



## 1.6. Trends in identification and characterisation of plastics

### 1.6.1. Dielectric Spectroscopy (DS)

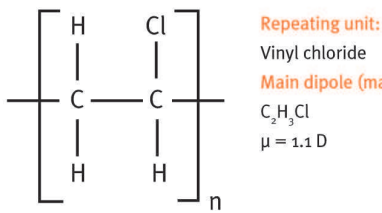
#### Introduction

DS is the investigation of the dipolar nature of materials through the study of the physical phenomenon known as dielectric relaxation. When applied to polymers, it provides information about the segmental mobility of a polymeric chain, allowing studying the dynamics of polymers with different molecular architectures.

Plastics are, with a few exceptions, insulating materials – in other words they are not able to conduct electric currents but, instead, they can accumulate charges.

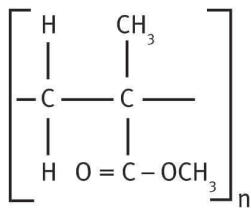
Electric permittivity (also known as dielectric constant) is a physical property of an insulating material that quantifies its capacity of polarizing when immersed in an electric field. Polarisation consists in the partial or total orientation of the molecules constituting the material. This phenomenon occurs in different ways, depending on the microscopic structure of the material. Materials composed of “polar” molecules, i.e. having a natural charge separation, exhibit a greater dielectric constant with respect to non-polar materials, where polarisation consists in the displacement of the centres of positive and negative charges (induced polarisation). Essentially there are two types of polarisation: the rotational polarisation, consisting in the alignment of permanent dipoles along the electric field, and the distortional polarisation, that consists in the induction of a dipole moment in a molecule normally not having it. The net dipole moment, or polarisation, is the vector summation over all molecular dipoles in the repeating units of the main chain, and in all other polymer chains in the system. Therefore, the spectral (dielectric)





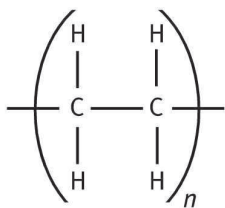
**Repeating unit:**  
Vinyl chloride  
**Main dipole (main chain):**  
 $C_2H_3Cl$   
 $\mu = 1.1 \text{ D}$

Figure 42. Structure and polar characteristics of PVC



**Two types of dipoles:**  
ester group ( $O = C-O$ )  
methyl group ( $CH_3$ )  
**Main dipole (side chain):**  
 $O = C-OCH_3$   
 $\mu = 1.8 \text{ D}$

Figure 43. Structure and polar characteristics of PMMA



**Monomer:**  
ethylene gas ( $C_2H_4$ )  
 $\mu = 0$

Figure 44. Structure of polyethylene

response of a polymer depends on the quality and on the quantity of the above molecular dipoles.

Polymers are mainly weakly polar materials: the dipole moment is due to the presence of polar bonds (covalent bonds in which electrons are unequally shared) in the polymeric chain. Examples of polar plastics are poly(vinyl chloride) (PVC), a thermoplastic existing both in rigid and flexible form, and poly(methyl methacrylate) (PMMA), a transparent thermoplastic often used in plastic artefacts also known as Plexiglas, Perspex or acrylic glass. Figures 42 and 43 respectively show the repeating units of PVC and PMMA.

It is well known that purely linear polymers are rather uncommon. Indeed, a plastic material usually consists of a main skeleton with secondary lateral chains. Both the principal and secondary chains can contain polar groups, contributing to the total dipole moment. Longer chains have more “inertia” and relax at lower frequencies. On the opposite, the shorter are the polar groups, the higher is their relaxation frequency. The phenomenon of relaxation is the non-instantaneous response of molecular dipoles to a time-varying electric field: the “bigger” is a molecule, the greater is the delay in polarizing itself. The relaxation frequency is the value at which the electric polarisation, and hence the dielectric constant, changes from an equilibrium condition to a different one. Relaxation is characterised by a peak in the dielectric losses.

Polyethylene, also known as polythene, is a non-polar thermoplastic that does not possess a permanent dipole moment, due to its molecular architecture (it is a long chain of identical, neutral, symmetric repeating units). Figure 44 shows the polyethylene molecule.

By comparing Figure 42 with Figure 44, it should be noted that the substitution of a hydrogen atom with a chlorine atom is responsible for the appearance of a dipole moment. As a consequence, the electrical behaviour of the two polymers is expected to be different and, thus, such to allow to distinguish polyethylene from PVC.

In summary, the dielectric properties (in particular the dipole moment) strongly depend on the molecular structure of a material. This, in turn, means that looking at the dielectric properties of a polymer it is possible to obtain information about its molecular structure and, for example, to ascertain the occurrence of changes in that structure.

