2.2. Surveying plastic artefact collections in museums

Reference dolls as a low-technological method for comparing the rates of degradation of plastics in museum environments

In the previous paragraph actual cases of deterioration that were found in different museums have been reported. However, one of the main issues that is of interest for conservators and curators is to assess which kinds of plastics are most vulnerable to deterioration and to what extent they can deteriorate under the environmental conditions normally encountered in museums. Although, one might expect that real time deterioration could be ascertained by a careful investigation of museum objects on display or in storage, real objects or artworks may not sampled due to ethical considerations. Their pre-collection history is often unknown. Finally, permanent monitoring disturbs the aesthetic environment of the object whilst on display.

Therefore, in recent years, different types of sensors have been proposed that mimic in some way the behaviour of an actual object, although in a simplified way and usually with much quicker responses (Bacci *et al.* 2008). Within this context it is of interest not only to ascertain the behaviour of a given plastic material in real time in various environments, but also to comparatively evaluate how identical, new objects comprising several plastics react to different environments. For these reasons a long-term experimental campaign specifically aimed at investigating the role and the variability of environmental agents on new plastics was initiated.

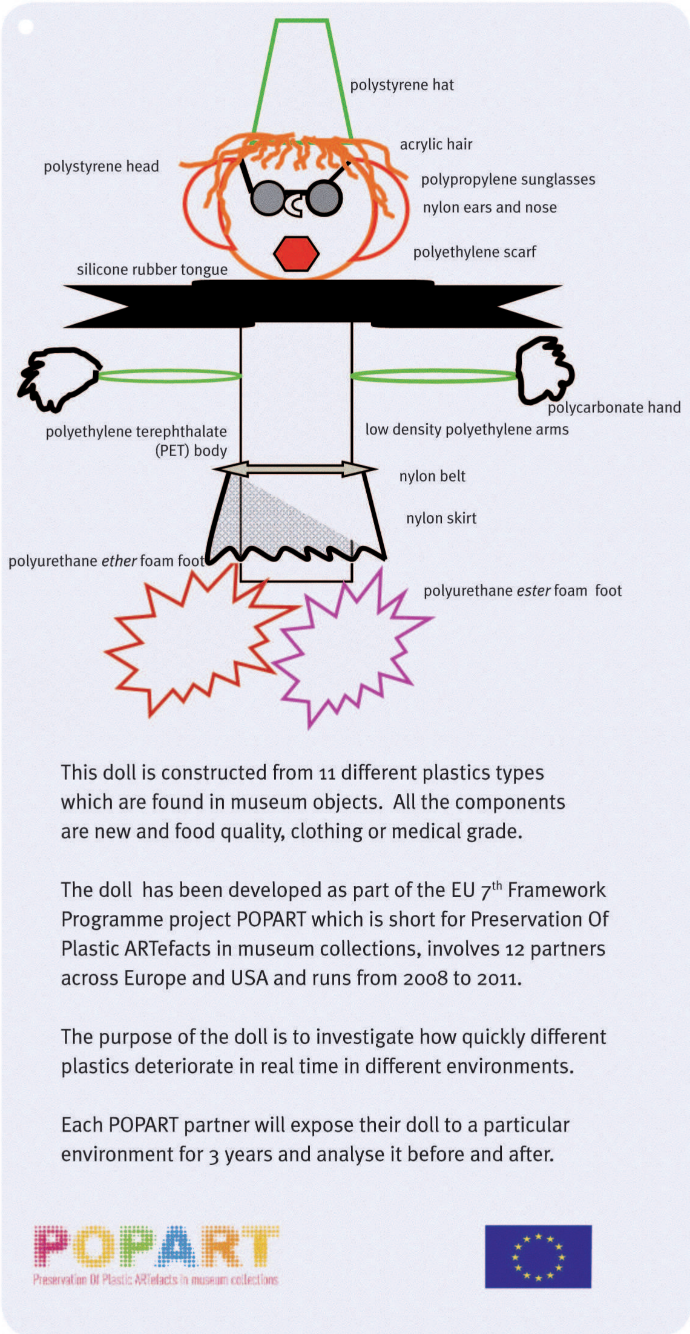

Figure 38. Leaflet adopted to explain the aims of the Popart project and the materials constituting the doll

Reference objects were prepared for simultaneous exposures in different environmental conditions. The reference object was designed and produced by Natmus in the form of a doll. Polly, as she was named, comprised of 11 different plastics representative of types typically found in modern museum collections. The plastics were polystyrene, poly(methyl methacrylate), poly(methyl acrylate), polypropylene, polyethylene terephthalate, low density polyethylene, silicon rubber, polycarbonate, polyamide, polyurethane ether foam and polyurethane ester foam. The plastics were represented by readily available, low cost medical, laboratory or food industry products so that Polly could readily be constructed by other researchers who wished to repeat or continue the research initiated. The products used were a polystyrene snaps glass as the hat, foamed polystyrene hobby ball as a head, acrylic fibre as hair, nylon screws as ears, polypropylene separating sheet as sunglasses, polyamide (nylon 6) tie as nose and belt, silicon baking form as tongue, polyethylene terephthalate soda bottle as body, polyethylene insulating tape as a scarf, low density polyethylene disposable pipettes as arms, polycarbonate sheet as hands, nylon net as a skirt and polyurethane -ester and -ether underwear padding foams as feet. Polly was assembled using polyamide fishing thread without any use of adhesives which might initiate degradation especially stress cracking of plastics.

