Understanding light sensitivity of plastics in heritage collections

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‘I, Anna Pokorska confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.’
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Abstract

Through an extensive and in-depth literature review five photostability ‘influencers’ were identified: polymer type, light stabilizers and/or antioxidants, colourants (dyes or pigments), impurities from manufacture and processing, and previous light exposure. Of those five, the effect of several colourants and previous UV exposure on cellulose acetate (CA) and polypropylene (PP) polymers was examined through a series of light-ageing experiments. The selected pigments are known to have a sensitizing effect on those polymers when exposed to UV radiation, however their influence under visible light, as found in a museum environment, has not been explored. Results obtained from these experiments show that, although many of the pigments did indeed accelerate molecular changes of the polymer when compared to uncoloured samples, the effect was not strong enough to lead to mechanical damage or even discolouration even after exposure corresponding to 200 years on display at 200 lux under similar light sources. The final study addressed the question whether previous light exposure of a plastic object can increase its sensitivity to visible light as found in museum displays. The results were similar to the previous experiment in that, although oxidation continued even without UV, its rate was not fast enough to cause significant degradation of the material. However, a growth in a hydroxyl FTIR band caused by UV exposure was linked to light sensitivity of PP when subsequently aged with visible radiation, which allows for simple screening of potentially photosensitive objects. Visible reflectance spectroscopy was also shown to be a promising tool for non-invasive identification of pigments used in plastics, particularly when combined with NIR spectroscopy to identify the polymer type. Finally, all the data and results from the experimental work as well as literature review were made available to the conservation community in the form of an online tool.
Impact Statement

Plastic materials have quickly become ubiquitous in our everyday lives, from ordinary use objects to high value works of art and design all of which can now be found in museum collections. The sheer amount of different plastics with various additives used throughout history creates considerable challenges to conservators. Although a wealth of literature on photodegradation of plastic materials and their additives has been published by both academia and industry, due to the methods used by the researchers, those findings are often difficult to translate for museum conservation purposes. This is particularly the case with the sensitivity of various types of plastics formulations to visible light since the vast majority of previous research has instead focused on the effect of UV radiation. Consequently, museum lighting guidelines for display of plastic objects remain somewhat vague.

The main goal of this project was to fill the gaps in knowledge relating to photostability of plastics from a heritage perspective by identifying the long-term effect of visible light on the physical appearance and chemical structure of selected modern materials. This was achieved by designing research questions that address concerns specific to the conservation domain and developing a suitable experimental methodology. Since it is rarely known what types of plastics are present in collections in the first place, a prioritising approach was employed with the aim of identifying factors which have the most influence over light stability of common plastics. The results obtained from the light-ageing experiments will help to better inform the currently insufficient museum display guidelines for plastics. Furthermore, the light-stability ‘influencers’ identified provide a useful and pragmatic framework for both designing further photodegradation studies with heritage in mind as well as screening for light-sensitive plastics in collections. Specific metrics which can help quantify photodegradation and spot potentially sensitive plastics were defined. These can be obtained through the use of infrared spectroscopy – a common analytical tool in the conservation sector.
Furthermore, Fibre Optic Reflectance Spectroscopy (FORS) was shown to have a lot of potential as a fast and non-invasive analytical technique to aid conservators in understanding their plastics collections and help in identifying potentially photosensitive objects.

The work carried out as part of this research was shared with museum professionals from major heritage institutions. Surveys of the conservation community carried out showed an overwhelming lack of access to resources and expertise on the subject. This led to the development of a free online tool which will help disseminate the knowledge gathered through this research. The application was designed in a way that helps conservators assess the light stability of an object by answering a few simple questions as well as provide access to the whole database.
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Chapter 1

Introduction to plastics preservation in heritage collections

1.1 Context

The word ‘plastic’ is a generic term which applies to a variety of materials and refers to their ability to be shaped or moulded. They can be natural, for instance amber and tortoiseshell, or man-made. The first man-made plastics, also called semi-synthetics, were derived from natural polymers, such as cellulose from wood pulp or casein from milk, during the second half of the 19th century to make cellulose nitrate and casein formaldehyde respectively. These were followed by fully synthetic plastics such as poly(vinyl chloride), acrylics and polystyrene in the early 1900s. Nowadays, both synthetic and semi-synthetic materials can be found in many heritage collections either as art, design or even examples of everyday objects (Figure 1-1 and Figure 1-2). Many early plastics were inherently unstable due to their experimental nature and were identified as such relatively quickly. However, objects made from those materials still form an important part of many museum collections and now pose significant conservation challenges.

Since those modern materials have a comparatively short history, research into their degradation and conservation is still ongoing. This is further impeded by the fact that plastics are very complex materials which comprise a base polymer and various additives. Inasmuch as the exact formulation of a plastic varies depending on the desired end-product and application, its properties and, therefore, ageing behaviour will also be different.
Figure 1-1. A 1929 celluloid clockwork toy figure of Popeye on display at the Museum of Childhood, London (source: the author, 2016).

Figure 1-2. Display of plastic dishware from the ‘Plasticity – a History of Plastics in Portugal’ exhibition at Museu de Leiria, Portugal (source: the author, 2019).
Several institutions now contain within their collections substantial numbers of historical and art objects made partly or entirely of various types of plastics. Artists and designers have experimented with many materials, often unaware of any inherent flaws in their chemical composition which would hinder their longevity. The plethora of polymeric materials which has been made available, and improved upon, throughout the years makes it a challenging area to research. In addition, certain objects which are significant to design history, such as packaging, would have been specifically created for temporary use. Not only does that create a daunting task for conservators attempting to preserve them but also poses ethical questions regarding their intrinsic nature and whether they should be preserved at all.

1.2 Complexity of plastics

The main difficulty when it comes to assessing stability of plastic materials lies in their inherent complexity. Despite the perfunctory way the word ‘plastic’ is often used to describe anything synthetic, in reality it applies to an extremely diverse group of materials. Unlike wood or metal, for example, plastics are made up of a number of different chemical compounds, a combination of which completely depends on the intended purpose of the finished product. Each of those compounds plays a very specific function of either altering the properties of the base polymer or providing additional ones. Table A-1 in Appendix A provides an overview of the main categories of additives found in common plastics to date with specific examples. Although it is not an exhaustive list, it clearly illustrates the broad range of chemicals that can comprise a single ‘plastic’. To complicate things even further, some polymers can also be mixed together to form copolymers. Even additives belonging to the same category can be chemically very different from each other, ranging from simple carbon to copolymers. In addition, when combined, those compounds can interact with each other, as well as the base polymer, to affect stability by either enhancing each other’s properties or weakening the whole system (see for example [1], [2]).

To make matters more complex still, heritage collections incorporate not only materials produced using modern practices and standards but also historic
examples of often experimental early plastics compositions. Furthermore, although details of specific formulations are particularly important to conservation due to their undeniable impact on stability, they are often trade secrets and rarely fully disclosed. In addition, the plastics industry has progressed and expanded so quickly, with new advances happening constantly, that it is very difficult to keep track of its history in the same way as has been done for other materials. It is also rarely feasible to identify the presence and/or composition of a particular additive/combination of additives analytically as this is hindered by lack of expertise and resources, the destructive nature of many analytical methods and very low additive concentration used.

Currently, the most commonly used approach for assessing stability of plastic museum objects is to use polymer type as the predominant indicator since it is, relatively speaking, the easiest component to identify. It also allows for simple categorization of plastics in collections in line with other material types. However, it has been shown that polymer type on its own is not a sufficient gauge of whether a particular plastic might be sensitive to light exposure [3]. Studies have shown that polymer photodegradation is wavelength dependent i.e., many polymers themselves do not absorb in the visible range. In fact many only absorb short-wavelength UV radiation (Figure 1-3) [4]. Table 1-1 demonstrates maximum absorptions for the most common polymer types and compares those with the wavelengths found to be most conducive to degradation. However, photodegradation is rarely a direct consequence of breaking of the polymer chain from UV absorption [4][5]. In fact, it more often results from a complex series of processes including excitation, energy transfer and oxidation, which can be induced by longer wavelengths of radiation. This is made possible by the presence of impurities, additives and even chromophores such as carbonyl and unsaturated groups within the polymer matrix [4]. This is particularly relevant in a heritage context, as the common practice of UV filtration makes the susceptibility of a plastic to wavelengths below 400 nm less important.
Table 1-1. Absorption maxima contributing to photodegradation of the most common polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Peak UV absorption [6]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>&lt; 200 nm</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>&lt; 200 nm</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>210-260 nm</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>200 nm</td>
</tr>
<tr>
<td>Acrylic (PMMA)</td>
<td>214 nm</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>260 nm</td>
</tr>
<tr>
<td>Polyester</td>
<td>240-290 nm</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>&lt; 250 nm</td>
</tr>
</tbody>
</table>

Figure 1-3. Example UV absorption spectra of several key polymers compared to the UV spectral distribution of sunlight (----). Reproduced from [7].
1.3 Plastics and museums

Plastic materials have become ubiquitous in our everyday lives, from ordinary household objects to high value works of art and design. They also have a contradictory reputation. On one hand plastics are thought of as durable due to the fact that many are not readily biodegradable, while at the same time they are often used as temporary and cheap substitutes for more valuable materials and not expected to last as long. In fact, many early plastics have intrinsic flaws which contribute to their degradation due to the largely experimental character of their production. Nevertheless, plastic objects of both natures can now be found in heritage collections, the most important being: cellulose acetate (CA), cellulose nitrate (CN), poly(vinyl chloride) (PVC), polyurethane (PUR), polyethylene (PE), polypropylene (PP), polycarbonate (PC), polystyrene (PS) and polyamides [8]. In addition, artists and designers have happily experimented with the use of the materials, creating innovative artworks and design objects while simultaneously posing considerable challenges for conservators.

Although a substantial amount of research on the topic of polymer light stability has already been carried out by the industry and academia, the vast majority of studies has focused on the use of UV radiation to accelerate degradation processes. This is less relevant to the needs of museums where UV is excluded as standard practice and, therefore, will be discussed in more detail in Chapter 2. While there is general consensus that short-wavelength radiation is harmful for plastics, little is known about the effect of visible light, which in turn results in very limited display and preservation guidelines for museums. Moreover, stability studies, particularly those driven by the industry, focus on new materials and their longevity in terms of usable lifetime dependent on application. In contrast, objects in heritage collections are rarely new and will have already been exposed to a variety of environmental conditions, which will have altered their stability.

Museums often do not know what types of plastics they actually hold as proper characterisation of a plastic artefact requires destructive analytical methods, time, and expertise, some or all of which are often lacking. Some collection
surveys have been carried out in the past and identified 5 key vulnerable plastics: cellulose nitrate, cellulose acetate, polyurethane foams, rubber and PVC [9]. However, detailed material information is often unavailable and museum objects are, more often than not, simply classified as made of ‘plastic’.

Signs of degradation in plastics, specifically caused by oxidation on light exposure, include: loss of mechanical properties such as toughness and impact strength, as well as deterioration of appearance through chalking, crack formation, crazing, yellowing and loss of gloss (Figure 1-4) [10]. Unfortunately, those can also result from other types of degradation and, thus, are often difficult to specifically identify as results of light damage.

![Image of degraded polycarbonate lamp cover](image1.png)  
**Figure 1-4.** [a] Polycarbonate lamp cover degraded by natural exposure to sunlight, showing significant cracking and yellowing of the polymer. [b] 3D microscope image of the cover showing detail of the cracks as well as surface crazing (source: the author, 2016).
1.4 Lighting guidelines

Despite a wealth of academic and industrial literature on the subject of polymer photodegradation, sensitivity of plastics to visible light\(^1\) remains largely unexplored. Consequently, institutional guidelines for display of those materials can be rather vague. Plastics are either completely omitted [11] or only partially covered [12][13]. For instance, the Victoria and Albert Museum (V&A) display guidelines classify ‘plastics’, as a group, as being both light-sensitive and light-durable (Figure 1-5) without providing any further details.

![V&A Guidelines](image)

**Figure 1-5.** Light sensitivity categories for various materials reproduced from the 2010 guidelines for the Victoria and Albert Museum, London.

Similarly, recommendations from the Canadian Conservation Institute written by Stefan Michalski [14] only refer to plastics sensitivity to UV and define two levels:

- low sensitivity is described as ‘cracking, chalking of modern plastics’

\(^1\) In a museum context that refers to the range between 400-700nm.
while

- medium sensitivity is specified as ‘cracking of most plastics’

However, no information is given on which plastic materials fall into which category and the table titled ‘Sensitivity of coloured materials to light and the number of years to cause fading’ does not mention plastics at all.

This trend is evident across other official recommendations. PAS 198 ‘Guidelines and procedures for choosing appropriate lighting for indoor exhibitions’ only mentions polyester as having low sensitivity to light, while nylon is deemed highly sensitive [12]. PD CEN/TS 16163 Technical Specification, which draws on the CIE\(^2\) 157:2004 Technical Report ‘Control of damage to museum objects by optical radiation’, places ‘some plastics’ in the low sensitivity category again without further explanation [13]. The CIE report itself acknowledges the complexity of plastic materials and the resulting difficulty in defining their light sensitivity, however it still lacks any concrete advice for conservators [15].

As demonstrated above, light sensitivity of plastics is an area that still requires more empirical evidence to help conservators make better informed decisions about the display of those materials. The majority of research that has already been done on that subject, both within academia and industry, was carried out using UV accelerated degradation. However, as previously stated it is standard practice in museums and galleries to completely exclude any UV radiation from displays. Therefore, data obtained in those studies is not particularly useful in terms of predicting the lifetime of objects in museums or choosing the right level of illumination and length of display.

A previous study carried out by the author, found that, in the case of some materials, results previously achieved with short wavelength UV radiation could be reproduced using visible light only [3]. In addition, results demonstrated that all plastics should not be treated the same and light display decisions cannot be

\(^2\)Commission Internationale de l'Eclairage (International Commission on Illumination).
based on polymer type only, but also that even plastics containing the same polymer can behave differently. Thus, it is clear that there is no shortcut or umbrella-like approach that can be adopted even for materials based on the same polymer, let alone all plastics.

1.5 Scope of work

The aim of this research was to investigate the stability of plastics common in heritage collections to visible light exposure by designing a pragmatic approach to assessment and classification of material sensitivity as well as an experimental methodology more suitable for heritage-focused accelerated ageing tests.

The principles of photochemistry and polymer photodegradation as well as the current state of the art of research on the subject necessary to the understanding of this thesis are laid out in Chapter 2. In addition, the idea of photodegradation ‘influencers’ and prioritisation of components when assessing light stability of plastics is introduced. It then goes into more detail in terms of the interaction of different components of a plastic and how that affects the overall stability of the material to light with a particular focus on colourants. It also introduces some common analytical techniques for characterisation of plastics. Based on the findings from Chapter 2 the following research questions were developed:

1. What effect do colourants have on the light stability of plastic materials when exposed only to visible light?
2. Does previous exposure to UV radiation increase the sensitivity of plastics to visible light?
3. How can the sensitizing colourants be non-invasively identified in museum objects?

These research questions were addressed through a series of accelerated visible light ageing experiments on polypropylene (PP) and cellulose acetate (CA) samples with potentially sensitizing pigments without any stabilizers or thermal antioxidants to fully assess the influence of these additives on the stability of each polymer. A subset of these samples was also subjected to UV pre-treatment at two
different doses before further visible light ageing to explore the contribution of degradation products to material sensitivity. PP was selected as a polymer with a relatively simple chemical structure which is also the best studied in terms of previous photodegradation research, including how various additives affect it. This made pigment selection and result comparisons easier. PP is also prone to developing oxidation impurities which can contribute to autocatalyzed photodegradation even at longer wavelengths of radiation [16]. On the other hand, CA is one of the polymers known to be intrinsically unstable and problematic to museums (see above). Although those issues are not known to be light-related, not much attention has been given to its behaviour with different colourants on light exposure.

Chapter 3 describes the experimental setup, analytical and data processing techniques used in the two light-ageing studies as well as details of surveys of museum professionals carried out and the online tool that was developed as part of this project. Chapters 4 and 5 describe and compare the results of the two photodegradation experiments focusing on the effect of colourants and previous UV exposure.

The assessment of various common analytical techniques in terms of their effectiveness in identifying light sensitive plastics formulations and suitability for heritage applications, specifically looking at the identification of polymers and colourants, is presented in Chapter 6.

Chapter 7 introduces a free online tool for conservators developed as one of the outcomes of this research as well as results of two surveys of conservation professionals.

Finally, Chapter 8 outlines the main conclusions drawn from the research performed and offers recommendations for conservators regarding display of plastics and identification of light-sensitive objects as well as suggestions for further work.
1.6 Bibliography


Chapter 2

Photodegradation and its influencers

This chapter introduces the principles of photochemistry and polymer photodegradation relevant to plastics conservation and understanding of this thesis, with a specific focus on PP and CA. It also covers the most up-to-date knowledge in the field of plastics light stability from the points of view of industry, academia and heritage while evaluating the differences between them. A way of reducing the complexity of the topic by prioritising plastic components most important for photostability is proposed. Subsequent sections explore the role of photodegradation influencers on light stability of plastics based on different polymers. Degradation pathways of the selected polymers are discussed first, followed by impurities and degradation products as those are tightly coupled with polymer type. A detailed literature review on the effect of colourants is then presented. Each of the components is assessed according to its impact, ease of detection and relevance to the heritage field. Light stabilizers were excluded from this work since their main function is protective and they are very difficult to identify and quantify using methods allowed in the heritage domain. A review of known cases where stabilizers have been found to react antagonistically with other additives, thus compromising the stability of the polymer, are included as additional information in Appendix B.

2.1 Principles of photochemistry and energy transfers

Light as electromagnetic radiation consists of oscillating electric and magnetic fields travelling through space (Figure 2-1) but it can also be thought of as a stream of particles called photons. Photon energy is proportional to its frequency (denoted by the Greek letter \( v \)), which is defined as the number of ‘wave peaks’
that pass through a particular point in one second, measured in Hz (or reciprocal seconds [s⁻¹]).

Figure 2-1. Graphic representation of electromagnetic radiation as oscillating perpendicular electric and magnetic fields.

The equation for energy of one photon of light (2-1) states that it is equal to frequency multiplied by Planck’s constant ($h = 6.63 \times 10^{-34}$ Js) which indicates that the higher the frequency, the higher the energy.

$$E = h\nu = hc/\lambda$$

(2-1)

Frequency can also be defined as the speed of light ($c \approx 3 \times 10^8$ m/s) divided by wavelength ($\lambda$) in m which is the distance between each wave peak or trough (Figure 2-2a). Thus, the shorter the wavelength, the higher the energy.
The parts of the electromagnetic spectrum most important from the museum perspective are UV, visible and infrared. In general, in the heritage context visible light is defined as radiation of wavelength between 400-700 nm.

The absorption of light by a molecule can cause modifications to the chemical structure of the material which then manifest themselves in changes to the physical appearance of the object. However, not all wavelengths were created equal when it comes to degradation and it takes fewer photons of blue light to cause the same amount of damage caused by red light (Figure 2-2b). In fact, the effectiveness of damage increases exponentially with decreasing wavelength. The damage function plotted in Figure 2-3 shows relative damage ($Y$) per wavelength ($X$) expressed as an exponential function:

$$s(\lambda)_{dm,rel} = e^{-0.012(\frac{\lambda}{[\text{nm}]}-300)}$$

It can be easily noted that UV radiation ($\lambda < 400$ nm) is significantly more damaging than visible light ($\lambda > 400$ nm). This explains why heritage organisations aim to eliminate all UV from their displays and storage areas. However, it is important to note that not all objects will absorb all wavelengths, therefore as well as this damage curve the absorption spectrum of the material and spectral power distribution of the light source also need to be taken into account.
Light can be described in two different ways:

- **radiometrically** – measuring the distribution of power in space
  or
- **photometrically** – characterizing the interaction of light with the human eye or, in other words, how humans perceive light in a space

Irradiance (a radiometric measure) and illuminance (a photometric measure) are the most important metrics from a conservation perspective, with the latter being prevalent in practice.

Irradiance is the radiant energy received by a surface area and can be expressed either as a graph of spectral power distribution (SPD), showing how much energy at each wavelength is being emitted, or as a total value calculated from the area under the curve in W/m². Alternatively, illuminance defines how much light falls onto a given surface and is expressed in lux.
However, neither value can tell the full story of the potential damaging effect of a light source. Illuminance, which is a particularly popular metric within the heritage community, is flawed in that respect as it places the most focus on what is actually perceived by the observer. As can be seen from Figure 2-4, humans are most sensitive to green wavelengths and after applying the $V(\lambda)$ curve in the calculation, the resulting value no longer reflects the full SPD of the light source i.e., the more damaging wavelengths are not given as much weight.

![Figure 2-4. Sensitivity of the human eye to visible light $V(\lambda)$.](image)

That can be a problem for selecting different light sources and setting display light levels as there is a balance to be struck between light sources that are less damaging and ones that provide a faithful representation of the object’s appearance.

Another crucial concept to mention is the reciprocity principle, which is the idea that light damage is cumulative, and exposure is defined as an integration of irradiance multiplied by time (2-II).

$$H = \int E \, dt \quad (2-II)$$
Where:

H is total exposure,

E is irradiance falling on a surface (W/m²),

\( t \) is time (h).

Although, traditionally, illuminance would have been used instead of irradiance in Equation 2-II to produce lux hours (lxh), the current standard unit is Wh/m². However, lxh are still often used by heritage institutions to define and control the exposure of their objects. This is done by having annual ‘exposure budgets’ for collections and sometimes even individual objects, which then determines how long and under what light levels a particular object can be displayed.

Yet it is not just the amount and type of light that determines how much damage can be caused to an object. Different materials have varied levels of sensitivity determined by their chemistry. The Grotthuss–Draper law (also known as the Principle of Photochemical Activation) states that only light which is absorbed by a system can cause chemical changes. For light to be absorbed by a material the energy of the emitted photon needs to match exactly that of a specific allowed electronic transition of a particular chemical bond in the molecule. When a photon of sufficient energy is absorbed, an electron can change its state from the ground singlet state \((S_0)\) or the highest occupied molecular orbital, HOMO) to an excited state (e.g., \(S_1\) or lowest unoccupied molecular orbital, LUMO) (Figure 2-5). The electron can also change its spin direction and, therefore, be excited to a triplet state (e.g., \(T_1\)). In addition, each electronic state consists of a range of different vibrational levels.

Once an electron is excited, there are several pathways through which the energy can be dissipated (Figure 2-5 and Figure 2-6). It can be released as heat to the surroundings via vibrational relaxation, which lowers the vibrational state of the electron, and/or internal conversion, which lowers the electronic state. Energy
can also be emitted in the form of a photon via fluorescence and phosphorescence processes. Other possible pathways include:

- physical quenching (deactivation) – the excited molecule collides with another molecule
- dissociation (or photolysis) - direct breaking of the bond
- direct reaction
- intermolecular energy transfer – the energy is passed onto another molecule
- intramolecular energy transfer – the same molecule enters a new electronic state

Figure 2-5. Jablonski diagram showing some of the possible energy transfer processes following absorption of a photon. $S_0$ – ground singlet state; $S_1$ – excited singlet state; $T_1$ – excited triplet state; $E$ - energy.

$S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow \text{phosphorescence}$

$1$ – ABSORPTION
$2$ – VIBRATIONAL RELAXATION
$3$ – FLUORESCENCE
$4$ – VIBRATIONAL RELAXATION & INTERNAL CONVERSION
$5$ – INTERSYSTEM CROSSING
$6$ - PHOSPHORESCENCE

3 Following inter-system crossing to an excited triplet state and vibrational relaxation.
Figure 2-6. Possible routes for loss of electronic excitation of an example species in an excited state (AB*). Reproduced from [2].

From the point of view of plastics photodegradation the most important processes are: photolysis, photosensitized reactions and intramolecular and intermolecular hydrogen atom abstraction [2]. However, high energies are required to break bonds found in polymeric molecules, so direct photolysis of molecular bonds is not relevant if a plastic object is only exposed to visible light (Figure 2-7). Consequently, this argument is often quoted in support of the theory that plastics should be stable under visible light. While this is certainly true, the other two pathways make it possible for polymer photodegradation to be induced with wavelengths longer than 400 nm. For instance, photo-oxidation often includes a sensitizing molecule in a triplet state which can react with oxygen or an unsaturated compound [2]. Those sensitizing molecules can be colourants or other additives included as part of the plastic material. This is of particular concern to museums and indicates that some plastics in heritage collections may, in fact, be sensitive to light.
2.2 Polymer photodegradation

Photodegradation of polymers is a chain reaction which can be induced by a variety of factors, such as UV radiation. It begins with an initiation reaction which produces a polymer radical through hydrogen atom abstraction (2-III) [4][5].

\[
\text{PH} \rightarrow \text{P}^\bullet + \text{H}^\bullet \tag{2-III}
\]

This polymer radical can then react with atmospheric oxygen to create a peroxo radical (2-IV) which continues the process of hydrogen atom abstraction to produce hydroperoxides (2-V) in what is called a propagation stage.

\[
\text{P}^\bullet + \text{O}_2 \rightarrow \text{POO}^\bullet \tag{2-IV}
\]
Hydroperoxides can be decomposed on exposure to light thus forming further radicals (2-VI).

\[ \text{POO} \cdot + \text{PH} \rightarrow \text{POOH} + \text{P} \cdot \] (2-V)

\[ \text{POOH} \rightarrow \text{PO} \cdot + \cdot \text{OH} \] (2-VI)

These reactions propagate until termination is reached and only inactive products result. This process can lead to molecular weight reduction in the polymer as well as chemical changes, such as introduction of new functional groups, thus affecting the physical properties of the material.

### 2.3 Research – current state of the art

Although there have been many advances in the subject of plastics conservation, there are still areas requiring further research. This is mainly due to the relatively short history of plastic materials in art and design compared to their more traditional counterparts. Although photodegradation of plastics has been studied previously both within academia and the polymer industry, there still exists a need for further work that directly addresses the needs of museums. As mentioned above, despite the general practices of excluding UV light from museum galleries and applying conservative light levels on display, our knowledge of the sensitivity of those artefacts to visible light has not been examined in much depth so far.

Theoretically, polymeric materials should be resistant to degradation by visible and, in some cases even near-UV radiation, which does not contain enough energy to break C-C or C-H bonds of the polymer chain [4], [6]. However, it is known that polymers can degrade in response to visible light due to impurities present from manufacturing or certain colourants which can initiate photodegradation with longer wavelengths [4], [7]–[9]. Some materials such as PUR foams are known to break down under museum conditions [10][11]. Despite that, research on the
photostability of polymers in museum collections within conservation has been limited and mostly devoted to paints and binding media, with a particular focus on acrylcs [12]-[22], which are widely used both by artists and conservators.

In general, UV is over-represented in irradiation tests with many researchers referring to well established laws of polymer chemistry which state that such materials are resistant to degradation by visible, and in some cases even near UV, radiation. In fact, out of a total of 106 papers reviewed for this thesis, as many as 87% of experiments used UV radiation (Figure 2-8). In addition, of the five articles where visible light was the focus [17], [23]-[26], two were industry driven [24], [25], one investigated the effectiveness of visible light exposure in preventing yellowing of acrylic paints [17], and one used visible radiation on acrylic resins used in conservation treatments [26]. The only study to examine stability of various plastics found in museum collections to visible light was that of Pastorelli et al. [23]. However, the conditions were only slightly accelerated and other environmental factors, such as pollution and temperature, were also monitored. In addition, colour change was the only method used for measuring degradation.

Figure 2-8. Chart showing the proportion of 106 polymer photodegradation studies reviewed for this thesis that used different types of radiation.
For ethical reasons most tests have been carried out on new materials, usually of commercial grade and occasionally compared to relevant museum objects with a relatively well-known history [27],[28]. However, brand new plastics behave differently to those which have been exposed to UV or other damaging factors prior to entering a controlled museum environment. It has also been noted that extended UV irradiation can cause a shift in the absorption of some materials into the visible range [29]–[33] and yet, as demonstrated by Figure 2-8, little attention has been devoted to how already aged objects may react to prolonged visible light exposure. It is therefore definitely an area which requires further exploration and examples of that need can be easily found in the institutional display guidelines discussed in Chapter 1.

Furthermore, research studies into light degradation of modern plastics to date show a lack of consistency between the aims, materials tested, methodologies and equipment, often very different to those relevant to a heritage context, making interpretation and comparison of results very difficult. In general, the main focus of academic research in this subject has been illuminating the photochemical processes that take place when a given material is exposed to some kind of radiation. On the other hand, industrial research is mostly pre-occupied with lifetime prediction and stabilization. However, ‘lifetime’ of a material from an industry perspective is not the same as that of a museum object. In fact, many museum artefacts may enter collections nearing or having already exceeded their useful lifetimes as defined by the industry. Similarly, chemical studies tend to concentrate on very specific issues which are difficult to relate to the physical attributes of a material, such as mechanical strength or discernible colour change. They also usually test known substances prepared in a lab under controlled conditions, which is the exact opposite of what can be found in museum collections, i.e., objects of unknown compositions and history or state of degradation.

When reviewing polymer photodegradation literature from a heritage point of view it is also imperative to know what kinds of conditions and equipment were used to accelerate degradation of a given material. Unfortunately, this is rarely
supplied in enough detail. Surprisingly, types of light sources used, their spectra and/or intensity are often missing from the sources reviewed (for example see [34]–[36]).

Another critical issue is the sheer number of different plastics with various additives now available and, while there is a wealth of literature on their stability from both academia and industry, due to the methods used those findings are often difficult to translate for conservation purposes. Thus, the sensitivity of various types of plastic formulations to visible light is not well understood and consequently museum lighting guidelines for them remain somewhat vague and under-researched [1], [37], [38].

Some studies explored the relationship between polymers and their additives, such as dyes and pigments, concluding that the latter have a varied effect on plastics deterioration. In addition, presence of visible light-absorbing impurities within the polymer matrix can work to initiate photodegradation with longer wavelengths. This is of particular significance to the conservation community where plastics stability needs to be considered holistically, taking into account all of the components and possible interactions between them. Therefore, these topics will be discussed in detail in the following section.

### 2.4 Component interaction and its role in photostability of plastics

In order to tackle the subject of plastics stability to light from a heritage standpoint it is, therefore, necessary to focus research efforts on the effect of visible light on those components which have the greatest impact on photostability. The insights gained from the in-depth review of literature convey that these can be narrowed down to five main ‘influencers’ as presented in Figure 2-9.
The type of base polymer remains the primary factor. However, research shows that on its own it is a poor indicator of the overall stability of a plastic [39]. Nevertheless, in order to assess how sensitive a material might be to light exposure, it is essential to identify the polymer. Colourants were ranked as second most important for three reasons:

- their presence is easy to determine, even if their exact nature is not
- they can be affected by light exposure even if the polymer is not, leading to deterioration of the objects’ appearance
- they can sensitize the polymer to visible light exposure

Light stabilizers are nowadays routinely added to plastics formulations to protect the material from UV and oxidation. However, they become depleted over time and it is currently impossible to assess the level of stabilization of a naturally aged object.

Chromophoric impurities are visible light absorbing chemical groups which can be formed along the polymeric chain during processing and manufacture due to high temperatures required. These are mostly relevant to polyolefins, however their impact on photostability of those polymers has been shown to be significant.
Finally, previous exposure to UV and other environmental stressors over time is a factor uniquely relevant to heritage conservation that can have a huge impact on the condition of an artefact yet has gone largely unexplored.