Dielectric properties may be affected by the following factors:

- Presence of polar groups in the molecular structure
- Degree of crystallinity

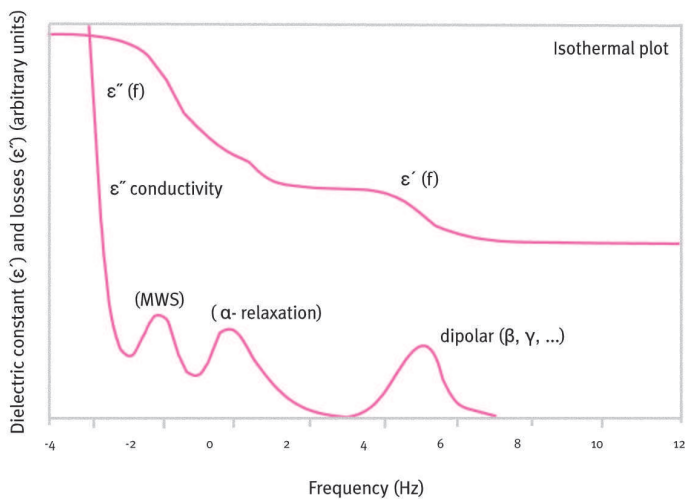


Figure 45. Schematic view of the relaxation processes in a polymer

- Temperature (in particular, the “distance” from the glass transition temperature)
- Humidity

The first one has been formerly discussed. The last one is rather obvious, as water is a very high dielectric constant material. The second and third characteristics are related to the molecular architecture and, as such, they affect the dielectric properties. The degree of crystallinity, for example, depends on the temperature but also on the structure: co-polymers are unlikely to be crystalline, whilst polymers whose lateral chains have a chemical composition similar to the backbone easily crystallise.

Processes producing a change in the above properties (deterioration/ageing) reflect on the dielectric properties of a polymer. In particular, environmental conditions (light, heat, moisture, pollutants) have effects on the polymeric chain structure and, as a consequence, they affect the dielectric properties of plastic materials (Menczel *et al.* 2009; MacCrum *et al.* 1967). As plastics usually consist of polymeric materials plus some kind of additive or filler, changes in these last materials can affect dielectric characteristics as well.

The main deterioration mechanisms – chain end degradation (shortening) and random degradation (chain scission) – are due to thermal and/or mechanical stress, light exposure, oxidation, and absorption of water.

Not all plastic materials used in artworks exhibit the same vulnerability to ageing factors (Shashoua 2008; Martuscelli 2010). Among them, a certain number has been recognised to be more prone to the effect of temperature changes, water uptake and exposure to light, like for example cellulose nitrate and acetate, polyurethane, plasticised PVC.

The rationale of DS as a technique for the study of plastic materials is the following. Plastics possess a complex dielectric response, exhibiting loss peaks (dielectric relaxation) at a number of frequencies. The location (and the amplitude) of the relaxation frequencies is strictly related to the molecular structure and to other factors, such as, for example, the fraction of amorphous/crystalline material and the glass-transition temperature. When the dielectric properties are observed over an extended frequency band (theoretically, from a few mHz to several tens of GHz), it is possible, in principle, to detect the changes in a plastic material by looking at the location and at the shape of the dielectric relaxations. Figure 45 is a schematic view of the expected dependence of the dielectric properties on frequency. The sequence of peaks in the dielectric loss



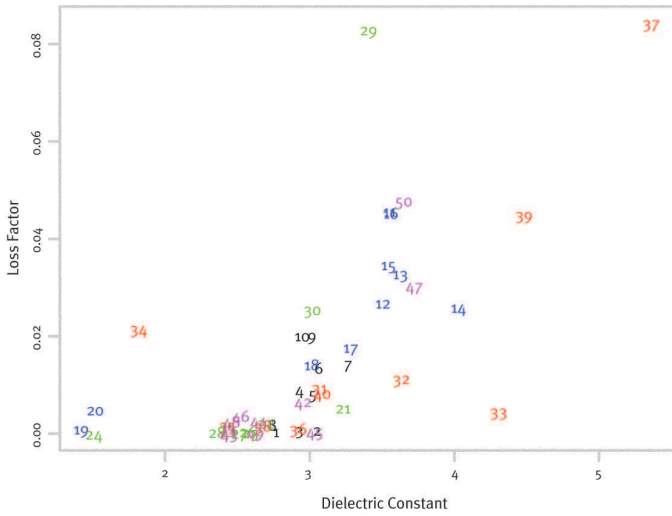


Figure 46. ResinKit™ samples on the ( $\epsilon'$ ,  $\tan\delta$ ) plane

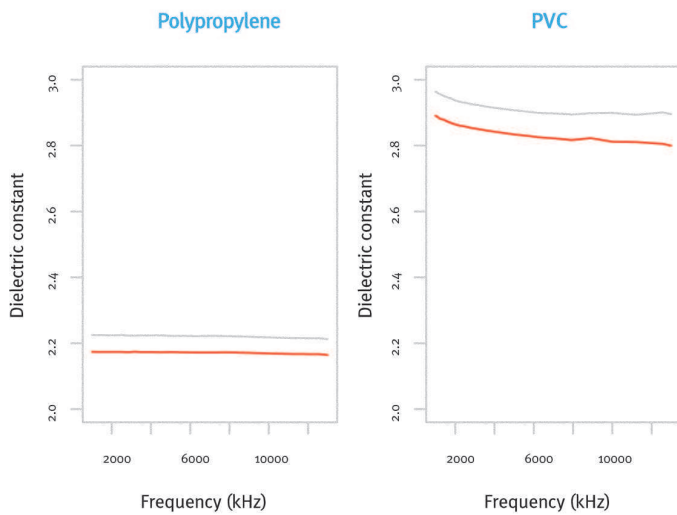


Figure 47. Measurement before (grey) and after (red) artificial ageing

factor  $\epsilon''$  is representative of the different relaxation mechanisms (e.g. the primary  $\alpha$  relaxation, and secondary  $\beta$ ,  $\gamma$ ,  $\delta$  relaxations representing secondary transitions in the polymer chain).