In Figure 38 a sketch of the doll is shown and the different plastics that were used are reported. The Figure 38 was also used to prepare a label in English and also in the language of the country, where the doll was displayed. This sign was placed beside each doll explaining the background and the aim of the project, the structure of the doll and the objectives of the display (see Figure 39).

Beside the scientific aim, the choice of Polly doll as reference object was especially effective in attracting public curiosity and thus turned out to be a powerful publicity and dissemination tool for the project.

The 16 identical dolls realized were exposed in different places, not only in normal exhibit conditions, but also in some selected extreme conditions to ascertain possible acceleration of the deterioration process. In most cases the environmental parameters were also measured. The dolls were periodically evaluated by visual inspection and in selected cases by instrumental analyses. Exposures were interrupted after 18-20 months. Instrumental analysis included non-invasive techniques, such as colorimetry and UV-VIS-NIR spectroscopy, which allowed the monitoring of the conservation state during the period of display without altering the dolls themselves, but additional micro-invasive and invasive

Figure 39. Arrangement of the doll Polly in the Conservation Department of Natmus, Denmark

analyses were made at the end of the exposure period to obtain more information about the deterioration mechanisms. Reference dolls were stored in dark or closed boxes for the entire exposure period to avoid external interferences.

Figure 40 summarizes the situation.

Some dolls were placed in environmental conditions not usually encountered in museums (for instance Polly 8, Polly 9 and Polly16). This was done to obtain further information about the general mechanism of deterioration of the investigated plastics.

In all sites the average temperature resulted in the range 20-25°C even if peaks as high as 42°C (Polly 1) were episodically recorded. Relative humidity was more variable than temperature, the mean values ranging from 36% to 53% during the period of exposure with large oscillations in many sites (for instance from 7% up to 75% for Polly 1) due to seasonal variability.

The mean values of illuminance appear to be generally kept within the limits recommended for museum exhibits. However, direct light for some periods of the year gave maximum illuminance values up to 26 klx on few Polly dolls. Ultra violet radiation was excluded or filtered by window glass and ranged from 0 to about 600 mW/m^2 with a mean value over the exposure period below 50 mW/m^2. The exception was Polly 16, which was irradiated deliberately at 248 nm in order to ascertain the behaviour of different plastics under UV radiation. Finally, in one site (Polly 6) exposure to pollutants (sulfur dioxide, nitrogen dioxide and ozone) were conducted. Their quantity was well above the recommended limits for museums with respect to nitrogen dioxide and ozone, while sulfur dioxide was always present in low concentrations.

Figure 41 reports the results of the visual evaluation of the different parts of the dolls at the end of the period of exposure.

In order to standardise the visual evaluation of the dolls by different operators, a reference scale was adopted based on four degrees of alteration:

- 0 = no visible change
- 1 = just noticeable change
- 2 = evident change
- 3 = very strong change

Despite its simplicity, this evaluation method could be also used to monitor possible alterations of actual works of art with time. In fact, if the monitoring is done periodically, this simple action is a useful tool to establish the health of the artefact and to alert conservators to take proper decisions and to prevent further damage. Although visual evaluation is a very rough method to

Polly N. 1

Exposure: 07/10/09 – 05/05/11

Site: Pecci Museum of Contemporary Art, Prato, Italy

Characteristics: Situated beside of the ticket office on a table in front of the entrance and of the glass walls of the building. The illumination is mixed, but mainly natural

Environmental monitoring (mean values):

T = 20°C
RH = 45%
I = 387 lx
UV = 50 mW/m²

Method of evaluation: Non invasive reflectance spectroscopy (FORS), colorimetry

Polly N. 2

Exposure: 07/10/09 – 05/05/11

Site: IFAC, Sesto Fiorentino Florence, Italy

Characteristics: Situated inside the IFAC library store-room, near the main entrance, in front of a glass partition wall. The illumination is mixed, but mainly artificial (fluorescent tubes)

Environmental monitoring (mean values):

T = 21°C
RH = 44%
I = 160 lx
UV = 15 mW/m²

Method of evaluation: Non invasive reflectance spectroscopy (FORS), colorimetry

Polly N. 3

Exposure: 04/11/09 – 16/05/11

Site: Science Lab. V&A Museum, London, U.K.