2.4.1 Effect of polymer type and exposure - photodegradation pathways of PP and CA

Since type of radiation and its effect is very closely linked to polymer type, it is very difficult to discuss them separately. Therefore, the role of these two influencers will be reviewed together, with a specific consideration of PP and CA.

PP and CA are commonly found in heritage collections containing plastics and were selected to be further investigated in this thesis in terms of their stability to museum lighting conditions. The reasons for their selection are discussed in Chapter 1, section 1.5. This section will describe the most important photodegradation processes of these two polymers.

2.4.1.1 Polypropylene

![Chemical structure of PP.](image)

Hydroperoxide decomposition plays a crucial part in photo-oxidation of PP and can lead to significant deterioration of the polymer. When PP is exposed to high-energy radiation, cross-linking and chain-scission reactions take place [40]. However, direct photolysis of bonds in a PP chain can only occur when radiation below 254 nm is used as longer wavelengths are not absorbed by the pure
polymer. While this kind of radiation is filtered out from sunlight before it reaches the earth, it does not mean that PP is immune to light exposure as it is never completely uncontaminated. Commercially produced PP will contain a number of impurities acquired during the manufacturing process which act as chromophores and extend the absorption spectrum of the polymer to longer wavelengths. These can be residual titanium or aluminium compounds from polymer synthesis reactions or oxidation products created during thermal processing (e.g. from extrusion or injection moulding) [4]. The high temperatures and amount of shear force required to melt, extrude and mould PP, as well as the presence of atmospheric oxygen can lead to the displacement of a tertiary hydrogen and the formation of hydroperoxides (2-VII) [4], [40], [41].

These hydroperoxides then decompose easily on light absorption into a macroradical and a hydroxyl radical, thus initiating a chain photodegradation reaction (2-VIII).  

At this point photodegradation can proceed in one of two ways, both resulting in the production of ketones [4], [41]. The first pathway is a process called β-scission in which a CO double bond is formed by breaking of the polymer chain and creation of a radical group (2-IX).
The remaining chain molecule undergoes a Norrish II reaction on additional light absorption which breaks it up further, creating CC double bonds and hydroxyls, followed by more carbonyl species.

The radicals produced via the β-scission process interact with oxygen and humidity to form more hydroperoxides which, in turn, absorb more light and initiate another cycle of reactions.

The second pathway also involves ketone formation but in this case a methyl radical is released and Norrish I reactions are initiated through more light absorption, leading to the breaking of the polymer chain and creation of more radicals (2-X and 2-XI)

![Chemical structures for reactions 2-X and 2-XI](image)

As can be seen, photodegradation of PP is a complex mechanism leading to many different reactions which result in formation of various carbonyl groups and chain scission. The extent of photooxidation damage is largely dependent on the amount of thermally-induced impurities from manufacture and processing [41] which in turn determines the degree and speed of mechanical deterioration of the material on light exposure. This is of particular importance to museums as plastic objects in their collections are likely to contain such impurities acquired either during the production process or general use.
2.4.1.2 Cellulose acetate

Similarly to PP, CA bonds can only be directly photolyzed with radiation of wavelength shorter than 254 nm [4][42]. However, there is less consensus as to what the light-induced degradation pathways actually are. In vacuum, deacetylation, chain scission and cross-linking are reported to be the major reactions, while in the presence of oxygen deacetylation does not occur and, instead, oxygen uptake is followed by chain scission, oxidation and cross-linking [4]. Jortner proposed that, since most chemical groups present in CA do not absorb radiation above 280 nm, any absorption at longer wavelengths and associated chromophoric behaviour should be attributed to the following chemical group [42]:

![Diagram of Chemical Structure](image)

Figure 2-11. Chemical structure of CA.

![Diagram of Chromophoric Group](image)

Figure 2-12. Chromophoric group proposed to be responsible for light absorption > 280 nm in CA.
Additionally, Kozmina et al. showed that photodegradation of CA in the presence of oxygen leads to the production of a higher number of ester peroxides than in its absence, and that carboxyl and carbonyl groups also appear alongside formaldehyde and seven other volatile compounds (CH₃COCH₃, CO₂, CO, H₂O, H₂, C₂H₆, CH₄) [43]. Their main conclusion was that on UV exposure CA degrades via a combination of hydrolysis, photolysis and oxidation leading to the breaking of the pyranose ring. On the other hand, Chen et al. identified ketene (CH₂=CH₂), CO, CO₂, H₂, H₂O and acetic acid (CH₃COOH) as volatile compounds released on UV irradiation in vacuum, and no volatile products when the irradiation was carried out in oxygen⁴. In both cases, however, residual moisture found inside the polymer contributed to degradation [44]. Finally, Hon tested stability of both cellulose diacetate and triacetate fibres in vacuum using different light sources (λ > 253.3 nm, λ > 280 nm, and λ > 340 nm) [45]. UV spectroscopy analysis revealed that absorption falls significantly above 260 nm for both types of CA, but that prolonged irradiation causes an increase between 250-310 nm which suggests that chromophores such as double bonds and ketones are being created. Investigating wavelength dependence showed that most free radicals were produced when samples were exposed to λ < 253.3 nm and when irradiation > 340 nm was used, no radicals were found [45]. The type and quantity of volatile products released varied according to light sources used and CA type. It is interesting to note however, that acetic acid and acetone were only detected in samples irradiated with λ > 280 nm. The appearance of these volatile compounds was attributed to decomposition of ester groups (deacetylation). In contrast to other experiments, ketene was not detected as a volatile product, nor was there any evidence of cross-linking or scission of the pyranose ring. Arguably, the most important takeaway from this study is that pure CA, regardless of its degree of substitution, does not absorb, and therefore degrade on exposure to, light of wavelength longer than 340 nm. Hence, daylight should not be harmful to pure CA. It is, however, necessary to bear in mind that this investigation was carried out in vacuum using pure grade CA samples. In real applications, not only would other compounds be present in the polymer matrix, but, as mentioned before, the

⁴ In this case the polymer tested was cellulose triacetate.
presence of oxygen, moisture, impurities, additives and possibly higher temperatures will have a significant effect on the type and rates of reactions that can be initiated with longer wavelengths of light. This is of particular relevance to museum objects which contain a variety of additives and will often have been previously exposed to a mixture of different conditions. This process was demonstrated by Hosono et al. via the addition of the photosensitizer benzophenone to the CA matrix and irradiation with simulated sunlight ($\lambda > 275$ nm) [46]. In this case benzophenone molecules absorb light $> 380$ nm and are excited to a triplet state. This is followed by hydrogen atom abstraction from the CA chain leading to radical formation and chain scission.

While the reactions proposed above refer to photodegradation initiated by a specific catalysing compound, they do illustrate that longer wavelengths, such as those found in daylight, can bring about deterioration of CA as long as the right conditions for energy transfer between molecules are met.

### 2.4.2 Effect of impurities and degradation products

There are several different types of impurities which can be found in plastics. They can be divided into two main categories:

- **Molecular** - degradation sites on the polymer chain either due to thermal oxidation during processing or from everyday use/exposure
- **Physical** - residues from polymer production or metal ions from processing equipment

Research has shown that polymer degradation is a complex process depending on many variables [4], [7], [47]. However, all polymers go through a phase called oxidation induction time (OIT) which defines a period during which oxygen absorption takes place but no detectable changes to the material occur. After the OIT has passed, degradation can proceed relatively fast via an autocatalytic process involving the formation of hydroperoxides [4]. This is a very important concept, particularly for heritage conservation, as it makes judging the stability of plastic objects very difficult. Studies have shown that only a very small amount
of initial oxidation (in the order of 0.01%) can cause chain reactions, eventually leading to cracking and embrittlement in PP [48]. Naturally, those reactions can be caused by a number of factors, impurities being one of them. At this moment, there are no non-invasive methods for measuring the state of oxidation or the presence of physical impurities in a plastic which would be suitable for conservation purposes. However, since oxidative processes are limited by the rate of diffusion of oxygen into the material [48][49][50], it could be possible in the future to use such techniques as hyperspectral imaging to map initial oxidation sites on the surface of an object in a similar way as has been done for plasticizer distribution [86].

Unfortunately, the detection of physical impurities, such as residual titanium or aluminium compounds from polymer synthesis or metal particles from processing, which might contribute to degradation of plastics is not possible in a museum object due to their extremely low concentration in the polymer [51]. Even extensive sampling and performing destructive analysis such as gas chromatography-mass spectrometry (GC-MS) might not give a real picture. As they are very difficult to identify analytically and not the most influential in terms of catalysing photodegradation reactions in polymers, they will not be explored further in this work. Instead, the impact of molecular impurities will be discussed in more detail as they are particularly important in initiating photo-oxidation mechanisms.

Polymers most prone to impurity-catalysed light-deterioration, and, therefore, best studied from this point of view, are polyolefins such as polyethylene (PE) and polypropylene (PP). Oxidised PP in particular can become susceptible to photodegradation at longer wavelengths than it would normally absorb due to the formation of carbonyl groups. PP is easily oxidised at the high temperatures used during processing. Hydroperoxide groups which can form through heat and absorption of oxygen play a crucial role in initiating further autocatalytic reactions leading to carbonyl group production and loss of molecular weight [41].
This issue is particularly relevant to plastics conservation since many museum artefacts could already be in an oxidation induction stage initiated by processing impurities and previous UV exposure during their lifetimes e.g., through display or use in a domestic environment. Although stabilizers are likely present in any commercially produced object, these might also be already depleted and not providing any protection. Additionally, as demonstrated in section 2.3, research carried out so far has not explored the effect that visible light may have on stability of plastics containing such impurities. Therefore, it is crucial to explore the influence of previous exposure on light stability in a museum context.

2.4.3 Effect of colourants

Colourants used in the plastics industry include both dyes, which are completely soluble organic compounds, and pigments, which are insoluble solid particles that impart colour when dispersed in a medium. While some colourants are known to protect polymers from the effect of light by either absorbing or reflecting harmful radiation, others can have a negative effect. The latter can happen via two distinct degradation pathways, summarized by Rånby and Rabek [4], in which colourants can act as either:

- **photo-initiators**, by producing free radicals\(^5\) on light absorption, which then attack the polymer causing direct breakage of the polymer chain or oxidation reactions (Figure 2-13)

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\(^5\) Atoms or molecules with an unpaired electron, which make them highly chemically reactive.

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**Figure 2-13: Photo-initiation of light degradation processes in polymers.**
• photosensitizers, which following excitation on light absorption transfer energy to the polymer directly or to oxygen, (forming singlet oxygen\(^6\)) which then attacks the polymer causing either direct breakage of the polymer chain or oxidation reactions (Figure 2-14)

![Figure 2-14: Progression of photosensitized degradation processes in polymers.](image)

The fact that different colourants can either stabilize or sensitize various polymers to light is not a recent discovery. As an important aspect of material longevity, it has been the subject of investigation for several industrial researchers whose work will be discussed in subsequent sections. The majority of commercial and academic research so far has focused on the deleterious effect of some dyes on natural and synthetic fibres, a phenomenon known as phototendering. The following sections will summarize the most important findings in terms of the effect of colourants on polymer photostability. Only the most relevant papers regarding dyes will be reviewed as it is a very large field of study, focusing mainly on textiles, with many different dyes tested and various analytical methods used, which makes comparisons challenging. Pigment related research led by industry will be discussed next, followed by heritage, drawing comparisons not only between materials and results but also methods and analysis. Since colourants can be described with different names (e.g. commercial, chemical), for clarity and ease of result comparison pigments mentioned in this work will, whenever possible, be referred to by their abbreviated Colour Index (CI) name. In the CI system, the first letter ‘P’ stands for

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\(^6\) High-energy form of oxygen which is particularly reactive towards organic compounds.
‘Pigment’, followed by another letter indicating the colour and a classification number. For example, PY83 corresponds to Pigment Yellow 83.

2.4.3.1 Dyes
As early as 1949, Egerton examined the mechanisms of dye-sensitized photodegradation of various textiles: natural, semi-synthetic and synthetic by exposing samples coloured with particular basic dyes to sunlight (λ > 340 nm) at 0% and 100% humidity for 15 days [52]. The effect of dyes: Thioflavin T, Auramine O, Acridine Orange LP, Fuchsine, Rhodamine S and Malachite Green A on the stability of the textiles was assessed by measuring loss of tensile strength and comparing it to undyed samples of the same materials. Although the paper mostly dealt with natural fibres, such as cotton and silk, some consideration was also given to synthetic polymers such as nylon and cellulose acetate rayon. The latter was shown to be considerably the more stable of the two materials, with Auramine O dye being the most sensitizing and causing a 12% loss of tensile strength in the cellulose acetate fibres at 100% RH, while the same dye on nylon caused a 63% decrease under the same conditions. Interestingly, Egerton found that the fading of dyes themselves reduced their photosensitizing properties.

Another study of dyes which is of note due to its scope, systematic approach and the use of visible light was conducted by Zweig and Henderson in 1975 [53]. Twenty-four dyes of various classes and two phthalocyanine pigments (PB15 and PG7) were examined for their ability to sensitize cellulose acetate film through the production of singlet oxygen when irradiated with light of wavelengths longer than 430 nm. However, the photosensitizing effect of the dyes was only measured by the % depletion of a chemical singlet oxygen trap included in each sample. Additionally, this was compared to the lightfastness of each colourant on its own under the same exposure conditions. No clear pattern can be discerned in the results in terms of a particular class, chemical structure or lightfastness of the most sensitizing dyes, although eight out of nine basic dyes of various classes included were particularly sensitizing. Azo appeared to be the least sensitizing of the group, followed by anthraquinone. In the second part of the paper, Disperse Red 15, which proved most effective at producing singlet oxygen in the first
experiment, was selected for testing on other polymers. Film samples were irradiated for 60 h with light that would only be absorbed by the dye and not the polymer\(^7\). The results showed that polymers which contained no olefinic unsaturation\(^8\), namely PVC, PMMA, PS, PC, PU, PP, atactic PP, CA, polyester, EPDM (rubbery copolymer of ethylene and propylene) did not experience any changes in infrared or ultraviolet spectra. On the other hand, the unsaturated polymers (polyisoprene, PMMA-polyisoprene rubber, polybutadiene, ABS, SBR rubber, PS, AB rubber, impact co-polymer of methyl methacrylate, acrylonitrile and polystyrene) showed rapid changes not only in their physical properties, such as brittleness of polybutadiene-containing polymers or tackiness of the ones including polyisoprene, but also development of new infrared absorption bands corresponding to hydroxyl and carbonyl groups being formed due to oxidation. All results were compared to undyed samples exposed in the same conditions to ensure that the effect was indeed due to the presence of the dye as the same dye can have a different effect on different polymers.

Apart from the two studies summarized above, many more were conducted which looked to assess other material combinations as well as to explain the exact chemical processes involved. The topic of dye phototendering has been very well covered. It is also less relevant to solid plastics which are the focus of this research and, therefore, will not be further discussed here. For more information the reader is directed to a review by Allen \cite{Allen9}. Pigments, on the other hand, have received much less attention. In fact, knowledge of sensitizing pigments in certain formulations often stems from industrial experience, making it difficult to find research studies referenced in some literature. For instance, yellow and red azo-based organic pigments as well as ultramarine, cadmium yellows and iron oxides have been mentioned as problematic for some polymers without any further details given \cite{Allen9}\cite{54}. In addition, industrial studies tend to focus on exploring the stabilizing properties of pigments, either alone or in conjunction with other additives, in order to find the most efficient stabilizing combination of additives which maximizes the material useful lifetime but does not affect the desired

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\(^7\) Specific range was not given.
\(^8\) Carbon-carbon double bonds.
properties. Other, more recent perspectives include utilizing photocatalytic and/or UV absorbing properties of some compounds for biodegradable materials and solar cells. In all cases, however, the pigment most studied in terms of its photoactivity is, by far, titanium white (PW6, titanium dioxide) [55]. It has two crystal structures, anatase and rutile, both of which have been widely used, either individually or in combination [56]. However, extensive research has shown that each type has very different properties due to their different UV absorption. As a result, anatase is a known photosensitizer, while rutile is very widely used as a stabilizer. A discussion of all the literature relating to the photoactive behaviour of titanium dioxide pigments would be outside the scope of this work and several comprehensive reviews on the topic exist which would be of interest to the conservation community [56]-[59]. Instead this chapter will consider the current knowledge on the effect of other white and coloured pigments on the light stability of various polymers. The review will be divided into two sections looking at research carried out within heritage and non-heritage (industry and academia) sectors in order to highlight their different needs and approaches.

2.4.3.2 Pigments - industrial and academic research

Industrial literature can be difficult to interpret as methods and practices are often standard within the sector but not clearly specified and rarely published. This is particularly the case with the older studies where experimental details are scarce. The most important results of research carried out in both these sectors are summarized in Table 2-1. The polymer most studied from the perspective of the effect of different pigments on its light stability is PP. The examination of pigments in an industrial or academic context will, therefore, be divided into a separate discussion on PP followed by one covering other polymers.

2.4.3.2.1 Polypropylene

Some of the results obtained from studies on PP are contradictory. Research by Uzelmeier examined the effect of various pigments on both the heat and light stability of unstabilized and heat-stabilized PP [60]. The pigments included:
Cromophtal red 3B⁹, quinacridone magenta, phthalocyanine blue and green, titanium dioxide (rutile), iron oxide (tan), cadmium yellow, chromium oxide green, mercadium red, ultramarine blue and three carbon black pigments. The UV screening ability of the pigments and mechanical strength of the samples were measured. However, the exact methodology was not described making it difficult to critically evaluate the results. Channel black was found to be the most effective for protecting unstabilized PP, with phthalo pigments and tan iron oxide next in line. Cromophtal Red and quinacridone magenta had no effect, while the remaining pigments had a moderately positive effect. In terms of stabilized PP, only ultramarine was found to have no impact. All other pigments contributed positively to a smaller or greater extent, with channel black and phthalo pigments being the most effective. Stabilizing ability was found to be proportional to pigment concentration.

Some of those results were confirmed four years later by Steinlin and Saar who studied the effect of the most important organic pigments on the light-stabilizing ability of a hindered amine light stabilizer (HALS) – Tinuvin 770, for spin-dyeing of PP fibres [61]. In this case the level of degradation was assessed by a breaking tenacity test and colour measurements. The impact of pigment concentration was also explored, as samples were prepared with 0.1/0.5/1.0/1.5% loadings. However, contrary to Uzelmeier’s findings, the effect of concentration varied according to the pigment. Increased loading of PY138 accelerated degradation, while the opposite was found for PY110 and PV37. Results for other pigments were less conclusive and were not presented. Instead, the paper moved on to focus on samples with 1% pigment concentration and different amounts of stabilizer. The influence on stability was judged by the amount of time needed to reduce the tenacity of each coloured sample by 50% relative to the unpigmented one. In order to compare the results obtained with and without Tinuvin 770, it is important to note that the addition of 0.75% HALS stabilizer increased the protection factor of the polymer from 1 to 4.6. Nonetheless, most of the pigments tested were found to stabilize the fibre samples when no light stabilizer was

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⁹ Most likely an anthraquinone pigment (PR177) but only the brand name was given in the publication.
added. In the presence of a light stabilizer most pigments had no effect either way, some reduced its effectiveness (these were exclusively yellow), and a few increased it (these were mostly violet, blue and green pigments). There was no link between the absorption curves of the colourants and the impact on light stability of the polymer. Chemical composition did not provide an explanation for the differing effect of the pigments as, for example, both the damaging yellow pigments as well as the stabilizing red ones contained azo groups. However, some pigments showed fading before the fibre tenacity reduced to 50%. This led the authors to propose that there could be a relationship between lightfastness of pigments and their effect on stability of the fibres. Their hypothesis proposed that the decomposition products of the pigments following light exposure could accelerate the degradation of the fibres.

On the other hand, work presented by Stengrevics on pigments used in PP fibres and tapes for outdoor applications contradicts some of those earlier findings [62]. In fact, there even seemed to be discrepancy between results obtained for the different forms of the polymer with the same pigment, as was the case with PY83 which was found to promote degradation under natural sunlight in fibre samples but had no effect in tapes. Furthermore, there was no clear correlation between the accelerated degradation and natural weathering experiments. Some pigments, such as PY93, were shown to diminish loss of tensile strength under artificial conditions but were sensitizing under sunlight. This paper is a good example of the typical industrial literature of the time as no sample preparation or analysis methods were provided. The issue of realistic weathering behaviour and lifetime prediction has since been under a lot of scrutiny, with researchers constantly looking for accelerated methods which best represent real complex scenarios [63]–[66]. In fact, in the work of Steinlin and Saar, as well as Allen, who looked at the performance of cadmium yellow, arylide yellow and phthalo blue in PP films, it can be observed that results obtained by accelerated degradation are also different to those achieved through natural weathering (see Table 2-1) [18], [24].
The issue of light stabilizer compatibility was further explored by Klemchuk who tested BZT\textsuperscript{10}, Nickel, BZP\textsuperscript{11}, HALS and BZA\textsuperscript{12} stabilizers against unstabilized coloured PP tapes containing PR101, PY37, PO20, PB29, PB15, PY93 and PR144\textsuperscript{[8]}. The samples contained 0.3% stabilizer to 0.4% colourant and were assessed by the amount of solar energy (in kLy\textsuperscript{13}) needed to reduce tensile strength by 50%. In the case of tapes without any stabilizer, all pigments exhibited varied levels of protection (with the exception of PB29 which had no impact) which is consistent with findings by Steinlin and Saar\textsuperscript{[61]}, Uzelmeier\textsuperscript{[60]} and Stengrevics\textsuperscript{[62]}. However, the results were drastically different when stabilizers were introduced. BZT was found to act antagonistically when combined with any of the tested pigments, while Nickel stabilizer only reacted badly when PR101 was included. BZP showed a much more mixed behaviour but only PR101 significantly reduced its effectiveness. PY93 and PR144 very strongly decreased the protective function of HALS – as much as by 50% in the case of the former, while PB15 greatly enhanced its abilities. Finally, PY93 was also the only pigment to react antagonistically with BZA stabilizer.

A slightly different approach was adopted by Ahmadi who instead of screening a variety of colourants focused on the effect of PR57:1 on PP\textsuperscript{[68]}. The stabilizing performance of the pigment was compared with two different light stabilizers. Film samples were made with varying concentrations of pigment (0.025, 0.05, 0.075 and 0.1). Every sample contained a different quantity of each stabilizer; however, their combinations appear random, i.e., for each pigment loading two different mixtures of stabilizers were used but were not consistent for all samples. This made the comparison of results more difficult. Overall, it was found that the pigment not only enhances PP stability but also improves the performance of HALS stabilizers when used together. Additionally, increasing pigment concentration can provide better UV protection than adding a benzophenone UV absorber. It is important to note, however, that all the film

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\textsuperscript{10} benzotriazole  
\textsuperscript{11} benzophenone  
\textsuperscript{12} benzylamine  
\textsuperscript{13} Kilo Langley - a unit of heat transmission often used to describe the rate of solar radiation received by the earth. Equivalent to approximately 11.662 Wh/m\textsuperscript{2}.  

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samples in this study contained an antioxidant and its influence was not decoupled from that of the pigment.

2.4.3.2.2 Other Polymers
Other polymer types have not been investigated in as much detail in terms of their relationship with colourants. Marvuglio et al. looked at the UV screening properties of various pigments in crystal PS for food packaging applications [69]. The samples were exposed to radiation between 300-400 nm and assessed with UV-Vis-NIR spectroscopy. Iron oxides were shown to be the most appropriate for screening as they effectively blocked out the UV at low content levels while maintaining transparency. Carbon black and phthalo blue were also effective but their higher colour contributions made them less suitable for the application. Colour change was also assessed and after prolonged sunlight exposure only samples containing carbon black and PR48 showed more significant ΔE values than pure PS (18.2, 99.9 and 9.4 respectively).

In another study, tensile strength, percent gel fraction and IR carbonyl index were measured in coloured LDPE films exposed to a carbon arc light source for 500 h [70]. All samples except those with chrome orange dark contained between 5-8% of titanium dioxide. The reason for including titanium dioxide, its type, and why its concentration varied between samples with different pigments were not discussed and its possible influence was not explored. Nevertheless, all pigments exhibited stabilizing properties in the following order of effectiveness: cadmium yellow < ultramarine blue < phthalocyanine green < chrome orange. The screening effect of cadmium yellow was significantly smaller than other colourants and, when a UV absorber was added to the plastic, the sample degraded faster than the stabilized uncoloured material. Most pigments significantly delayed, as well as reduced the level of, crosslinking.

However, the impact of ultramarine blue is worth noting, as it only delayed the reactions - the sample reached the same level of crosslinking after 500 h compared to the unpigmented sample after 250 h of exposure. In addition, ultramarine was found to accelerate degradation in HDPE [71] when films
coloured using two commercial masterbatches, blue and green\textsuperscript{14}, containing different amounts of the pigment were exposed to natural ageing. The results showed that the blue masterbatch significantly promoted photodegradation of PE, while the green was only sensitizing at the start of exposure. The tensile tests showed that sunlight reduced the strength of the films by 52\% for uncoloured, 70\% for blue, and 35\% for green films. The authors did not attempt to separate the possible impact of the other additives present in each masterbatch analytically. However, they concluded that ultramarine blue is sensitizing even in the presence of carbon black and copper phthalocyanine, both of which were included in the masterbatches and act as UV absorber and radical scavenger respectively.

Only two pigments were found to accelerate degradation of PVC, zinc oxide and phthalocyanine blue, both of which have been found to promote surface degradation of the polymer [34], [72]. Finally, despite acting as a stabilizer for most polymers, copper phthalocyanine has a significant photocatalytic effect on PC [73]. It significantly reduces impact resistance of the polymer and accelerates the formation of degradation products such as hydroxy and carbonyl groups. Scanning electron microscopy (SEM) images also showed considerable surface deterioration compared to unpigmented samples which were only cracked. The proposed degradation mechanism excluded copper phthalocyanine as an intrinsic singlet oxygen or free radical producer but instead suggested that interactions between the excited energy states of pigment and polymer are the cause of the accelerated degradation.

It is clear that the effect of pigments varies greatly not only depending on the polymer they are incorporated in but also on what other additives and/or pigments are present. In addition, no clear connections can be seen between photoactivity and type of pigment either in terms of hue or type (e.g. organic vs inorganic; chemical structure). This creates an incredibly complex situation where each individual formulation might have to be tested individually. It is, however, possible to tackle the subject by adopting a strategic approach of

\textsuperscript{14}The green masterbatch mixture included a halogenated copper phthalocyanine pigment.
drawing upon the current knowledge and conducting light degradation tests designed to answer the most important questions relating to light stability of heritage plastics.

The following table summarizes the photodegradation studies discussed above in respect of the radiation and analytical methods. The data is organized by pigment and, where possible, light doses were calculated or converted to the same units in order to better visualize the findings on each colourant’s effect on various polymers when exposed to light. This table distils information from industrial literature that is most relevant to the plastics conservation field: material details (polymer, pigment, stabilizers), type and amount of radiation employed, type and goal of analysis, and most important findings. It also categorizes each result into stabilizing, sensitizing or neutral, based on whether the pigment slowed/decreased or sped up/increased the level of polymer photodegradation compared to an uncoloured sample. This also includes samples containing light stabilizers.

Although the methods used in photodegradation studies are quite varied, the most important points to note are that the vast majority of these experiments used UV radiation to promote photodegradation in their samples. This makes the results difficult to interpret from the point of view of conservation as it does not necessarily reflect how the same material would behave on extended visible light exposure, especially if it has already been naturally aged. In addition, most tested pigments have been found to be stabilizing which might reflect the fact that sensitizing pigments were likely identified in practice and are, therefore, of limited interest to the industry. Stabilizing colourants, on the other hand, could provide practical benefits and thus were studied in more depth. Furthermore, 6 out of the 12 reviewed studies explored the stability of PP in various forms, with just 2 investigating PVC and only one each for LDPE, HDPE, PS and PC. This hardly presents a good overview of types of polymers that can be found in heritage collections.
Results can also be inconsistent, e.g. the studies conducted by Steinlin and Saar [61] and Stengrevics [62] each identified different behaviours for pigments: PY83, PY93, P031, P061, PR48, PR149 and PR166 in PP, even though similar methods were employed. This further highlights the complexity of the subject and the need for a more tailored approach for plastics conservation. However, it also emphasizes the importance of considering all components, particularly pigments, when contemplating light stability of a plastic object.

It can also be noted that 8 of the papers reviewed were published in the 1970s and 1980s and since then there have been considerably fewer experiments carried out on the topic with the 2 most recent articles dating from 2008. Taking into consideration the rapid growth in the development of synthetic organic pigments during the 20th century [74], it begs the question whether photodegradation tests for many new colourants were carried out but not published, and whether pigments that might have eventually been shown to be sensitizing were ever used in production before being withdrawn and thus could be present in modern collections. Of course, it could also be the case that internal studies simply eliminated any pigments that were not up to standard, but trade secrets make it almost impossible to find out without carrying out analysis on every object.
Table 2-1. Effect of pigments on light stability of polymers. Results from non-heritage research.