A relevant literature (Pratt *et al.* 1997; Moteleb *et al.* 1999; Kima *et al.* 2006; Gubanski *et al.* 2003; Wetton *et al.* 1992) in different application fields exists concerning the detection and the quantification of polymers degradation due to different factors, such as water absorption, heat and exposure to ultra violet radiation. For example, the effect of ageing on polymers used in cables or in transformers as insulating materials has been investigated by DS by studying the frequency-dependent characteristics of their dielectric properties as a function of temperature, ultra violet radiation exposure and water absorption.

The experience in technological sectors far from that of the cultural heritage can be therefore exploited in the conservation field, making DS a useful diagnostic tool for monitoring the plastic artefacts.

### Instrument

Measurements on ResinKit™ samples have been made using a Low-Frequency Impedance Analyzer HP 4192A equipped with an Agilent Probe 16451 B.

An innovative time-domain technique, using an electrometer Keythley 6517A, is currently under development. The first prototype requires samples identical to the former measurement method but, in perspective, the method should allow to take measurement on site directly on artworks, non-destructively.

### Sampling size

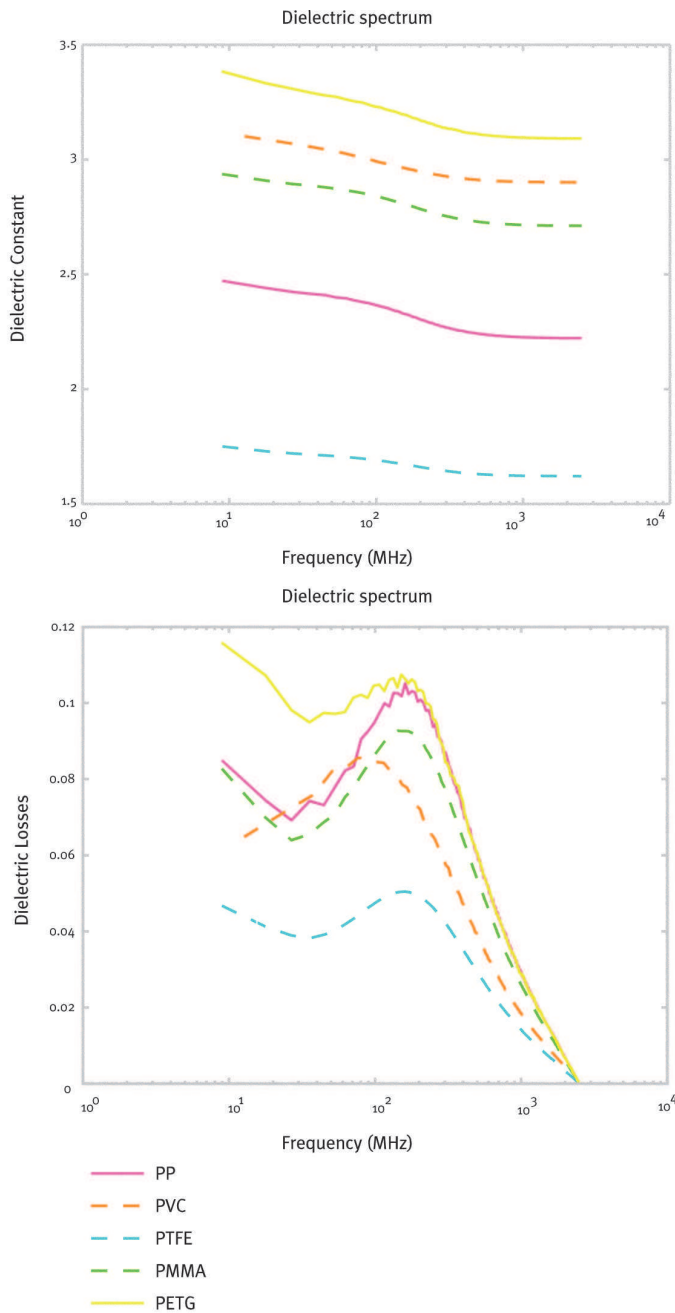
Circular or rectangular shape, diameter (or diagonal) from 10 to 56 mm. Required almost uniform thickness, from 0.1 to 10 mm. Other requirements: flat, smooth surface.

### Examples and results

Measurement on the ResinKit™ samples allowed to classify plastics on the “dielectric plane” (whose axes are the dielectric constant,  $\epsilon'$ , and the loss tangent,  $\tan\delta$ ) as shown in Figure 46. The numbers in Figure 46 identify to the fifty materials included in the ResinKit™ collection. Different colours have been assigned to groups of ten: black for materials from 1 to 10, blue from 11 to 20, etc.







**Figure 48.** Dielectric spectra of several polymers at ultra-low frequency

The dielectric data refer to the frequency band 1-10 MHz, where all measured polymers exhibit a “flat” behaviour (Figure 46).

It may be observed that different polymer classes are usually well separated (horizontally and/or vertically). For example, material 20 (polycarbonate) is very “far” from 37 (urethane elastomer), while it is close to 19 (poly(propylene oxide)). However, a classification based only on point wise dielectric properties is not an easy task: indeed, the exploitation of the full dielectric spectrum would be needed for the purpose of material identification.