Characteristics: Situated in a museum display case Artificial light

Environmental monitoring (mean values):

T = 22.8°C
RH = 35.8%
I = 107.1 lx
UV = 88 μW/lumen

Method of evaluation: Visual

Polly N. 4

Exposure: 20/10/09 – 01/05/11

Site: C2RMF, Petite Ecurie du Roy, Versailles, France

Characteristics: On the ground floor on a shelf in front of a window looking on the south site of the building

Environmental monitoring (mean values):

T = 21.6°C
RH = 46.4%
I = 95.8 lx
UV = 44 μW/lumen

Method of evaluation: Visual

Polly N. 5

Exposure: 20/10/09 – 01/05/11

Site: C2RMF library, Petite Ecurie du Roy, Versailles, France

Characteristics: On the ground floor stored in a cardboard box on a shelf

Environmental monitoring (mean values):

T = 21.6°C
RH = 46.4%
(due to space constraints T and RH were measured outside the cardboard box)

Method of evaluation: Visual

Polly N. 6

Exposure: 01/10/09 – 23/05/11

Site: University College (UCL), Heritage Science Laboratory, London, U.K.

Characteristics: Sealed glass reactor simulating the showcases environment

Environmental monitoring (mean values):

T = 22°C
RH = 41%
I = 28 lx
O_3 = 5.23 ppb
SO_2 = 0.28 ppb
NO_2 = 23.48 ppb

Method of evaluation: Visual

Polly N. 7

Exposure: 20/10/09 – 15/05/11

Site: CRCC, Paris, France

Characteristics: Stored in a closed cardboard box. No light

Environmental monitoring (mean values):

T = 22°C
RH = 34%

Method of evaluation: Visual, Py-GCMS

Polly N. 8

Exposure: 08/09/09 – 27/05/11

Site: ARC-Nucléart, Grenoble, France

Characteristics: Situated above the water pool of gamma ray irradiation facility (humid atmosphere and no direct light)

Environmental monitoring (mean values):

T = 20°C
RH = 40%
(reference period: 29/12/10 – 27/04/11)

Method of evaluation: Visual

Figure 40. Distributions of the 16 dolls Polly

Polly N. 9

Exposure: 08/09/09 – 27/05/11

Site: ARC-Nucléart, Grenoble, France

Characteristics: Situated on the side of an impregnation tank for wet archaeological artefacts (aqueous solution of polyethylene glycol, humid environment, and period of sunshine)

Environmental monitoring (mean values):

T = 20°C
RH = 40%
(reference period: 29/12/10 – 27/04/11)

Method of evaluation: Visual

Polly N. 10

Exposure: 01/10/09 – 01/05/11

Site: PISAS, Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia

Characteristics: Kept behind a window at room temperature

Environmental monitoring (mean values): No

Method of evaluation: Visual, DSC, Thermogravimetry, Non isothermal chemiluminescence

Polly N. 11

Exposure: 01/09/09 – 02/05/11

Site: NATMUS, Lingby, Denmark

Characteristics: Situated in a closed glass showcase in the Conservation Department together with samples of the materials used to construct her, with no environmental control

Environmental monitoring (mean values):

T = 22.6°C
RH = 51%
(reference period: 08/12/09 – 02/05/11)

Method of evaluation: Visual

Polly N. 12

Exposure: 07/08/09 – 20/05/11

Site: GCI, Los Angeles, USA

Characteristics: Situated in the south-facing window in the GCI labs; light exposure is not monitored

Environmental monitoring (mean values): No (Natural light, Air conditioning)

Method of evaluation: Visual

Polly N. 13

Exposure: 07/08/09 – 20/05/11

Site: GCI, Los Angeles, USA

Characteristics: Indoors in an enclosed box

Environmental monitoring (mean values): No (Away from light and heat sources, Air conditioning)

Method of evaluation: Visual

Polly N. 14

Exposure: 31/08/09 – 13/04/11

Site: ICN, Ateliergebouw, Amsterdam, The Netherlands

Characteristics: Situated in the partner office in front of a window with UV filter and red light excluded

Environmental monitoring (mean values):

T = 22°C
RH = 53%
I = 5000 klx during the entire period

Method of evaluation: Visual and FTIR/ATR

Polly N. 15

Exposure: 31/08/09 – 13/04/11

Site: ICN, Ateliergebouw, Amsterdam, The Netherlands

Characteristics: Kept in the dark in a box inside a cabinet of the partner office

Environmental monitoring (mean values):

T = 22°C
RH = 53%

Method of evaluation: Visual and FTIR/ATR

Polly N. 16

Exposure: 31/08/09 – 03/06/11

Site: SOLMATES, High Tech Factory, Enschende, The Netherlands

Characteristics: Kept in the enclosure of a high power pulsed UV laser (500 mJ per pulse at 248 nm). It is irradiated by the diffuse scattering of the UV laser light

Environmental monitoring (mean values): No (controlled temperature around 20°C)