(✓ stabilizing effect, × sensitizing effect, = no effect, * information not explicitly provided in the original publication)

<table>
<thead>
<tr>
<th>Pigment</th>
<th>CI Name</th>
<th>Polymer</th>
<th>Radiation</th>
<th>Total Dose</th>
<th>Analysis</th>
<th>Findings</th>
<th>Overall Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc white (zinc oxide)</td>
<td>PW4</td>
<td>PVC</td>
<td>UV</td>
<td>Unknown</td>
<td>FTIR, weight loss measurements, SEM</td>
<td>SEM images show surface damage. Adding sensitizer to pure PVC caused an increase in weight loss of 5%, while further addition of zinc oxide increased it to 20%. FTIR: decrease in the C-Cl band at 695 cm⁻¹; increase at ~1600 cm⁻¹ (formation of carboxylic acids); carbonyl groups detected at 1700 cm⁻¹ &amp; 2858 cm⁻¹; 1768 cm⁻¹ - production of carbamates.</td>
<td>×</td>
<td>[72]</td>
</tr>
<tr>
<td>Monolite yellow (monoazo, arylamide)</td>
<td>PY 1:1</td>
<td>PP (film)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>IR (embrittlement time – time to reach a carbonyl index of 0.6)</td>
<td>Stabilizing factor of 11.0 (compared to 1.0 of pure unpigmented polymer)</td>
<td>✓</td>
<td>[67]</td>
</tr>
<tr>
<td>Diarylide yellow (disazo, benzidene)</td>
<td>PY17</td>
<td>PP (fibre)</td>
<td>Natural and artificial sunlight</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Significantly decreased time needed to achieve 50% drop in tensile strength in accelerated ageing and promoted degradation under natural sunlight. Significantly reduced the efficiency of a HALS stabilizer.</td>
<td>×</td>
<td>[62]</td>
</tr>
<tr>
<td>Pigment</td>
<td>Sample</td>
<td>Matrix</td>
<td>Illumination</td>
<td>Interaction</td>
<td>Reaction Description</td>
<td>Reference</td>
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<tr>
<td>Chrome yellow (lead chromate)</td>
<td>PY34*</td>
<td>PVC (rigid)</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Discolouration, induction time before rapid HCl evolution on heating</td>
<td>[34]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium yellow (cadmium zinc sulphide)</td>
<td>PY35*</td>
<td>LDPE</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Elongation loss (tensile testing), degree of crosslinking (gel fraction), IR spectroscopy</td>
<td>[70]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium yellow (cadmium sulphide)</td>
<td>PY37*</td>
<td>PP (heat-stabilized)</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>[60]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium yellow (cadmium sulphide)</td>
<td></td>
<td>PP (un-stabilized)</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample, UV screening ability at 375 nm</td>
<td>[60]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Increased time to start of discolouration and 10% residual surface stability compare to unpigmented unstabilized sample.
- Accelerated photooxidation reactions in unstabilized samples, evidenced by the formation of carbonyl groups (increase of FTIR absorbance at 1715 cm$^{-1}$). [Samples contained 5% titanium dioxide]

- Reported an increase in UV stability between 70% at 0.1% concentration and 890% at 2% concentration.
- An increase in UV stability (2:1).
<table>
<thead>
<tr>
<th>Color</th>
<th>PP (film)</th>
<th>PP (fibre)</th>
<th>PP (tape)</th>
<th>IR (embrittlement time – time to reach a carbonyl index of 0.6)</th>
<th>Stabilizing factor of 2.0 (compared to 1.0 of pure unpigmented polymer)</th>
<th>Protection factor: pigmented fibre stability/unpigmented fibre stability</th>
<th>Stabilizing factor of 1.4 without any stabilizer, 1.04 with 0.75% Tinuvin770 (HALS stabilizer).</th>
<th>Mostly increased the total amount of energy required to reduce tensile strength by 50% with and without various light stabilizers.</th>
<th>Protection factor: pigmented fibre stability/unpigmented fibre stability</th>
<th>Stabilizing factor of 1.2 without stabilizer, 0.70 with 0.75% Tinuvin 770 (HALS stabilizer).</th>
<th>Decreased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing and promoted degradation under natural sunlight. Reduced the efficiency of a HALS stabilizer.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine yellow</td>
<td>PY42</td>
<td>PS (crystal)</td>
<td>Natural sunlight; artificial λ = 300-400 nm</td>
<td>UV-Vis-NIR spectroscopy, discoloration</td>
<td></td>
<td></td>
<td></td>
<td>Effectively screened out UV radiation even at low concentrations.</td>
<td></td>
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</tr>
<tr>
<td>Material</td>
<td>PP (tape)</td>
<td>PS (crystal)</td>
<td>PP (fibre)</td>
<td>PP (fibre)</td>
<td>PP (tape)</td>
<td>Tensile strength</td>
<td>Effect of Light on Tensile Strength</td>
<td></td>
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<tr>
<td></td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Same amount of solar energy was needed to reduce tensile strength to 50% as for an unpigmented unstabilized sample. Significantly reduced the efficiency of a HALS stabilizer.</td>
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<tr>
<td></td>
<td>100,000 langleys of solar radiation; unknown</td>
<td>Unknown</td>
<td>UV-Vis-NIR spectroscopy, discolouration</td>
<td>Effectively screened out UV radiation even at low concentrations.</td>
<td></td>
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</tr>
<tr>
<td>Cromophtal yellow 3G</td>
<td>PY93</td>
<td>PP (fibre)</td>
<td>Natural and artificial sunlight</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.6 without stabilizer, 0.65 with 0.75% Tunuvin 770 (HALS stabilizer).</td>
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<tr>
<td></td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm²*</td>
<td>Tensile strength</td>
<td>Increased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing but promoted degradation under natural sunlight. Significantly reduced the efficiency of a HALS stabilizer.</td>
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<tr>
<td></td>
<td>Unknown</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Significantly increased the total amount of energy required to reduce tensile strength by 50% without any light stabilizers but behaved antagonistically with BZP, BZA and BZT stabilizers and greatly reduced the effectiveness of HALS.</td>
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<tr>
<td>Colorant Name</td>
<td>PY</td>
<td>Form</td>
<td>Wavelength (nm)</td>
<td>Energy (kJ/cm²)</td>
<td>Protection Factor: Pigmented Fiber Stability/Unpigmented Fiber Stability</td>
<td>Stabilizing Factor: 0.75% Tinuvin 770 (HALS Stabilizer)</td>
<td>Reference</td>
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<tr>
<td>Cromophthal yellow GR (disazo condensation)</td>
<td>PY95</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.2 without stabilizer, 0.52 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>✔️</td>
<td>[61]</td>
<td></td>
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</tr>
<tr>
<td>Isoindole yellow (tetrachloro-isoindolinone)</td>
<td>PY109</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.6 without stabilizer, 0.83 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>✔️</td>
<td>[61]</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Isoindolinone yellow (tetrachloro-isoindolinone)</td>
<td>PY110</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.2 without stabilizer, 0.91 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>✔️</td>
<td>[61]</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Irgazin yellow (azomethine copper complex)</td>
<td>PY129</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.7 without stabilizer, 1.52 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>✔️</td>
<td>[61]</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Dye/Orange</td>
<td>Product Type</td>
<td>Polymer</td>
<td>λ (nm)</td>
<td>γ (kJ/cm²)</td>
<td>Protection Factor: Pigmented Fiber Stability/Unpigmented Fiber Stability</td>
<td>Stabilizing Factor</td>
<td>Notes</td>
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<tr>
<td>Quinophthalone yellow (isoindoline)</td>
<td>PY138</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1 (i.e. same as unpigmented polymer) without any stabilizer, 0.57 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>[61]</td>
<td></td>
<td></td>
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<tr>
<td>Cadmium orange (cadmium seleno-sulphide)</td>
<td>PO20</td>
<td>PP (tape)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Increased the total amount of energy required to reduce tensile strength by 50% with and without various light stabilizers.</td>
<td>[8]</td>
<td></td>
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</tr>
<tr>
<td>Chrome orange (lead chromate)</td>
<td>PO21</td>
<td>LDPE</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Tensile testing, % gel fraction, IR spectroscopy</td>
<td>Delays, and reduces the level of, crosslinking as well as production of photooxidation products (carbonyl).</td>
<td>[70]</td>
<td></td>
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</tr>
<tr>
<td>Chromo orange 4R (disazo condensation)</td>
<td>PO31</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.6 without stabilizer, 0.76 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>[61]</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* Indicates the energy required for a 50% decrease in tensile strength.
<table>
<thead>
<tr>
<th>Isoindolol orange</th>
<th>PO61</th>
<th>PP (fibre)</th>
<th>$\lambda = 340-700$ nm</th>
<th>300 kJ/cm$^2$ *</th>
<th>Protection factor: pigmented fibre stability/unpigmented fibre stability</th>
<th>Stabilizing factor of 1.3 without stabilizer, 1.04 with 0.75% Tinuvin 770 (HALS stabilizer).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tetrachloroisoindolinone)</td>
<td>PP (fibre)</td>
<td>Natural and artificial sunlight</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Increased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing but promoted degradation under natural sunlight. Reduced the efficiency of a HALS stabilizer.</td>
<td></td>
</tr>
<tr>
<td>Permanent red BB (monoazo)</td>
<td>PR48</td>
<td>PS (crystal)</td>
<td>Natural sunlight; artificial $\lambda = 300-400$ nm; 100,000 langleys of solar radiation; unknown</td>
<td>UV-Vis-NIR spectroscopy, discolouration</td>
<td>Effectively screened out UV radiation even at low concentrations.</td>
<td></td>
</tr>
<tr>
<td>PR48: 2 (Ca salt)</td>
<td>PR48</td>
<td>PP (fibre)</td>
<td>$\lambda = 340-700$ nm</td>
<td>300 kJ/cm$^2$ *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.2 without stabilizer, 0.98 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (fibre)</td>
<td>Natural and artificial sunlight</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Significantly decreased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing and strongly promoted degradation under natural sunlight. Reduced the efficiency of a HALS stabilizer.</td>
</tr>
<tr>
<td>Pigment</td>
<td>PR No</td>
<td>Matrix</td>
<td>Light</td>
<td>Tensile strength</td>
<td>Effect</td>
<td>Ref</td>
</tr>
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<td>-------</td>
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<td>----------------------------------------------------------------------*</td>
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</tr>
<tr>
<td>PR48: 3 (Sr salt)</td>
<td>PP (tape)</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Decreased amount of solar energy needed to reduce tensile strength to 50% compared to an unpigmented unstabilized sample. Significantly reduced the efficiency of a HALS stabilizer.</td>
<td>[62]</td>
</tr>
<tr>
<td>Lithol rubine (monoazo)</td>
<td>PR57: 1 (Ca salt)</td>
<td>PP (film)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>transmission FTIR (carbonyl, hydroperoxide &amp; crystallinity indices), tensile test, contact angle measurements, DSC, density measurements (ASTM D105-68)</td>
<td>Pigment found to enhance polymer stability as well as performance of HALS stabilizers. Index values not given.</td>
</tr>
<tr>
<td>Thioindigo violet</td>
<td>PR88</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm²</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.5 without stabilizer, 0.85 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
</tr>
<tr>
<td>Iron oxide red</td>
<td>PR101 * or PR102 *</td>
<td>PVC (rigid)</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Discouralation, induction time before rapid HCl evolution on heating</td>
<td>Increased time to start of discouloration and 10% residual surface stability compare to unpigmented unstabilized sample.</td>
</tr>
<tr>
<td>Material</td>
<td>PR Number</td>
<td>Description</td>
<td>Sample Type</td>
<td>Conditions</td>
<td>Test Method</td>
<td>Result</td>
</tr>
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</tr>
<tr>
<td>PR101</td>
<td>PP</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Increased the total amount of energy required to reduce tensile strength by 50% without any light stabilizers. Slight antagonistic behaviour with BZP and BZT stabilizers.</td>
<td>✓</td>
</tr>
<tr>
<td>Cadmium red PR108</td>
<td>PVC</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Discolouration, induction time before rapid HCl evolution on heating</td>
<td>Increased time to start of discolouration and 10% residual surface stability compare to unpigmented unstabilized sample.</td>
<td>✓</td>
</tr>
<tr>
<td>(cadmium sulphide selenide)</td>
<td>PS</td>
<td>Natural sunlight; artificial $\lambda = 300$-400 nm</td>
<td>100,000 langleys of solar radiation; unknown</td>
<td>UV-Vis-NIR spectroscopy, discolouration</td>
<td>Effectively screened out UV radiation even at low concentrations.</td>
<td>✓</td>
</tr>
<tr>
<td>Mercadium red PR113</td>
<td>PP</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>Reported an increase in UV stability between 70% at 0.1% concentration and 890% at 2% concentration.</td>
<td>✓</td>
</tr>
<tr>
<td>(cadmium sulphide-mercuric sulfide)</td>
<td>PP</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample,</td>
<td>An increase in UV stability (2.75:1).</td>
<td>✓</td>
</tr>
<tr>
<td>Pigment</td>
<td>PR Number</td>
<td>Stabilizer</td>
<td>UV Screening Ability</td>
<td>Weatherometer Exposure to Achieve Brittle Flex Failure Relative to Uncoloured Sample</td>
<td>Stabilizing Factor</td>
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</tr>
<tr>
<td>Quinacridone magenta</td>
<td>PR122</td>
<td>PP (heat-stabilized)</td>
<td>λ &gt; 295 nm*</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>✓ [60]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (un-stabilized)</td>
<td>λ &gt; 295 nm*</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>= [60]</td>
<td></td>
</tr>
<tr>
<td>Azo condensation red</td>
<td>PR144</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm*</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>✓ [61]</td>
<td></td>
</tr>
</tbody>
</table>

*保護因數：著色纖維穩定性/無著色纖維穩定性

- Stabilizing factor of 1.4 without stabilizer, 0.87 with 0.75% Tinuvin 770 (HALS stabilizer).
<table>
<thead>
<tr>
<th>Pigment</th>
<th>PR No.</th>
<th>Type</th>
<th>Emission range</th>
<th>Dose</th>
<th>Protection factor: pigmented fibre stability/ unpigmented fibre stability</th>
<th>Tensile strength</th>
<th>Effect of sunlight on tensile strength</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perylene red</strong></td>
<td>PR149</td>
<td>PP (fibre)</td>
<td>$\lambda = 340$-700 nm</td>
<td>300 kJ/cm² *</td>
<td></td>
<td>Stabilizing factor of 1.2 without stabilizer, 0.98 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>Increased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing. No effect under natural sunlight. Slightly reduced the efficiency of a HALS stabilizer.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (tape)</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td></td>
<td>Slightly increased the total amount of energy required to reduce tensile strength by 50% without any light stabilizers. Slight antagonistic behaviour with BZT stabilizer. Greatly reduced effectiveness of HALS.</td>
<td></td>
</tr>
<tr>
<td><strong>Cromophtal scarlet</strong></td>
<td>PR166</td>
<td>PP (fibre)</td>
<td>$\lambda = 340$-700 nm</td>
<td>300 kJ/cm² *</td>
<td></td>
<td>Stabilizing factor of 1.5 without stabilizer, 0.91 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>Decreased amount of solar energy needed to reduce tensile strength to 50% compared to an unpigmented unstabilized sample. Reduced the efficiency of a HALS stabilizer by more than 50%.</td>
</tr>
<tr>
<td>(azo condensation red)</td>
<td>PP (tape)</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>Same amount of solar energy was needed to reduce tensile strength to 50% compared to an unpigmented unstabilized sample. Reduced the efficiency of a HALS stabilizer by 50%.</td>
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<td>[62]</td>
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<tr>
<td>Anthraquinone red</td>
<td>PR177</td>
<td>PP (heat-stabilized)</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>Reported an increase in UV stability between 20% at 0.1% concentration and 160% at 2% concentration.</td>
<td>✔</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (un-stabilized)</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample, UV screening ability</td>
<td>No increase in the UV stability compared to unpigmented sample.</td>
<td>✔</td>
</tr>
<tr>
<td></td>
<td>PR177</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 2 without any stabilizer, 1 (i.e. same as unpigmented polymer) with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>✔</td>
</tr>
<tr>
<td>Pigment</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Irgazin red BPT (perylene)</td>
<td>PR224</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1 (i.e. same as unpigmented polymer), 0.80 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td></td>
</tr>
<tr>
<td>Phthalo-cyanine blue (Cu)</td>
<td>PB15*</td>
<td>PC</td>
<td>λ = 315-400 nm</td>
<td>Unknown</td>
<td>FTIR, SEM, mechanical testing</td>
<td>Oxidation bands in the carbonyl and hydroxyl regions appear much quicker in pigmented samples. Surface is intensely corroded as opposed to just crazed in pure PC. Both impact resistance &amp; elongation at break decrease much faster in pigmented samples.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (heat-stabilized)</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>Reported an increase in UV stability between 170% at 0.1% concentration and 900% at 2% concentration.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (un-stabilized)</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample,</td>
<td>An increase in UV stability (3.5:1).</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Source of Light</td>
<td>UV screening ability</td>
<td>Tensile strength</td>
<td>Effect</td>
<td>Stabilizer Interaction</td>
<td></td>
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<tr>
<td>----------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PP (tape)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Increased the total amount of energy required to reduce tensile strength by 50% without any light stabilizers. Slight antagonistic behaviour with BZT stabilizer. Greatly enhanced effectiveness of HALS, nickel and BZA stabilizers.</td>
<td>✓</td>
<td>[8]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP (film)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>IR (embrittlement time – time to reach a carbonyl index of 0.6)</td>
<td>Stabilizing factor of 4.8 (compared to 1.0 of pure unpigmented polymer)</td>
<td>✓</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>PVC (rigid)</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>Discolouration, induction time before rapid HCl evolution on heating</td>
<td>Increased time to start of discolouration but accelerated surface degradation compared to unpigmented unstabilized sample.</td>
<td>x</td>
<td>[34]</td>
<td></td>
</tr>
<tr>
<td>PS (crystal)</td>
<td>Natural sunlight; artificial $\lambda = 300$–$400$ nm, 100,000 langleys of solar radiation; unknown</td>
<td>UV-Vis-NIR spectroscopy, discolouration</td>
<td>Effectively screened out UV radiation.</td>
<td>✓</td>
<td>[69]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB15: 3 (beta Cu)</td>
<td>$\lambda = 340$–700 nm</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.6 without any stabilizer, 1.30 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>✓</td>
<td>[61]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>PP (fibre)</td>
<td>PP (tape)</td>
<td>PB16 (metal-free)</td>
<td>Ultramarine blue (heat-stabilized)</td>
<td>Tensile strength</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
</tr>
<tr>
<td>---------------------</td>
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<td>------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>Natural and artificial sunlight</td>
<td>Natural sunlight</td>
<td>$\lambda = 340-700 \text{ nm}$</td>
<td>$\lambda &gt; 295 \text{ nm}$</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Unknown</td>
<td>Unknown</td>
<td>$300 \text{ kJ/cm}^2$</td>
<td>Unknown</td>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Literature</td>
<td>[62]</td>
<td>[62]</td>
<td>[61]</td>
<td>[60]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Significantly increased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing and reduced degradation under natural sunlight. Significantly enhanced the efficiency of a HALS stabilizer.

More solar energy was needed to reduce tensile strength to 50% compared to an unpigmented unstabilized sample.

Stabilizing factor of 1.2 without any stabilizer, 1.33 with 0.75% Tinuvin 770 (HALS stabilizer).

Reported a 0% increase in UV stability at 0.1, 0.5 & 2% concentrations.
<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration</th>
<th>Incidence</th>
<th>Methodology</th>
<th>UV Stability</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (unstabilized)</td>
<td>Unknown</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown, Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample, UV screening ability at 375 nm</td>
<td>No change in UV stability compared to an uncoloured sample.</td>
<td>[8]</td>
</tr>
<tr>
<td>PP (tape)</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Tensile strength</td>
<td>No change in the total amount of energy required to reduce tensile strength by 50% without any light stabilizers. Slight antagonistic behaviour with BZT and BZT stabilizers. Slightly enhanced effectiveness of HALS, nickel and BZA stabilizers.</td>
<td>[8]</td>
</tr>
<tr>
<td>HDPE</td>
<td>Natural sunlight</td>
<td>Unknown</td>
<td>FTIR (carbonyl index); tensile testing; % gel fraction</td>
<td>Increase of carbonyl absorption at 1715 cm⁻¹ as well as % gel fraction (polymer crosslinking). 70% reduction in tensile strength.</td>
<td>[71]</td>
</tr>
<tr>
<td>LDPE</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Tensile testing, % gel fraction, IR spectroscopy</td>
<td>Delayed crosslinking and photooxidation reactions. [Samples contained 8% titanium dioxide.]</td>
<td>[70]</td>
</tr>
<tr>
<td>Indanthrone blue</td>
<td>PB60</td>
<td>PP (fibre)</td>
<td>λ = 340-700 nm, 300 kJ/cm² * Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.6 without any stabilizer, 1.65 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>[61]</td>
</tr>
</tbody>
</table>

* Spectral data.
<table>
<thead>
<tr>
<th>Phthalo-cyanine green</th>
<th>PG7* PP (heat-stabilized)</th>
<th>λ &gt; 295 nm*</th>
<th>Unknown</th>
<th>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</th>
<th>Reported an increase in UV stability between 80% at 0.1% concentration and 900% at 2% concentration.</th>
<th>✓</th>
<th>[60]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS (crystal)</td>
<td>Natural sunlight; artificial λ = 300-400 nm</td>
<td>100,000 langleys of solar radiation; unknown</td>
<td>UV-Vis-NIR spectroscopy, discoloration</td>
<td>Effectively screened out UV radiation even at low concentrations.</td>
<td></td>
<td>✓</td>
<td>[69]</td>
</tr>
<tr>
<td>LDPE</td>
<td>λ &gt; 295 nm*</td>
<td>Unknown</td>
<td>Tensile testing, % gel fraction, IR spectroscopy</td>
<td>Delays, and reduces the level of, crosslinking as well as production of photooxidation products (carbonyl). [Samples contained 6% titanium dioxide.]</td>
<td></td>
<td>✓</td>
<td>[70]</td>
</tr>
<tr>
<td>PG7 (poly-chlorinated Cu)</td>
<td>Natural and artificial sunlight</td>
<td>Tensile strength</td>
<td>Significant increased number of hours needed to achieve 50% drop in tensile strength in accelerated ageing and reduced degradation under natural sunlight. Significantly enhanced the efficiency of a HALS stabilizer.</td>
<td></td>
<td></td>
<td>✓</td>
<td>[62]</td>
</tr>
<tr>
<td>PP (fibre)</td>
<td>λ = 340-700 nm</td>
<td>300 kJ/cm² *</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Stabilizing factor of 1.8 without any stabilizer, 1.09 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td></td>
<td>✓</td>
<td>[61]</td>
</tr>
<tr>
<td>Material</td>
<td>Unstabilized PP</td>
<td>$\lambda &gt; 295$ nm$^*$</td>
<td>Stabilized PP</td>
<td>$\lambda &gt; 295$ nm$^*$</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample, UV screening ability</td>
<td>An increase in UV stability (3.5:1).</td>
<td>[60]</td>
</tr>
<tr>
<td>--------------------------</td>
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<td>---------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>Chrome green (chrome oxide)</td>
<td>PG17$^*$ PP (heat-stabilized)</td>
<td>$\lambda &gt; 295$ nm$^*$</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>Reported an increase in UV stability between 40% at 0.1% concentration and 510% at 2% concentration.</td>
<td>[60]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PP (un-stabilized)</td>
<td>$\lambda &gt; 295$ nm$^*$</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>An increase in UV stability (2.75:1).</td>
<td>[60]</td>
<td></td>
</tr>
<tr>
<td>Pigment</td>
<td>Acronym</td>
<td>Additive</td>
<td>Wavelength</td>
<td>Exposure Time</td>
<td>UV Stabilization</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
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<td></td>
</tr>
<tr>
<td>Brown earth (iron oxide)</td>
<td>PBr7*</td>
<td>PP (heat-stabilized)</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>Reported an increase in UV stability between 30% at 0.1% concentration and 610% at 2% concentration.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PP (un-stabilized)</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample, UV screening ability</td>
<td>An increase in UV stability (3.25:1).</td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td>PBk6*</td>
<td>PS (crystal)</td>
<td>Natural sunlight; artificial $\lambda = 300\text{-}400$ nm</td>
<td>100,000 langley's of solar radiation; unknown</td>
<td>UV-Vis-NIR spectroscopy, discolouration</td>
<td>Effectively screened out UV radiation even at low concentrations.</td>
<td></td>
</tr>
<tr>
<td>Lamp black (carbon)</td>
<td>PBk7*</td>
<td>PP (heat-stabilized)</td>
<td>$\lambda &gt; 295$ nm*</td>
<td>Unknown</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td>Reported between a 70% increase in UV stability at 0.01% concentration to 1300% increase at 1% concentration.</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>PP (un-stabilized)</td>
<td>PP (fibre)</td>
<td>PVC (rigid)</td>
<td>Vine black (carbon)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>UV range</td>
<td>λ &gt; 295 nm*</td>
<td>λ = 340-700 nm</td>
<td>Natural sunlight</td>
<td>λ &gt; 295 nm*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weatherometer exposure</td>
<td>Unknown</td>
<td>300 kJ/cm²</td>
<td>Unknown</td>
<td>Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brittle flex failure</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample, UV screening ability</td>
<td>Protection factor: pigmented fibre stability/unpigmented fibre stability</td>
<td>Discolouration, induction time before rapid HCl evolution on heating</td>
<td>Hours of Weatherometer exposure to achieve brittle flex failure relative to an uncoloured sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV stability</td>
<td>A significant increase in UV stability (12:1).</td>
<td>Stabilizing factor of 2.5 without any stabilizer, 1.52 with 0.75% Tinuvin 770 (HALS stabilizer).</td>
<td>Increased time to start of discolouration and 10% residual surface stability compare to unpigmented unstabilized sample.</td>
<td>Reported an increase in UV stability between 50% at 0.1% concentration and 70% at 2% concentration.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Literature</td>
<td>[60]</td>
<td>[61]</td>
<td>[34]</td>
<td>[60]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:
- PP: Polypropylene
- PVC: Polyvinyl chloride
- Vine black (carbon): A pigment used for UV protection
- PBk8*: A specific pigment used in PP (heat-stabilized)
2.4.3.3 Pigments - heritage research

In contrast to academic and industrial literature, research on the effect of pigments on polymers carried out within, or for, the heritage sector has focused exclusively on modern paints. This can be seen in Table 2-2, which summarizes the methods and outcomes of the studies discussed below. No research regarding pigment effect on light sensitivity of solid plastic materials has been published that answer questions and concerns relevant to conservation, a gap this thesis aims to address. Commercial binders based on polymers such as acrylic, styrene-acrylic, polyester and vinyl have been examined, often as a result of investigation of a particular artist’s practice or artwork [15]. Unlike the industrial researchers, heritage scientists are more interested in finding any formulations which might be more sensitive to light exposure. Pigments tested so far have been those most commonly used in commercial paints. However, samples are not always lab-made and commercial paints contain many additives which are not always known. Additionally, traditional artists’ paints tend to include inorganic pigments. Where organic colourants are used, they are often not the same as those used for solid plastics due to high temperatures and compatibility issues during processing. Therefore, most of these results cannot be translated directly to plastic objects.

As can be observed in Table 2-2, phthalocyanine pigments were again amongst the most studied and confirmed that the effect of a colourant varies with polymer type. When exposed to UV radiation, Di Crescenzo et al. found that phthalocyanine green had no effect on vinyl or acrylic binders but was sensitizing when mixed with a styrene-acrylic co-polymer causing an increase in the hydroxyl and carbonyl regions of the FTIR spectra due to photooxidation of the polymer [12]. This is in agreement with Papliaka, who tested both blue and green pigments from that family and found that, in general, they accelerated the formation of hydroxyl groups, while PB15 also contributed to chain scission of the acrylic portion of the binder which was evidenced in an increase of FTIR absorption at 1640 cm\(^{-1}\) (peak corresponding to unsaturated chain ends) [18]. However, phthalocyanines do not pose a problem in alkyd binders\(^{15}\). Anghelone et al. tested both lab-made paints containing an alkyd binder and various

\(^{15}\) Oil-modified polyester resins.
phthalocyanine pigments\textsuperscript{16} as well as commercial alkyd paints\textsuperscript{17} \cite{75}. All pigments were found to have a stabilizing effect on the paints as compared with pure alkyd medium films, though the level of stabilization varied with pigment type. PG36 was found to be the least effective of all, while PG7 and the PB15:x pigments were the most protective. Interestingly, comparison between self-made and commercial paints showed that additives present in the latter did not have any influence on the degradation.

There seems to be less agreement on the effect of ultramarine blue on various binders. It was found to promote photooxidation in vinyl, acrylic and styrene-acrylic paints, leading to significant colour changes and surface roughness demonstrated by SEM \cite{12} as well as degradation of both binder and surfactant in two different acrylic media on exposure to UV \cite{18}. In contrast, Ferreira et al. noted a decrease in chain scission in some vinyl samples containing ultramarine pigment \cite{15}. However, these samples used a commercial aqueous vinyl emulsion, and in pure PVAc binder ultramarine seemed to increase the rate of polymer chain scission. However, those results were not supported by FTIR analysis which did not detect any molecular changes in either polymer.

Another contentious group of pigments are iron oxides. It also appears evident that even binders belonging to the same family will react differently with the same pigment. Brown iron oxide pigment was found to protect PVAc as well as commercial vinyl emulsion samples from chain scission when exposed to a xenon arc light source for 3500 h \cite{15}. On the other hand, Wei et al. reached an opposing conclusion. After subjecting commercial PVAc samples containing a brown iron oxide colourant to a lower overall radiation dose using a similar light source, they detected a greater amount of oxidation, deacetylation and chain scission products than in the uncoloured samples \cite{76}. Moreover, when a yellow iron oxide pigment was tested with acrylic, styrene-acrylic and vinyl-based binders, it caused an increase of absorption in the hydroxyl and carbonyl regions of the FTIR

\textsuperscript{16} PB16 - metal free pigment; 3 polymorphs of copper phthalocyanine: alpha (α) PB15:1 - chlorine stabilized, beta (β) PB15:3, and epsilon (ε) PB15:6; green phthalocyanine; fully chlorinated copper phthalocyanine; PG7; chlorinated and brominated copper phthalocyanine; and PG36.

\textsuperscript{17} PB15:1, PG7 and PG36.
spectra, corresponding to formation of oxidation products in the acrylic paints [12]. It also contributed to the reduction on the polymer signal after aging of the vinyl samples. However, this experiment not only tested a commercial PVAc copolymer resin different to the other studies but was also carried out using UV radiation exclusively. This complicates matters considerably as the composition of the paints, and thus their absorption and stabilization levels, will differ. It is, therefore, impossible to tell what exactly caused such different reactions in the vinyl paints.

More consistent results were acquired for cadmium red and yellow pigments, which were shown to be sensitizing in acrylic [19] and PVAc paints [76], as well as organic quinacridone colourants which accelerated photodegradation in acrylic and styrene-acrylic media [12], [18].

It is important to note that all experiments were carried out using UV-Vis irradiation to accelerate the degradation, keeping with the convention of fading studies despite the proven wavelength dependence of polymer degradation [4], [7], [77]. In fact, Papliaka [18] and Di Crescenzo [12] only used UV radiation in their studies, while Anghelone [75] extended exposure into near-IR (up to 3000 nm) in order to simulate solar ageing. While many commercial products are expected to be exposed to at least some amount of UV during their lifetime, objects which are part of a heritage collection are subjected to much more gentle and controlled environments, with UV filtration as standard practice [1][38]. Keeping in mind that polymers have been shown to react differently to radiation of different wavelengths, this calls into question the suitability of the methods as results obtained this way may not be relevant in a museum situation. Therefore, an approach specifically tailored to the needs of heritage conservation is necessary to assess plastics stability.

Furthermore, despite the many similarities between the studies, the methods of degradation assessment differ somewhat between research teams. While in most cases FTIR was used to assess molecular changes due to exposure, and colour measurements were carried out to define changes to the visual properties of the
material, techniques used to further describe the stability of samples under exposure were much more varied. These included: GC-MS [19], [75], [76], SEM [12], size-exclusion chromatography (SEC) [15], UV-Vis spectroscopy [15], molecular weight measurements [15], weight loss measurements [15], Raman spectroscopy [18] and nuclear magnetic resonance (NMR) [78]. Unlike industrial research, there appear to be less standardization when it comes to methods of assessing mechanical or physical properties of materials that would answer conservation concerns.
Table 2-2. Effect of pigments on light stability of polymers. Results from heritage research.

