulated materials by fabricating conductive polymer nanocomposites is increasingly present. The second part of the thesis was focused on the dispersion of the functionalized CNTs, together with pristine grade (CNT), in two different polymer matrices, one thermoset epoxy resin and two different perfluoropolyether (PFPE) aqueous dispersions. A dispersion method of the CNTs in a DGEBA (diglycidil ether of bisphenol A) based resin was developed with mechanical stirring and ultrasonication. Calorimetry characterizations were investigated to observe the effects of the insertion of different functionalized carbon nanotubes inside the nanocomposites. Extensive rheological characterizations showed at first a good reproducibility of the dispersion process. Nanocomposites

containing COOH-CNT showed a lower effect on viscosity (easier processability) than the other CNT grades (NH<sub>2</sub>-CNT and pristine CNT). Moreover, rheological measurements (steady and dynamic) were exploited to monitor the efficiency of the CNTs dispersion in the epoxy matrix. The percolation threshold between viscous liquid and solid-like behavior was investigated and related to the different functionalities and to the different CNTs' structure morphologies formed. Electrical characterization was also performed. A percolation threshold was observed when pristine CNTs and NH<sub>2</sub>-CNTs were inserted. These observations suggested that CNTs could interact with the resin in different ways, depending on the type of functionalities present on their external wall. Conductivity induced by carbon nanotubes in those nanocomposites make them ideal candidates as damage evolution sensor. A promising defect's sensitivity was registered even at low crack length, and the electrical response was found to be related on the concentration and on the different functionalities of carbon nanotubes inserted into the nanocomposites. Two different perfluoropolyether

polymers were investigated, inserting carboxylic functionalized CNTs. Those matrices are widely used to impart hydrophobic and oleophobic repellence and as lubricant in critical conditions. The creation of nanocomposites with the insertion of carbon nanotubes is realized in order to enhance the peculiar high performances of those polymers. COOH-CNTs were efficiently mixed with different perfluoropolyether polymers with mechanical stirring and ultrasonication. A shear thinning behavior was observed for the nanocomposites' dispersions and a presence of interconnected microstructures of CNTs was suggested. A clear enhancement of dynamic mechanical properties was observed at increasing carbon nanotubes concentration, with a more wide temperature range in which those nanocomposites could be efficiently used. These improvements were obtained without modifying the peculiar hydro/oleo-phobicity of those nanocomposites. Moreover, the insertion of carbon nanotubes clearly induced an electrical conductivity in those nanocomposites. The induced conductivity observed for those nanocomposites could open their exploitation in different applications. One

of the most promising is the exploitation of fluorinated CNT based nanocomposites as advanced hydrophobic surface treatments of Gas Diffusion Layer (GDL) for PEM fuel cells. GDL requires different and controversial properties, that could be fulfilled by using those nanocomposites as coating of carbon cloth, permitting to enhance the performances of pollutant free PEM fuel cell. Carbon cloths treated with perfluoropolyether polymer modified with COOH-CNT, showed a good hydrophobicity as required by GDL components. Moreover, an improvement in conductivity, respect to the standard PTFE coating method, was obtained at increasing concentration of carbon nanotubes. An high water vapor permeability was observed with limited film formation of perfluoropolyether coatings, marginally effected by CNTs insertion. GDLs hydrophobized with those fluorinated nanocomposites showed a clear improvement in electrochemical performances when used in PEM fuel cell systems, in comparison with standard GDL coated with PTFE.

## LIGHT-TRIGGERED OPTICAL ELEMENTS: PHOTOCROMISM GAINS NEW OPPORTUNITIES

Giorgio Pariani

The possibility to light-trigger their physical-chemical properties makes photochromic materials particularly attractive for the development of smart devices, that find application in optics, opto-electronics, and biology. By date, the only commercially relevant application of photochromism regards photochromatic lenses for sunglasses, which are realized with thermally reversible (T-type) photochromic compounds.

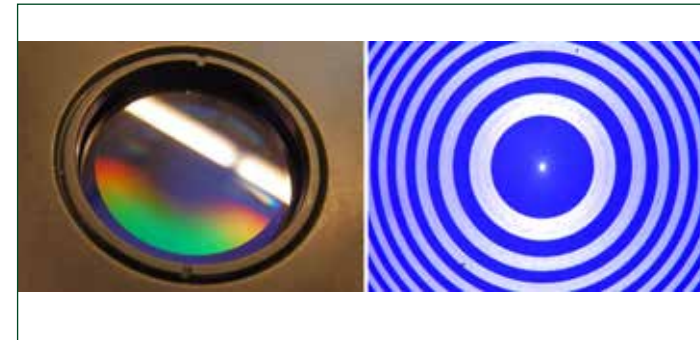
In this research work, we focused our attention to optical applications, in the framework of a fruitful collaboration between the Politecnico di Milano and the Osservatorio Astronomico di Brera started more than 10 years ago, aiming in the development of switching optical elements based on photochromic materials. Coming into play the difference between the demonstration of a proof of concept device and the realization of reliable prototypes, huge efforts have been required to fill this gap and achieving the goals was not counted on. When applied in optics, materials have to meet strongly demanding requirements. In particular, photochromic compounds must show large response of the desired property (which usually means large absorbance) and high optical

quality, i.e., homogeneity, flatness, etc., in order to obtain efficient devices.