Method of evaluation: Visual

Material	Doll portion	Change observed during the entire period of exposure							
		Polly 1	Polly 2	Polly 3	Polly 4	Polly 5	Polly 6	Polly 7	Polly 8
Polystyrene	head	2	2	0	0	0	0	0	0
Silicone rubber	tongue	1	0	0	1	0	0	0	0
Polyurethane ether foam	right foot	2	3	2	3	3	2	2	0
Polyurethane ester foam	left foot	2	2	1	2	1	1	1	0
Nylon	skirt	1	1	0	0	0	0	1	0
Nylon 6.6	belt	1	1	0	0	2	0	1	0
Low density Polyethylene	arms	0	0	0	0	0	0	0	0
Polycarbonate	hands	1	1	0	0	0	0	1	0
Polyethylene terephtalate	body	0	0	0	0	0	0	1	0
Polyethylene	scarf	0	0	0	0	0	0	0	0
Nylon	ears	1	1	1	0	2	0	1	0
Nylon	nose	0	0	0	0	2	0	1	0
Polypropylene	sunglasses	1	0	0	0	0	0	0	0
Polyacrylonitril + Polyvinyl acetate	hair	1	0	0	1	0	0	0	0
Polystyrene	hat	0	0	0	0	0	0	0	0

Material	Doll portion	Change observed during the entire period of exposure							
		Polly 9	Polly 10	Polly 11	Polly 12	Polly 13	Polly 14	Polly 15	Polly 16
Polystyrene	head	0	0	0	0	0	0	0	3
Silicone rubber	tongue	0	0	2	2	0	2	0	0
Polyurethane ether foam	right foot	2	1	2	3	0	2	0	3
Polyurethane ester foam	left foot	2	1	2	2	0	2	0	3
Nylon	skirt	1	0	0	1	0	0	0	0
Nylon 6.6	belt	1	0	1	2	0	1	0	1
Low density Polyethylene	arms	0	0	0	0	0	0	0	0
Polycarbonate	hands	1	0	0	0	0	0	0	2
Polyethylene terephtalate	body	0	0	0	0	0	0	0	0
Polyethylene	scarf	0	0	0	0	0	0	0	0
Nylon	ears	1	0	0	1	0	1	0	2
Nylon	nose	1	0	1	1	0	1	0	0
Polypropylene	sunglasses	0	0	0	0	0	0	0	0
Polyacrylonitril + Polyvinyl acetate	hair	0	0	1	3	0	2	0	1
Polystyrene	hat	0	0	0	0	0	0	0	0

Figure 41. Visual evaluation of the alterations observed in the different materials constituting the dolls Polly after the period of exposure (0 = no changes; 1 = just noticeable changes; 2 = evident changes; 3 = dramatic alterations)

assess the damage, because it strongly depends on the sensitivity of the observer and cannot be considered an objective indication of the extent of the damage, it remains one of the most used methods to assess the conservation state of three dimensional artworks and it was considered favourably for use in this context. Actually, the introduction of a reference evaluation scale turned out to be effective in reducing the degree of arbitrariness. In spite of the fact that a change could be considered by one person as insignificant and rated

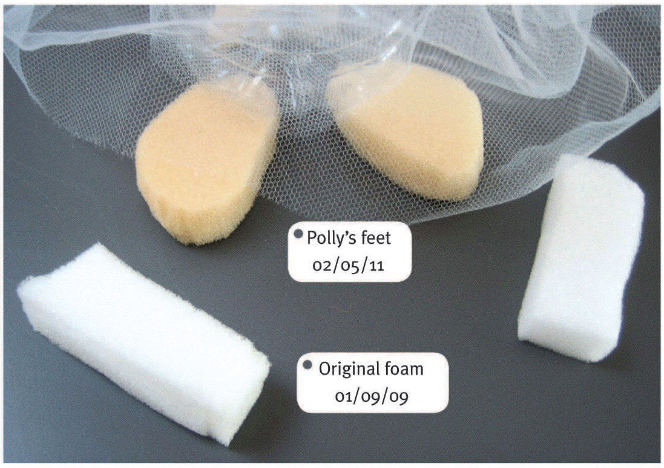

Figure 42. Alterations observed in the Polly's feet (polyurethane foam) after exposure and compared with the original materials

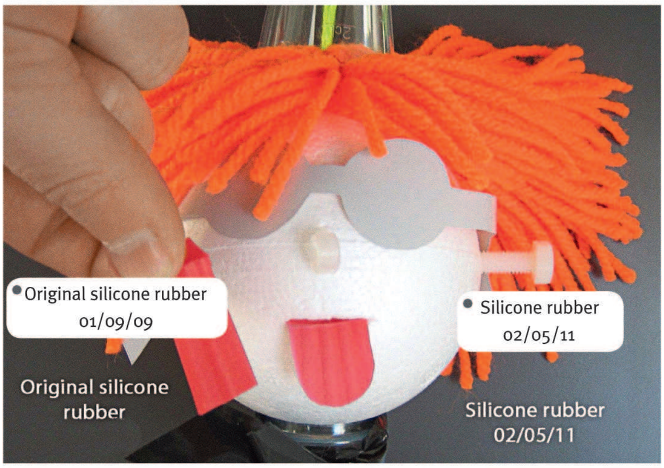

Figure 43. Alterations observed in the Polly's tongue (silicone rubber) after exposure and compared with the original material

as "0", while another could rate the same change as "1", all the results of the experimentations were consistent.

