



**Experiment title: Analysis of the stratigraphic distribution of phtalate-based plasticisers in Poly-vinyl Acetate in model samples and museum objects with Micro-FTIR"**

**Experiment number:**  
EC977

<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 16/05/2012 to: 20/05/2012	<b>Date of report:</b> 05/09/2013
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## **Report:**

### **Introduction**

The failure of polymeric design objects includes the degradation of the main polymeric component and the modification of the blend (which include also the presence of additives such as plasticizer, colorants and stabilizers). The modification of the molecular structure due to aging of the polymer as well as the loss of plasticizer due to migration of the small molecules, leads to a rapid failure of the design objects, which may become brittle and fragile, preventing the possibility of use or exposition.

Two of the most important polymers used in design objects are polyvinyl acetate (PVAc) and acrylonitrile styrene butadiene (ABS) and have been the subject of this research. Both PVAc and ABS aged standard specimen and samples from historical Italian design objects from the 1960's were analyzed. The design objects made in PVAc, coming from the collection of the *Triennale Design Museum* (TDM) in Milan (Italy), are Taraxacum and Fantasma lamps, produced in the 1960's using a commercial resin traded as Cocoon®, a polymeric spray coating [1,2].

The two design objects made in ABS, coming from a private collection, are the Grillo telephone, designed by Marco Zanuso and Richard Sapper for *Siemens* in 1967, and the E63 lamp designed by Umberto Riva for *Francesconi* in 1963.

The degradation of PVAc occurs through the elimination of acetic acid and the formation of unsaturated bonds and polyenes through Norrish Type-II Photodegradation [3]. Recent studies based on FTIR from model samples suggest that thermal degradation of PVAc proceeds with a series of different reactions [4]. The elimination of acetate side chains leads to the formation of C=C double bonds, which occurs along the polymer backbone and with chain termination.

ABS is susceptible to photo-oxidative degradation. This instability is due to the butadiene, and in particular to the presence of residual double bonds along the polymer chains, which lead to molecular modifications localized preferentially on material surface [5]. This degradation generally involves an autocatalytic free radical chain mechanism where the allylic radicals react with oxygen to form hydroperoxides products. Labile oxygen–oxygen bonds break to form RO·radicals, precursor of typical oxidation product such as aldehydes, ester, carboxylic acids and ketones.

The aim of our research was to study the stratigraphic distribution and migration of additives in such polymeric matrices as a function of natural and artificial ageing by SR- $\mu$ FTIR analysis. In the specific case of PVAc we wanted the study of the migration properties of the plasticizer dibutylphthalate both in model and objects samples. In addition, SR- $\mu$ FTIR was employed to study the material blend in the case of specific historical ABS objects, mapping the distribution of additives and heterogeneities on the micrometric scale.

## Experiment description

### Materials:

- **PVAc samples:** a series of samples of reference PVAc doped with increasing concentrations of DBP were prepared. Samples have been naturally and artificially aged in steps in thermal-oxidative (60°C) and photooxidative (UV>380 nm) conditions with a maximum ageing condition of 3000 hours. In addition, samples from design objects (made of Cocoon ® which contains both PVAc and a phthalate plasticizer) have been studied.
- **ABS samples:** a series of samples of reference ABS were aged in photo-oxidative (UV>380 nm) conditions at different intervals of time for up to 1000 hours. In addition, samples from two design objects were taken from different areas of the objects using a scalpel and analyzed.

For PVAc, sample preparation was a limiting factor. Due to the high elasticity of the material which tended to curl onto itself, and stretch elastically during cutting, it was not possible to obtain microsamples with the appropriate thickness using a microtome. PVAc is a strongly absorbing material in the IR and hence transmission FTIR analysis was possible only for samples which were placed in a diamond compression cell. As a result, analysis of fragments of PVAc did not yield the expected results. In some samples in the diamond compression cell, it was possible to observe a heterogeneous distribution of additives and degradation, but this could not be correlated directly with the shape of the sample as all spatial information as lost upon compression of this low T<sub>g</sub> polymer.

For samples of ABS, thin-sections of different thickness were obtained, ranging from 1 to 4  $\mu\text{m}$ , where one side of the microtomed slice corresponded precisely to the side exposed to UV radiation while the other side was from the unexposed side.

SR- $\mu\text{FTIR}$  analyses were performed at the ID21 FTIR end-station, ESRF [6]. The beam line was designed to exploit the edge radiation emitted from the short straight section (focusing electron lenses) upstream of a bending magnet. A set of a tens of mirrors is used to collect, to collimate, to transfer the beam, and finally to provide a parallel source to the FTIR spectrometer (Nexus, from Thermo). This spectrometer is coupled to a Thermo Continuum microscope that uses reflecting Schwarzschild objectives and a set of apertures to define the spot size. The signal coming from the sample (in transmission or reflection) is detected by a liquid  $\text{N}_2$  cooled single element MCT detector. In the present experiments, analyses were carried out in transmission, on thin sections and various types of scans were acquired – point analysis, line scans and maps of points. The line-scans and map-scans allow the visualization of the distribution of the main functional groups, in particular the formation and disappearance of some species in the vicinity of the surface.