Conversely, the detection of deterioration or ageing phenomena appears to be simpler. Preliminary tests on a small set of plastics subjected to artificial ageing supported the potentiality of DS for detecting and quantifying degradation before it is visible suggesting that DS could be used as a diagnostic technique synergistically with more established ones, like GC-MS, X-ray fluorescence, FTIR Spectroscopy etc.

Figure 47 shows the change in dielectric constant, in the frequency range 1-13 MHz for samples of polypropylene and PVC before (black line) and after (red line) artificial ageing.

In the development of a portable DS system specifically designed for applications in museums, different technological issues have to be solved.

At the laboratories of IFAC-CNR the development of a portable DS system, operating in the time-domain and aimed at reconstructing the relaxation spectrum by means of a Laplace/ Fourier transformation, is in progress. Preliminary results obtained in the testing phase are reported in Figure 48 that shows a comparison between the dielectric spectra obtained applying a FFT to the time-domain signals on polypropylene PP, PVC, PTFE, PMMA and PETG.

**Roberto Olmi, Costanza Cucci and Mauro Bacci**

### 1.6.2. NIR imaging

Plastic artefacts represent a significant challenge to conservation, as many synthetic materials are naturally unstable in the long term (Keneghan *et al.* 2008). Certain types are particularly susceptible to degradation induced by environmental conditions and deteriorate rapidly, requiring specialist care, regular monitoring or even isolation. For their successful preservation it is essential that chemical properties of plastic artefacts are understood. However, their nature significantly restricts the possibilities for sampling. It is often difficult to ethically justify the use of destructive analytical





techniques and non-destructive analysis is essential where sampling is not permitted. Even if it is possible, many degraded objects are difficult to analyse without further damage or potential loss because of handling during the process of analysis.

A solution may be offered by the use of two-dimensional (2D) near infrared (NIR) chemical imaging, a technique that is both non-contact and non-invasive and hence valuable for visualisation of damage on historic plastic materials. Being able to quantitatively image degraded areas of plastic objects would be of huge advantage to their successful conservation.

With NIR imaging, tens of thousands of NIR spectra are collected in a measurement, each relating to a specific area or a pixel on the sample surface, resulting in spatially resolved information on the nature and quantity of chemical species. The immense quantity of data resulting from the application of this method and contained within a single image necessitates a variety of processing techniques to assist with image interpretation.

Therefore, multivariate analysis techniques, such as principal component analysis (PCA) and partial least square (PLS), are often applied to expose trends that would be otherwise undetectable (Geladi *et al.* 1989; Burger *et al.* 2006).

The near infrared spectral region (1000–2500 nm) has not been exploited to the same extent as the visible or mid infrared regions in imaging studies yet. It has already been demonstrated that NIR spectroscopy has a significant potential in the field of organic heritage material characterisation and greatly enhances heritage collection management replacing destructive and micro-destructive methods. In this section, an application of NIR spectroscopy to quantitative imaging of chemical properties and damage mapping on plastic objects is introduced.

In this work (Cséfalvayová *et al.* in print), a collection of 91 plastic reference samples and objects (SamCo) has been assembled by the partners RCE, V&A and Natmus and imaged. The ResinKit™, a commercial available collection of 50 specimens of various plastics, was also available for imaging experiments. An additional set of plastics from the UCL Centre for Sustainable Heritage extended collection of historic plastic materials was analysed.

NIR images were acquired using the hyperspectral chemical imaging workstation SisuCHEMA (SPECIM Spectral Imaging Ltd.), which employs a SPECIM MCT based Spectral Camera. The spectral range recorded was 970–2500 nm, with 10 nm spectral resolution, producing images with 320 spatial pixels combined with 256 wavelength channels. The length of the scanning can be set freely according to the sample in question and is not limited to image





shape. The spectral camera builds the image one line at a time while the sample is scanned on a moving sample tray. Total image acquisition time including reference acquisition was about 4 s. Applying this “push-broom” approach these imaging systems require only a line of illumination. Combining this with the fact that data is collected in a short time, the heat load for sensitive samples is minimised. The height of the available measurement compartment presently restricts the size of objects that can be studied to 100 x 100 x 40 mm (W x L x H).

Each resulting image, composed of a set of absorption spectra, was processed to eliminate pixels with experimental artefacts such as shadow, specular reflection, background and spikes, thus reducing physical or instrumental contributions to spectral variations. A spectral matching correlation algorithm was developed for identification. Spectral matching compares the shape of each spectrum with each library spectrum and assigns a “degree of match” value ranging from -1 (perfectly antimatched) to +1 (perfectly matched) using an algorithm. The library entries with the highest match values with the unknown sample were used to identify the unknown.