An examination of Figure 41 shows that the values attributed by different observers to each plastic material constituting the 16 dolls are indeed uniform, the only exception being Polly 7, for which alteration of both feet was evaluated as significant though the doll was kept in the dark

The most degradation was seen in the right and left feet, which comprised polyurethane ether and polyurethane ester foams, respectively. The second most frequently changed material was polyamide (nylon 6), which was reported to be yellowed in several cases. The other polymers were visually unaltered.

In Figure 42 the feet of Polly 11 at Natmus after 20 months of exposure are compared with the original foam to show the strong colour change. Similar extents of yellowing were observed for all the dolls exposed to natural or artificial light, while no change occurred in the dolls kept in the dark. When colour change was quantified, values as high as ΔE › 8 to 10 (CIELab76) were found. The instability of polyurethane materials to light and the consequent formation of coloured degradation products are well documented in the literature (Shashoua 2008, 188). On the other hand, low density polyethylene, polypropylene and polyethylene terephthalate did not appear changed by exposure and instrumental evaluation of the colour change showed it to be below detection limits. All the other materials were altered by exposure and the visual evaluation confirmed by the instrumental measurement of colour. In particular, major changes were observed for nylon and silicone rubber (see Figure 43).

Colour change measured by non-invasive reflectance spectroscopy (FORS) is only indicative owing to the difficulty in repositioning the optical probe and to the transparency or softness of some constituting materials. Some colour changes are not due to alteration of plastic material, but only to the pigment/dye added to the plastics. This is likely to be the case with silicone rubber. Of course, this aspect that does not imply instability of the plastic material is important when it is considered in the context of an actual work of art, which is constituted by a complexity of materials (different plastics, pigments and dyes, other organic/inorganic compounds) and for which colour is an intrinsic and essential factor of the artefact. Anyway, in spite of the difficulties inherent to the non-invasive monitoring of colour changes in a three dimensional object (see also Chapter 1) this kind of measurement represents a valuable early warning tool for changes. Besides colour, the use of FORS in the UV-Vis-NIR range is in principle useful for obtaining information about the material degradation with time by examining the decrease of the typical absorption bands

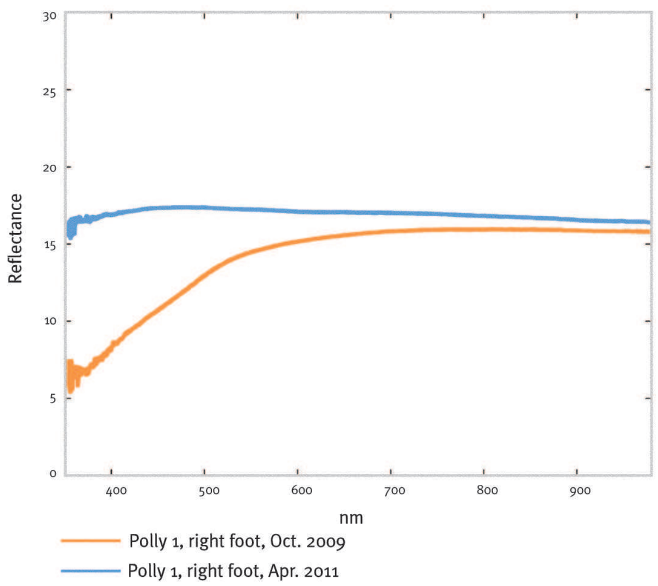

Figure 44. Reflectance spectrum recorded non-invasively by means of FORS on the Polly right foot (polyurethane ether foam) before and after exposure

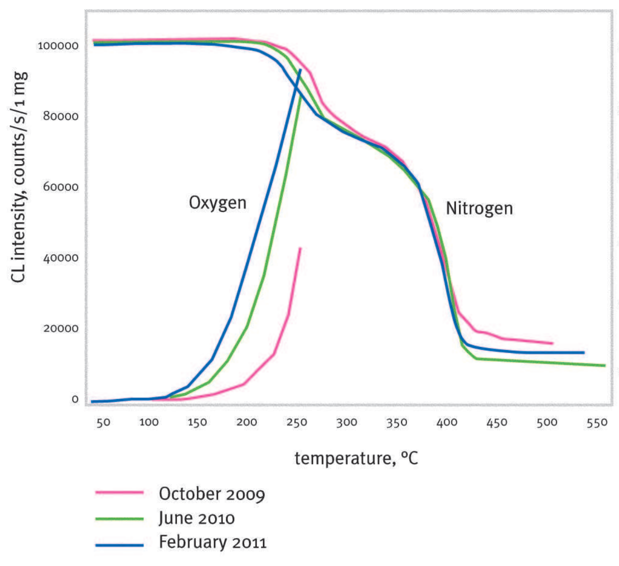

Figure 45. The development of the non-isothermal chemiluminescence (in oxygen) and thermogravimetry (in nitrogen) runs with the polyester urethane shoe ageing under laboratory conditions, rate of heating 5˚C/min

of that material or the increase of new bands due to deterioration products (see Chapter 1). The experimental campaign on Polly dolls resulted on spectral changes observable only in the UV-Vis region, whereas the NIR region did not exhibit any meaningful change for all the material investigated. In Figure 44 the FORS spectra measured on the polyurethane ether foam (right foot) before and after the exposure on Polly1 are reported.