The beam size was reduced from  $10 \times 10 \mu\text{m}^2$  down to  $3 \times 3 \mu\text{m}^2$ . Analysis carried out at ID21 FTIR end-station is described elsewhere [6]. The beam line was designed to exploit the edge radiation emitted from the short straight section (focusing electron lenses) upstream of a bending magnet. A set of tens of mirrors is used to collect, to collimate, to transfer the beam, and finally to provide a parallel source to the FTIR spectrometer (Nexus, from Thermo). This spectrometer is coupled to a Thermo Continuum microscope that uses reflecting Schwarzschild objectives and a set of apertures to define the spot size. The signal coming from the sample (in transmission or reflection) is detected by a liquid  $\text{N}_2$  cooled single element MCT detector. In the present experiments, analyses were carried out in transmission, on thin sections and various types of scans were acquired – point analysis, line scans and maps of points. The line-scans and map-scans allow the visualization of the distribution of the main functional groups, in particular the formation and disappearance of some species in the vicinity of the surface.

An asymmetric beam ( $10 \times 3 \mu\text{m}^2$ ) had the advantage of providing a good balance between flux ( $10 \mu\text{m}$  in the direction parallel to the surface) and lateral resolution ( $3 \mu\text{m}$  in the direction perpendicular to the surface). Spectra were acquired as the sum of 25 scans, with a spectral resolution of  $4 \text{cm}^{-1}$ , over the  $4000\text{--}900 \text{cm}^{-1}$  range.

## General conclusions

Sample preparation is of fundamental importance and represents the critical point for the success of analysis, both for the microtoming of ABS and the analysis of more elastic polymers like PVAc.

SR- $\mu\text{FTIR}$  microspectroscopy is an effective approach for the assessment of degradation of ABS polymers. The historical samples and the aged specimens were mapped with a step size of  $3 \times 3 \mu\text{m}^2$ ; maps were elaborated using suitable data analysis software (PyMCA) for the generation of functional images. The depth of oxidation was evaluated; different degradation products, such as ketones, aldehydes, esters, and  $\alpha$ - $\beta$  unsaturated carbonyl compounds, were identified while the loss of additives was studied. A comparison between the artificially aged samples and the samples coming from historical objects has been carried out; in

addition specific microscopic inclusions and stabilizers were identified and mapped. Specifically, for ABS standard a maximum level of oxidation was found in the first 50-60  $\mu\text{m}$  in depth with a chemoselectivity for 1,4 over 1,2 C=C of polybutadiene.

Further applications of SR- $\mu$ FTIR are foreseen for the mapping of the migration of additives and the study of modern plastics and paints.

## References

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5. R. M. Santos et al. J. Appl. Polym. Sci. 2010,116: 2005–2014
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## **Publications (submitted)**

**1.** Saviello D., Pouyet E., Cotte M., Toniolo L., Nevin A. “Synchrotron FTIR microspectroscopy for the mapping of photo-oxidation and additives in ABS model samples and historical objects”, *Polymer*, submitted 09/2013

### **Abstract**

Synchrotron-based Fourier transform infrared micro-spectroscopy (SR- $\mu$ FTIR) was used to map photo-oxidative degradation of acrylonitrile-butadiene-styrene (ABS) and to investigate the presence and the migration of additives in historical samples from important Italian design objects. For standard ABS an accelerated UV ageing process was carried out. Samples were prepared using a microtome, and high resolved ( $3 \times 3 \mu\text{m}^2$ ) molecular maps were generated by FTIR microspectroscopy in transmission mode. The depth of oxidation in samples was evaluated and accompanied by the formation of ketones, aldehydes, esters, and  $\alpha,\beta$  unsaturated carbonyl compounds. This study demonstrates selective surface oxidation and a probable passivation of material against further degradation. In samples of design objects made of ABS from the 1960s, deterioration was evaluated and microscopic inclusions and UV-stabilizers were identified and mapped, in particular, a proteinaceous material was found and mapped for the first time in an historical design object.

**2.** E. Pouyet, M. Cotte, B. Fayard, C. Gervais, J. Kieffer, A. Lluveras, J. Mass, F. Meirer, A. Nevin, M. Salomè, D. Saviello, F. Sette, J. Susini, Y. Taniguchi “Synchrotron-based micro-spectroscopic analysis of thin sections” *Analytica Chimica Acta*, submitted 09/2013

### **Abstract**

Over more than a century, the analyses of painting fragments have been mainly carried out through the preparation of thick cross-sections in resin. With the development of innovative analytical instruments, alternatives to this standard method should be considered. Synchrotron radiation-based techniques such as SR- $\mu$ FTIR, SR- $\mu$ XRF,  $\mu$ XANES and SR- $\mu$ XRD are increasingly used for the study of artistic materials, as they offer enhanced spatial resolution and sensitivity. The capabilities of these techniques can be significantly improved if carried out on painting thin sections ( $30 \mu\text{m}$  and below). In this context, getting thin sections of painting fragments is essential but it represents a critical step in the complete analytical process. The present paper evaluates the pros and cons of sample preparation methods largely used and described in the literature and proposes new alternatives aiming at limiting chemical and analytical interferences introduced during sample preparation. In addition to the optimization of the procedures for each SR micro-analytical techniques quoted above, a specific discussion is focussed on the challenges and solutions for the combination of these techniques.