(✓ stabilizing effect, × sensitizing effect, = no effect, * information not explicitly provided)

<table>
<thead>
<tr>
<th>Pigment</th>
<th>CI Name</th>
<th>Polymer</th>
<th>Radiation</th>
<th>Total Dose</th>
<th>Analysis</th>
<th>Findings</th>
<th>Overall Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalk (calcium carbonate)</td>
<td>PW18</td>
<td>Vinyl (PVAc)</td>
<td>λ ≥ 300 nm</td>
<td>280 Wh/cm²</td>
<td>SEC, FTIR (transmission), colorimetry, UV-Vis spectroscopy</td>
<td>Caused yellowing (ΔE = 2.6) and promoted reduction in molecular weight (chain scission) in pure PVAc.</td>
<td>×</td>
<td>[15]</td>
</tr>
<tr>
<td>Hansa Yellow (monoazo, arylamide)</td>
<td>PY3</td>
<td>Styrene-acrylic copolymer</td>
<td>λ = 300-400 nm</td>
<td>50 Wh/cm²</td>
<td>FTIR</td>
<td>No differences in FTIR spectra compared to pure binder.</td>
<td>=</td>
<td>[18]</td>
</tr>
<tr>
<td>Cadmium yellow (cadmium sulphide)</td>
<td>PY37</td>
<td>Acrylic [p(EA/MMA) &amp; p(n BA/MMA)]</td>
<td>λ = 295-800 nm</td>
<td>181 Wh/cm²</td>
<td>FTIR, Py-GC-MS</td>
<td>Increase of FTIR absorptions corresponding to photooxidation products and degradation of surfactant.</td>
<td>×</td>
<td>[19]</td>
</tr>
<tr>
<td>Iron oxide yellow</td>
<td>PY42</td>
<td>Acrylic [p(n BA/MMA)]</td>
<td>λ = 295-370 nm</td>
<td>Unknown</td>
<td>FTIR, SEM, colour measurements</td>
<td>Increase of FTIR absorption in the hydroxyl and carbonyl regions corresponding to formation of oxidation products.</td>
<td>×</td>
<td>[12]</td>
</tr>
<tr>
<td>Material (color)</td>
<td>Formulation</td>
<td>Wavelength Range (nm)</td>
<td>Power (Wh/cm²)</td>
<td>Methods</td>
<td>Observations</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl</td>
<td>[poly(vinyl acetate-co-vinyl versatate)]</td>
<td>λ = 295-370 nm</td>
<td>Unknown</td>
<td>FTIR, SEM, colour measurements</td>
<td>Caused a reduction in the FTIR polymer bands after aging</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arylide yellow (monoazo, arylamide)</td>
<td>PY74</td>
<td>Styrene-acrylic copolymer</td>
<td>λ = 300-400 nm</td>
<td>50 Wh/cm²</td>
<td>FTIR</td>
<td>No differences in FTIR spectra compared to pure binder.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel azo yellow (azo metal complex)</td>
<td>PY150</td>
<td>Vinyl (PVAc binder and commercial paints)</td>
<td>λ = 295-800 nm</td>
<td>131 Wh/cm²</td>
<td>Py-GC-MS, ATR-FTIR</td>
<td>Lowered the ratios of oxidation, chain scission and deacetylation products compared to pure binder.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthol AS red (monoazo)</td>
<td>PR9</td>
<td>Acrylic binder (EA/MMA)</td>
<td>λ = 280-320 nm</td>
<td>&lt; 50 Wh/cm²</td>
<td>FTIR (ATR and transmission), NMR</td>
<td>Smaller peak intensity variation for ester, carbonyl &amp; lactone bands in ATR-FTIR spectra than in pure binder.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium red (cadmium sulphide selenide)</td>
<td>PR108</td>
<td>Acrylic binders [p(EA/MMA) &amp; p(nBA/MMA)]</td>
<td>λ = 295-800 nm</td>
<td>181 Wh/cm²</td>
<td>FTIR</td>
<td>Increase of FTIR absorptions corresponding to photooxidation products and degradation of surfactant.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vinyl</td>
<td>λ = 295-800 nm</td>
<td>131 Wh/cm²</td>
<td>Py-GC-MS, ATR-FTIR</td>
<td>Increased the ratios of oxidation, chain scission and deacetylation products compared to pure binder.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References: [12], [18], [76], [78], [19]
<table>
<thead>
<tr>
<th>Color</th>
<th>Number</th>
<th>Binder</th>
<th>λ = 300-400 nm</th>
<th>Wh/cm²</th>
<th>Method(s)</th>
<th>Effect of Photodegradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthol red AS-D (monoazo)</td>
<td>PR112</td>
<td>Styrene-acrylic copolymer</td>
<td>300-400 nm</td>
<td>50</td>
<td>FTIR, colorimetry</td>
<td>Accelerated photodegradation of the binder (formation of carbonyl products, reduction of C-H, C-O and C-C peaks).</td>
</tr>
<tr>
<td>Quin-acridone magenta</td>
<td>PR122</td>
<td>Styrene-acrylic copolymer</td>
<td>300-400 nm</td>
<td>50</td>
<td>FTIR, colorimetry</td>
<td>Accelerated photodegradation of the binder (formation of carbonyl products, reduction of C-H, C-O and C-C peaks).</td>
</tr>
<tr>
<td>Quin-acridone violet</td>
<td>PV19</td>
<td>Styrene-acrylic copolymer</td>
<td>300-400 nm</td>
<td>50</td>
<td>FTIR, colorimetry</td>
<td>Accelerated photodegradation of the binder (formation of carbonyl products, reduction of C-H, C-O and C-C peaks).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vinyl [poly(vinyl acetate-co-vinyl versatate)]</td>
<td>295-370 nm</td>
<td>Unknown</td>
<td>FTIR, SEM, colorimetry</td>
<td>No changes were detected in the FTIR spectra.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acrylic [p(n BA/MMA)]</td>
<td>295-370 nm</td>
<td>Unknown</td>
<td>FTIR, SEM, colorimetry</td>
<td>No changes were detected in the FTIR spectra.</td>
</tr>
<tr>
<td>Dioxazine violet</td>
<td>PV37</td>
<td>Styrene-acrylic copolymer</td>
<td>300-400 nm</td>
<td>50</td>
<td>FTIR, colorimetry</td>
<td>Reduced the level of photodegradation of the binder.</td>
</tr>
</tbody>
</table>

[12] [18]
<table>
<thead>
<tr>
<th>Phthalo-cyanine blue</th>
<th>PB15 (Cu)</th>
<th>Styrene-acrylic copolymer</th>
<th>λ = 300-400 nm</th>
<th>50 Wh/cm²</th>
<th>FTIR, colorimetry</th>
<th>Accelerated photodegradation of the binder (formation of carbonyls and hydroxyls, reduction of C-H, C-O and C=C peaks). Weak absorption at 1640 cm⁻¹ corresponding to formation of unsaturated chain ends due to chain scission.</th>
<th></th>
<th>[18]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PB15:1, 15:3 and 15:6</td>
<td>Alkyd binder (polyester)</td>
<td>λ = 295-3000 nm</td>
<td>51 &amp; 262 Wh/cm²</td>
<td>FTIR, THM-GC-MS</td>
<td>Reduced photodegradation of the binder, particularly the polyester part.</td>
<td>✓</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>PB16 (metal-free)</td>
<td>Alkyd binder (polyester)</td>
<td>λ = 295-3000 nm</td>
<td>51 &amp; 262 Wh/cm²</td>
<td>FTIR, THM-GC-MS</td>
<td>Reduced photodegradation of the binder, particularly the polyester part.</td>
<td>✓</td>
<td>[75]</td>
</tr>
<tr>
<td>Cobalt blue (cobalt aluminate blue spinel)</td>
<td>PB28</td>
<td>Vinyl</td>
<td>λ = 295-800 nm</td>
<td>131 Wh/cm²</td>
<td>Py-GC-MS, ATR-FTIR</td>
<td>Increased the ratios of oxidation, chain scission and deacetylation products compared to pure binder.</td>
<td>✓</td>
<td>[76]</td>
</tr>
<tr>
<td>Ultramarine blue</td>
<td>PB29</td>
<td>Vinyl (PVAc)</td>
<td>λ ≥ 300 nm</td>
<td>280 Wh/cm²</td>
<td>SEC, FTIR (transmission), colorimetry, UV-Vis spectroscopy</td>
<td>Promoted reduction in molecular weight (chain scission) in pure PVAc.</td>
<td>✓</td>
<td>[15]</td>
</tr>
<tr>
<td>Material</td>
<td>UV Range</td>
<td>FTIR</td>
<td>Change in FTIR Absorptions</td>
<td>References</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Acrylic binders [p(EA/MMA) &amp; p(n BA/MMA)]</td>
<td>λ = 295-800 nm</td>
<td>FTIR</td>
<td>Increase of FTIR absorptions corresponding to photooxidation products and degradation of surfactant.</td>
<td>[19]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl [poly(vinyl acetate-co-vinyl versatate)]</td>
<td>λ = 295-370 nm</td>
<td>FTIR, SEM, colorimetry</td>
<td>Caused a reduction in the FTIR polymer bands after aging, with an additional broadening of the carbonyl band. Significant surface roughness and discolouration (ΔE = 18.11, 26.16 and 13.02).</td>
<td>[12]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylic [p(n BA/MMA)]</td>
<td>λ = 295-370 nm</td>
<td>FTIR, SEM, colorimetry</td>
<td>Increase of FTIR absorption in the hydroxyl and carbonyl regions corresponding to formation of oxidation products. Significant discolouration and surface roughness.</td>
<td>[12]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene-acrylic copolymer</td>
<td></td>
<td></td>
<td>Increase of FTIR absorption in the hydroxyl and carbonyl regions corresponding to formation of oxidation products. Significant discolouration and surface roughness.</td>
<td>[12]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phthalo-cyanine green</td>
<td>PG7 (poly-chlorinated copper)</td>
<td>Styrene-acrylic copolymer</td>
<td>λ = 300-400 nm</td>
<td>50 Wh/cm²</td>
<td>FTIR, colorimetry</td>
<td>Accelerated photodegradation of the binder (formation of carbonyls and hydroxyls, reduction of C-H, C-O and C-C peaks). Weak absorption at 1640 cm⁻¹ corresponding to formation of unsaturated chain ends due to chain scission.</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acrylic [p(n BA/MMA)]</td>
<td></td>
<td>λ = 295-370 nm</td>
<td></td>
<td></td>
<td>No changes were detected in the FTIR spectra.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vinyl [poly(vinyl acetate-co-vinyl versatate)]</td>
<td></td>
<td>λ = 295-370 nm</td>
<td></td>
<td></td>
<td>No changes were detected in the FTIR spectra.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PG36 (bromated chlorinated copper)</td>
<td>Alkyd binder (polyester)</td>
<td></td>
<td>λ = 295-3000 nm</td>
<td>51 &amp; 262 Wh/cm²</td>
<td>FTIR, SEM, colorimetry</td>
<td>Reduced photodegradation of the binder, particularly the polyester part.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkyd binder (polyester)</td>
<td></td>
<td>λ = 295-3000 nm</td>
<td>51 &amp; 262 Wh/cm²</td>
<td>FTIR, THM-GC-MS</td>
<td>Reduced photodegradation of the binder, particularly the polyester part.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Pigment</td>
<td>Acrylic binders</td>
<td>λ = 295-800 nm</td>
<td>E = 181 Wh/cm²</td>
<td>Spectroscopy</td>
<td>Photooxidation Products</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------</td>
<td>-----------------</td>
<td>----------------</td>
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<td></td>
</tr>
<tr>
<td>Viridian (hydrated chromium oxide)</td>
<td>PG18</td>
<td>Acrylic binders [p(EA/MMA) &amp; p(n BA/MMA)]</td>
<td>λ = 295-800 nm</td>
<td>181 Wh/cm²</td>
<td>FTIR</td>
<td>Increase of FTIR absorptions corresponding to photooxidation products and degradation of surfactant.</td>
<td>[19]</td>
<td></td>
</tr>
<tr>
<td>Brown iron oxide</td>
<td>PBr7*</td>
<td>Vinyl</td>
<td>λ = 295-800 nm</td>
<td>131 Wh/cm²</td>
<td>Py-GC-MS, ATR-FTIR</td>
<td>Increased the ratios of oxidation, chain scission and deacetylation products compared to pure binder.</td>
<td>[76]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vinyl (PVAc)</td>
<td>λ ≥ 300 nm</td>
<td>280 Wh/cm²</td>
<td>SEC, FTIR (transmission), colorimetry, UV-Vis spectroscopy</td>
<td>Significantly reduced chain scission in pure PVAc.</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>Manganese brown (manganic hydroxide)</td>
<td>PBr8</td>
<td>Acrylic binders [p(EA/MMA) &amp; p(n BA/MMA)]</td>
<td>λ = 295-800 nm</td>
<td>181 Wh/cm²</td>
<td>FTIR</td>
<td>Increase of FTIR absorptions corresponding to photooxidation products as well as degradation of surfactant.</td>
<td>[19]</td>
<td></td>
</tr>
<tr>
<td>Bone black (carbon)</td>
<td>PBk9</td>
<td>Acrylic binders [p(EA/MMA) &amp; p(n BA/MMA)]</td>
<td>λ = 295-800 nm</td>
<td>181 Wh/cm²</td>
<td>FTIR</td>
<td>Increase of FTIR absorptions corresponding to photooxidation products as well as degradation of surfactant.</td>
<td>[19]</td>
<td></td>
</tr>
<tr>
<td>Mars black (iron oxide)</td>
<td>Styrene-acrylic copolymer</td>
<td>λ = 300-400 nm</td>
<td>50 Wh/cm²</td>
<td>FTIR, colorimetry</td>
<td>Reduced the level of photodegradation of the binder.</td>
<td>✓</td>
<td>[18]</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
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<td></td>
</tr>
<tr>
<td>PBk11</td>
<td>Styrene-acrylic copolymer</td>
<td>λ = 300-400 nm</td>
<td>50 Wh/cm²</td>
<td>FTIR, colorimetry</td>
<td>Accelerated photodegradation of the binder (formation of carbonyls and hydroxyls, reduction of C-H, C-O and C-C peaks). Weak absorption at 1640 cm⁻¹ corresponding to formation of unsaturated chain ends due to chain scission.</td>
<td>✗</td>
<td>[18]</td>
<td></td>
</tr>
</tbody>
</table>
2.4.3.4 Summary

Examining both tables as a whole, there are 28 pigments which can be categorized as purely stabilizing and 10 which act as prodegradants. This would be a very simplistic analysis, however, as the latter were all isolated studies on a single polymer. In terms of the stabilizing pigments, 19 were only tested in a single experiment on one polymer, while only 7 colourants were investigated by multiple teams, with just 4 tested on more than one polymer.

Where other polymer types were included or different methods and additives were used, the results vary considerably, and the picture becomes less clear. With different polymer types the effect could be easily explained by the differences in chemical structure and, therefore, varying absorbance spectrum, which will in turn alter the availability of particular energy transfer processes. In terms of experimental methods, however, the disparity in results is not easily understood. In most cases, due to the many variables:

- material type (from fibres to film to solid samples\(^{18}\))
- exposure conditions (from type and intensity of illumination to temperature, relative humidity and length of exposure)
- properties tested (such as tensile strength, molecular weight loss, oxidation levels, colour change)

the results are often very difficult, if not impossible, to compare, especially as the method descriptions are often lacking in relevant detail.

As demonstrated by the literature, the exact effect of a colourant on the light stability of a polymer depends on their particular combination as well as the exposure conditions. Other additives also play a role, for example inclusion of light stabilizers can actually be unnecessary with some plastics formulations. So

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\(^{18}\) In fact, a standard method in polymer photochemistry is to test in different solvents, i.e. liquid form \([4]\).
far, not many colourants have been researched in terms of their influence on the light stability of particular polymers. The exceptions are titanium dioxide and carbon-based black pigments which have been extensively researched in academia, industry, and heritage. Additionally, the negative effect of some dyes has been researched within the textile industry while the majority of heritage studies have been focused on the stability of paint systems. However, the knowledge of the sensitizing combinations of colourant and polymer is still limited, considering the possible number of formulations. Comparison of results is also problematic due to the differences in light source intensity and spectral power distribution, length of exposure, sample preparation, temperature, and humidity conditions, as well as methods of analysis used to assess degradation. It is, therefore, necessary to assess whether the same results can be achieved without UV, i.e., whether plastic objects containing sensitizing pigments and exposed in museum conditions would be vulnerable to light damage, which is exactly what this thesis addresses.

It is clear that variations in composition can greatly influence the overall photostability of plastics and classifications based only on polymer type could be misleading. A broader approach is therefore necessary to identify particular compounds and/or factors which could contribute to photodegradation of plastics in museum conditions so that better recommendations can be given for their display. Since no UV is present in museum displays and pure polymers do not absorb visible light, it is reasonable that the focus of research should fall on those components of a plastic material that do absorb in the visible range. This includes colourants as well as chromophoric groups within the system, be it from manufacture or previous exposure.
2.5 Analytical techniques for identification of plastic components

Based on previous research, which showed that polymer type is not the only factor influencing the light stability of a plastic system, a decision was made to focus on four main influencers and how they interact with other components of the material on exposure to visible light. Although many additives are present in a commercially manufactured plastic, most of them, apart from the base polymer and fillers, are added in small quantities, which makes them very difficult to detect and identify. However, the final appearance of a plastic as well as its intended application can provide a large clue as to which polymer and colourants might have been used. Since identification of plastic components is essential for an effective assessment of an object’s light stability, the following sections introduce analytical techniques most commonly used within conservation with a particular focus on identification of polymer type and colourants.

2.5.1 Visible reflectance spectroscopy

Visible reflectance spectroscopy holds significant potential in helping to identify colourants in plastics, which is an essential step in understanding the material’s stability to light. Several studies have already been carried out [79]–[81], and the technique has been shown to be a useful non-destructive tool, particularly for the identification of artists’ pigments. Libraries and databases of reference spectra for the most common colourants are readily available [82]–[84]. Cavaleri et al. showed that visible reflectance can also characterize some inorganic coloured pigment mixtures (such as a combination of smalt and azurite) as well as mixtures with lead white [80]. However, historic pigments are mostly inorganic compounds and, therefore, easier to distinguish due to very characteristic reflectance curves, distinct chemical compositions and relatively small variety. Matters become more complicated with 20th century synthetic organic colourants whose chemical structures are much more complex and rarely include elements other than carbon, hydrogen and nitrogen. They are also much more
numerous, with pigments belonging to the same family having similar properties and chemical composition. A recent study [85] on organic dye identification using UV-Vis-NIR fibre optic spectroscopy (FORS) showed that the technique can be useful to at least identify the dye category if not the specific colourant, which is particularly the case with red dyes. However, a good reference library and/or an additional analysis such as XRF was needed to perform a full identification in this case.

2.5.2 NIR spectroscopy

Near Infrared (NIR) spectroscopy uses radiation in the range of 700-2500 nm (or 14000-4000 cm⁻¹) which can be achieved using quartz optics and is the reason why it is often combined with UV-Visible spectrometers. NIR spectra are much more complex to interpret than mid-IR ones as they contain many overtones and combination bands. All organic substances absorb in the NIR range and produce many overlapping bands so assignment of individual absorption bands to specific chemical bonds is not possible and statistical analysis is often needed to extract information from the data. However, it is non-invasive, portable and easy to use, and thus has been extensively explored for use within the heritage sector [86]-[88]. NIR has been widely investigated for fast non-destructive analysis of plastics in heritage collections and reference databases are being currently developed and expanded [89], [90].

2.5.3 FTIR spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy uses mid-IR¹⁹ radiation to measure changes in the vibrational energy of molecules. Absorption of a particular portion of IR radiation by a molecule can cause: stretching (increase or decrease of bond length between atoms), bending (changes to the angle of the bonds relative to each other or the rest of the molecule) or torsional vibrations (twisting of the molecule backbone). These vibrations can also be symmetric or

¹⁹ In most cases that ranges between 4000-500 cm⁻¹ or 2.5-20 µm.
asymmetric and are related to the structure of the molecule itself. Therefore, a substance can be identified by examining locations, intensities and shapes of peaks in an IR spectrum. The three most notable types of FTIR are: transmission, Attenuated Total Reflectance (ATR) and reflectance. While the first two methods provide the best quality data, they are not always suitable for use within conservation. In order to collect a transmission spectrum, a sample must be taken from the object which then needs to be ground and mixed with an inert powder, such as potassium bromide (KBr), to produce a pellet. This process is not only time-consuming but also rarely possible. On the other hand, an ATR attachment allows for analysis of surfaces and requires minimal preparation, but the pressure required to obtain a good quality spectrum can leave a small dent in a softer material. It is possible to use FTIR non-destructively with the use of a reflectance attachment [91], which only requires that the object being analysed is held closely in contact with the instrument. However, it is much more difficult to obtain good quality, comparable spectra this way due to the variability of the contact. It is also more difficult to interpret the data directly due to the significantly higher signal to noise ratio. Finally, the aperture of the instrument can be rather large and, therefore, unsuitable for smaller objects.

2.5.4 Raman spectroscopy

Unlike FTIR, Raman spectroscopy utilizes lasers to emit radiation of narrow range (from near-UV to near-IR) and examines how that radiation is scattered by a sample. Scattering occurs when radiation is not absorbed and results from the same type of molecular vibrations observed with IR spectroscopy. Thus, the two techniques provide complementary information.

Raman spectroscopy is the most widely used analytical method for the identification of pigments. Its application to the analysis of artists’ paints has been so extensive that several sources of reference spectra exist for both organic and inorganic colourants [92]–[96]. It has also been used to identify polymers [97],
and the availability of portable instruments makes it an ideal technique for heritage applications.

2.5.5 **XRF spectroscopy**

X-ray fluorescence provides information regarding electronic transitions of electrons in atoms, which are particular to specific elements. Consequently, it is the most suitable technique for the analysis of inorganic materials. It is also particularly suited for conservation applications as non-destructive means of pigment identification and portable instruments are widely available.

2.6 **Summary**

Based on the extensive literature review on the state of current knowledge on photodegradation influencers presented above, this thesis explores the impact of four out of five main factors affecting light sensitivity of two polymers commonly found in museum collections: PP and CA. The following chapters describe two accelerated ageing studies which explore the effect of: polymer type, colourants, chromophoric impurities and previous exposure history on polymer photodegradation. Both experiments were designed to answer heritage specific questions using only visible light exposure and ambient conditions as well as analytical methods prevalent in the conservation domain. Figure 2-9 is used throughout this document as signposting for the reader to indicate which of the five influencers will be addressed by highlighting the relevant component.
2.7 Bibliography


29, no. 1, pp. 73–92, 1990.


[92] M. C. Caggiani, A. Cosentino, and A. Mangone, “Pigments Checker version


Chapter 3

Methodology

This chapter lays out the experimental setup used for the two light-ageing studies including the selection and preparation of materials, photodegradation equipment, analytical methods and procedures and data processing. It also gives details of surveys carried out among conservation professionals as well as the development of an online tool for conservators.

3.1 Materials

In order to establish the influence of pigments on polymer photodegradation, it was essential to produce new samples of known composition. Isotactic PP (M_w ~ 340,000, M_n ~ 97,000, product no. 427861) and CA (M_n ~ 30,000, product no. 180955) powders without any additives were purchased from Sigma Aldrich (London, UK). Average degree of substitution for the CA powder was calculated by da Ros et al. to be 2.45 [1].

PP samples were made by first compounding the pure polymer powder or coloured mixture in a HAAKE MiniLab II compounder/extruder (Thermo Fisher Scientific, Waltham, USA) at 195°C for approximately 10 mins. Next, the melted polymer was extruded into a cylinder of a HAAKE MiniJet II injection moulder (Thermo Fisher Scientific, Waltham, USA) and moulded into rectangular samples (30 x 10 x 2 mm) using 400 bar pressure. The temperature of the cylinder and the mould were 200°C and 60°C respectively. No antioxidants or other stabilizers were used so the temperature settings were established experimentally and were the best compromise of the lowest possible values that still produced well-mixed samples in order to reduce thermal oxidation of the polymer. All coloured
samples contained ~0.25% pigment, except for PB29 which has a much lower tinting strength so a higher loading of 0.5% was used instead. The extruder was purged before each change of pigment, first with a PP/PE copolymer to remove most of the colourant and then with the PP powder, however some contamination was still possible.

CA samples were prepared by dissolving the polymer powder in acetone, with and without pigments (at 1% loading), in reflux for 4 h. Once fully incorporated, the mixture was allowed to cool for 1 h and diethyl phthalate (DEP) plasticizer (99.5% purity from Sigma Aldrich) was added to all the coloured solutions and one of the uncoloured at 20% wt concentration. The addition of plasticizer was intended to render samples with properties more representative of real CA objects, however pure CA, without any additives was also produced for comparison. These were then left to stir for 30 mins before being poured out into a flat glass tray and left to slowly dry under a glass lid for a week. Finally, the trays were placed in a vacuum oven for 72 h at 20 °C and 150 mbar.

Figure 3-1. Chemical structure of DEP plasticizer.

Fourteen pigments covering a variety of colours and chemical structures were selected for accelerated ageing tests. These have either previously been found to be sensitizing in either PP or CA or are commonly used with those polymers (see Chapter 3). Details of each pigment are included in Table 3-1, while specific sample formulations for each experiment can be found in the relevant sections below.
<table>
<thead>
<tr>
<th>Pigment</th>
<th>CI Number</th>
<th>Type</th>
<th>Lightfastness</th>
<th>Manufacturer</th>
<th>Chemical Structure [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB29</td>
<td>77007</td>
<td>synthetic sulphur-containing sodium aluminium silicate</td>
<td>8 (light stable at any loading)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
<td><img src="image" alt="Chemical Structure PB29" /></td>
</tr>
<tr>
<td>PO13</td>
<td>21110</td>
<td>pyrazolone</td>
<td>6</td>
<td>Sun Chemical (New Jersey, US)</td>
<td><img src="image" alt="Chemical Structure PO13" /></td>
</tr>
</tbody>
</table>

20 Blue Wool Scale rating as provided by the manufacturer.
<table>
<thead>
<tr>
<th>Color Index</th>
<th>CAS Number</th>
<th>Type</th>
<th>Tint</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR48:2</td>
<td>15865:2</td>
<td>monoazo calcium lake</td>
<td>6-7 (full tint)</td>
<td>BASF (Ludwigshafen, Germany)</td>
</tr>
<tr>
<td>PR88</td>
<td>73312</td>
<td>thioindigoid</td>
<td>7-8 (medium), 7-8 (light), 8 (full tint)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
<tr>
<td>PR166</td>
<td>20730</td>
<td>azo condensation</td>
<td>7 (medium), 6-7 (light), 8 (full tint)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
<tr>
<td>125</td>
<td>PR220</td>
<td>20055</td>
<td>disazo condensation</td>
<td>7-8 (full tint)</td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
<td>-------</td>
<td>---------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>125</td>
<td>PY14</td>
<td>21095</td>
<td>disazo</td>
<td>6 (full tint)</td>
</tr>
<tr>
<td>125</td>
<td>PY35</td>
<td>77205</td>
<td>cadmium zinc sulphide</td>
<td>8 (light stable at any loading)</td>
</tr>
</tbody>
</table>

Zn=S  
Cd=S
<table>
<thead>
<tr>
<th>Color Code</th>
<th>126</th>
<th>Formula</th>
<th>Description</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY42</td>
<td>77492</td>
<td>hydrated iron oxide</td>
<td>8 (light stable at any loading)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
<tr>
<td>PY83</td>
<td>21108</td>
<td>disazo condensation</td>
<td>8 (light stable at any loading)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
<tr>
<td>PY95</td>
<td>20034</td>
<td>disazo condensation</td>
<td>7-8 (full tint)</td>
<td>BASF (Ludwigshafen, Germany)</td>
</tr>
<tr>
<td>Color Code</td>
<td>Number</td>
<td>Type</td>
<td>Tint</td>
<td>Supplier</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>----------</td>
<td>----------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>PY151</td>
<td>13980</td>
<td>benzimidazolone</td>
<td>8 (light stable at any loading)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
<tr>
<td>PY154</td>
<td>11781</td>
<td>benzimidazolone</td>
<td>8 (medium), 7-8 (light), 8 (full tint)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
<tr>
<td>PV23</td>
<td>51319</td>
<td>dioxazine</td>
<td>7 (medium), 7 (light), 8 (full tint)</td>
<td>Kremer Pigmente (Aichstetten, Germany)</td>
</tr>
</tbody>
</table>
In addition, commercially produced coloured plastics from various objects, both new and naturally aged, were used to assess common analytical techniques for their ability to identify specific colourants in plastics. Details of the materials sampled are included in Table 3-2. Plastic samples used to assess analytical techniques for identification of pigments.

Table 3-2. Plastic samples used to assess analytical techniques for identification of pigments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Colour</th>
<th>Condition</th>
<th>Source/Object</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>Violet</td>
<td>Aged(^{21})</td>
<td>Ruler</td>
</tr>
<tr>
<td>CN</td>
<td>Cream</td>
<td>Aged</td>
<td>Imitation ivory box</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>New</td>
<td>Table Tennis Ball</td>
</tr>
<tr>
<td></td>
<td>Orange</td>
<td>New</td>
<td>Table Tennis Ball</td>
</tr>
<tr>
<td></td>
<td>Dark Brown</td>
<td>Aged</td>
<td>Imitation tortoiseshell cigarette case</td>
</tr>
<tr>
<td></td>
<td>Light Brown</td>
<td>Aged</td>
<td>Imitation tortoiseshell box</td>
</tr>
<tr>
<td>CA</td>
<td>Red</td>
<td>New</td>
<td>Awl tool handle</td>
</tr>
<tr>
<td></td>
<td>Brown</td>
<td>New</td>
<td>Sheet</td>
</tr>
<tr>
<td>PU</td>
<td>Black</td>
<td>Aged</td>
<td>Foam</td>
</tr>
<tr>
<td></td>
<td>Grey</td>
<td>Aged</td>
<td>Foam</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>Aged</td>
<td>Foam</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td>Aged</td>
<td>Foam</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td>Aged</td>
<td>Foam, inside of a Mickey Mouse doll</td>
</tr>
<tr>
<td></td>
<td>Orange</td>
<td>Aged</td>
<td>Foam, inside of a Noddy doll</td>
</tr>
<tr>
<td>PS</td>
<td>Clear</td>
<td>New</td>
<td>Sheet</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>New</td>
<td>Styrofoam</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>New</td>
<td>Foam</td>
</tr>
<tr>
<td></td>
<td>Pink</td>
<td>Aged</td>
<td>Box</td>
</tr>
<tr>
<td>ABS</td>
<td>Brown</td>
<td>Aged</td>
<td>Aladdin doll</td>
</tr>
</tbody>
</table>

\(^{21}\) naturally
### 3.2 Light-ageing setup

Visible light ageing was carried out in small custom-made metal chambers (120 x 106 x 157 mm) (Figure 3-2) fitted with Philips Fortimo SLM ES 3000 lm 930 PW L15 Gen1 LED lamps (Eindhoven, the Netherlands) emitting between 400-780 nm with a CRI of 90 and 3000K CCT (Figure 3-3).

Temperature control inside the chambers was achieved with the use of a custom-made cooling system positioned beneath the sample stages. The system comprised of 128.7 W thermoelectric Peltier modules (Adaptive, UK) combined with WH7016K temperature controllers from Shenzhen Willhi Electronics Co., Ltd. (Shenzhen, China) and Corsair Hydroseries Liquid CPU Coolers (Fremont, USA). RH was not controlled and corresponded largely to ambient conditions. Temperature and RH conditions were monitored using iButton Hygrochron data loggers (Measurement Systems Ltd., UK) placed next to the samples (Figure 3-4).
Figure 3-2. Custom-made LED chambers with sample cooling system used for visible light-ageing.

Figure 3-3. Spectral power distribution of the Philips Fortimo SLM ES 3000 lm 930 PW L15 Gen1 LED lamp used for visible ageing compared to the xenon lamp with Xenochrome 320 filter array to simulate sunlight through window glass, normalized to 100 W/m² for the 300-400 nm range (data courtesy of Atlas Material Testing Technology).
UV pre-treatment was carried out in an Atlas Xenotest Alpha+ weathering chamber (Mount Prospect, USA) equipped with a xenon light source and a set of Xenochrome 320 filters simulating daylight through window glass (Figure 3-3).