It is clear that non-invasive measurements are necessary during the period of exposure, while successively much more information can be obtained by invasive or micro-invasive investigations. In the case of Polly dolls, non-isothermal chemiluminescence and thermogravimetry studies (see also Chapter 3) were completed just after the exposure. Each polymer gives a specific response of the chemiluminescence intensity with temperature. Some polymers give rather high chemiluminescence signal e.g. polyurethane ethers polypropylene, polyethylene and nylon while polyethylene terephthalate (PET), silicone rubber and poly(methyl methacrylate) give a relatively weak signal. Very sharp increase of the light emission at temperatures above 200°C indicates that the sample is heavily stabilised and is seen particularly with polypropylene and polyethylene. Visual alterations were confirmed (see Figure 45), but significant changes were also measured for other polymers apparently slightly affected by natural ageing. In the Figure 46 a summary of the results obtained for the polymers constituting Polly is reported. Here, a temperature difference between the results obtained before and after exposure is evaluated according to the following considerations (see also Chapter 3). As the maximum intensity of chemiluminescence depends on the polymer type, it seemed to be quite useful to plot the respective runs in the normalised coordinate of the intensity, which was the actual intensity, divided by the maximum intensity of chemiluminescence instrument. In such a way the intensity at the maximum always equal to 1 and the differences in the lower temperature regions due to sample ageing could be differentiated readily.

With respect to long term stability of polymers, results suggest that lower temperatures are of higher interest. To have a uniform approach the section of normalised graphs up to 10% of the maximum chemiluminescence intensity at 250°C measured at the beginning and the end of the doll monitoring was chosen. As scale of the changes in each polymer, the temperature corresponding to 10% of I_{max} was determined arbitrarily. The most significant changes were observed not only for polyurethane ester foam (32°C) and polyurethane ether foam (23°C), but also for the polystyrene head (31°C), and polyethylene terephthalate body (22°C), while the items

Polymer	Temperature (°C) of 10% uptake of CL intensity related to I_{max}, October 2009	Temperature (°C) of 10% uptake of CL intensity related to I_{max}, February 2011	Difference (°C)	Evaluation of the alteration
Acrylic hairs	127.2	123.0	4.2	1
Polycarbonate hands	159.8	152.0	7.8	1
Silicone rubber tongue	169.9	154.3	15.5	2
Nylon belt	184.8	174.7	10.1*	1* June 2010
Polyurethane ester foam foot	188.0	155.9	32.1	3
PS head	195.5	164.6	30.9	3
Nylon skirt	200.8	198.0	2.8	0-1
PP sunglasses	209.0	199.7	9.3	1
PE scarf (carbon black)	211.5	199.7	11.8	2
PET body	213.6	191.2	22.4	3
Low density PE arms	215.5	208.8	6.7	1
PS hat	222.1	211.4	10.7	
Polyurethane ether foam foot	232.6	210.0	22.6	3
Nylon ears and nose	-	-	-	Not tested
PMMA tray	-	-	-	Not tested

Figure 46. Temperatures of 10% value of maximum chemiluminescence intensity Imax for polymers composing the doll that were exposed during the period October 2009 to February 2011

least affected by ageing were the polyamide skirt, acrylic hair and low density polyethylene arms.

One more analytical technique that was used to follow possible degradation processes was Fourier transform infrared spectroscopy (FTIR) at the RCE. FTIR is one of the most used spectroscopic methods for the identification and quantification of oxidation products (van Oosten 2008). Oxidation can be monitored by the increase in carbonyls on the polymer chain from carboxylic acids, dicarboxylic acids, aldehydes and ketones. Photo-oxidation of polymers causes a development of surface cracks, discolouration, darkening and decrease in molecular weight, which results in gradual loss of mechanical properties and ultimate embrittlement. Chemical changes will lead to decrease in molecular weight and eventually in gradual loss of mechanical properties and ultimate embrittlement.

At the RCE, FTIR was used to follow photo-oxidation of Polly's polymers. Indeed, Polly's plastics are highly sensitive to spectral radiation, especially high energy UV radiation and absorb wavelength above 285 nm due to impurities, in particular oxygen containing species and trace levels of metals and other species present, arising from production processes. Photons react with the polymer surface to form radicals. These radicals react rapidly with atmospheric oxygen and hydro peroxide is formed. The decomposition of the hydro peroxide groups produces oxygen functional groups on the surface including C-OH, C=O and COOH. The amount of oxidized materials created on polymer surface increases at the exposure to light. Therefore, FTIR is particularly suitable for this kind of investigation.