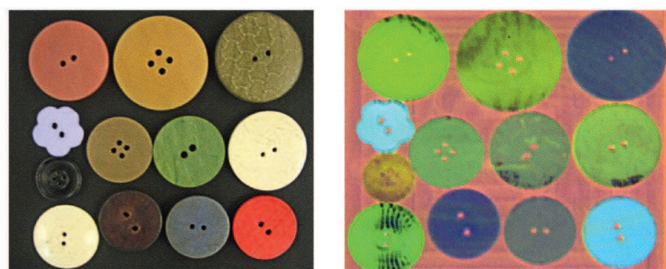
The numerous sample objects covered all major classes of plastics found in museum collections, and a library of reference images and spectra was acquired. A suitable classification algorithm was created on homogeneous regions of each plastic sample. Such filtering of spectra was also justified by the large number of spectra in a typical image (102,000). The contributions of shadows and specular reflections to spectroscopic images were reduced by identifying and subsequently separating these patterns from the sample absorption pattern within the image.

By applying a classification algorithm, most synthetic polymers can be reliably identified independently of their shape, reflective surface, colour or thickness. Only materials that have low-intensity or unstructured absorption bands cannot be classified satisfactorily. High scattering and absorbing samples such as those containing carbon black fillers increase spectral interferences and reduce the NIR signal, although they do not always prevent positive identification.

Using a statistical approach to examine NIR imaging data, spectral variations between individual samples are automatically identified and exploited to generate image contrast in a useful and intuitive way. PCA efficiently compresses a large number of variations into a finite number of factors while suppressing the effects of spectral interferences and removing noise from the data set. As a case study to demonstrate the potential of this approach in contrast



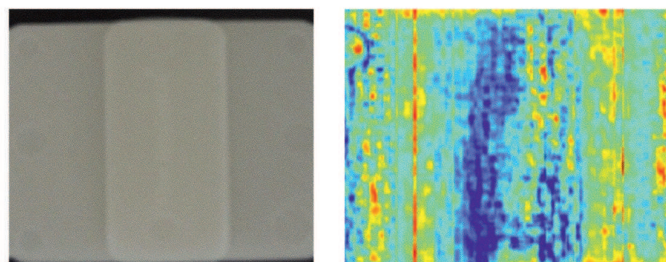




49.



50.



51.

**Figure 49.** Twelve randomly chosen buttons for the identification experiment using NIR qualitative imaging, left: VIS image, right: pseudo-colour NIR image, showing PE buttons in green, PE with carbon black in dark green/blue, casein formaldehyde in light blue, and wood in brown

**Figure 50.** A crinoline lady brush from 1950's/1960's, left: VIS image, right: pseudo-colour qualitative NIR image, showing the body to be of CA and bristles to be of nylon

**Figure 51.** The flexible PVC sample from the ResinKit™ collection, left: b/w image, right: pseudo-colour semi quantitative NIR image, showing areas with more plasticiser in red and those with less in blue

to NIR spot analysis, a set of twelve buttons has been subjected to NIR imaging analysis.

Likely composed of several different types of polymer materials, this collection proved to be an ideal example to explore the potential of NIR imaging to investigate multiple samples simultaneously and identify their composition.

Another case study is shown in Figure 50. As the areas with different spectral attributes show up in different colours in the pseudo-colour image, the two plastic materials are clearly distinguished from the aluminium background. A comparison with the NIR spectral library revealed the materials to be cellulose acetate and polyamide.

In museum collections, PVC objects also frequently require attention due to rapid degradation (Shashoua 2001). Despite being of relatively recent origin, many PVC objects show exudation of plasticiser in the form of surface accretions. Previously flexible PVC may thus become stiff and sometimes cracked. Exuded plasticiser may interact with other plastic materials such as polystyrene (Marcilla *et al.* 2004) for which it is a solvent and where PVC is in contact with polystyrene, the latter may therefore become damaged. NIR imaging can be used to map the distribution of chemical composition of flexible PVC objects, allowing the location and identification of plasticiser

The examples highlight several advantages of the NIR imaging technique, such as the possibility to overcome sampling limitations encountered in Raman or mid-IR imaging which may require samples to be flat. Imaging also significantly reduces tedious sampling requirements associated with single-point collection methods, with no requirement of any prior knowledge about the sample composition or location of a particular component. While computation intensive quantitative NIR imaging will without doubt secure its place in examination of artworks, having access to properly characterised reference sample sets is likely to remain the main limitation of this highly attractive analytical technique.

**Gianluca Pastorelli, Linda Cséfalvayová,  
Harri Karjalainen and Matija Strlič**





### 1.6.3. FTIR imaging

#### Introduction

FTIR-ATR imaging was a niche in the market at the end of the last century and only used at sophisticated laboratories. Nowadays it is daily practice for the identification and characterisation of multi-layered samples from cultural heritage objects. Not only photo-oxidation on the surface of degraded modern and contemporary art objects can be measured, nowadays it is common practice to observe the depth of the oxidation.

Degradation and oxidation profiles in degraded plastics can be visualised, condition of an object can be established and adequate conservation measures advised.

FTIR Imaging uses a multiple element detector with the purpose to develop an infrared image for a certain area of interest, so that for each pixel of the area of choice, a FTIR spectrum is recorded.

FTIR imaging can be performed through 2 dimensional experiments such as line scans (taking up spectra for marked points along a line) and maps (2-dimensional grids). Mapping is often used when examining the homogeneity of some chemical function spread over a defined area. A linear array detector is used at which high amounts of spectral data can be taken up in a very limited time. Besides transmittance and reflectance imaging, ATR imaging has been developed. ATR uses a germanium crystal, which offers the opportunity to achieve higher spatial resolution at a given wavelength than using standard transmission techniques.