Light measurements were taken using an GL Optic Spectis 1.0 Touch spectrophotometer (Poland) with a CMOS image sensor, a range of 340-780 nm and ~1.7 nm spectral resolution. Black current compensation was carried out before each set of measurements and integration time was set to automatic. For the regular monitoring of light intensity in the visible ageing chambers the instrument sensor was placed centrally at sample level and repositioned before each measurement. This method was tested for repeatability with twenty consecutive measurements and displayed an RSD of 0.32%. However, the four separate lamps used were subject to intensity fluctuations over time, therefore an average irradiance level was calculated from eight spectra collected for each chamber on different days. Details of average irradiance and illuminance for each experiment are given in the relevant sections below.
Due to the small size of the chambers, light distribution was evaluated using a WaveGo spectrophotometer (Ocean Optics, USA) and calculated as % of maximum measured irradiance. Figure 3-5 shows the spread of light intensity based on twenty-six measurements covering the sample shelves inside of each chamber.

Figure 3-5. Light distribution plots for each visible light chamber. X and Y axes represent the dimensions of the bottom surface of the chamber, while the dots show measurement spots. Colour map values are in % of the max measured irradiance.
3.2.1 Experiment 1 - Effect of pigments

Two identical samples sets were aged to ensure repeatability of results. Control samples of the same materials were included in each chamber but were wrapped in aluminium foil to exclude light. Due to the small size of the chambers, samples were further divided into two sets and aged separately Table 3-3.

Table 3-3. Samples used in Experiment 1.

<table>
<thead>
<tr>
<th>Set 1</th>
<th>PP</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO13</td>
<td>PO13</td>
</tr>
<tr>
<td></td>
<td>PR48:2</td>
<td>PR48:2</td>
</tr>
<tr>
<td></td>
<td>PV23</td>
<td>PR88</td>
</tr>
<tr>
<td></td>
<td>PY14</td>
<td>Pure</td>
</tr>
<tr>
<td></td>
<td>PY35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PY42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PY154</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pure</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Set 2</th>
<th>PP</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PB29</td>
<td>PB29</td>
</tr>
<tr>
<td></td>
<td>PR88</td>
<td>PY35</td>
</tr>
<tr>
<td></td>
<td>PR166</td>
<td>PV23</td>
</tr>
<tr>
<td></td>
<td>PR220</td>
<td>DEP</td>
</tr>
<tr>
<td></td>
<td>PY83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PY95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PY151</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pure</td>
<td></td>
</tr>
</tbody>
</table>

The total irradiance dose was 69 Wh/cm² (or 197 Mlxh) which corresponds to approximately 270 years on display at 200 lx based on 3650 opening hours per year reported for the Victoria and Albert Museum, London [3]. Average temperature and RH values across the four chambers throughout the experiment are reported in Table 3-4.
Table 3-4. Environmental conditions experienced by the samples during ageing.

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Relative Humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Average</td>
</tr>
<tr>
<td>Set 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2a</td>
<td>20.6</td>
<td>26.1</td>
</tr>
<tr>
<td>C2b</td>
<td>22.6</td>
<td>26.6</td>
</tr>
<tr>
<td>Set 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2a</td>
<td>21.1</td>
<td>24.4</td>
</tr>
<tr>
<td>C2b</td>
<td>19.5</td>
<td>25.0</td>
</tr>
</tbody>
</table>

3.2.2 Experiment 2 - Effect of previous UV exposure

Based on the results of the previous experiments on PP, three of the most sensitizing pigments were selected for further study with UV-pre-exposure alongside pure PP: PO13, PR220 and PY151. CA samples contained either PO13, PY35, PB29 or PR88 as well as samples of pure polymer and plasticized samples with no colourants. Two new sample sets were produced and included uncoloured samples of both polymers and control samples wrapped in aluminium foil for comparison. All samples were analysed with ATR-FTIR and Vis-NIR prior to any light exposure. Unlike Experiment 1, no repeats were carried out and only one sample of each formulation was exposed to each set of conditions.

UV pre-ageing was carried out in a Xenotest chamber described above. Temperature and RH were set to 25°C ± 5°C and 55% ± 10% respectively. Irradiance intensity between 300-400 nm was specified as 100 W/m² which gives a total irradiance value of 1553.5 W/m². Two different UV exposure doses were administered: 5 and 50 h, which were determined from a review on oxidation induction time for PP provided by François-Heude et al. [4], especially research conducted by Yang and Ding [5]. These were then confirmed experimentally using PP samples since no such data was available for CA. The low dose was designed to cause the minimal amount of oxidation detectable by ATR-FTIR, while the higher dose was meant to show significant molecular changes.
with no obvious damage to the material detectable with the human eye. After the UV exposure, all samples were analysed again and then moved to the visible light ageing chambers for approximately 9 weeks to simulate 200 years on museum display at 200 lx (total dose of 49 W/cm²). Temperature and relative humidity conditions during the experiment are summarized in Table 3-5. Environmental conditions experienced by the two sets of samples during visible light exposure.

Table 3-5. Environmental conditions experienced by the two sets of samples during visible light exposure.

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Relative Humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Average</td>
</tr>
<tr>
<td>UV low</td>
<td>20.1</td>
<td>23.0</td>
</tr>
<tr>
<td>UV high</td>
<td>21.1</td>
<td>24.7</td>
</tr>
</tbody>
</table>

3.3 Analytical techniques

Analytical techniques were used for two different purposes in this research:

- To monitor changes in molecular structure following degradation experiments (Chapters 4 and 5)
- To explore techniques for identifying sensitive formulations (Chapter 6)

Alterations to molecular structure were monitored mainly using ATR-FTIR, complemented with visible reflectance spectroscopy to assess colour change.

In order to establish which techniques (or combinations of techniques) are best suited to identification of pigments in historic plastics, analytical results from samples of commercial materials and those of known composition were compared. XRF was used to detect any inorganic elements, visible reflectance provided details of colour profiles, while NIR and Raman spectroscopy yielded information regarding molecular structure. In each case, single measurements
were collected from the centre of each sample as no quantitative analysis was needed.

### 3.3.1 ATR-FTIR spectroscopy

ATR-FTIR spectroscopy was done with a Bruker Alpha instrument (Billerica, USA) equipped with a diamond crystal. 32 cumulative scans were collected with a resolution of 4 cm\(^{-1}\) in absorbance mode in the range of 4000-400 cm\(^{-1}\).

During the light-ageing experiment, samples were analysed with FTIR weekly and the number of measurements for both techniques was 5 per sample. Spectra were collected across each sample and, in order to ensure that the same spot was targeted every week, a 3D printed nylon template was used. The template had 5 holes the size of the tip of the ATR-FTIR anvil and allowed for much more exact positioning of the samples thus ensuring spectra from the same spot were collected each time.

### 3.3.2 Visible-NIR spectroscopy

For the analysis in the visible and NIR range an ASD LabSpec 5000 spectrometer (Boulder, USA) was used with a 2 mm spot diameter fibre optic cable, measuring in the 350-2500 nm range. The spectral resolution of the instrument is 3 nm at 700 nm and 10 nm at 1400/2100 nm, while the sampling interval is given as 1.377 nm between 350-1050 nm and 2 nm between 1000-2500 nm, with a scanning time of 100 ms.

Five measurements were taken across the exposed surface of each sample before and after ageing using a similar template to the one for FTIR but adapted to the size of the fibre-optic probe (Figure 3-6).
3.3.3 **Raman spectroscopy**

Raman spectroscopy was evaluated through the use of several benchtop instruments equipped with different laser wavelengths:

- 632.8 nm (Jobin Yvon, Horiba, Kyoto, Japan)
- 785 nm (inVia Raman Microscope, Renishaw, Wotton-under-Edge, UK)
- 514 nm (as above)

In each case a single scan of 10 s at 50x magnification was collected in the range of 100-3200 cm⁻¹. The laser power was varied according to the sample. Additionally, the performance of a handheld spectrometer (Pharma ID, Analytik Ltd., Cambridge, UK) with a 785 nm laser, resolution of ~12-15 cm⁻¹ FWHM across range, spectral range 300-2500 cm⁻¹, and laser spot size < 50 μm, was compared to that of the inVia microscope.

3.3.4 **XRF spectroscopy**

X-ray fluorescence analysis was carried out using a handheld XRF spectrometer (Delta DP4000, Olympus, Southend-on-Sea, UK) in soil mode, scanning with
beams 1, 2 and 3 for 20 s. Whatman filter paper was used as a background. One measurement was taken per sample.

### 3.4 Data analysis

#### 3.4.1 Processing of spectral data

Baseline correction of averaged and normalized FTIR spectra of PP, shown in all figures throughout this thesis, was done by applying a rubberband function in Opus software (version 7.5, Bruker, USA) as it provided an even and consistent baseline for presentation purposes (Figure 3-7). All other processing of spectral data, including averaging and standard deviation, was carried out in Matlab (version R2018a, MathWorks, USA) (Figure 3-7). Spectrum normalization for figures was done by dividing each absorbance value by the value of a reference peak: 2915 cm\(^{-1}\) for PP and 1033 cm\(^{-1}\) for CA. Reference peaks selected correspond to methylene and cellulose backbone absorptions respectively as these are not expected to be affected much, if at all, by the exposure conditions.

![Processing steps of FTIR data and associated software used for figures (top) and peak ratio analysis (bottom).](image)

Peak ratios (both intensity and area) for PP were calculated by subtracting a baseline and dividing the relevant peak value by the reference peak as defined above for each individual measurement. These were then used to obtain an average value with standard deviation (Figure 3-7). Intensity was used to obtain peak ratios in most cases, however peak area was deemed more suitable for the
hydroxyl band where peak maximum often shifts, and the band can also broaden out as more hydroxyl groups develop. Peak area was also used to capture all the different carbonyl products being created. The reasoning behind that is discussed in Chapter 4.

In order to remove the effect of various shifts in PP spectra specific baselines were established for each FTIR band. For the reference peak a local baseline was defined as 3000 and 2100 cm\(^{-1}\) with the value at 2100 cm\(^{-1}\) calculated as an average absorbance between 2200 and 2000 cm\(^{-1}\) (Figure 3-8). The hydroxyl band baseline boundaries were defined as 3600 and 3020 cm\(^{-1}\), while the group carbonyl peak area was calculated between 1800 and 1500 cm\(^{-1}\). Where peak intensity was taken as the value (carbonyl, vinyl and ester II peaks), average absorbance between 2200 and 2000 cm\(^{-1}\) was subtracted as a baseline instead.

![Figure 3-8. Local baselines for the hydroxyl and reference FTIR bands used in peak ratio calculations.](image)
In order to prepare the data for PCA, average FTIR spectra before and after ageing were first normalized to the reference peak at 2915 cm$^{-1}$. First derivative spectra were then calculated using the Savitzky-Golay smoothing filter with a quadratic polynomial and a five-point moving window average in order to eliminate baseline effects (3-III).

$$\frac{dy}{d\lambda} = \frac{y_{i+1} - y_i}{\Delta \lambda} \quad (3-\text{III})$$

The next step involved applying Standard Normal Variate (SNV) transformation which is a weighted normalization technique that amplifies the variation between samples [6][7]. To carry out SNV, a mean of the values of each spectrum was first calculated, and subsequently subtracted from, the values of the spectrum. The resulting spectra were then divided by their standard deviation. The final stage of pre-processing involved removing data points between 2700-1800 cm$^{-1}$ and < 700 cm$^{-1}$ as they do not contribute useful information for PCA and contain a significant amount of noise.

### 3.4.2 Principal Component Analysis (PCA)

PCA is a standard chemometric method for the study of spectroscopic data, where traditional approaches to interpretation are not suitable. It is a multivariate analysis technique used to separate large sets of data into smaller, more manageable subsets, and can show how those subsets are either similar to or different from each other. It does this by calculating ‘Principal Components’ (PCs) which are essentially uncorrelated variables obtained from the whole data set that explain the most variance in the data [8].

To do this, PCA first centres the data around the origin (0,0). It then tries to find a line of best fit that goes through the origin, and projects all the data points onto it. The best fitting line, called the first principal component (or PC1), is found by maximizing the sum of squared distances from the projected points to the origin (also known as the eigenvalue). The slope of PC1 tells us the ratio between the variables which in turn describes which variable is most important when it comes to how the data is spread out. When doing PCA with singular value decomposition
(SVD), loading scores for each variable along the PC1 dimension are calculated by scaling their values so that a singular vector, or an eigenvector, is obtained. The loading scores can be used to determine which variable is most valuable for separating the data. To obtain the second principal component PCA creates a line perpendicular to PC2 that also goes through the origin. Depending on the dataset, the number of PCs is either equal to the number of variables or the number of samples, whichever is smaller. The only constraint is that the lines are all orthogonal, which ensures that the variables are uncorrelated. The eigenvalues for all PCs can also be converted into variation around the origin by dividing them by the sample size - 1 (n-1). This is expressed as a percentage of the total variation around the PCs.

PCA analysis was executed in OriginPro 2019 software (version 9.6.0.172, Academic, OriginLab Corporation, USA) using a PCA plugin by extracting 4 components as a covariance matrix.

### 3.4.3 Colour analysis

Changes to the colour of the tested samples were mainly determined from visible reflectance spectra before and after exposure and quantified by calculating CIELab and ΔE2000 values.

CIELab is a three-dimensional colour space which allows for measuring both lightness (along the L axis) and chromaticity of samples (along the a and b axes) [9]. The L dimension scales between 0-100 with values increasing with lightness. The a axis describe the level of redness (positive end) and greenness (negative end), while the b axis defines yellowness (positive end) and blueness (negative end). Hence, by using the CIELab system one can characterize colour in much more detail. The first step was multiplying the visible reflectance spectrum of a sample by the spectrum of the D65 standard illuminant and the response of the 1964 10° standard observer, to obtain the XYZ tristimulus values. CIELab values were then calculated in Matlab using equations in scheme 3-IV. Illuminant D65 was chosen as it corresponds to daylight of 6500K CCT which is representative of average midday light in Western and Northern Europe. The CIE 10° standard
observer refers to the response of an average human observer to wavelengths of the visible range.

\[ L = 116f \left( \frac{Y}{Y_n} \right) - 16 \]

\[ a = 500 \left[ f \left( \frac{X}{X_n} \right) - f \left( \frac{Y}{Y_n} \right) \right] \]

\[ b = 200 \left[ f \left( \frac{Y}{Y_n} \right) - f \left( \frac{Z}{Z_n} \right) \right] \]

where

\[ f(I) = \begin{cases} \frac{1}{3} & \text{for } I > 0.008856 \\ f(I) = 7.7871 + \frac{16}{116} & \text{otherwise} \end{cases} \] (3-IV)

Additionally, total colour change between two measurements can also be simplified by utilizing the \( \Delta E_{2000} \) equation (3-V) which is also commonly used in the conservation sphere [3]. Detailed steps of the full calculation can be found in Luo et al. [10]. This process was also carried out in Matlab using a function from ‘Computational Colour Science Using MATLAB’ add-on created by Stephen Westland (version 1.0.0.0).

\[ \Delta E_{2000} = \sqrt{\left( \frac{\Delta L'}{K_L S_L} \right)^2 + \left( \frac{\Delta C'}{K_C S_C} \right)^2 + \left( \frac{\Delta H'}{K_H S_H} \right)^2 + R_T \left( \frac{\Delta C'}{K_C S_C} \right) \left( \frac{\Delta H'}{K_H S_H} \right)} \] (3-V)

### 3.5 Surveys of museum professionals

An anonymous survey of heritage professionals working with plastics collections was conducted online using UCL’s Opinio platform between 25th April and 31st August 2019. It contained a total of 44 questions with some designed specifically for conservators, conservation scientists and curators. Since the specific job role was not relevant to the conclusions of this thesis, it was not decoupled from the
84 total entries. Instead, the number of responses for each individual question was used.

Additional data was collected via a paper survey handed out to 14 heritage professionals who attended a Plastics Workshop held at UCL and co-facilitated by the author. The questionnaire contained 6 open questions relevant to this thesis which are listed in Chapter 7.

Due to a relatively small amount of data in both cases all processing was done either manually or in Microsoft Excel 2016. Appropriate ethics approval was obtained prior to the survey as well as the workshop.

### 3.6 Application development

The free online database application for conservators P/Light was developed using Java 8, the Spring MVC (version 5.1.8) and Hibernate (version 5.4.3) open source frameworks and MySQL database with a simple HTML and CSS frontend. The app is hosted on AWS EC2 instance via AWS Elastic Beanstalk and can be accessed via the following URL: [www.plight.online](http://www.plight.online).

### 3.7 Bibliography


Chapter 4

Experiment 1 - Effect of pigments on stability of PP and CA

The main goal of this study was to establish the effect of particular pigments on the photostability of plastics based on two different polymers. Additionally, since the PP samples all contained different levels of oxidation caused by thermal processing during manufacture, contribution from chromophoric impurities was also taken into account. A total of fourteen different pigments was selected for this experiment based on their compatibility with the polymers under test and what is already known about their sensitizing capabilities. This method provided a good mix of colourants with varied chemical structures (both organic and inorganic) as well as lightfastness. Six of those pigments (PB29, PO13, PR48:2, PR88, PV23, PY35) were added to both polymers for comparison. As can be seen in Chapter 2, the catalysing action of PB29, PR48:2, PR88, PR166, PY83 and PY95 on PP has already been studied under UV irradiation. However, the remaining eight pigments have not been investigated in these formulations so far. In addition, this experiment fills the research gap identified in Chapter 2 by using LED lamps emitting only visible light.
for the accelerated ageing. This makes it much more relevant to the needs of the heritage sector which have not been addressed in previous studies.

Due to the large collection of samples, they were divided into two sets each of which was exposed to intense visible light for 12-13 weeks to achieve a total irradiance dose equivalent to 270 years on museum display at 200 lx. Each set of samples contained pure polymer specimens for reference. It was also duplicated and aged in a separate chamber to test reproducibility of results. Further details of the methods can be found in Chapter 3.

Despite the relatively large dose of visible radiation none of the samples showed signs of perceptible physical damage such as embrittlement, cracking or flaking after exposure. Colour change was difficult to assess visually, especially in the pigmented samples as any yellowing of the polymer caused by chemical changes would be masked by the colourant and there was no perceptible yellowing of the uncoloured samples. The following sections will report on the results of analysis to confirm whether any molecular or colour alterations took place after ageing.

4.1 FTIR analysis

Based on the current knowledge of degradation processes summarized in Chapter 2 the expected changes to PP structure on irradiation are related to oxidation. This should result in the formation of various hydroxyl and carbonyl groups. Although mostly associated with thermal degradation of PP, creation of CC double bonds was also investigated in this work by following the evolution of vinyl species which absorb around 1650 cm\(^{-1}\). Table 4-1 lists specific FTIR peaks which were used for the final analysis. The peak at approximately 2915 cm\(^{-1}\), representing methylene asymmetric stretching within the polymer backbone [1], was used as a reference.

In terms of CA, lack of agreement in literature means that it is not clear what can be expected after prolonged irradiation with visible light in the presence of pigments. Therefore, different processes were investigated with FTIR: deacetylation (via degree of substitution), plasticizer degradation and oxidation,
by comparison to a reference peak at 1033 cm\(^{-1}\) corresponding to the stretching vibration of the C-O-C bonds within the pyranose ring (Table 4-1).

**Table 4-1. FTIR bands selected for monitoring of chemical changes during and after photodegradation.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Peak Location (cm(^{-1}))</th>
<th>Vibration</th>
<th>Functional Group</th>
<th>Expected Behaviour</th>
<th>Quantification Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>2915*</td>
<td>CH(_2)</td>
<td>-</td>
<td>No change or decrease</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>3600-3020</td>
<td>OH</td>
<td>Hydroxyl</td>
<td>Increase</td>
<td>Area</td>
</tr>
<tr>
<td></td>
<td>1740</td>
<td>CO</td>
<td>Carbonyl</td>
<td>Increase</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>1650</td>
<td>CH(_2)-CH</td>
<td>Vinyl</td>
<td>Increase</td>
<td>Intensity</td>
</tr>
<tr>
<td>CA</td>
<td>1033*</td>
<td>C-O-C</td>
<td>Cellulose backbone</td>
<td>No change</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>3700-3200</td>
<td>OH</td>
<td>Hydroxyl</td>
<td>Increase</td>
<td>Area</td>
</tr>
<tr>
<td></td>
<td>747</td>
<td>DEP (plasticizer)</td>
<td>-</td>
<td>Decrease</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>1730</td>
<td>CO</td>
<td>Carbonyl</td>
<td>Decrease</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>1369</td>
<td>CH(_3)</td>
<td>Methyl</td>
<td>Decrease</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>1215</td>
<td>C-O-C</td>
<td>Acetate ester</td>
<td>Decrease</td>
<td>Intensity</td>
</tr>
</tbody>
</table>

* Reference peak

4.1.1 Polypropylene

Four pigments emerged as being particularly sensitizing to PP on visible light exposure: PV23, PR48:2, PY154 and PO13 (Figure 4-1). In terms of PR48:2 this result is consistent with previous findings by Stengrevics [2] who found it reduced the tensile strength of PP fibres by 50% under natural and simulated sunlight. The other three pigments have not been previously studied from this perspective.
Figure 4-1. PP samples with: [a] PO13, [b] PR48:2, [c] PV23 and [d] PY154 from chamber C2b before (black) and after (red) exposure to visible light.
Pure PP samples experienced the smallest amount of chemical change (Figure 4-2), indicating that, in the formulations prepared for this research, all pigments acted as sensitisers to a certain extent. The results of this work are, therefore, evidence that chemical changes to PP can occur even when UV radiation is excluded and may be further accelerated by the presence of certain colourants.

![Figure 4-2. Uncoloured PP sample from chamber C2b before (black) and after (red) exposure to visible light.](image)

Aside from the expected increases in various carbonyl and hydroxyl groups caused by light exposure in the coloured samples, there was also significant growth of the bands between 1300 and 1000 cm\(^{-1}\) (Figure 4-1). Among those the biggest change can be noted to the peak at around 1017 cm\(^{-1}\). These bands are not easy to assign as they correspond to several overlapping vibrations relating to different parts of the polymer structure, including the molecule backbone (carbon-carbon bonds) (Table 4-2). Wen et al. observed a similar behaviour after exposure to a high pressure mercury lamp (\(\lambda > 290\) nm) with temperature of 50 ± 1°C and attributed it generally to the formation of carbonyl degradation products [3]. In fact, the C-O bonds of esters and carboxylic acids, formed in PP due to thermal and light degradation, emit IR peaks in the 1275-1185 cm\(^{-1}\) and 1160-1050 cm\(^{-1}\) regions [4]. For brevity, the absorption at 1255 cm\(^{-1}\) will be referred to as ester I band for the remainder of this thesis, while the 1017 cm\(^{-1}\) peak specifically will be termed the ester II peak.
Table 4-2. FTIR band assignments for PP between ~1300 and 1000 cm\(^{-1}\) [5].

| 1305  | CH\(_2\) wagging, CH\(_2\) twisting |
| 1296  | CH\(_2\) wagging, CH\(_2\) twisting, CH bending |
| 1255  | CH\(_2\) twisting, CH bending, CH\(_3\) rocking |
| 1220  | CH\(_2\) twisting, CH bending, CC backbone stretching |
| 1164  | CH bending, CC backbone stretching, CH\(_3\) rocking |
| 1154  | CH bending, CC backbone stretching, CH\(_3\) rocking, C-CH\(_3\) stretching |
| 1101  | CH twisting, CC backbone stretching, CH\(_3\) rocking, CH\(_2\) wagging, CH bending |
| 1045  | C-CH\(_3\) stretching, CH bending, CC backbone stretching |
| 998   | CH bending, CH\(_3\) rocking, CH\(_2\) wagging |

The data obtained was complex, with some differences between the results obtained in each chamber. PB29, PR166 and PR220 from chamber C2b had more intense carbonyl absorptions than their C2a counterparts, while for the remaining specimens all photodegradation bands were more intense after being aged in chamber C2b. These differences are discussed in the following sections and Principal Component Analysis was used to further explore the data, given the complexity of the results (section 4.1.1.1). Following visual examination of the FTIR spectra after visible light ageing, samples from chamber C2b can be divided into three groups based on the level of increase in absorption in three main areas: hydroxyl, carbonyl and ester (Figure 4-3). As discussed in more detail above, changes to the latter are not usually monitored as standard practice when studying degradation of PP, however they have been shown to occur in response to the creation of various carbonyl species.
Figure 4-3. FTIR spectra of all samples from chamber C2b after visible light ageing showing three groups according to photodegradation level. Red – group I; blue – group II; green – group III; black – uncoloured PP.
Group I which clearly shows the biggest levels of photodegradation includes the four pigments mentioned above. In group II, putting the pigments in order of the most sensitising was more difficult as not all monitored peaks increased in absorption for every sample. However, of those, PY35 was distinctly the most sensitising. Other pigments falling within this category are: PY14, PY42, PR166 and PB29. The final group is comprised of: PR220, PR88, PY151, PY95, PY83 and uncoloured PP. Except for an increase in hydroxyl absorption, which was slightly higher in pure PP than in samples containing PY83 and PR88, as stated above the uncoloured sample had the lowest level of photodegradation as detected by ATR-FTIR in chamber C2b.

In terms of the other chamber (C2a), there is no such clear distinction between the different samples after exposure. The most sensitizing pigments from this set of samples did not have as strong an effect as corresponding samples in C2b. However, pigments PV23, PY154 and PR48:2 still appear amongst the most sensitizing colourants. Overall, there is less consistency in the changes to the three absorption areas monitored within each sample compared to chamber C2b. In fact, PY95 appears to have had the biggest photocatalytic effect on PP within this set of samples. PY35, PY14 and PY42 all seem to have had little effect on PP in this set, contrary to C2b. PR220, PB29, PR166, PR88 and PO13 were very inconsistent in that they only caused increases in absorption of some FTIR peaks but not others.

The inconsistency in results between the chambers could have been caused by the varied levels of thermal oxidation due to the way the PP samples were produced. This possibility is further explored in section 4.1.1.2. It is also important to note that due to the small size of the chambers and a large number of pigments being tested, PP samples were further divided into two sets which were aged separately (see Chapter 4). This means that each set experienced slightly different environmental conditions caused by fluctuations in ambient temperature and humidity, which could be another possible explanation for the differences between the same samples aged in different chambers and will be discussed in more detail in section 4.1.1.3.
4.1.1.1 Principal Component Analysis (PCA)

Due to the varied behaviour between the samples and the considerable number of variables that could have contributed towards it, it was necessary to employ statistical analysis to identify and better describe any patterns in the results. Principal Component Analysis was chosen as the most suitable method for reducing dimensionality of large datasets.

The first round of PCA was carried out on unaged sample data and shows that there are identifiable differences between samples produced in different Sets. PC1 accounts for 95.6% of total variance, while PC2 covers 1.7%. Consequently, using only two PCs is sufficient to explain as much as 97.3% of sample variance.

Interestingly, PC1 primarily distinguishes the samples by the intensity\(^{22}\) of the peak around 1376 cm\(^{-1}\) which is, in part, related to the bending vibrations of CH\(_3\) groups (Figure 4-4). The samples were divided into two separate groups along the PC1 axis (Figure 4-5). The first group, which received negative scores, includes spectra of the following samples: uncoloured PP, PB29, PR88, PR166, PY83 and PY95. These were all specimens from Set 2 of the experiment. Sets 1 and 2 were produced at different times and, for the most part, samples from Set 1 had less initial degradation from thermal processing\(^{23}\) judging by the amount of absorption in the hydroxyl and carbonyl regions of the FTIR data before ageing.

PC2 gave negative loadings to absorbance around 2941 and 2859 cm\(^{-1}\) and positive loadings to values around 2910 and 2844 cm\(^{-1}\) (Figure 4-4). These loadings essentially describe the shape of the convoluted bands between 3000-2760 cm\(^{-1}\), which comprise various CH\(_2\) and CH\(_3\) stretching vibrations. Other significant loadings for PC2 are: 1751 cm\(^{-1}\) (-), 1735 cm\(^{-1}\) (+), corresponding to the inflection points of the main carbonyl band, as well as 1010 and 1002 cm\(^{-1}\) (+). Additionally, three samples stand out from the other two groupings: PO13 from both chambers and PY42 from chamber C2b, as they received much lower negative scores on PC2 (Figure 4-5). This is to do primarily with the height of the

\(^{22}\) relative to the reference band at 2915 cm\(^{-1}\)

\(^{23}\) with the exception of PY151 and PR220
main carbonyl peak (~1742 cm⁻¹) as these samples exhibit even more signs of oxidation in their FTIR spectra than other specimens from the same set.

Figure 4-4. Loading plot of PC1 and PC2 of all PP spectra before ageing. [Bottom plot shows a processed derivative spectrum of one of the uncoloured samples for reference.]
PCA of samples after ageing calculated percentages of total variance of 92.8% and 3.5% for PC1 and PC2 respectively, which cumulatively accounts for 96.3% of variation within the samples.

Similarly to the case of the unaged samples, PC1 separated the aged spectra based on the peak at 1376 cm⁻¹, while PC2 used the shape of the convoluted bands between 3000-2760 cm⁻¹ (Figure 4-6). However, ageing introduced new significant sources of variation, therefore PC2 further differentiated the data according to the changes to, and relationship between, various degradation markers, namely the different peaks found in the carbonyl area, as well as small peaks at 1258, 1046 and 1017 cm⁻¹.
Figure 4-6. Loading plot of PC1 and PC2 of all PP spectra after ageing. [Bottom plot shows a processed derivative spectrum of one of the uncoloured samples for reference.]

Four main groupings can be distinguished in the score plot (Figure 4-7):

- Cluster I – samples which scored negatively on PC1 and between 0.76 and -2.03 on PC2
- Cluster II – samples which scored positively on PC1 and negatively on PC2
- Cluster III – samples which scored positively on both PCs
- Cluster IV – samples which scored similarly to Cluster I on PC1 but even higher on PC2

The samples from Cluster IV do not form as clear a grouping on the score plot as the other clusters but all four are from chamber C2b. Cluster II is comprised exclusively of uncoloured PP spectra from both sample sets, while Cluster III includes: PR220, PY95, PB29 and PY151 from both chambers. Cluster IV is made
up of PV23, PR48:2, PY154 and PO13 which from chamber C2b and have already been identified as the most degraded samples earlier in this chapter.

Figure 4-7. Score plot of PC1 vs PC2 of all PP spectra after ageing.

Investigation of the score plot with the samples categorized according to the pigment type did not reveal any patterns which would link sensitizing action of particular pigments to their chemical structure (Figure 4-8). However, it is apparent that uncoloured PP behaves differently on light exposure than pigmented PP.
The most sensitizing pigments as identified by visual inspection of the before and after spectra and confirmed by PCA are: PV23, PR48, PY154 and PO13, from chamber C2b. They experienced the most significant changes to their molecular structure and show considerable increases across all the peaks relating to photodegradation markers (Figure 4-12). Samples from Cluster I display similar changes but to a lesser extent (Figure 4-9), while Cluster III samples experienced chiefly an increase in the main carbonyl band (Figure 4-11). Pure PP samples primarily exhibited an increase in carbonyl absorption at 1743 cm⁻¹ as well as simultaneous decrease of the band at 1376 cm⁻¹ (Figure 4-10). However, this effect was less prominent than in any of the coloured samples.
Figure 4-9. FTIR spectra of PP with PY14 (C2b) from Cluster I before (black) and after (red) visible ageing.