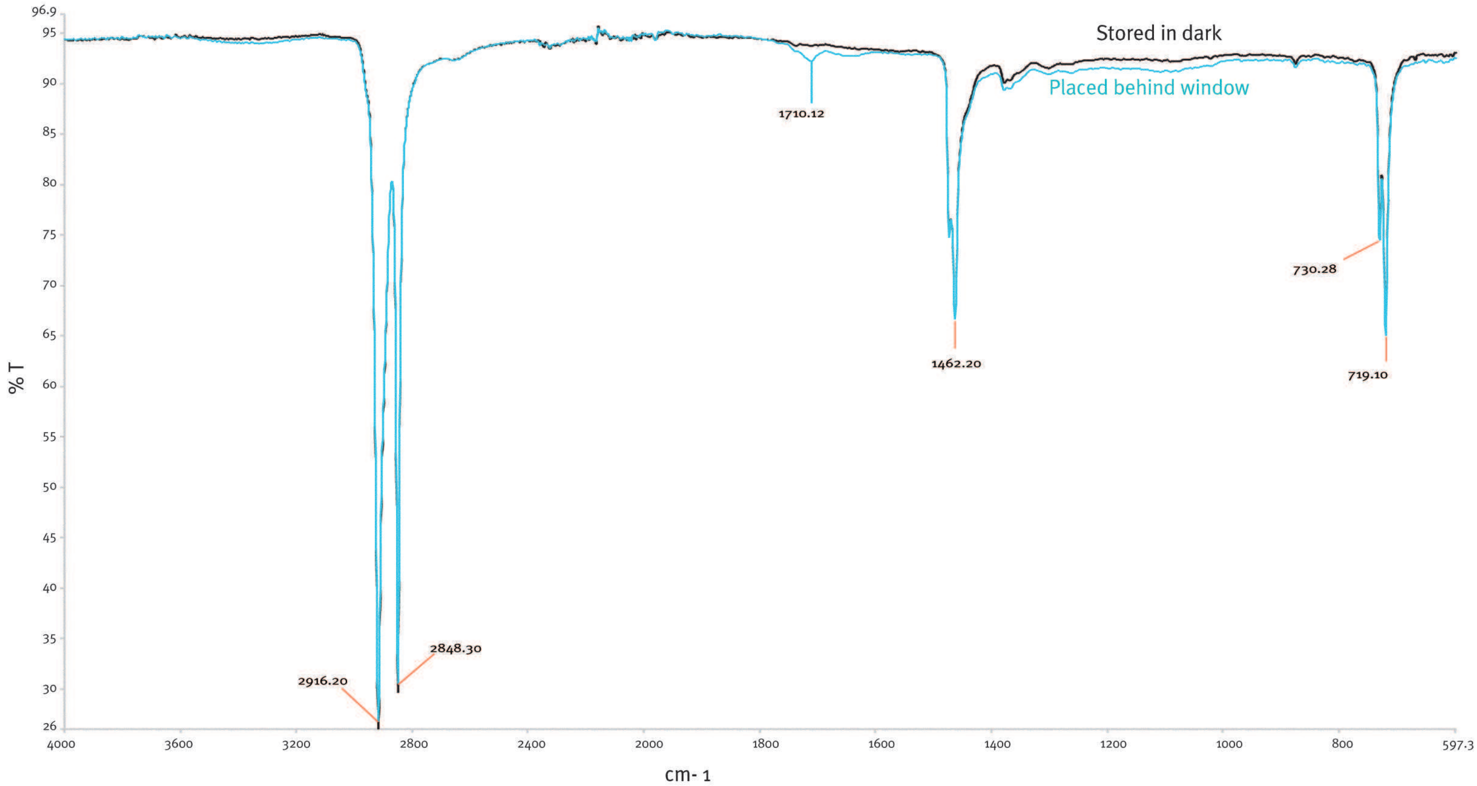

Figure 47. FTIR spectra of PE constituting Polly's scarf exposed to light (blue spectrum) and stored in dark (black spectrum)

Spectra were recorded from 4000 to 600 cm^{-1}, over 40 scans at a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum 1000 FTIR Reflectance accessory (ATR, Graseby spectrometer combined with a Golden Gate single Reflection Diamond Attenuated Total Specac, sample size 0.6 mm^2, see also Chapter 1). ATR analysis only penetrates a thin layer of the sample and measures, amongst other oxidation products, the carbonyl and hydroxyl formation on the surface of the material.

It takes time for oxygen to diffuse into the bulk of the material. The process determining step is the diffusion-limited oxidation in materials thicker than 100 µm. Under 40 µm thicknesses, diffusion is independent of film thickness.

At the RCE, all Polly's plastics before and after natural light ageing were analysed using FTIR. All FTIR spectra of the naturally aged were compared with the FTIR spectra of the plastics of Polly that was kept in the dark. After ageing, increase in carbonyl absorption and OH absorption was observed in PUR ether of one of Polly's feet and slightly oxidation in PE of Polly's scarf (see Figure 47).

After ageing, increase in crystallinity of amorphous polymers was observed in PA, PET, PS and PAN of Polly's components (see Figure 48) at sharper absorption bands and changes in intensities. No changes in the FTIR spectra was obvious in PP,SI, PE of the arms and PS of Polly's hat.