#### Instrument

FTIR spectral data were collected on a Perkin Elmer Spectrum 100 FTIR spectrometer combined with a Spectrum Spotlight 400 FTIR microscope equipped with a 16x1 pixel linear Mercury Cadmium Telluride (MCT) array detector. A Perkin Elmer ATR imaging accessory consisting of a germanium crystal was used for ATR imaging.

#### Sample preparation

To obtain high quality data, preferably the sample should be embedded in a resin. The resin with embedded sample can be sectioned and polished using abrasive sheets. Generation of images occurs using a linear MCT detector array, combined with an automated moving stage/ATR crystal. The sample contact area is defined by the surface area of the germanium crystal of







a.



b.

**Figure 52.** a) Andres Slominski, “Untitled” (1992), bicycle with plastic bags and suitcases (Waitz Hanburg), (photo Katharina Haider). b) degraded white polyethylene (PE) bag

approximately 600  $\mu\text{m}$  in diameter. Images of maximum 500 by 500  $\mu\text{m}$  can be readily obtained as well as any other rectilinear areas that fit into this crystal surface area. Image pixel sizes can be 6.25 by 6.25  $\mu\text{m}$  or 1.56 by 1.56  $\mu\text{m}$ . The number of sample scans per pixel (usually varying from 1 to 16), defines the total image acquisition time and the spectral quality of the data.

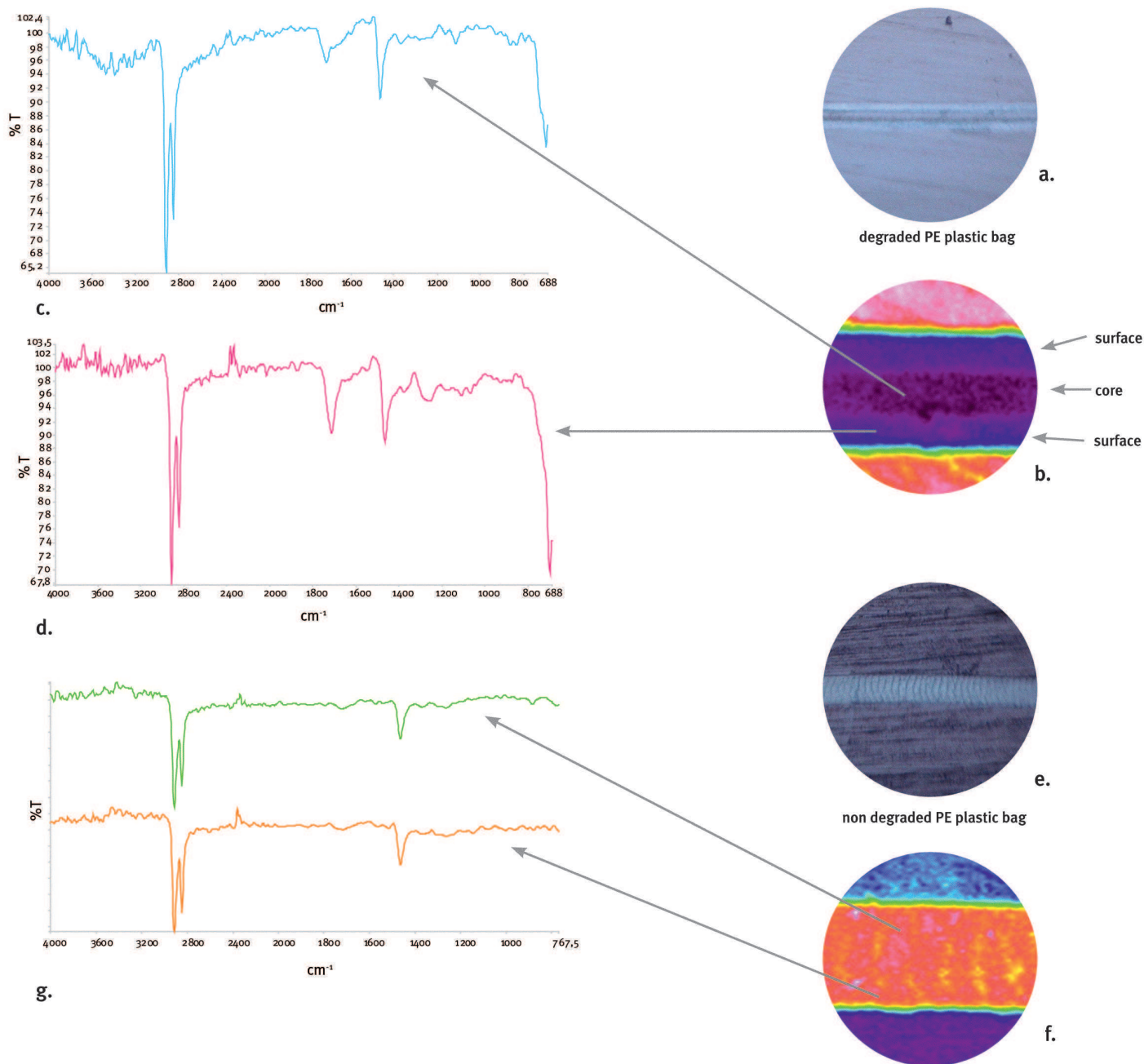
A first way of processing the data is making use of the “show structure” feature. After performing a base line correction and principal component analysis (PCA), this PCA function highlights the gross features in the image by overlaying the resulting principal component score images. A second way to process the data is using spectral frequency information.