Figure 4-10. FTIR spectra of pure PP (C2a) from Cluster II before (black) and after (red) visible ageing.
Figure 4-11. FTIR spectra of PP with PY151 (C2a) from Cluster III before (black) and after (red) visible ageing.

Figure 4-12. FTIR spectra of PP with PV23 (C2b) from Cluster IV before (black) and after (red) visible ageing.
4.1.1.2 Peak ratio analysis

Figure 4-13 shows the magnitude of change in the carbonyl and vinyl peak ratios for samples from both chambers after ageing. Unsurprisingly, the pigments which caused the most degradation according to PCA (Cluster IV) and visual examination of FTIR spectra, exhibit the largest increase in both carbonyl and vinyl as well as hydroxyl (see Appendix C) absorptions. However, the initial levels of absorption of the three monitored FTIR bands as relating to thermal oxidation from manufacture does not appear to be the main factor determining the catalysing action (see Appendix C). Although sample PO13 from chamber C2b did have one of the highest levels of initial oxidation before photo-ageing, the other sensitizing pigments are much lower on the list and the presence and intensity of the carbonyl, hydroxyl and vinyl peaks prior to the experiment varied within each sample. In addition, the unpigmented PP samples had higher initial levels of hydroxyl and vinyl absorption than samples containing PV23, PY154 and PR48.

One of the features the four most degraded samples have in common, is the evolution pattern over time (Figure 4-14). In all four cases a significant increase in carbonyl absorption can be observed after three to four weeks of visible light exposure, before gradually decreasing for a further few weeks, and finally picking up again towards the end of the experiment. This is also the case for the hydroxyl and vinyl peak ratios for samples PV23 and PR48. Samples with other pigments are less consistent with each other. However, coloured specimens from Set 2 do split into two groups in terms of the peak ratio evolution. PB29, PY95 and PY151 follow a similar pattern with a significant increase in hydroxyl and vinyl absorption towards the final weeks of exposure in chamber C2b, before lowering slightly again. PR88, PR166 and PY83 also display similarities in how, and when, certain degradation products were formed. Interestingly, the evolution patterns for the same sample in both chambers are not the same, although identical groupings can be observed within the same sample set.
Figure 4-13. Ratios of carbonyl (1740 cm\(^{-1}\)) and vinyl (1650 cm\(^{-1}\)) peaks relative to the reference band (2915 cm\(^{-1}\)) before (black) and after (red) ageing.
Figure 4-14. Carbonyl peak ratio evolutions calculated relative to the reference peak: [a] PV23, [b] PO13, [c] PR48, [d] PY154.
Figure 4-15. Ratios of carbonyl (1800-1500 cm\(^{-1}\)) area and ester II peak (1017 cm\(^{-1}\)) relative to the reference band (2915 cm\(^{-1}\)) before and after ageing.
Although carbonyl index is considered a standard method for quantification of oxidation in polyolefins [1], [6], [7] this analysis demonstrates that it is not representative of the full scope of photodegradation products. The four categories of FTIR change revealed by PCA analysis in the previous section as well as Figures 4-9 to 4-12 illustrate that carbonyl groups produced in various samples after ageing are not limited to an increase in absorption at 1740 cm\(^{-1}\). Aside from the main carbonyl and vinyl peaks, two small bands around 1577 and 1540 cm\(^{-1}\) can also be observed to alter on exposure. However, it is not the case that all of these peaks increase or even change in the same way. For example, the carbonyl peak ratios for PR88, PY14 and PY35 from chamber C2a increase after exposure while there is little to no change in the vinyl peak ratio. On the other hand, the opposite is true for PR220 and PY83. Therefore, in order to capture the full extent of photooxidation products, two new peak ratios were calculated: carbonyl area, defined as total absorbance between 1800 and 1500 cm\(^{-1}\), and peak intensity at 1017 cm\(^{-1}\) relating to the formation of double bonds (Figure 4-15).

4.1.1.3 Effect of temperature
Since the discernible differences between the results obtained from each chamber do not appear to be related to the amount of initial oxidation, it would suggest that, although small, variations in environmental conditions could explain the disparity between the level of sensitized oxidation caused by samples containing the same pigment. Despite the use of a custom cooling system during the study, changes to ambient temperature and humidity had a strong effect on the experimental conditions. Samples from Set 1 which were aged in chamber C2b, on average experienced temperatures higher by only 0.5°C compared to their counterparts in chamber C2a. Since the former included the most degraded samples this small increase in temperature may have had a significant effect, however it does fall within the ±0.5°C accuracy level for this model of data logger. The temperature range recorded for the C2b chamber in the first part of the experiment was also slightly higher than for other samples. On the other hand, relative humidity seems to have had no impact.
4.1.2 Cellulose Acetate

In general, CA samples experienced much less deterioration than PP ones. Pigments which proved most sensitizing for PP, such as PV23, had little effect on CA. After subtracting the baseline\(^{24}\) and normalizing the average FTIR spectra to the C-O-C peak at 1033 cm\(^{-1}\), most of the pigmented samples show only very slight decreases in the bands corresponding to the DEP plasticizer. This is mainly visible in the peak at 747 cm\(^{-1}\) and shoulder around 1282 cm\(^{-1}\). However, for the most part, this is very similar to the uncoloured DEP samples and does not appear to be caused by a sensitizing action of the pigments. Only PR88 seems to cause slightly more degradation to CA compared to other colourants (Figure 4-16). Apart from the changes to the plasticizer peaks, there was a noticeable drop in the carbonyl band. This peak was originally selected for monitoring of alterations to the acetate groups attached to the polymer chain. However, since no changes to other bands relating to acetate substitution (1250 and 1369 cm\(^{-1}\)) can be observed it is more likely that this reduction is linked to the degradation of plasticizer as DEP also emits a strong band in that location. In addition, no significant increases in the hydroxyl area were observed, indicating that oxidation or deacetylation did not take place.

\(^{24}\) Calculated as an average between 2200 and 2000 cm\(^{-1}\).
Figure 4-16. FTIR spectra of CA: [a] PV23, [b] PR88, [c] uncoloured with DEP, [d] pure. Black – before; red – after ageing.
4.2 Colour analysis

One of the ways molecular changes to polymer structure manifest themselves outwardly is through colour change. Yellowing and darkening of a polymer often precedes structural damage such as crazing and cracking of the material surface. In addition, all of the components of a plastic contribute to the colour properties and external appearance of an object. Therefore, colour plays a crucial part in the overall condition of an artefact.

There are many ways of measuring and describing colour difference but the most commonly used systems within conservation are the ISO Blue Wool Scale and the CIELab colour space. The former is a method of defining rate of fading of a material compared to a collection of eight wool samples dyed with colourants of known lightfastness where the each dye is twice as sensitive to light as the preceding one. ISO 1 being the most fugitive and ISO 8 being most stable [8]. While this straightforward approach is a standard for describing light stability of various materials in heritage collections it is not suitable for use with plastics since it only estimates change in lightness. Therefore, the CIELab colour space is much more suitable for complex materials whose behaviour can vary between darkening, yellowing and hue variations.

In fact, $\Delta E_{2000}$ value of 1.5 was determined to be a threshold for ‘perceptible change’ (PC) in a study at the Victoria and Albert Museum, London (V&A) [9] and was used to inform the lighting policy of the museum with a maximum fading rate established as 1.5 PC per 50 years. This assumes a total lifetime of an object to be 500 years or 10 PC. It is, however, important to note that, in the case of fading, consecutive PCs are not equal since this type of colour change is exponential. Nevertheless, it is a well-known metric within the conservation community and alterations to colour appearance of plastics are not limited to fading. This methodology was therefore deemed a valuable measure for assessing the colour change of PP and CA samples aged in this experiment.

Data presented in Figure 4-17 shows that the most significant colour change can be seen in PP samples containing PY14, with average $\Delta E_{2000}$ values of 10.15 and
9.23 for each chamber. Examining the individual Lab (see Appendix C) values reveals that both samples experienced a large decrease along the b axis, becoming less yellow, as well as a decrease in lightness and a small increase along the a axis. This corresponds to the pigment itself fading thus allowing for the darker yellowing of the polymer to show through which can be observed in the lowering of the main reflectance peak in the visible spectrum (Figure 4-18).

The next most affected colourant was PO13 both in CA and PP, although it appears to be more sensitive in the former medium as both CA samples scored above 6 for ΔE2000. In terms of the Lab values, all samples show a decrease along all three axes, becoming less yellow and red as well as darker after ageing (Figure 4-19).

Samples which experienced 1-2 perceptible colour change values were: PR48:2 (CA and PP), PV23 (CA and PP) and PY42 (PP). Two pigments stand out as having significantly different results between the two chambers: PY35 and PY154. In both cases samples from chamber C2b had a total colour change of 1.7, while the values from chamber C2a were much lower (0.5 and 0.8 respectively). This is also consistent with all of the uncoloured PP samples and, again, appears to be related to the slightly higher oxidation levels obtained in the C2b chamber.

Unsurprisingly, most of the pigments which experienced significant colour change after ageing are considered less lightfast (see Table 4.1). However, even colourants classified as having an ISO Blue Wool ratings of 7 and 8, specifically PV23, PY35, PY42 and PY154, experienced loss of colour after prolonged exposure to visible light.

Using the V&A’s guidelines, the total exposure in this experiment equates to half an object lifetime and a max acceptable level of colour change would be 5 PCs or 7.5 ΔE2000 units. The only pigment which exceeded that value was PY14, while the next most faded pigment – PO13 fell within the tolerable limits of colour change.
Figure 4-17. CIELab $\Delta E_{2000}$ for all PP (a – C2a; b – C2b) and CA (c – C1a; d – C1b) samples after ageing. Red line - perceptible colour change.
Figure 4-18. Visible reflectance spectra of PP sample with PY14 from chamber C2a before and after ageing.

Figure 4-19. Visible reflectance spectra of CA sample with PO13 from chamber C1a before and after ageing.
4.3 Discussion

The results of this study show that visible light is sufficient to induce both chemical and colour change, although these effects did not translate into serious visible damage. The mechanical properties of the samples did not appear to be affected by ageing, although they were not assessed analytically during this study. Further analysis of the surface of the tested plastics would be necessary to quantify these observations. Nevertheless, PP was found to be more susceptible to visible light degradation than CA due to its tendency to develop chromophoric degradation products during processing. It was also demonstrated that certain pigments accelerate degradation of PP even on exposure to visible light alone. As pointed out in the literature review in Chapter 2, very few studies have looked at the effect of visible light to date. Therefore, these results comprise significant findings specifically relevant to the conservation community.

Out of the samples tested, the most sensitizing pigments for PP are: PV23, PO13, PR48:2 and PY154. However, most of the pigments included in the experiment accelerated photooxidation reactions in PP to a certain extent. The final results in terms of molecular changes vary between pigments with no discernible pattern as to pigment type or initial level of oxidation from processing. In general, degradation was stronger in chamber C2b, particularly for pigments aged in the first round (Set 1). The most feasible explanation for this is the slightly higher temperatures experienced by these samples and will be further explored in the analysis of Experiment 2.

Of the six pigments which have been previously studied for their sensitising effect, only PR48:2 and PY83 had been formerly shown to significantly affect the tensile strength of PP fibres when exposed to UV [2]. However, this experiment showed that each one can accelerate photodegradation reactions in unstabilized PP even with the use of visible light alone. In addition, eight colourants featured in this study had not been tested for their sensitizing ability before: PV23, PO13, PY151, PY154, PY14, PY35, PY42, PR220. They have all been shown to accelerate photodegradation reactions in PP to a various extent.
In CA, only PR88 appears to have a notable sensitizing effect, however only on the DEP plasticizer. Moreover, no clear evidence of oxidation or deacetylation was detected in any CA samples, pigmented or unpigmented. This demonstrates that, although CA is considered by conservators to be one of the most unstable plastics, visible light exposure is not a significant degradation factor for this polymer, even in pigmented samples without any stabilizers. This is a useful finding for conservators, as there have been no previous studies exploring the impact of light on CA museum artefacts.

Additionally, the use of the carbonyl index as a standard method of establishing levels of photodegradation in PP was shown to be inadequate in encompassing the full extent of oxidation. Peak area in the general carbonyl absorption region (1800-1500 cm\(^{-1}\)) as well as intensity of a band linked to ester absorption (≈ 1017 cm\(^{-1}\)) should be adopted instead.

Molecular alterations were accompanied by degradation of colour properties. Several pigments experienced colour change greater than 1.5 ΔE\(2000\) units, defined as 'perceptible change'. The most light-sensitive colourant was PY14 which exceeded admissible levels of fading as defined by the V&A 2001 lighting policy.

Interestingly, the most sensitizing pigments for PP as established through ATR-FTIR and PCA analysis (PV23, PR48:2, PO13 and PY154) were also the ones with the lowest levels of lightfastness. The only exception was PY14 which was classified by the manufacturer as ISO 6 on the Bluewool scale and was clearly the most light-sensitive but not the most sensitizing towards the polymer. However, although even seemingly lightfast pigments caused degradation in PP, there appears to be some indication that lower light stability of a colourant contributes to its catalysing action as previously suggested by Steinlin and Saar [10].
4.4 Bibliography


Objects which have a history before entering a collection might behave differently to ones made from brand new materials. Degradation processes could be initiated with previous exposure to UV or other environmental factors and, due to long induction times in plastics, might not be detectable until it is too late. Therefore, for the purposes of conservation, it is imperative to investigate whether photodegradation reactions initiated by previous UV exposure would continue under visible light. Many heritage artefacts will have been used prior to entering museum collections, which in turn makes them likely to have been exposed to UV radiation from daylight. While the influence of thermal treatment during processing and the resulting oxidation of PP have already been discussed in Chapter 5, this is only one of possible material states. Given the role of UV in polymer photodegradation, the goal of this experiment was to establish whether reactions initiated during prior exposure to UV radiation could continue under visible light in the presence and absence of colourants for two very different polymer types.
Subsets of samples of PP and CA similar to the ones from the previous experiment were exposed to two different levels of UV pre-treatment with radiation simulating daylight through window glass. The two UV exposure levels of 0.78 Wh/cm² and 7.77 Wh/cm² will simply be referred to as low and high dose respectively. The first dose was experimentally determined as the least amount of exposure to cause perceptible change in FTIR spectra, while the high dose was intended to produce significant deterioration as detected by FTIR. The purpose of two different levels was to determine if there is a particular threshold amount of UV exposure necessary for photodegradation reactions to continue under visible light only.

5.1 FTIR analysis

Once again FTIR was used as the main analytical method as it allows for fast and efficient analysis of samples while providing information regarding chemical composition, and changes to it, as well as a good indication of any reactions that might have taken place. All spectra were baseline corrected and normalized using the same methods as in the previous study (Chapter 3, Section 3.2.2).

5.1.1 Polypropylene

PP samples selected for this experiment included three of the pigments found to be among the most sensitizing in the effect of colourants study: PO13, PR220 and PY151, as well as uncoloured PP for reference. Similar to Experiment 1, each sample had some thermal degradation from processing (see Appendix D) which can be seen as various carbonyl peaks in the FTIR spectra. All FTIR band assignments referred to in this chapter can be found in Chapter 4 (Table 5-1).

The results of low UV exposure as detected by FTIR were comparable to the subsequent treatment with visible light in that they mainly comprise the production of more carbonyl species, as shown by the formation or increase of bands at 1696, 1653, 1577 and 1547 cm⁻¹. The main carbonyl peak at 1746 cm⁻¹ either decreased or remained the same after UV ageing. The uncoloured, PO13 and PY151 samples also displayed an increase in the 1047 and 1018 cm⁻¹ peaks, but only uncoloured PP had any discernible increase in the hydroxyl absorption
due to UV treatment. Interestingly, subsequent visible light exposure appears to have reversed at least some of the effects of UV absorption. Spectra of samples PO13 and PY151 show that all the peaks which increased after pre-treatment shifted back to the initial levels after being exposed to visible light (Figure 5-1 and Figure 5-2). However, in sample PR220 only the main carbonyl peak was reduced, while uncoloured PP experienced a slight decrease in most of the peaks associated with degradation except the band at 1047 cm$^{-1}$, which did not change, and the main carbonyl peak (1744 cm$^{-1}$), which increased.

The high UV dose produced more consistent results and, unsurprisingly, stronger degradation across all samples. The most significant difference between the two sets is the considerable increase in the hydroxyl absorption after UV exposure in samples treated with the high UV dose.

![Figure 5-1. ATR-FTIR spectra of PP with PO13 before (black), after pre-treatment with low UV dose (blue) and after subsequent visible ageing (red).](image)
Change in the spectra also points to a decrease in the main carbonyl band at 1744 cm\(^{-1}\) (except for PO13 where it remained the same) and simultaneous increase in the other carbonyl peaks (Figure 5-3). In addition, UV pre-treatment caused a general increase between 1250 and 1000 cm\(^{-1}\) indicating formation of various carbonyl groups due to oxidation of the polymer chain. In contrast to the low UV set, subsequent visible light exposure did not reverse the effects of the high UV dose, although the final results vary slightly between the different samples. Uncoloured PP shows a large further increase in all peaks between 1250 and 1000 cm\(^{-1}\), while in the pigmented samples this is limited mainly to the bands at 1259, 1047 and 1018 cm\(^{-1}\). The level of hydroxyl absorption did not change, however, except for a slight reduction in PR220. The main variation in this set after visible ageing lies in the carbonyl peaks: all of the bands increased for PO13 and PY151 (Figure 5-4), while in PR220 and uncoloured PP only the main carbonyl band increased. No pigment appears to be significantly more sensitizing than the others in this case, however all coloured samples exhibited significantly more degradation than pure PP.
Figure 5-3. ATR-FTIR spectra of PP with PO13 before (black), after pre-treatment with a high UV dose (blue) and after subsequent visible ageing (red).

Figure 5-4. ATR-FTIR spectra of PP with PY151 before (black), after pre-treatment with a high UV dose (blue) and after subsequent visible ageing (red).
5.1.1.1 Peak ratio analysis

The differences between the behaviour of the low and high UV exposure sets supports the accelerating effect of previous UV exposure being largely dependent on its amount. For photodegradation reactions initiated by UV to continue under visible light, a sufficient amount of the right degradation products is required. In the case of PP, it appears that the presence of hydroxyl groups leads to further photodegradation under visible light. Trends in the data demonstrate that the larger the initial hydroxyl band the stronger the degradation on subsequent exposure, particularly for the high UV dose samples.

Plotting intensities of the vinyl and ester II bands after both UV and visible light ageing against the area of the broad hydroxyl band after UV treatment shows a very good correlation (Figure 5-5 and Figure 5-6). However, the intensity of the main carbonyl peak after visible ageing is not as well correlated to the hydroxyl absorption level (Figure 5-7). This supports the conclusion from Experiment 1 that a carbonyl index based solely on the intensity of the peak around 1730 cm\(^{-1}\) is not a reliable metric of photodegradation in PP. Instead, the area between 1800-1500 cm\(^{-1}\) should be used (Figure 5-8) in conjunction with the intensity of the ester II peak around 1017 cm\(^{-1}\) to capture all peaks related to carbonyl degradation products.
Figure 5-5. Hydroxyl absorption (measured as peak area) after UV pre-treatment [(♦) – low; (●) – high versus the intensity of the vinyl band after subsequent visible ageing.

Figure 5-6. Hydroxyl absorption (measured as peak area) after UV pre-treatment [(♦) – low; (●) – high versus the intensity of the ester II band after subsequent visible ageing.
Figure 5-7. Hydroxyl absorption (measured as peak area) after UV pre-treatment [(♦) – low; (●) – high versus the intensity of the main carbonyl band after subsequent visible ageing.

Figure 5-8. Hydroxyl absorption (measured as peak area) after UV pre-treatment [(♦) – low; (●) – high versus the area of all carbonyl bands after subsequent visible ageing.
These are significant findings as they demonstrate that the hydroxyl band could be used to determine whether a particular PP object might be sensitive to visible light exposure. As mentioned above, samples exposed to the lower dose of UV did not develop a hydroxyl band and, consequently, did not experience further degradation after visible ageing. In addition, uncoloured PP from the high UV dose sample set developed a lower hydroxyl band than the pigmented samples and subsequently experienced less photodegradation. Following calculation steps detailed in Chapter 3 to obtain peak area in the hydroxyl absorption region of an ATR-FTIR spectrum a threshold value of 9 a.u. could be used as an indicative measure to help identify a light sensitive PP object. Given that FTIR spectroscopy is a relatively accessible analytical tool for museums, this provides the plastics conservation community with a useful metric that could be used to identify PP objects whose past history has exposed them to a sufficiently high dose of UV radiation to make them particularly light sensitive.

5.1.1.2 Effect of temperature

Temperature and relative humidity data collected for each chamber throughout this experiment supports the conclusion from Chapter 4 that temperature could be one of the most important factors in promoting photodegradation. The high UV dose samples experienced average temperatures of 24.7 °C during subsequent visible ageing, while for the UV low samples that value was 1.7 °C lower. Furthermore, maximum temperatures were lower than in the visible ageing study: 27.1 °C versus 31.1 °C. Unlike Experiment 1, these values fall outside of the reported error of ±0.5°C for the data loggers. A detailed comparison of average temperature conditions experienced by each sample during ageing in both studies can be seen in Figure 5-9 which shows a good correlation between temperature and final amount of photodegradation (as defined by the score on the PC1 axis). These results highlight the importance of temperature control both during accelerated ageing studies and display of plastic objects in museums.
In addition, comparison of the amount of all carbonyl groups produced during Experiment 1 with visible light ageing only shows a very good correlation between chamber C2a and low UV pre-treatment set, as well as chamber C2b and the high UV samples (Figure 5-10). Considering that the total visible light dose from Experiment 1 was approximately 20 Wh/cm² higher than in this study, temperature appears to have a stronger influence over rate of photodegradation in coloured PP than amount of previous UV exposure. For samples containing PR220, PY151 and no pigment, the carbonyl area after visible light exposure in chamber C2b is the same as that after high UV exposure, followed by visible light exposure. The higher temperature combined with a larger dose of visible light appears to cause the same amount of photooxidation as inclusion of UV pre-treatment. For the sample containing PO13, the impact of a higher temperature and visible light dose have an even more pronounced effect. This sample belonged to Set 1 and experienced average temperatures of 26.6 °C in chamber
C2b, while for the corresponding sample from the high UV set the temperature was 1.9 °C lower.

Figure 5-10. Comparison of carbonyl area peak ratios after visible light ageing only (Experiment 1) and after UV pre-treatment followed by visible exposure (Experiment 2).

5.1.1.3 PCA

PCA analysis of aged sample spectra from both experiments, shows that the UV treated pigmented PP behave very similarly to their counterparts which were only aged with visible light (Figure 5-9). It is worth keeping in mind, however, the difference in total visible light exposure for each set of samples used for PCA as the UV set was exposed to a total visible light dose 20 Wh/cm² lower than the visible only experiment.

All of the UV samples got negative scores on the PC1 axis, placing most of them in the same cluster as the samples whose largest changes related to the main carbonyl absorption peak in Experiment 1. Additionally, the low UV dose samples with PY151, PO13 and uncoloured PP scored higher on PC2, placing them closer
on the plot to the uncoloured visible-aged samples as they experienced less degradation. Finally, PO13 exhibits the largest disparity between experiments since the samples aged with visible light only scored positively on PC1 and were amongst the most degraded. However, this could be due to the higher amount of total visible light exposure.

Interestingly, direct comparison of the FTIR spectra of the high UV dose samples with the corresponding samples from the previous experiment after a similar dose of visible light, reveals that a comparable level of photodegradation can be achieved even without adding UV. Figure 5-11 shows normalized spectra of PP with PO13 from week 8 of Experiment 1 plotted against the corresponding high UV sample. One notable difference between the results obtained with and without UV in the case of pigmented samples is that the former is more efficient in promoting formation of hydroxyl groups, while the latter produces slightly higher levels of carbonyl absorption. In contrast, uncoloured PP is most degraded when UV is used (Figure 5-12). This suggests that, although previous UV exposure does have a sensitising effect on photodegradation of PP in general, similarly to thermal oxidation from processing, it is not as important as the presence of certain pigments.
Figure 5-11. Comparison of ATR-FTIR spectra of PP with PO13 from both experiments: after 8 weeks of visible ageing only (C2a - grey, C2b - black), after pre-treatment with a high UV dose and subsequent visible ageing (red).
Figure 5-12. Comparison of ATR-FTIR spectra of uncoloured PP from both experiments: after 8 weeks of visible ageing only (C2a - grey, C2b - black), after pre-treatment with a high UV dose and subsequent visible ageing (red)
5.1.2 Cellulose Acetate

Since CA samples were largely unaffected by visible only light exposure in the previous experiment, the final selection of pigments for UV testing included:

- PB29 and PY35 which are often mentioned in literature to be photosensitizing to CA [1], [2]
- PR88 which was the only colourant that appeared to negatively affect CA on extended visible light exposure
- PO13 which was among the most sensitizing pigments to PP as well as one of the least lightfast

All the coloured samples included DEP and, for comparison, uncoloured CA with and without plasticizer was also tested. Samples were exposed to the same conditions as PP and examined with ATR-FTIR for any molecular changes. Since visual examination of FTIR spectra did not reveal any obvious alterations, several peak ratios were calculated and plotted over time to confirm that deacetylation, plasticizer loss or oxidation of the polymer did not happen.

Figure 5-13 shows peak ratios for the acetate ester, carbonyl and hydroxyl groups relative to the reference peak for PO13, PR88 and PB29 respectively, plotted over time. It can be seen that the values do not change after UV pre-treatment or after visible light exposure even for the higher UV level samples. This is consistent across all CA specimens and further proves that degree of substitution did not change. Only hydroxyl absorption appears to fluctuate. Additionally, plasticizer levels do not decrease substantially, only the uncoloured CA appears to lose a small amount of DEP (Figure 5-13d).
Figure 5-13. Peak ratios over time for low (black) and high (red) UV dose CA samples after subsequent exposure to visible light: [a] – PO13, acetate ester; [b] – PR88, carbonyl; [c] – PB29, hydroxyl; [d] – no pigment, DEP.
5.2 Colour analysis

Colour change relative to measurements taken before ageing was calculated after UV pre-treatment and after 9 weeks of total visible light exposure using the CIELab colour space and can be seen in Figure 5-15. Most samples, both of CA and PP, did not appear to experience noticeable colour change, as defined in the previous chapter using the V&A model, either after UV exposure or following further visible light treatment. However, PO13 consistently exhibited significant colour change of between 3.47 ± 0.37 and 4.57 ± 0.27 ΔE2000 units after being aged with both UV and visible radiation. This is the case for both polymers as well as both UV dose levels, although the pigment appears to be more sensitive to light damage in PP than in CA. This colour change falls below the maximum acceptable damage of 6 ΔE2000 units for exposure corresponding to 200 years at 200 lx as defined by the V&A. Average visible reflectance spectra of PO13 in PP from the high UV set demonstrate that the initial fading of the pigment after UV exposure was followed by the reduction in the main chromatic peak around 600 nm (Figure 5-14). This suggests that fading of the colourant allowed the darker yellow/brown of the degraded polymer to show through.

![Figure 5-14. Average visible reflectance spectra of PP with PO13 before (black), after high dose UV pre-treatment (blue) and after subsequent visible ageing (red).](image)

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Figure 5-15. Total colour change (CIE ΔE<sub>2000</sub>) after UV pre-treatment (blue) and after subsequent visible light ageing (black) of: [a] – CA, low UV, [b] – CA, high UV, [c] – PP, low UV, and [d] – PP high UV. Red line – perceptible colour change.
Some colour change can also be observed in unpigmented CA samples; however, the standard deviation (SD) is much higher (0.51-0.79). The high measurement SD of certain samples is likely to be due to the inhomogeneity of the material as the values presented are an average of five spectra collected from different spots across each specimen. This is particularly the case for CA which was produced in a lab via the casting process without the help of compounding equipment. The chosen production method contributed not only to formation of aggregates but also migration of pigment particles towards the drying surface of the material due to solvent evaporation resulting in an overall non-uniform colourant distribution and variation in colour measurements. Similar issues affected the dispersion of plasticizer which, although does not change the colour of the plastic, increases transparency of CA (Figure 5-16). In PP on the other hand, some impurities transferred from the processing equipment as well as uneven yellowing caused by thermal degradation during injection moulding are more apparent in uncoloured samples, again leading to higher variation in colour across each specimen.

Figure 5-16. Individual visible reflectance spectra of uncoloured CA with DEP plasticizer collected from 5 spots across the sample before (black) and after UV and visible ageing (red) showing the variation in the measurements caused by the inhomogeneity of the material.
5.3 Discussion

Investigation of the effect of two different UV exposure levels on visible light stability of pigmented and unpigmented PP and CA has shown that it can be a contributing factor towards photodegradation of plastics. However, it plays a less significant role than polymer and colourant type. This experiment demonstrated that while degradation products of previous UV exposure can indeed sensitize further photodegradation of PP, the amount of UV exposure is crucial. Formation of a sufficient amount of hydroxyl groups (> 9 a.u.) as detected by FTIR appears to be an indicator of light sensitivity for coloured PP as the area of the FTIR band after UV pre-treatment was shown to be closely linked to the overall degradation level after visible light ageing. Additionally, temperature plays a very significant role in photodegradation of PP as even a 1.9 °C increase combined with additional 20 Wh/cm² of visible light exposure can cause a similar amount of photodegradation as UV treatment.

On the other hand, CA was not affected by radiation of wavelengths longer than 320 nm and further visible light exposure did not cause any detectable degradation, although some small loss of plasticizer was experienced by uncoloured samples. This is further evidence that CA is not as sensitive to light exposure as previously thought, even under temperatures above 25 °C and in the presence of pigments and absence of light stabilisers.

Finally, samples containing PO13 showed the largest colour change after visible light ageing and, although the pigment was sensitive in both polymers, it appears less lightfast in PP than CA.
Previous chapters clearly showed the importance of not only identifying the polymer type but also the colourants present in a given plastic object in order to more accurately assess that object’s level of sensitivity to visible light exposure. Therefore, this chapter focuses on how polymer and colour identification can be achieved within the constraints of conservation and limited resources. However, it is not an easy question to answer and methods most suitable for polymer identification often do not provide any information regarding colourants. The following sections explore the viability of using visible reflectance spectroscopy as a non-invasive, fast and easy way of identification of pigments in plastics. Its combination with NIR spectroscopy as a single tool for the characterisation of plastics in collections will also be evaluated. Finally, as a comparison, the most common techniques currently used to identify pigments in other materials, specifically: Raman and XRF spectroscopy, will be discussed and assessed in terms of their usefulness for heritage plastics.
6.1 Visible reflectance spectroscopy for identification of colourants in plastics

In order to explore the potential of visible reflectance spectroscopy, both on its own and in conjunction with NIR, for plastics conservation average spectra collected from unaged samples of PP and CA during previous experiments were examined. In order to enable a better comparison of the shape of the spectra it was necessary to account for variations in overall intensity of the measurements. Spectra were first normalized to minimum and maximum values by using the following equation:

\[ y = \frac{x - \text{min}}{\text{max} - \text{min}} \]

where \( x \) is the raw spectral data matrix.

Before assessing the reflectance curves of the various coloured samples, it is important to consider the influence of the polymer on the final colour of the plastic. As can be seen from Figure 6-1, samples of pure polymers show clear differences in reflectance, with the PP reflectance curve increasing with wavelength values and absorbing considerably more light in the violet-blue-green regions of the spectrum.