Among the different families of photochromic systems, we specifically referred to diarylethenes, which show efficient thermally irreversible photochromism at the solid state (P-type photochromism). Moreover, photochromic polymers, in which the chromophore is covalently linked to the main polymeric chain, are considered as the most convenient candidates for applications in the optical field, showing large responses and high optical quality. Specifically, we developed a two components polyurethane coating based on 1,2-diarylethene derivatives and an aliphatic diisocyanate. The deposition is carried out with common solution techniques (e.g. spin coating) and process parameters finely tune the thickness of the photochromic layer. The polymerization takes place in situ, providing amorphous films with remarkable optical properties (surface flatness and bulk homogeneity). The versatility of the formulation allows to vary the amount and the chemical structure of the photochromic monomer without affecting the reactivity of the polymerization, thus tuning over a wide range

the optical properties of the material.

Once verified that polyurethane coatings fulfill the requirements of optical quality and high sensitivity, two different holographic devices based on these films have been yielded. The former, namely amplitude Computer-Generated Hologram (CGH), based on the transmittance change of the photochromic film in the visible region, is an effective device used as reference surface in the null interferometric test of aspheric and free form optics. We produced Fresnel Zone Plates (FZPs), as prototypes of more complex CGHs, on the photochromic coatings (see fig. 1), and the functionality of devices has been proved, successfully testing the photochromic FZPs as respect to spherical reference surfaces. The latter, based on the modulation of the refractive index in the near-IR region, is called Volume Phase Holographic Grating (VPHG). By using the photochromic coatings, we produced VPHGs with a Lloyd mirror configuration set-up. The functionality of the devices has been demonstrated and diffraction efficiencies up to 8% have been measured in the Near-IR region of the spectrum, where the material is transparent and the grating is a phase only,



1. A  $f_{1,5}$  Fresnel Zone Plate realized onto a photochromic polyurethane film.

which is the largest value of diffraction efficiency due to phase modulation ever obtained with photochromic materials. Beside the design of new diarylethene-based materials, a deep understanding of the conversion upon exposure was considered of great relevance to be aware of the actual highlights and the limit of applying photochromism into optics. Accordingly, we studied the kinetics of conversion of diarylethene systems first in solution, where we determined the cycloreversion quantum yield of three diarylethenes in solvents with different polarity, and then at the solid state. In this case, we developed an analytical model describing the kinetics of photoconversion inside the volume of the material. Quantum yields of photochromic systems at the solid state have not been so far reported, and no standard techniques can

be found in the literature. We successfully applied the model to determine the ring-opening quantum yield of polyurethane films under different laser beam profiles and at different wavelengths. A lowering of the ring opening quantum yield while increasing the wavelength of the exposure light, which has been already reported for diarylethene derivatives in solutions, has been here observed for the first time at the solid state. Moreover, the model revealed to be a useful tool to determine the conversion profile inside the volume of the photoactive material while the device is realized. A complete conversion into the colored form of the whole film is not always possible and all the properties related to absorbance are consequently affected. Considering the decoloration reaction, the conversion is not uniform

through the film thickness and the profile depends on the exposure time. Moreover, the conversion profile in the film thickness can be completely different from the illumination profile because of the highly non-linearity, with great consequences on the properties of the final device.

## POLYMERIC MATERIALS USED FOR INDUSTRIAL DESIGN DURING XX CENTURY: degradation study, structure/ proprieties relations and conservation strategies

Francesca Toja

Polymeric materials have been extensively used in works of art and in design objects since last century. Technological innovation has had a high and direct impact both on art and on industrial production. Polymers were introduced as novel binding media for paint, and successively, as well as new materials in industrial design project.

One of the most fortuitous outcomes of polymers technology was indeed the mass production of design objects by means of plastics. In the 50s of the 20<sup>th</sup> century designers explored numerous uses and transformations of plastics for their works, creating thus forms, colours and functions unconceivable to achieve with the previous materials available to them. In a short time, plastics permeated everyday life, in a radical way transforming the choices, the habits and the common utilities of the modern society, and influencing quickly its fashions, brands and symbols. A large number of handmade and industrial objects, made of polymeric materials, represent today the development of the 20<sup>th</sup> century society, and are conserved in museums and private collections.