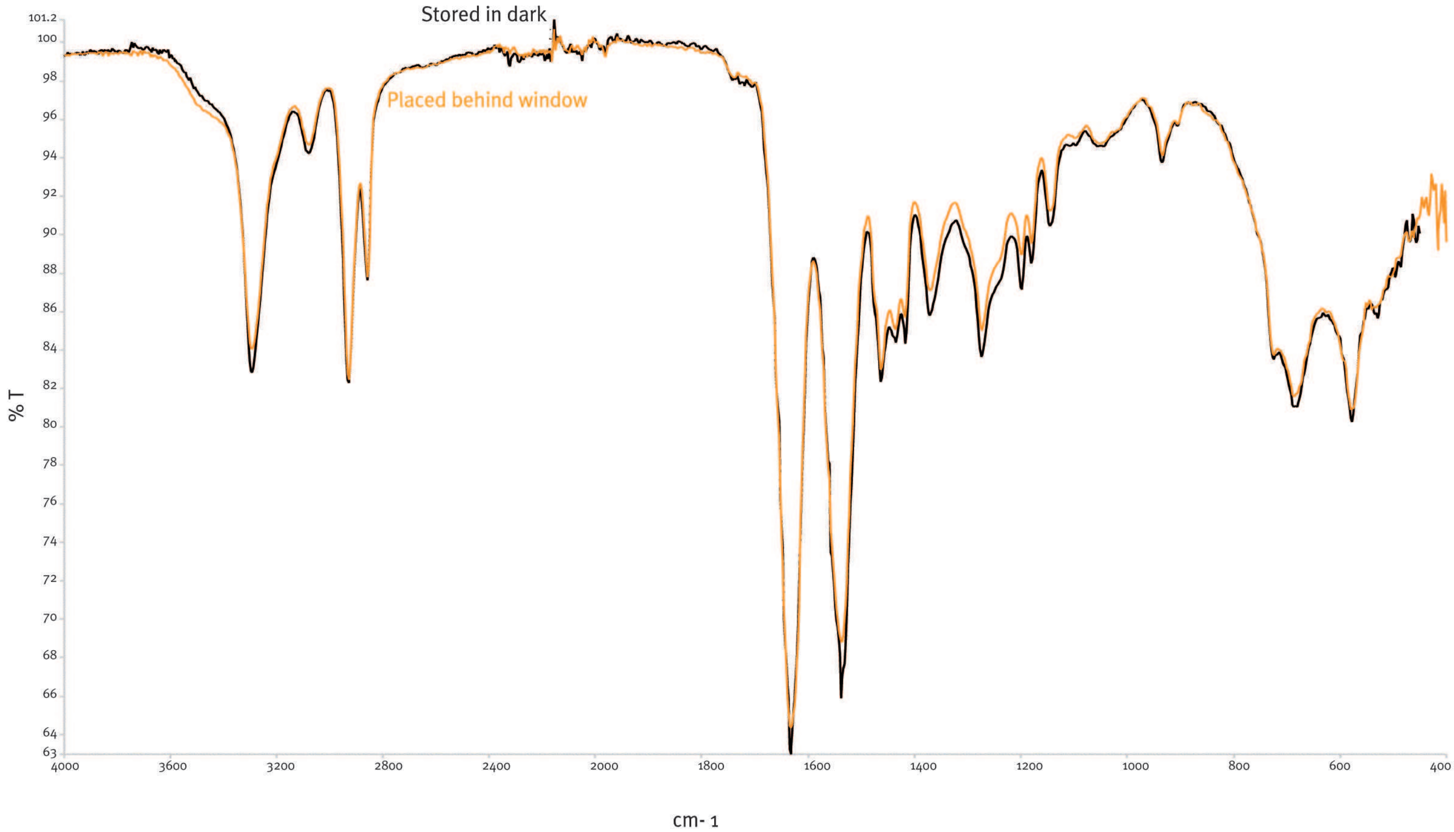

Figure 48. FTIR spectra of PA constituting Polly's nose exposed to light (orange spectrum) and stored in dark (black spectrum)

In conclusion the experimental campaign carried out with Polly dolls can be viewed as a pilot study aimed at tackling the practical issues related to the monitoring of real three dimensional plastic artworks and the surrounding environment.

The overall exposure period (one year and half) was sufficient to observe initial changes in the more susceptible polymers, such as polyurethane ethers and esters, and polyamide, with detectable chromatic changes and surface effects. Conversely the other polymers were shown to be stable in the same conditions over this time period.

The experimentation was also an occasion for testing and comparing different approaches for the assessment of degradation on real objects, from the easiest method based on visual evaluation to the non-invasive techniques, such as the colorimetric analysis and the micro-analytical and analytical techniques commonly used in laboratories (FTIR, chemiluminescence).

Last but not least, the educational and communication benefits of an object like Polly facilitated the dissemination of the project results to the public, and increased the awareness of issues associated with plastics in museum collections.

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