![Figure 6-1. Visible reflectance spectra of uncoloured CA and PP samples.](image)
This means that PP reflects proportionally more yellow-orange-red wavelengths than the two CA samples and this is caused by two factors. Firstly, PP is a naturally opaque milky white plastic compared to the transparent CA. Secondly, the PP samples used in the experiments did not include any antioxidants to prevent heat degradation during processing which, despite best efforts, still caused some yellowing of the material. In contrast, CA is a transparent polymer with a much more even distribution of reflectance across the visible range. It is interesting to note, however, that adding DEP plasticizer increases the plastic’s transparency further. These differences will cause variations between spectra of the same pigment within a different medium and must be taken into account when attempting identification using visible reflectance. This can be clearly seen in the spectra of CA and PP samples coloured with PR88 (Figure 6-2) where the shape of the reflectance curve between 650-800 nm closely resembles that of the uncoloured PP and CA.
Figure 6-2. Visible reflectance spectra of all unaged red samples (see Section 4.1 for more details about pigment types).
Figure 6-3. Visible reflectance spectra of all unaged yellow samples.
However, other factors will also have an influence. Due to different production methods, as outlined in Chapter 3, it was not possible to ensure the same concentration and distribution of the pigments within each polymer. Although the measured quantity of colourant was the same in both cases, due to the nature of the compounding and extrusion equipment in the case of PP, the final loading achieved is likely different from the measured quantity. Conversely, CA was prepared in a lab without the use of proper compounding equipment, which caused a much less even distribution of the colourant particles within the polymer matrix and some aggregates were formed. This is likely the reason for the significant decrease of reflectance at 638 nm for the CA sample of PR48:2 compared to the same pigment in PP (Figure 6-2). The pigment aggregates in CA can be clearly seen with the naked eye and most likely contributed to higher colour saturation of the sample. This makes the pigment difficult to visually distinguish from PR220 and PR166 whose spectra are more similar, with reflectance maxima at 630 and 623 nm respectively (Figure 6-2).

Another example of this phenomenon can be seen in the samples of PY35 (Figure 6-3). In this case, one would expect the PP sample to exhibit higher reflectance in the orange-red parts of the spectrum, however it is the other way around. This can be explained by the yellowing of the polymer itself due to the production method contributing to the darker, more saturated appearance of the PP sample. However, this issue is unlikely to be encountered in real museum objects since those would have been produced to a much higher standard of consistency. Figure 6-3 also demonstrates that it may be challenging to distinguish between two organic pigments belonging to the same family. Spectra of PY151 and PY154, both benzimidazolone Hansa yellows, are almost identical. Chemically these are also very similar, with the only difference being the substitution of fluorine in PY154 for a carboxylic acid group (COOH) in PY151. In those cases, a more invasive type of analysis might be necessary if the pigment needs to be specifically identified.

As discussed above, visual comparison of two visible spectra is not always easy or sufficient to determine whether the measurements are of the same material.
even after normalization. However, using derivative spectra it is possible to describe this type of data in more detail and, thus, simplify the process. Calculating derivative spectra is a standard method of improving data resolution, resolving combination bands and removing baseline shifts in reflectance spectroscopy [1].

First derivatives show the rate of change over wavelength calculated as:

$$\frac{dR}{d\lambda} = f'(\lambda)$$

where R is reflectance and \( \lambda \) is wavelength.

First order derivatives help to identify peaks as well as describe slopes either side of a reflectance curve. The latter can be done by identifying minima and maxima in a first derivative spectrum the locations of which correspond to inflection points\(^{25}\) in the raw data. The derivative value of an inflection point characterizes the slope of a peak in the original spectrum (Figure 6-4). Positive and negative signs indicate rising or falling slopes respectively, while their values reflect the sharpness of the slope, i.e. the higher the value the steeper the slope\(^{26}\).

\(^{25}\) A point of a curve at which it changes from being convex to concave or vice versa.

\(^{26}\) The opposite is true for negative slopes.
Figure 6-4. Visible reflectance [a] and corresponding first derivative spectrum [b] of PP with PR48:2 showing inflection points.

Summaries of derivative analysis for the samples are shown in Table 6-1 and Table 6-2. The pigments were combined into two groups with similar features. The reflectance curves of yellow, orange and red colourants have been described according to the wavelength at which reflectance begins, location of any peaks present, and the direction and sharpness of relevant slopes.
Table 6-1. Characteristics of the reflectance curves of the yellow, orange and red samples. (IP – inflection point)

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Type</th>
<th>Polymer</th>
<th>Reflectance Start $\lambda$</th>
<th>$\lambda$ of Max Reflectance</th>
<th>Left IP</th>
<th>Right IP</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\lambda$</td>
<td>Derivative Value</td>
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<tr>
<td></td>
<td></td>
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<td>515 nm</td>
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<td>577 nm</td>
<td>537 nm</td>
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</tr>
<tr>
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<td>603 nm</td>
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<td>Reflectance Valley $\lambda$</td>
<td>Left IP $\lambda$</td>
<td>Derivative Value</td>
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<td>---------</td>
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<td>-----------------</td>
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<td>N/A</td>
<td>0.0019</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>609 nm</td>
<td>N/A</td>
<td>591 nm</td>
<td>0.0007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N/A</td>
<td></td>
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<td>0.0020</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>N/A</td>
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<tr>
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<td>610 nm</td>
<td>N/A</td>
<td>595 nm</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>650 nm</td>
<td>0.0027</td>
</tr>
</tbody>
</table>
Conversely, measurements of blue and violet samples have characteristic reflectance bands on either side of the spectrum, with a valley in between where little or no reflectance occurs. The violet samples show additional small peaks in that area. For visible reflectance and relevant derivative plots for each sample see Appendix E.

The values presented in Tables 6-1 and 6-2 can be used to describe data and aid identification more accurately. By using derivatives and taking into consideration all of the spectral features mentioned above, the process is simplified, and a more objective match can be obtained. Naturally, the polymeric medium has to be taken into account since it can cause shifts in locations of certain features, as demonstrated in the tables. Additionally, the data presented here was derived from averages of five spectra, so including more data and error boundaries would improve the accuracy of this method. Further assessment of the applicability of visible reflectance data to pigment identification will be carried out in section 6.3 with the aid of Principle Component Analysis (PCA).

6.2 NIR spectroscopy for identification of polymers in plastics

Despite the complexity of NIR spectra and difficulty in band assignment to particular chemical groups, polymer types can be easily identified by comparison to a known reference. Figure 6-5 shows spectra of two polyurethane samples from a previous photodegradation experiment and clearly illustrates that each polymer type has a very distinct spectral fingerprint in the NIR region. In combination with visible reflectance in non-invasive instruments such as Fibre Optic Reflectance Spectroscopy (FORS), NIR spectroscopy can be a very useful tool for analyse of heritage plastics as it could simultaneously characterize both polymer and colourant. Chemometric techniques such as PCA could be utilized to create models which would make identification faster and less reliant on expertise and experience. The potential of the combined method for the purposes of plastics characterization in heritage will be explored in detail in the next section.
Figure 6-5. NIR reflectance spectra of two chemically different types of polyurethane foam.

6.3 Chemometric evaluation of Vis-NIR spectroscopy

Based on the above assessment, visible reflectance combined with NIR spectroscopy offers great potential for the identification of sensitive plastics formulations in museums, including both polymer type and colourant identification. Both types of analyses require very little, if any, contact and are very fast to perform (one measurement takes only a few seconds). By combining the two, one can obtain information about the colourants present and the base polymer. In addition, there is no need to carry out two separate analyses since instruments exist which combine the two. Fibre Optic Reflectance Spectroscopy (FORS) would be particularly useful in this case as it is portable, relatively inexpensive, and easy to use. By using a fibre optic probe to both emit and collect the light one can avoid any sampling of or even contact with the object. It also allows the analyst to carry out measurements on even the most irregular surfaces without compromising on data quality to an extent usually associated with similar techniques such as reflectance FTIR.
However, data interpretation methods would have to be developed in order to maximize the potential of Vis-NIR spectroscopy for plastics characterization in museums and make it more user-friendly. The next sections will discuss how PCA can help evaluate the suitability of the technique for the purpose of polymer and pigment identification, what kind of information one can extract from this sort of data and any pre-processing required for best results. As described in Chapter 3, PCA is a very effective data separation technique which can also be utilized to create models for material identification. Spectral data used in this section included coloured and uncoloured PP and CA after different stages of light ageing collected during Experiment 1 and 2.

6.3.1 Data pre-processing

All spectra were trimmed at either end to remove noise, so that each spectrum ranged from 400 to 2300 nm. The visible range was defined as 400-830 nm, while the NIR range was defined as 830-2300 nm as per colour measurement range recommended by CIE [2] and supported by most colorimetric equipment.

The most frequently used pre-processing method for NIR data is Standard Normal Variate (SNV) [3]. However, in terms of visible reflectance data, it is much more common to see derivatives as a way of improving interpretation. Therefore, in order to establish whether SNV would be better suited for visible data pre-processing than first order derivative, initial PCA was carried out on all visible reflectance spectra available, first without any processing (Figure 6-6), followed by derivatives (Figure 6-7) and, finally SNV spectra (Figure 6-8).
The main observation when comparing score plots of the first two PCs is that derivative spectra are sorted in a completely different way to the unprocessed and SNV normalized ones. While the derivative data appears to be well separated by hue, PC1 in the SNV analysis differentiates colours in a similar way to the y axis of the CIE 1931 chromaticity diagram (Figure 6-9) with the hues in the following order: yellow, orange, red, violet and blue. It also significantly improved data separation compared to PCA without any pre-processing. SNV normalization was, therefore, selected as the preferred pre-processing method for both visible and NIR data prior to PCA analysis.
Figure 6-7. PC1 versus PC2 scores of all the derivative visible reflectance spectra (aged and unaged).

Figure 6-8. PC1 versus PC2 scores of all the SNV normalized visible reflectance spectra (aged and unaged).
6.3.2 PCA of visible reflectance spectra

Average spectra of unaged samples of coloured PP were divided into two categories according to their main hue: yellow and red. PCA was performed on each of these categories to reveal which wavelengths were the most important for the identification of each pigment in PP. All data was prepared using methods outlined in Chapter 3 prior to PCA. Spectra of blue, orange and violet samples, as well as those in CA, were excluded from the PCA as too few examples of each of the colours were available to produce meaningful analysis. The following sections present the results of this analysis. The way in which this information can be used by practitioners will be discussed in section 6.5.

6.3.2.1 Yellow

In the case of yellow samples, PCA was carried out on seven average spectra containing 431 data points each. From Table 6-3 it can be observed that the first three PCs explain 98% of variance in the data, with the largest contribution coming from the first PC at 87.57%. By selecting only three principal components, the original data matrix of 7 spectra x 431 data points at 1 nm intervals, can be compressed to 7 spectra x 3 principal components in dimension, with the new matrix accounting for the majority of spectral variance.
Table 6-3. Variance and cumulative variance related to the first five PCs from the analysis of yellow samples.

<table>
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<th>Principal Component</th>
<th>Percentage of Variance (%)</th>
<th>Cumulative (%)</th>
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</thead>
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<tr>
<td>1</td>
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<td>87.57</td>
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<tr>
<td>2</td>
<td>6.93</td>
<td>94.50</td>
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<tr>
<td>3</td>
<td>3.56</td>
<td>98.06</td>
</tr>
<tr>
<td>4</td>
<td>1.18</td>
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</tr>
<tr>
<td>5</td>
<td>0.72</td>
<td>99.97</td>
</tr>
</tbody>
</table>

Scores corresponding to the first two PCs are reported in Figure 6-10 and it can be clearly seen that, for the most part, the data is very well separated. The only exceptions are PY14 and PY151 which score closely on both PC1 and 2. Examination of loadings for PC1 (Figure 6-11) reveals that the pattern closely resembles that of the example reflectance spectrum. This component divides the spectra into two main sections: 480-650 nm and 650-830 nm. In the first instance, the spectra are scored on the overall intensity of reflectance within that range, with the most significant wavelength being approximately 522 nm. The second range corresponds to the direction and angle of the reflectance slope above 650 nm, with increasing slopes receiving negative scores and vice versa.

The second component further divides the spectra into three sections: 470-550 nm, 550-750 nm, and 750-830 nm. The most important wavelengths for data separation and, therefore pigment identification, are 520 and 580 nm which give opposite sign scores. This suggests that PC2 is primarily related to where in the yellow part of the visible spectrum the reflectance starts and how steep the left slope of the curve is. This essentially amounts to how sharp/broad the dominant reflectance band is. However, this only helps to distinguish PY42, PY35 and PY154 as all the other pigments score very closely on the PC2 axis.
Figure 6-10. Score plot relating to PC1 and PC2 calculated from seven spectra of yellow PP samples.
Figure 6-11. Loadings for the first three PCs plotted against wavelength for yellow PP samples. Bottom plot shows normalized reflectance.
PC3 is better able to distinguish between PY14 and PY151 (Figure 6-12), which score -1.8 and 2.2 respectively. It also divides the pigments into two very distinct groups according to where the reflectance starts, the sharpness of the left slope and the overall intensity between 505 and 540 nm. However, pigments within each group, with the exception of PY154, received very similar scores on the PC3 axis and can only be further distinguished if plotted against PC1 scores. In fact, one could dispense with PC2 entirely and only use the first and third components to distinguish between the seven sample pigments, thus reducing the data matrix further by one dimension.

Figure 6-12. Scores relating to PC1 and PC3 calculated from seven spectra of yellow PP samples.
6.3.2.2 Red

The red category of PCA samples contained four different spectra and, in this case, only two PCs were needed to cover over 99% of variance in the data, with PC1 accounting for 90%.

Table 6-4. Variance and cumulative variance related to the first three PCs from the analysis of red PP samples.

<table>
<thead>
<tr>
<th>Principal Component</th>
<th>Percentage of Variance (%)</th>
<th>Cumulative (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90.64</td>
<td>90.65</td>
</tr>
<tr>
<td>2</td>
<td>8.71</td>
<td>99.36</td>
</tr>
<tr>
<td>3</td>
<td>0.64</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 6-13. Scores related to PC1 and PC2 calculated from four spectra of red PP samples.
Although the first component covers a vast majority of the spectral variance, it still fails to differentiate between PR220 and PR166, which received very similar scores of -5.39 and -5.63 respectively (Figure 6-13). This axis discriminates spectra mainly according to their reflectance intensity at 615 nm: the more intense the peak, the lower the score. In addition, the characteristics of the slope above 700 nm are taken into consideration. For instance, PR88 has the lowest reflectance between 570 and 700 nm and an increasing slope above 700 nm, and, therefore, can be seen in the lower right corner of the score plot. This is in contrast to the remaining samples whose behaviour is opposite and thus they appear on the negative side of the PC1 axis.

In order to fully differentiate the red samples, it is necessary to calculate the second PC, which identifies three crucial regions of the visible spectrum (in order of importance): 555-615 nm, 615-750 nm, and 750-830 nm (Figure 6-14). The wavelength with the highest loading for PC2 is 590 nm, followed by 640 nm. This component appears to consider the start of the reflectance curve, the intensity around 590 nm and the direction of the slope above 615 nm. Therefore, it is able to better distinguish between PR166 and PR220.
6.3.3 PCA of NIR spectra

NIR spectroscopy has already been shown to be an easy and effective non-destructive method for identification of historic plastics. However, some signal from additives, including colourants might be included in the data as well. Visual inspection of NIR spectra of only PP samples (Figure 6-15) revealed that the area between 830 and 1000 nm is the only one showing clear variability. Above 1000 nm the spectra only differ in intensity with no discernible pattern. PCA was used
to more accurately establish whether any NIR wavelength ranges could be used to add extra information regarding possible pigments present and thus characterize a particular plastic sample with respect to the base polymer and additives.

**Figure 6-15. NIR reflectance spectra of all PP samples (831-2300 nm, SNV normalized).**

PCA was first applied to spectra of coloured PP and CA samples where the same pigment was present in each polymer (PY35, PO13, PR48:2, PR88 PB29 and PV23). The first three PCs explain 97.6% of variance in the supplied data (68.4%, 29.6% and 2.7% respectively). The scores show that PC1 clearly differentiates between the two polymer types (Figure 6-16), with samples belonging to the CA group scoring positively on the PC1 axis and those belonging to the PP group scoring negatively. There is also more variation within the PP group of samples than those containing CA. This could once again be related to the production method of each material and the fact that PP samples have a certain varied level of oxidation obtained during processing, whereas the CA samples are much more homogenous. The second PC discriminates data according to pigment type, although it can be observed that scores for samples made with PP are shifted
slightly to more negative/smaller values compared to CA samples of the same pigment, with the exception of PR88.

Figure 6-16. Score plot of the first two PCs from the analysis of pigments present in both PP and CA samples.

Since the second PC appears to be more efficacious for pigment identification, the most important conclusion from the loadings plot (Figure 6-17) is that PC2 places the most significance on wavelengths below 1040 nm. This means that, in order to get the best results when using visible reflectance spectroscopy to identify pigments, it would be beneficial to extend the range to 1040 nm if possible. The loadings for PC1 show the areas most important for distinguishing between the two polymers, while there are no clearly discernible patterns within scores and loadings for PC3 (it likely only looks at the two polymers in more detail).
The next step was to carry out PCA on each polymer group separately to allow for a more detailed analysis of the NIR range data. This time all the pigmented and unpigmented samples for each polymer were included.

6.3.3.1 Polypropylene
Loadings plot for the PP group above 1450 nm (Figure 6-18) largely resembles the shape of the NIR spectrum and the loadings clearly correspond to reflectance intensities with peaks getting positive values and troughs getting negative ones. Additionally, below 1450 nm the loadings increase with decreasing wavelength. The spectra are thus divided into two main areas at the 1450 nm mark, where the total reflectance of the left side of the spectra is inversely related to the intensity of the broad bands between 1450-1685 nm and 1830-2250 nm. The second component separates the data mainly according to the intensity of reflectance below 1050 nm. In this range the data is scored positively if the reflectance
increases with decreasing wavelength and less positively if it decreases. The remaining range reflects the shape of the spectrum subdivided into two areas at the 1800 nm mark, with the wavelengths below obtaining negative values and those above positive ones.

![Figure 6.18. Loadings plot for PC1 and PC2 obtained from the PP group data. Bottom plot shows an example SNV normalized NIR spectrum.](image)

### 6.3.3.2 Cellulose acetate

PCA of CA samples also revealed that the most important wavelength range for data separation lies below 1050 nm, although in this case, due to the previously mentioned homogeneity of the samples, the broadest variation lay in the different pigments included, and was, therefore, picked up by the first PC. The remainder of the PC1 loadings plot resembles the NIR spectrum with the second most important range being 1050-1650 nm. The area between 830 and 1050 nm differentiates the spectra according to the direction and steepness of the reflectance slope, i.e. the steeper the slope with the wavelength increasing, the
lower the score. PC2 further divides the area below 1050 nm into two subsections at the 927 nm mark. The left side has loadings increasing with decreasing wavelength, while the right side behaves in an opposite way. This corresponds to two small reflectance peaks found at approximately 900 and 960 nm and their intensity relative to each other. The rest of the axis appears to mainly distinguish the data according to peaks and troughs found above 1325 nm, while between 1050 and 1325 nm the loadings correspond to overall intensity. Finally, PC3 divides the data into two main areas: 1125-1640 nm, which looks at two broad bands and associated troughs in that range, and above 1640 nm with values above 2215 nm receiving negative loadings with increased reflectance.

![Figure 6-19. Loadings plot for the first three PC obtained from the CA group data. The bottom plot shows and example spectrum of uncoloured CA with DEP plasticizer.](image-url)
6.3.4 PCA of extended visible reflectance spectra

Following the results of PCA on NIR spectra for each individual polymer, the visible range was extended by including wavelengths from 400 to 1050 nm for yellow PP samples from the original SNV normalized spectra. PCA was then carried out again to assess whether that would improve data interpretation. In this case, the first three PCs calculated explained a total of 98.4% of variance. The score plot of the first two PCs (Figure 6-20) clearly shows that much better data separation can be achieved by including longer wavelengths in the analysis. This is particularly the case with the pairs: PY151/PY14, and PY95/PY83 which plotted much closer together on the PC2 axis when the visible boundary was defined as 830 nm (Figure 6-10).

![Figure 6-20. Score plot of PC1 versus PC2 calculated from extended visible reflectance spectra (400-1050 nm).](image_url)

A closer examination of the loadings revealed that PC1 divides the extended visible reflectance spectra into two portions at approximately 860 nm. The most important region relates to the intensity of reflectance at 528 nm, which
corresponds to the main reflectance peak as well as the sharpness of its left slope in the raw data. The remaining loadings (i.e., above 860 nm) decrease steadily with increasing wavelength. PC2 on the other hand, identifies two main areas of the spectra, which fall on either side of 565 nm. Slightly more significance is given to the area between 470-565 nm. Referring back to derivative data (Table 6-1) suggests that this could be related to the sharpness of the left slope in the main reflectance curve. The area above 565 nm appears to be inversely related to the one below it, with the intensity of reflectance around 750 nm receiving the highest loadings.

Finally, the third PC focuses on two areas: 500-650 nm and \( \lambda > 770 \) nm. The first range is further subdivided at 553 nm into two inversely related sections. The one to the left of the 553 nm mark, with a peak at 525 nm, received more significant loadings than the one to the right, with a peak at 577 nm. Once again it could be inferred from the derivative data that those two peak locations could be describing the sharpness and direction of the slopes found in the original spectra.

![Figure 6-21. Loadings plots for PC3, PC2 and PC1 of all unaged visible reflectance spectra of yellow samples. The bottom plot shows an example spectrum.](image)
6.3.5  Effect of ageing on PCA results

Since all previous analysis focused on unaged samples, it was important to also explore the effect light ageing might have on the colour of the samples and, thus, PCA results. As a preliminary exploration, average measurements of the same yellow PP samples taken after different types of light exposure were subjected to PCA alongside their unaged equivalents. As may be expected, the score plot shows differences between aged and unaged samples (Figure 6-22), the degree of which varies between different pigments. However, for the most part they do cluster together and different pigments can be distinguished between regardless of whether they had aged. The greatest variance can be seen in samples that experienced a high dose of UV radiation. However, closer examination of the PCA loadings and the raw data, demonstrates that the variance is mostly related to changes of intensity of the entire spectrum, i.e. a shift in baseline which is not corrected by SNV.

Figure 6-22. Score plot of PC1 versus PC2 obtained from PCA of yellow PP spectra in the extended visible range (400-1050 nm) from Experiment 1 and 2.
Furthermore, adding the NIR range to the PCA analysis together with the visible did not improve data separation of aged samples.

While more research is necessary to create useful identification models, this short study has shown that pigment identification using PCA of visible-NIR reflectance data with the right combination of normalization techniques such as min/max, derivatives and SNV is feasible even after ageing. Ability to non-invasively and quickly identify both polymer and colourant present in a plastic object, regardless of its level of ageing would be immensely valuable to the conservation community and is definitely worth exploring further.

### 6.4 Other analytical techniques

Several other techniques have been more widely used for the purpose of pigment identification in other materials and as complementary analysis in studies of visible reflectance spectroscopy. Each of these techniques was tested throughout the duration of this work in terms of their suitability for plastics characterisation. It is, therefore, worth briefly discussing their advantages as well as shortcomings, since they are often the only methods available to a museum conservator or scientist.

#### 6.4.1 Raman spectroscopy

An investigation of various laser wavelengths on known plastic samples revealed that, although Raman can be used to identify some pigments in plastics, there is no one size fits all solution and various laser wavelengths work better or worse for different pigment/polymer combinations (not necessarily related to colour). Additionally, the concentration of pigment in a plastic is usually lower than 1%, which means that the polymer signal still dominates in some Raman spectra. However, there is less overlap between the pigment and polymer bands compared to FTIR spectroscopy and some pigments can be identified even with the use of a low-resolution handheld instrument. For instance, PO13 can be easily identified in PP using just four characteristic bands at 1600, 1560, 1530 and 1285 cm\(^{-1}\) which do not overlap with the polymer signal (Figure 6-23). Those same
bands can also be seen in a spectrum obtained using a handheld instrument (Figure 6-24).

Figure 6-23. Raman spectrum of PP with PO13 (top) against a reference spectrum of PO13 (bottom) showing distinctive peaks due to the pigment in the plastic sample.

Figure 6-24. Raman spectrum of PP with PO13 sample obtained with a handheld instrument (red) against a reference spectrum of pure PP collected with a benchtop instrument. The characteristic pigment peaks can be seen at 1600, 1560 and 1285 cm⁻¹.
6.4.2 XRF spectroscopy

The usability of XRF for characterisation of plastics was tested by analysing a number of samples of unknown composition. The results are summarized in Table 6-5 and were, for the most part, inconclusive. Most of the elements detected could not be assigned to known inorganic pigments, which suggests that the colourants used were indeed organic. Furthermore, data interpretation can be complicated by other additives present, such as stabilizers, which can contain barium, cadmium or lead salts, or fillers, such as barium sulphite or calcium carbonate [4]. As can be seen from Table 6-5, titanium was detected in 10 out of 17 samples analysed indicating the presence of titanium white pigment, which is also often used as a UV absorber, extender and opacifier. However, it is impossible to identify with this technique whether it is present in its anatase or rutile form, which is important since uncoated anatase is a known photocatalyst [5]–[7].

Although unambiguous pigment identification in a plastic using XRF is not possible in most cases, it can still be very useful when combined with other techniques, especially as it is non-invasive and can be portable. XRF could help to distinguish between different organic pigments based on metal salts or containing metal ions within their structure (e.g., copper in copper phthalocyanine pigments).
Table 6-5. Results of XRF analysis of unknown composition plastic samples. Element quantities in ppm (LOD – limit of detection).

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### 6.5 Discussion

Regardless of its limitations, visible reflectance would be very valuable for plastics characterisation, particularly if combined with NIR spectroscopy and chemometric methods. The ability to identify the two most important components of a plastic in terms of light sensitivity: colourant (visible) and the polymer (NIR), simultaneously and non-destructively would be of great value to the field.

Sample spectra used for the above evaluation were not produced with a goal of creating a reference library, therefore a much higher variation of the data can be expected when real objects are analysed. However, owing to the large quantity of data collected it is still possible to draw some useful conclusions. PCA showed that many pigments, organic and inorganic, can be identified from their visible reflectance spectra when compared to known references and the right normalization techniques are applied.

To create a good identification model, a set of samples produced in a way that simulates real industrial processes would be ideal. Unfortunately, the model would then be limited to the number of plastics formulations it was feasible to create. An even better and faster approach would be to collect reflectance spectra of pure pigments used in plastics production and establish the influence of concentration, pure polymer colour and ageing mathematically to obtain a predicted spectrum. A complete toolkit could be created to identify polymer, colourant and possibly even some additives by using a non-destructive vis-NIR reflectance technique such as FORS. A number of already created and freely-available databases could be used to help build and validate the model. Ideally, one would first use the NIR spectrum to identify the polymer type (and possibly some additives or any ageing). The next step would involve using PCA to extract any NIR data not resulting from polymer absorption and adding it to the visible reflectance spectrum which should be modified to again take into account the effect of the polymer, concentration and ageing if possible. Finally, the model spectrum would be compared against a subset of the reference library of relevant pigment spectra. The subset would be selected based on the colour of the object.
and what is known of the plastic (i.e., polymer type and date of production, if known, as that will narrow down the list of possible matches even further).

6.6 Bibliography


Chapter 7

Development of an online application for assessment of light stability of museum plastics

A broad survey of conservation professionals was carried out to better understand the needs of the sector in terms of plastics preservation knowledge. In addition, a workshop was delivered to a group of conservators and conservation scientists from major heritage institutions holding plastics collections. The information obtained helped in directing the development of an online tool providing state of the art knowledge on light stability of coloured plastics.

7.1 Plastics Survey Project

The survey project was originally initiated and managed by the author before being handed over to a fellow PhD student as a means of investigating how the traditional museum acquisition process influences the challenges conservators face when dealing with their plastics collections, specifically related to lack of
material knowledge. However, a broader potential was identified within UCL’s Institute for Sustainable Heritage (ISH) Plastics Research Group to find answers to both general and more specific questions relevant to topics already being studied. Therefore, the scope was extended to include questions relating to conservation challenges, identification methods, symptoms and signs of degradation as well as expertise and access to relevant knowledge. The author’s contribution was in creating the first drafts of the survey questions, leading of the initial meetings and project direction as well as dissemination. The project lead was later taken over by another PhD student who revised the questions, uploaded the survey to live and prepared a separate publication based on the results. The information presented in this chapter is based on analysis by the author of the raw data obtained from the survey with a specific focus on questions relevant to the topic of this thesis.

The finalized online survey contained a total of 44 questions and was available to complete between 25th April and 31st August 2019. It was promoted via the ISH professional network, Institute of Conservation (ICON), and during the Plastic Heritage Congress Lisbon 2019 (Figure 7-1).

Figure 7-1. Part of the leaflet distributed to heritage professionals promoting the survey.
The survey was filled out by 84 participants, out of whom 60 were conservators, 15 conservation scientists and 10 curators\textsuperscript{27} with a broad range of experience working with plastics collections from 1 to 45 years. Although the survey did not specifically collect identifiable data regarding the institutions partaking, there was a good mixture of organizations holding various sizes of plastics collections from all over the world (Figure 7-2).

Out of 73 responses to a question asking the respondent to rate their level of concern regarding their plastics collection, only 4 participants were not concerned (Figure 7-2).

![Figure 7-2. Survey results showing the proportion of plastics relative to the rest of the collection in the participants' institutions and level of concern for plastic artefacts.](image)

Concerns raised in the free text follow-up question varied, however, as can be seen from Figure 7-3, they most often related to storage as well as degradation generally and more specifically its speed and signs. Lack of knowledge and understanding were also on the forefront which correlates well with the state of the art in plastics conservation and inadequate guidelines discussed in Chapters 1 and 2 of this thesis. Shortage of various resources, such as staff, time and budget combined with a large number of plastic objects and difficulties with

\textsuperscript{27} One respondent marked both curator and conservation scientist fields.
identification also appear to be common. In fact, in most cases only portions of the collection have been already identified (Figure 7-4).

Figure 7-3. Word cloud of answers to question 12 of the survey relating to concerns surrounding plastics.

Figure 7-4. Proportion of plastics already identified within collections.

These results further confirm that heritage institutions struggle with managing their plastics collections as they often do not know what types of plastics they hold. Combined with lack of resources such as time and expertise on top of difficulty in accessing relevant data or knowledge, plastics conservation poses a major challenge to the heritage sector. While this project has already ensured to
address particular needs of the conservation community through the review of literature from the relevant point of view as well as light-degradation studies to answer heritage specific questions, there appears to be a strong demand for better sharing of such knowledge. The first step in addressing this was to deliver a free workshop for heritage professionals dealing with plastics collections in order to share this research as well as gather feedback regarding a proposal for an online tool.

7.2 Plastics Workshop

A workshop for conservators and conservation scientists involved with plastics collections was co-organized by the author with the help of a fellow PhD researcher. It was hosted at UCL on 27th Jul 2019 and attended by 14 heritage professionals from the following institutions: Tate, British Museum, British Library, Science Museum, V&A, National Trust, Museum of London, Wellcome Collection and Museum of Design in Plastics. The group included both conservators and conservation scientists of varied levels of plastics expertise. In addition, the organizations represented hold diverse plastics collections of different sizes and including artwork, toys, design objects, furniture, homeware and scientific equipment among others.