The polymeric material, if not suitably protected, may rapidly deteriorate: the knowledge about the stability and condition (state of conservation, restoration and



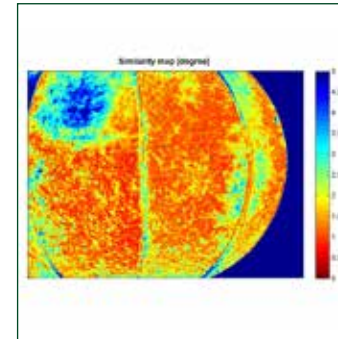
**1. Taraxacum lamp (left) manufactured by Flos starting from 1959 and Nesso lamp (right) manufactured by Artemide starting from 1965— copyright Photographic Archive Triennale Design Museum © photoAmendolagine-Barracchia.**

treatment) of such objects is still limited and only few examples of protocols for the investigation and management of these items are available.

The PhD project was carried out in the framework of a recent collaboration between the *Triennale Design Museum* of Milano (TDM) and the *Centre for the Conservation and Valorisation of the Cultural Heritage* of the *Politecnico di Milano*, the conservation issues of the *Triennale Design Museum* of Milano have been thoroughly investigated. A selection of very famous objects has been chosen for the scientific examination on the basis of the most urgent conservation needs (Fig.1). The items of the museum have been studied and compared to other items coming from a private collection.

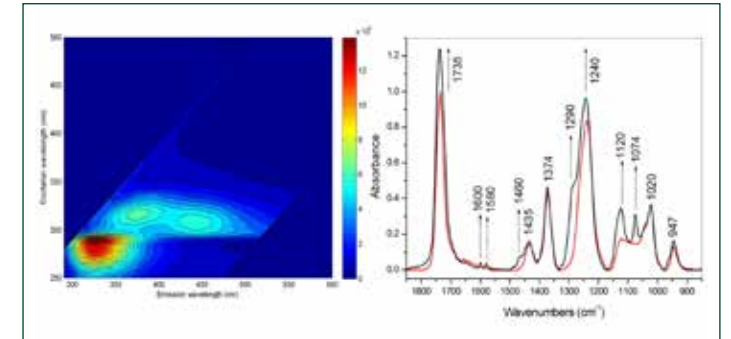
Starting from selected case-studies, three different polymeric materials have been analysed -poly(vinylacetate), ABS and cellulose acetate - with the aim of achieving enhanced competences in the field of polymer degradation in museum environment.

The goal of this thesis is to define and test a micro- and non-invasive protocol for polymer characterization and degradation assessment: vibrational spectroscopic techniques have proved to be suitable for the analysis of micro-samples of few mg and combination with innovative imaging techniques (Fluorescence Multispectral imaging, Fluorescence Life Time Imaging) has been used extensively to assess the degradation of polymers under



**2. Fluorescence Multispectral imaging: Similar Angle Maps of the Zucca lamp. The analysis permits the observation of two areas of the lamp (upper side of the object) in which the fluorescence emission spectra differ from that of the reference one.**

mild artificial and natural aging conditions. The degradation of PVAc in natural ageing condition proved to lead to the deacetylation of the polymer and to its localised deep oxidation (Fig. 2). The degradation patterns under photo and thermal-oxidative aging have been studied since the initial degradation steps, revealing differences in the degradation behaviour: the phenomenon is mainly a temperature driven process, which leads to increasing unsaturation content. The presence of the plasticiser (DBP) enhances the deacetylation of the polymer and modifies the degradation pattern of the polymer (Fig. 3). Design objects made of ABS present diffuse phenomena



**3. Poly(vinylacetate) with 30% wt. of DBP plasticizer: (left) Fluorescence excitation/emission spectrum of the unaged sample; (right) FTIR spectrum of standard PVAc (red line) and standard PVAc with 30% of DBP (black line) (arrows indicate the modification of the FTIR spectrum due to the presence of the plasticiser).**

of degradation of the rubber constituent and mechanical failure is a diffuse conservation problem. The assessment of the molecular modification have been implemented by the systematic analysis of specimens under mild and controlled aging treatment: ABS resin have been proved to be stable in thermal-oxidative conditions, while the photo-oxidative treatment leads to rapid degradation of the rubber phase, with formation of increasing content of oxidised groups. The analysis of cellulose acetate case-study revealed slight degradation phenomena affecting the internal side of the lamp. The analysis of the aged specimens revealed that cellulose acetate is stable under thermal-oxidative aging and only a partial

degradation have been evidenced by spectroscopic data; on the other hand the photo-oxidative treatment leads to a greater modification of the polymer. The correlation between FTIR, NMR and fluorescence data permits the comprehension of the degradation phenomena of the studied polymers. Fluorescence multispectral imaging has proved to be a reliable method for the monitoring activity on site for polymeric works of art, granted that the degradation pathway of the polymeric material had been thoroughly elucidated.