### Results (a case study)

In the series Bicycles made between 1991 and 2005 by the German artist Andreas Slominski, the bicycles are loaded with filled plastic polyethylene (PE) bags, suitcases and many other items. Due to constant load, daylight and ultra violet radiation and former use, some of the polyethylene bags were severely damaged (Haider and van Oosten 2011, Figure 52 a and b).

The most important degradation process of polyethylene is photo-oxidation. The uv stability of a product depends on the structure of the polymer, on the stabilisers that were added and on the properties imparted to it during production, processing and after treatment. Upon oxidation, chain scission and cross-linking occur, resulting in the formation of carbonyl groups, carboxylic acids, vinyl and vinylidene groups which can be observed using FTIR. Cross-sections were made of a white polyethylene plastic bag of the work of art “Bicycle for the Homeless” by the artist Andres Slominski





**Figure 53.** Visual images of embedded polyethylene bags (a and e). FTIR ATR spectra of cross sections (c, d and g). PCA score image as a total absorbance image (b and f).

and of a new pristine polyethylene bag. Visual images were made of these imbedded polyethylene bags (Figure 53a and e). FTIR ATR imaging was performed on these cross sections as described above.

The FTIR ATR image of the cross section was subjected to Principal Component Analysis (PCA) resulting in the PCA score image presented on the right as a total absorbance image (Figure 53b and f). Corresponding FTIR spectra of the various areas of the



polyethylene bag of the cross section are shown in Figure 53c, d and g.

The FTIR ATR image of a cross section of a degraded PE plastic bag from the work of art of the artist Slominsky visualises the degradation of polyethylene by increasing carbonyl absorption at  $1712\text{ cm}^{-1}$ , from core to surface of the bag. In Figure 53b this can be seen as the light blue areas on both the outer sides of polyethylene bag, corresponding with the higher C=O content to be seen in the FTIR spectrum at  $1712\text{ cm}^{-1}$  in Figure 53d. In contrast to the core of polyethylene bag visualised as the darker blue colour in Figure 53b, corresponding with lesser oxidation (C=O, carbonyl absorption) in the FTIR spectrum (Figure 53c).

A new pristine, not degraded PE bag showed no increase in carbonyl absorption at  $1712\text{ cm}^{-1}$  shown in Figure 53g and no colour change in the total absorbance image corresponding with no change in chemical composition.

## Conclusion

Visualising oxidation profiles of plastics using FTIR ATR Imaging is an important and helpful tool at estimation the condition of a plastic. The establishment of the condition of a plastic is one of the key issues at conservation a modern and contemporary work of art.

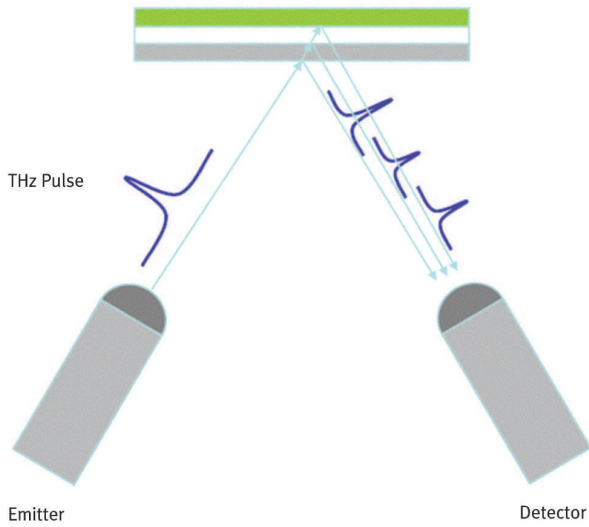
Thea van Oosten

### 1.6.4. 3D terahertz imaging

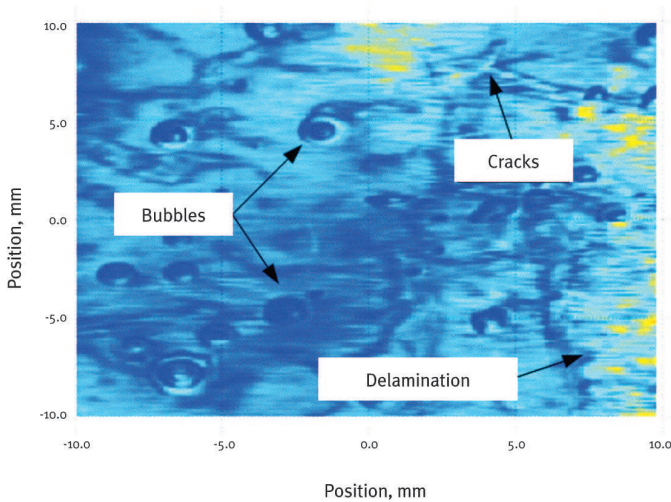
In the past few years the way for terahertz (THz) technology into heritage science and conservation has been paved slowly but securely (Fukunaga 2009). Terahertz radiation occupies the band between microwaves and the far infrared ( $1\text{ mm} - 100\text{ }\mu\text{m}$ ,  $\sim 0.3 - 3\text{ THz}$ ) and its recent advance is related to development of the necessary radiation sources and detectors.