The event opened with presentations of research carried out by the facilitators and state of the art in each specific field, followed by a general discussion guided by these questions:

1. How do you think the perception of plastics, within the heritage community, has evolved over the past 10-15 years?
2. Do you think as a community we are doing enough to preserve plastic objects?
3. Is lack of information regarding treatments or analysis methods hampering your work with plastics?
4. If you could know more about one aspect of plastic artworks, what would that be?
5. How much time do you have to identify the type of plastic within an object?

The ensuing debate began with an assertion of the complexity of plastics as materials and how the role of composition and manufacturing methods in stability has only recently began to be appreciated. It was also agreed that the use of the generic term ‘plastics’ within the conservation sphere is not adequate. The attendees touched upon the topic of acquisition and lack of detailed knowledge on materials composing objects being brought into collections. Often artists are not fully aware of the stability or composition of the materials they use which creates challenges for conservators. The biggest challenge identified by the participants was identification. Question 4 was designed to flag up the most important needs of the heritage sector from the perspective of plastics preservation that could be addressed through research. Most participants agreed that best storage practices for managing complex and mixed collections with limited resources, lifetime predictions and slowing down of degradation should be prioritized. Finally, the group was unanimous in admitting they have very little time to devote to plastics identification due to other priorities and limited resources. In fact, smaller institutions do not have access to analytical equipment and must rely on various academic collaborations which limits the process even further.

The attendees were also asked to fill out a short questionnaire to capture more specific answers about issues of particular interest to each facilitator. Questions relevant to this thesis are listed below:

1. How is the light stability of plastic objects currently assessed in your institution? (e.g., during the acquisition process, condition surveys or prior to display)
2. What guidelines or materials, if any, do you use to inform those decisions?
3. Do you think you have sufficient knowledge or information on light stability of plastics, or access to such, to assess objects in your collection?
4. Are there any challenges involved in making these assessments? If ‘yes’, what are they?
5. What would be helpful in overcoming these challenges?
6. Are you aware of light-damaged plastic objects in your collection? What is needed?

It is important to note that the 14 participants represented 9 different institutions, therefore some answers refer to the same organisation. However, due to the anonymous nature of the questionnaire it was impossible to distinguish them and remove duplicates. Nevertheless, the information obtained still gives a useful picture of the realities and challenges of conservation practice.

In terms of current practice of light stability assessment (Q1) it is most consistently done before display or loan (Figure 7-5). The acquisition process was also identified as the ideal time to identify risks to light stability with an implication that it is not always the case for some institutions. This was particularly interesting considering previously raised concerns regarding material knowledge and identification. The following quotes shed more light on the process and confirm that, due to lack of data, plastics as a group are treated as light sensitive.

‘*We recommend a blanket display requirement of max 80 lux.*’

‘*…all plastics are treated as sensitive organic materials and displayed at 50-200 lux. Some plastics are however on permanent display.*’

‘*…the range of plastics and their different reactions dependent upon unknowns (such as plasticizers and other additives used) makes predicting the light stability of the object tricky…*’

Unsurprisingly, the main resources for knowledge of the subject are official museum guidelines and standards (e.g., the BSI PAS198 standard was specifically mentioned), conservation literature and experience and expertise of colleagues. Despite that, when asked if they believe their knowledge of plastic light stability
is sufficient, 12 out of 14 participants replied ‘No’ and only 1 responded with a ‘Yes’.

The main challenges to making an informed judgement were identified as:

- Lack of resources (such as staff expertise and time) (8 responses)
- Lack of data and information (6 responses)
- Collection size and need to prioritize (5 responses)
- Material composition (4 responses)

Other important factors mentioned were ambiguous guidelines and not knowing about the previous life of an object.

Figure 7-5. Current process for assessment of light stability of a plastic object.
There was a clear need for more knowledge and easily digestible information to help conservators deal with materials as complex as plastics. Clear guidelines, more widely available resources and academic collaborations were amongst the most listed as solutions to overcoming the challenges named above. With an emphasis on ease of use and availability, online tools and frameworks as well as pragmatic approaches were also mentioned.

‘Plastics are some of the objects that we have the least information regarding their light stabilities. Any new information, publications would be very useful.’

‘Not enough information available to make informed decisions on lighting. As a result, we tend to adopt a cautious approach, lighting plastics at low level. This is a challenge because we are potentially not getting the best out of our collections or creating the best visitor experience. Some plastic objects would have a bigger impact if brightly lit…’

‘Clarity of guidance is helpful - to give a reason/purpose in undertaking assessments - because they are costly/time consuming for such a large collection i.e., if we know that certain plastics are more vulnerable as a result of new research then we can more easily justify a project to assess plastics.’
'More online tools/easily accessible equipment and software.'

'Some sort of risk management tool or framework for understanding and managing light exposure.'

These insights further corroborated the author's opinion that research carried out as part of this thesis should be more widely shared. The workshop ended with a presentation of a proposed software application which would not only make available a database of all current research on light stability of pigmented plastics collected as part of this project but also help conservators assess plastic objects in their collection by looking at their colour. After viewing mock-ups of the application, the participants were asked to vote using a free online tool to provide feedback which is presented in Figure 7-7. The results show an overall very positive reception of the proposal with every participant believing it would be at least somewhat helpful in their job and seeing potential in further expanding the scope of the app to include more and different types of data. 66.7% of respondents preferred an online application to a desktop or mobile version, however some expressed concern over usability in storage areas where Internet connectivity is not ideal.
Figure 7-7. Results of a short online survey on the proposed application.

1. How useful would such an app be in helping you assess light stability of plastics?
   - Very helpful: 46.2%
   - Helpful: 23.1%
   - Somewhat helpful: 30.8%
   - Not helpful: 0%

2. What would be the best format for the application?
   (you can select multiple answers)
   - Online: 66.7%
   - Desktop: 33.3%
   - Mobile: 16.7%
   - Tablet: 16.7%

3. Would it be useful to be able to add your own data?
   - Yes: 66.7%
   - No: 33.3%

4. Would it be worthwhile expanding the application into an online platform for plastics conservation including other data such as plasticizer loss, data from accelerated ageing experiments, etc.?
   - Yes: 100.0%
   - No: 0%
7.3 P/LIGHT Application

Based on feedback from the workshop as well as results of the survey and general knowledge of the field a web application was developed to help conservators in assessing light sensitivity of plastic objects in their collection (Figure 7-8). The app can be accessed via www.plight.online and brings together data collected in the literature review from Chapter 3 as well as results of Experiments 1 and 2. To make the process even simpler and faster, the app allows a conservator to filter the data by polymer type, object colour and date of production (if known).

![P/Light application home page](image)

**Figure 7-8. P/LIGHT application home page.**

Each pigment record contains information about its chemical structure, general properties, polymer compatibility and its effect on plastics’ stability to light exposure (Figure 7-9). For transparency, every entry regarding sensitivity is provided with a reference to the relevant study with a short summary of the most important methods used (Figure 7-10). The database currently only contains details of pigmented plastics; however, it could be extended to include information on stability of uncoloured polymers as well as general resources on photodegradation that would be of interest to conservators and other heritage professionals.
Figure 7-9. Pigment details page.

### Properties:
Very high molecular weight. Good to excellent light, weather, solvent bleed, chemical attack and heat resistance. Excellent light and solvent fastness; good heat resistance. Expensive to produce.

### Effect on polymer:
- Stabilizing factor of 12 without stabilizer, 0.52 with 0.75% Tinuvin 770 (HALS stabilizer).  

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**Reference**


**Experiment Details**
Chamber T = 27°C. Stabilizing effect of each HALS/pigment formulation was defined as ‘protection factor’ - calculated by comparing the half-value radiation energies of the pigmented/stabilized samples and a reference (unstabilized and uncoloured).

**Analysis**
Breaking tenacity test. Colour measurements using a T vs coordinate system.

**Exposure Details**
Radiation - UV-Vis 340-700 nm. Light chamber - Weatherometer 600.

Back to Pigment
7.4 Discussion

Data obtained from a wide international survey of heritage professionals as well as the information gained from a workshop delivered to conservators and conservation scientists responsible for the most prominent plastics collections in the UK points emphatically to a general lack of knowledge. This pertains both to degradation processes and signs as well as guidelines on how to prevent or slow down deterioration of plastics. Limited budgets, staff and time combined with large numbers of objects also contribute to conservators’ insufficient understanding of their own collections. This project addressed all of these issues not only by providing new data on light stability of two common polymers but also making that data easily available in simple format on a free web application.
Chapter 8

Conclusions

Despite their relatively short history synthetic and semi synthetic materials have very quickly penetrated every facet of modern society. The incredible versatility of plastics has enabled artists and designers to express their creativity like never before. Even everyday objects are fast becoming heritage due to the way they have completely transformed how we live our lives. Plastics have become ubiquitous; however, our knowledge of their longevity is still lacking, particularly with regards to the stability of plastic artefacts in museums. This especially applies to their relationship with visible light as opposed to UV radiation so often used in accelerated degradation tests. This lack of evidence leads to missing or vague display guidelines for plastics in collections. This project looked at the effect of visible light on plastic artefacts in the context of a museum environment. The main goal was to identify components in plastics formulations that could increase sensitivity of the material to visible light as well as find methods of easily identifying those sensitive plastics formulations in museum collections.

Since very few studies investigated the effect of colourants on the base polymer without the use of UV radiation, a different approach to the assessment of light-stability of plastic objects in a heritage context is needed. As discussed in Chapter 2, there are many factors determining the stability of a polymer to light, therefore, the goal of this thesis was to prioritize them and focus on the ones which exert the strongest influence. An in-depth literature review on plastics photodegradation revealed five main light stability ‘influencers’:
These factors were then used to guide this project in order to fill gaps in research relevant to heritage as well as provide a pragmatic approach to assessment of light stability of plastics.

The effect of colourants as well as chromophoric impurities on PP and CA was investigated in the first study (Chapter 4). The history of an object and possible previous UV exposure, a variable uniquely important to the conservation community, was explored in Chapter 5.

Results presented in Chapter 4 proved that all 14 of the tested pigments, 8 of which had never been studied from that perspective before, can accelerate photodegradation of PP even when only visible radiation is used. While the intensity of sensitizing action of each colourant varied, the most sensitizing pigments were PV23, PR48:2, PY154 and PO13. The six colourants whose photosensitising action had previously been investigated under UV radiation, were also shown to be sensitizing under visible light. In addition, samples containing PO13 were most susceptible to colour change across both polymers, reaching ΔE_{2000} values ranging between 2.99 ± 0.09 and 6.85 ± 0.36. However, considering that the total light dose corresponds to 270 years on museum display at 200 lx, this amount of colour change still falls within acceptable levels of 7.5 ΔE_{2000} units as defined by the V&A policy. The only pigment to exceed that limit
was PY14 in PP which experienced colour change of $9.23 \pm 0.06$ and $10.15 \pm 0.14 \Delta E_{2000}$ units.

Nevertheless, these chemical reactions do not proceed at a rate fast enough to cause substantial damage to the material within timeframes significant to heritage institutions. Therefore, one might be tempted to conclude that even extensive visible light exposure is not harmful to plastics. However, one objection that can be raised as to the relevance of Experiment 1 is that it was carried out on new samples with very limited number of additives. This kind of approach reduces the potential number of energy absorption and/or transfer channels and, therefore, resulting chemical reactions. It is unsurprising that one of the main criticisms conservation professionals raise towards results of scientific studies is that the objects in their collections are rarely new. In fact, the most unstable early plastics will have been acquisitioned after having been exposed to any combination of various environmental and storage conditions, as well as handling and physical stresses, which are largely unknown and not easy to quantify. Thus, stability predictions based on scientific research, where variables are intentionally limited and strictly controlled, can be seen as lacking and even unreliable from the conservation perspective. This is particularly true of materials as complex as plastics, where degradation is not always visibly obvious or even homogenous. Furthermore, assessing the real state of a plastic object, often composed of more than one type of polymer, analytically is not only time-consuming and, usually, destructive but requires knowledge and expertise that might not be readily available within heritage institutions. Therefore, the focus of Experiment 2 was previous UV exposure. Two different pre-treatment doses of simulated daylight through window glass (> 320 nm) were followed by visible light ageing of a smaller subset of coloured and uncoloured PP and CA samples. Examination of FTIR data revealed that higher UV exposure stimulated the production of sufficient amounts of hydroxyl groups which, in turn, allowed photodegradation reactions to continue under visible light. A threshold value of 9 a. u. calculated as the area of the hydroxyl band was identified as a simple means of screening for potentially light-sensitive plastics in collections. Since FTIR is one of the most commonly found analytical methods in heritage institutions and is
non-destructive it would allow many institutions to easily identify sensitive artefacts. No similar methods have previously been proposed.

Moreover, carbonyl index was shown to be inadequate as a metric for quantification of photooxidation in PP as other peaks corresponding to the formation of carbonyl groups were detected by FTIR. In order to capture those additional peaks and account for their varied behaviour between samples, a ratio of the area between 1800 and 1500 cm\(^{-1}\) normalized by the reference band at 2915 cm\(^{-1}\) is recommended instead. Additionally, the peak around 1017 cm\(^{-1}\) corresponding to the formation of C-O bonds in ester and carboxylic acid products has also been shown to increase on degradation.

A strong impact of ageing temperature on PP was also noted across both experiments. Even small differences between average values were able to accelerate degradation of coloured samples in particular. In fact, an increase of 1.9 °C combined with an extra 20 Wh/cm\(^2\) of visible light exposure produced a higher amount of carbonyl groups than inclusion of a high dose of UV pre-treatment in samples containing PO13.

CA, the other hand, demonstrated higher light stability than was expected bearing in mind that it is counted amongst the most unstable heritage plastics. No changes relating to the reduction in degree of substitution, oxidation or loss of plasticizer were detected by FTIR with and without the use of UV. Even average temperatures above 25 °C did not affect CA in the same way as PP. This is important as CA would normally be considered sensitive and displayed at low light levels. However, the polymer samples used in these studies were new and created in a lab, therefore not subjected to typical manufacturing methods where higher temperatures and shear force would have been used. Furthermore, CA is known to be particularly sensitive to moisture and temperatures and to naturally degrade over time. It would be beneficial to perform similar tests as in Experiments 1 and 2 on either naturally or artificially aged samples. In the case of accelerated thermal ageing, if those samples were found to be more light sensitive, it might be possible to determine a level of degree of substitution at
which CA becomes susceptible to photodegradation in a similar way as was done in Chapter 5 for PP. This would allow conservators to identify potentially photosensitive CA plastics in their collections. On the other hand, if light was shown to not be a contributing factor to CA degradation, museum guidelines for this polymer could be updated and allow for display of CA objects at higher light levels.

Based on the results of the two photodegradation studies a new hierarchy of light stability ‘influencers’ was proposed:

- Polymer type
- Colourant
- Temperature
- Amount of previous UV exposure/degradation products
- Chromophoric groups from thermal degradation
- Light stabilizers

This list can be used by conservators and researchers alike for assessing photo-stability of plastics in collections either as part of the conservation process or for planning of experiments.

In order to take advantage of the data and methods presented in this thesis, it is essential to be able to identify the ‘influencers’ present in a plastic objects. However, full characterization of museum artefacts is not only very difficult but also impractical, as was shown by the responses to the online survey of museum professionals. Furthermore, identification of other photodegradation ‘influencers’, such as processing impurities and light stabilizers would be even more challenging, if not impossible, under conservation restraints. However, identifying sensitive materials by focusing on pigment/polymer formulations will allow conservators to visually assess plastic objects since the colour of a pigment could provide a significant clue towards its light stability. The online application developed as part of this project will further help with that by providing easy access to the current knowledge on the subject and could be further extended to provide more information on plastics stability and
conservation as well as a means of communication and sharing of expertise for the heritage community.

Exploration of common analytical techniques for identification of pigments in heritage objects presented in Chapter 6 showed that visible reflectance spectra can be used in conjunction with PCA to distinguish between pigments of the same colour even after ageing. Visible reflectance spectrometers are often combined with NIR which has been effectively used for polymer identification. In addition, many Vis-NIR instruments employ fibre optic non-contact technology, are fast and relatively easy to use, which makes them ideal for screening of light sensitive plastics in museum collections. Future work could focus on creating identification models using visible reflectance and NIR data combined with PCA to make the process automated and not requiring scientific knowledge to interpret the results.

Finally, current trends in lighting for museum and gallery spaces include the use of LED technology combined with UV-filtered natural daylight. As heritage institutions in the UK come under increasing pressure from the government to reduce their carbon footprint, this strategy falls right within the sustainability guidelines. However, LEDs have not been used much in accelerated degradation studies to date and would definitely benefit from in-depth research. This is particularly important as they are likely to be the prevalent light source in the years to come and the potential of tuning them for a particular application could provide considerable benefits to the heritage sector. It is, therefore, strongly recommended that any future accelerated ageing studies use LED lamps emitting in the visible range only.
Appendices
## Appendix A

### Additional data for Chapter 1

**Table A-1. Common additives used in plastic materials [1], [2].**

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<thead>
<tr>
<th>Additive Type</th>
<th>Main Role</th>
<th>Common Examples</th>
</tr>
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<tbody>
<tr>
<td>Plasticizers</td>
<td>Reduce hardness, increase flexibility, improve processing.</td>
<td>Phthalate esters (e.g., diethyl phthalate), phosphate esters (e.g., triphenyl phosphate), aliphatic diesters, benzoates, epoxidized oils.</td>
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<tr>
<td>Fillers/extenders</td>
<td>Increase bulk to lower cost of production, opacification.</td>
<td>Chalk (calcium carbonate), plaster (barium sulphate), carbon black, talc (magnesium hydroxide), kaolin, clays, silicates, titanium dioxide, organic fillers (e.g., cellulose, wood flour), glass microspheres, glass fibres, carbon fibres, metal powders (e.g., stainless-steel alloys).</td>
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<tr>
<td>Heat stabilizers/antioxidants</td>
<td>Prevent oxidation/degradation of polymer during processing, manufacture and use.</td>
<td>Metallic salts (lead, cadmium, zinc, barium), hindered phenolics, secondary aromatic amines, phosphites/phosphonites, thioethers, carbon black.</td>
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<tr>
<td>Category</td>
<td>Effect</td>
<td>Examples</td>
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<td>----------------------------------</td>
<td>---------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
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<tr>
<td>Flame retardants</td>
<td>Prevent ignition and generation of smoke,</td>
<td>Aluminium trihydrate, magnesium hydroxide, phosphates, polybrominated</td>
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<tr>
<td></td>
<td>reduce burning rate.</td>
<td>diphenyl ether, pentabromobenzyl acrylate.</td>
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<tr>
<td>Impact modifiers</td>
<td>Increase impact strength.</td>
<td>Styrenics, polybutadiene, polybutenes, acrylic elastomers, dimer acids,</td>
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<td></td>
<td>calcium carbonate, talc, silicones.</td>
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<tr>
<td>Curing agents/initiators/accelerants</td>
<td>Initiation and control of cross-linking</td>
<td>Organic peroxides, cobalt/amine/vanadium compounds, aliphatic amines,</td>
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<td>reaction rate in thermoset polymers.</td>
<td>ketones, anhydrides, salicylates.</td>
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<td>Dispersing agents</td>
<td>Help equally distribute colourants, prevent</td>
<td>Polyethylene/polypropylene waxes, low molecular weight ionomers.</td>
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<td>agglomerates.</td>
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<tr>
<td>Clarifying/nucleating agents</td>
<td>Improve transparency (particularly in polypropylene).</td>
<td>Dibenzylidene sorbitol, sodium and potassium benzoates.</td>
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<td>Antistatic agents</td>
<td>Reduce/eliminate of a polymer tendency to</td>
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<td>hold charge.</td>
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<td>Processing aids/lubricants</td>
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<td>Calcium carbonates, styrenes, acrylics, calcium stearate, lead stearate,</td>
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<td>make polymer melt run faster and thinner.</td>
<td>clarifying/nucleating agents, fluoropolymers, silicone oils, engineered</td>
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<td>silicones.</td>
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<td>Reinforcements</td>
<td>Increase hardness and strength.</td>
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<td>Light stabilizers/UV absorbers</td>
<td>Protect against photodegradation.</td>
<td>Pigments (titanium dioxide, calcium carbonate, carbon black), benzophenones/benzotriazoles, nickel compounds, salicylates, hindered amines (HALS).</td>
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<td>Blowing agents</td>
<td>Introduce gas to the polymer to produce foams.</td>
<td>Low-boil hydrocarbons, fluorocarbons, sodium bicarbonate/citric acid, azo compounds.</td>
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<td>Biocides/anti-bacterial agents</td>
<td>Prevent mould growth.</td>
<td>Oxybisphenox arsine, quarternary ammonium salts, N-(trichloromethylthio)phthalimide, isothiazolin.</td>
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**Bibliography**


Light stabilizers

Stabilizers are the most obvious additives to consider when talking about light sensitivity and degradation. They are added to most plastics, especially those expected to be exposed to outdoor conditions. Nowadays, there are many different types of commercial light stabilizers available. Some can be used with most polymers, but many are particularly suitable and designed for specific applications [3]. This is due to the fact that polymer photodegradation processes vary greatly and need to be addressed individually. They are also often complex with several different possible pathways, therefore photostabilization is commonly achieved through a combination of various additives which work to delay or prevent certain chemical reactions.

Although, many light stabilizers are thought to operate by multiple mechanisms, some of which are still not fully understood, they can be generally divided into three main categories:

- UV screeners and/or absorbers
- Excited state quenchers
- Radical scavengers and/or hydroperoxide decomposers (antioxidants)

Perhaps the simplest, though not always the most desirable, way to hinder photodegradation is to include opacifying additives or pigments which prevent penetration of harmful radiation to the bulk of the polymer by either reflecting or absorbing it. Carbon black is by far the most commonly used additive in this category as it not only converts strong UV into less damaging wavelengths but is also capable of deactivating any excited states and inhibiting the production of free radicals [4][5][6]. Other pigments often employed for that purpose include: iron oxides, phthalocyanines, ultramarine blue, calcium carbonate, zinc oxide and titanium dioxide in rutile form [7][5][8]. However, negative interactions of these
colourants leading to photodegradation have also been reported for some polymers and will be further discussed in paragraph 2.4.3. Despite being the cheapest from of photostabilization, using opacifiers is not always appropriate for applications where retaining transparency or achieving a specific colour is important. This issue can be solved by the employment of colourless UV absorbers derived from compounds such as benzophenones, benzotriazoles and salicylates. While the latter provide protection by decomposing into UV-absorbing species on photolysis, the other two dissipate the absorbed energy mainly through a reversible reaction which allows them to retain their chemical structure and undergo the same process many times [3]. Unfortunately, their effectiveness is limited by the need for high concentrations and the thickness of the final product. It is often uneconomical or even impossible to include enough UV absorber to provide sufficient UV absorption, e.g. in films or fibres [1].

The second type of photostabilization - quenching of photoexcited states, is a complex process which can include a variety of transfer mechanisms and many UV stabilizers are believed to act, at least in part, as energy quenchers. The exact methods of deactivation depend on the polymer in question and are still not fully understood. However, decades of industrial research found that chelates of transition metals, such as nickel, work particularly well in this regard despite their relatively low UV absorption [3].

Finally, it is important to discuss antioxidants despite their being mostly associated with heat stability during manufacture and processing. However, oxidative reactions are very important when photodegradation is induced with longer wavelengths of radiation [9], therefore presence of antioxidant additives will also contribute to light stabilization. Antioxidants work by inhibiting the propagation phase of chain reactions through scavenging of free radicals or decomposing hydroperoxides being produced on light absorption. Nonetheless, the single most important and effective type of light stabilizer to date are hindered amines (HALS). High efficiency and extensive compatibility with many polymers and other additives contribute to their vast popularity. Commercially available since the 1970s, HALS still dominate the industry despite exhibiting
hardly any near-UV absorption or energy quenching properties. Although still not completely understood, their high performance is most likely connected to outstanding radical scavenging and hydroperoxide decomposition performance combined with their regenerative ability [1].

As mentioned above, it is now standard industry practice to combine several additives into one stabilizing system designed for a specific polymer and application. The complex chemical nature of both polymers and additives, as well as their varied photochemical behaviour, means that there are many photostabilizer systems available with different levels of compatibility for a particular polymer. In some cases, combining certain compounds can yield an unwanted result. For instance, a benzotriazole UV absorber (commercial name - Tinuvin 328) was discovered to behave antagonistically when combined with a HALS [10], reducing the effectiveness of both compounds. Additionally, other additives, such as certain pigments, can weaken the performance of a particular stabilizer when included in the same formulation. Klemchuk found that Cromophthal yellow 3G and Cromophthal red BR28 diminished the effectiveness of a hindered amine stabilizer by as much as 50% and 27.5% respectively [8]. This negative effect could also be seen in the combinations of a benzotriazole stabilizer with iron oxide red, cadmium yellow, rutile titanium dioxide, ultramarine blue, phthalocyanine blue and the two azo pigments mentioned above. Other antagonistic pairs included: a nickel-based stabilizer with iron oxide red; a benzophenone compound with cadmium yellow, Cromophthal yellow 3G and iron oxide red; and a benzoate light stabilizer with Cromophthal yellow 3G.

Furthermore, stabilizer presence may alter the progress of the deterioration through the material. An accelerated degradation study of on the effect of HALS and titanium dioxide pigment on depth profiles in injection moulded PP, showed that inclusion of HALS allowed oxidation to spread uniformly throughout the thickness of the samples on irradiation with UV [11]. This was explained by the decelerated degradation rate on the surface due to the stabilizer action, which

28 Commercial names of an azo condensation yellow pigment (PY93) and bisazo red pigment (PR144) respectively.
allowed more oxygen to diffuse into the bulk of the material. In contrast, unstabilized samples showed strong oxidation on the top layer with little penetrating deeper into the polymer. Caused by a much faster consumption of oxygen at the surface, the degraded layer eventually acts to block absorption of radiation further into the sample.

Regardless of the complications, however, light stabilizers as a photodegradation ‘influencer’ only have a positive effect on the durability of the overall material. Even when antagonistic behaviour with other additives occurs, resistance to UV is still higher than for an unstabilized system.

The final issue to consider is that, although UV stabilizers act to retard photodegradation, they do not last indefinitely. With continued exposure they will eventually become depleted, thereby allowing for deterioration of the polymer chain. This is an important concern from a heritage point of view as objects acquired for a collection are rarely brand new and need to be preserved past their expected useful lifetime. However, identification and quantification of protective additives in a plastic object in order to assess the level of stabilization is a formidable challenge not only for the museum sector. Reingruber and Buchberger reviewed methods and approaches to this type of analysis within the industry [12]. Their main findings were that the most effective and, therefore, most commonly used analytical tools include separation techniques such as liquid chromatography (LC) coupled with UV spectroscopy or pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). Unfortunately, all of these come with serious drawbacks from the point of view of conservation, the main being that it is necessary to obtain samples from the object to be assessed, although the need for specialised equipment and expertise is also a significant issue for many heritage organisations. For LC, the compounds of interest need to be extracted with solvents, which is time-consuming, requires specific knowledge and, sometimes, equipment which might not be standard in a conservation lab. Py-GC-MS dispenses with the sample preparation and allows for higher molecular weight compounds to be identified but because the entire sample is pyrolyzed, it is much more difficult to interpret the results as analytes from the
polymer and all the additives will be present. Other techniques, such as Fourier Transform Infrared Spectroscopy (FTIR) are mentioned as having a lot of potential for monitoring stabilizer content but with non-destructiveness and greater ease of use, comes lower sensitivity and reproducibility. The case becomes even more complex if degradation products of the consumed additives in question are also present alongside the intact stabilizers. The authors conclude that there is great demand for the development of more reliable and robust multi-analyte methods.

Bibliography


Appendix C

Additional data for Chapter 4

Figure C-1. Hydroxyl peak ratios before (black) and after (red) visible light ageing for both chambers (C2a – above, C2b - below).
Table C-1. Levels of oxidation before ageing in order of largest to smallest. [S1 – set 1, S2 – set 2]

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Table C-2. Colour change of all PP and CA samples after ageing given as average ΔCIELab values with standard deviation.

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<th>Δa ±</th>
<th>Δb ±</th>
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Appendix D

Additional data for Chapter 5

Table D-1. Thermal oxidation of PP samples before ageing measured as peak ratios relative to a reference band at 2915 cm⁻¹.

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Appendix E

Additional data for Chapter 6

Figure E-1. Visible reflectance spectrum of a CA sample with PB29.

Figure E-2. First derivative of a visible reflectance spectrum of a CA sample with PB29.
Figure E-3. Visible reflectance spectrum of a CA sample with PO13.

Figure E-4. First derivative of a visible reflectance spectrum of a CA sample with PO13.
Figure E-5. Visible reflectance spectrum of a CA sample with PR48:2.

Figure E-6. First derivative of a visible reflectance spectrum of a CA sample with PR48:2.
Figure E-7. Visible reflectance spectrum of a CA sample with PR88.

Figure E-8. First derivative of a visible reflectance spectrum of a CA sample with PR88.
Figure E-9. Visible reflectance spectrum of a CA sample with PV23.

Figure E-10. First derivative of a visible reflectance spectrum of a CA sample with PV23.
Figure E-11. Visible reflectance spectrum of a CA sample with PY35.

Figure E-12. First derivative of a visible reflectance spectrum of a CA sample with PY35.
Figure E-13. Visible reflectance spectrum of a PP sample with PB29.

Figure E-14. First derivative of a visible reflectance spectrum of a PP sample with PB29.
Figure E-15. Visible reflectance spectrum of a PP sample with PO13.

Figure E-16. First derivative of a visible reflectance spectrum of a PP sample with PO13.
Figure E-17. Visible reflectance spectrum of a PP sample with PR48:2.

Figure E-18. First derivative of a visible reflectance spectrum of a PP sample with PR48:2.
Figure E-18. Visible reflectance spectrum of a PP sample with PR88.

Figure E-9. First derivative of a visible reflectance spectrum of a PP sample with PR88.
Figure E-10. Visible reflectance spectrum of a PP sample with PR166.

Figure E-22. First derivative of a visible reflectance spectrum of a PP sample with PR166.
Figure E-23. Visible reflectance spectrum of a PP sample with PR220.

Figure E-24. First derivative of a visible reflectance spectrum of a PP sample with PR220.
Figure E-25. Visible reflectance spectrum of a PP sample with PV23.

Figure E-26. First derivative of a visible reflectance spectrum of a PP sample with PV23.
Figure E-27. Visible reflectance spectrum of a PP sample with PY14.

Figure E-28. First derivative of a visible reflectance spectrum of a PP sample with PY14.
Figure E-29. Visible reflectance spectrum of a PP sample with PY35.

Figure E-30. First derivative of a visible reflectance spectrum of a PP sample with PY35.
Figure E-31. Visible reflectance spectrum of a PP sample with PY42.

Figure E-32. First derivative of a visible reflectance spectrum of a PP sample with PY42.
Figure E-33. Visible reflectance spectrum of a PP sample with PY83.

Figure E-34. First derivative of a visible reflectance spectrum of a PP sample with PY83.
Figure E-35. Visible reflectance spectrum of a PP sample with PY95.

Figure E-36. First derivative of a visible reflectance spectrum of a PP sample with PY95.
Figure E-37. Visible reflectance spectrum of a PP sample with PY151.

Figure E-38. First derivative of a visible reflectance spectrum of a PP sample with PY151.
Figure E-39. Visible reflectance spectrum of a PP sample with PY154.

Figure E-40. First derivative of a visible reflectance spectrum of a PP sample with PY154.