The particular advantage of THz radiation in comparison to other optical techniques is that it induces interactions between large molecules, thus rendering itself particularly suitable for characterisation of macromolecular structures, such as plastic objects. Thus, THz spectroscopy has been used for determination of glass transition temperature of polymers (Jansen *et al.* 2010), has recently been shown to contain quantitative chemical information on the composition of historic paper (Trafela *et al.* 2011) and has been





**Figure 54.** When a THz pulse is reflected from a material with structure (or with interfaces with different refractive indices) then some of the pulse will be reflected from each layer



**Figure 55.** THz image of a degraded cellulose acetate photograph negative: frequency image at 2 THz shows bubbles and other structures in a cellulose acetate negative appearing as a consequence of degradation

used to study the sorption of water into synthetic materials (Jördens *et al.* 2010).

On the other hand, due to its properties, THz radiation can also be used for three-dimensional (3D) THz imaging, which combines a substantial depth of penetration into opaque organic materials with a significant amount of chemical information and it could significantly contribute to the present practice of structural and chemical monitoring of materials of organic origin. In this work, the first 3D images of historic plastic objects are presented using the state-of-the-art THz pulsed semiconductor-based imaging system (TeraView Ltd. Cambridge) specifically to monitor the thickness, uniformity and density of laminar and coated structures and to identify structural features such as cracks, dislocations and delamination. The emitter and receiver are based on a particular laser system working in the range of 0.06 THz – 3 THz.

The resolution of the system depends on the wavelength employed, and is typically in the range of several 10  $\mu\text{m}$ . This system has been described in detail elsewhere (Ho *et al.* 2009).

The imaging system operates on the principle of reflection of THz pulses from subsurface phase boundaries, i.e., boundaries between materials with different refractive indices (Figure 54).

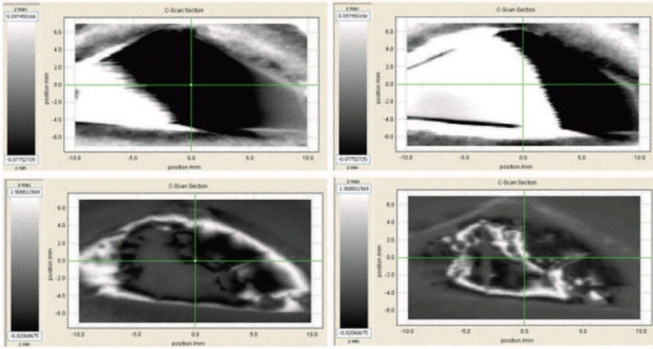
When a THz pulse sent by the emitter is reflected from a material with structure or with interfaces characterised by different refractive indices, the sequence of the reflected pulses from each layer is known as an “A-scan”. If the emitter and the detector are moved across a sample in the x direction, individual pulses at each position are received. The received pulses can be plotted either on a grey-intensity or coloured scale, which results in a cross sectional imaged called a “B-scan”. The resolution of a B-scan depends on pulse acquisition rate and speed of travel in the x direction. A C-scan is simply a scan over an area of a sample in the x-y direction, where at each point a sequence of pulses is recorded, thus a 3D image of an object can be obtained.

Several case studies were selected to explore the capabilities of 3D THz imaging, particularly plastic heritage objects. Using a degraded CA negative, it was possible to image the typical delaminations and other structures, such as bubbles and cracks, observed as a consequence of advancing degradation (Figure 55).

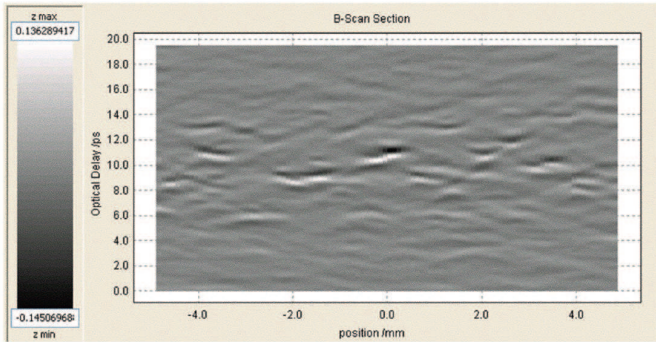
On CN objects, depth distribution of cracks can be observed very effectively. In Figure 56, two identical CN objects are shown, one still in a good physical condition, where no subsurface features can be observed, and another object where crazing can be easily observed







**Figure 56.** C-scans showing depth distribution of cracks in CA objects: object not severely degraded (above), severely crazed object (below)



**Figure 57.** B-scan representing the sub-surface cell shape and structure of polyether-based PUR foam

in the C-scans, representing horizontal cross sections of the object at different depths.

Using THz imaging, the subsurface cell shape and structure of polyether-based PUR foam (Figure 57) can be imaged in terms of optical delay of the THz beam measured in picoseconds (ps). The B-scan namely shows a vertical cross-section which however in future research would need to be translated into pathlength in order to allow for visualisation of the cell size in PUR foam (Figure 57).

THz imaging provides 3D images of polymers in a non-destructive and rapid manner and it shows significant potential for visualisation of the internal structure of plastic heritage objects.

**Gianluca Pastorelli, Phil Taday,  
David Lowe and Matija Strlič**

