1.1. Introduction

Since the introduction of the first semi-synthetic plastics about 140 years ago, an incredibly wide range of plastics has become available for use in cultural heritage. This would include works of art (sculpture in particular, but paintings and other types also), art and crafts, collectable household items, architectural models, industrial design and even built heritage, to name just a few. Artists, designers, engineers and architects have all appreciated the broad range of special qualities that this class of material has offered. For example, they can be light-weight, strong and low-cost, and yet offer high versatility – they are easily moulded or carved into any desired shape – and unique optical properties. It is perhaps, therefore, no surprise that the demand for plastics within cultural heritage continues to increase (www.plastiquarian.com).

As with all areas of conservation, one of the first requirements to understand better and study a class of material is to establish effective ways of analysis. This would include the ability to identify the chemical composition of a plastic object, as well as a better knowledge about its physical and chemical stability. But this is perhaps even more important for plastics than other types of material, due to the enormous range and variety of synthetic polymers that fall under the umbrella term “plastic”, and hence the very wide range of ageing behaviour, display and storage requirements, and response to conservation treatments. For example, some plastics can be harmful when in contact with other materials, some are sensitive to water when cleaning, some are easily scratched, some are extremely vulnerable to light and some to moisture.

In general terms, it is relatively straightforward to detect if an object is made of plastic or not, except for the early semi-synthetic plastics (e.g. cellulose nitrate), which can be extremely similar in appearance and feel to the natural materials that they were designed to mimic (such as tortoiseshell or horn).

However, it is often very difficult to identify the type of modern plastic by appearance and feel, especially in cases where dyes, pigments, stabilisers, plasticisers or other additives have been added to the base polymer, which can modify or mask its general properties.

That said, some plastics do have a characteristic look, or a distinctive feel, or show characteristic signs of manufacture, like evidence of the injection moulding sprue, enabling rough identification. An experienced conservator might be able to recognise some types of plastic by their transparency – such as acrylics, polyesters, polystyrenes and polycarbonates – or the noise they make when gently tapped, or even by smell when warmed gently by rubbing. It is also true that most plastics can be identified via simple destructive tests such as burning and dissolving samples (Coxon 1993), but – needless to say – such testing is not an option for objects of cultural heritage.

It is also common for there to be some level of documentation on the type of plastic used in a work of art, either from the collection or the artist. Other useful information that can help with the non-analytical identification process includes a knowledge of the history of plastics, an understanding of a particular artist's methods and materials, an awareness of when an object was acquired and/or was made, a familiarity with trade names or trademarks, and a knowledge of the Resin Identification Code on some objects (www.plasticsindustry.org). The nature of degradation itself can help to characterise an aged plastic. However, all these sources of information can be absent, or incomplete, or certainly unreliable. It is also known that various plastics can show the same characteristics as each other, so even simple tests may give false answers (Shashoua 2008; Waentig 2008).

Manufacturing techniques for plastics such as injection and blow moulding and vacuum forming are commonly used, and plastic objects can be identified by the marks of those techniques. Nowadays, developments of manufacturing of plastics include the application of new technologies such as 3D rapid prototyping under which fused deposition modelling (FDM) a manufacturing technology commonly used for modelling, prototyping, and production applications. This technology was developed by S. Scott in the late 1980's and was commercialised in 1990 (Scott 1992). Furthermore selective laser sintering (SLS) is a manufacturing technique that uses a high power laser to fuse small particles into a mass that has a desired 3-dimensional shape (Deckard 1989). Another innovative technique is PolyJet 3D printing technology developed since 2000 (www.object.com). This technique works by jetting a photopolymer in ultra-thin layers (16 μm) onto a build tray until the part is completed. Each photopolymer layer is cured by ultra violet radiation immediately after it is jetted, producing fully cured objects. Due to these new technologies and techniques to fabricate plastic objects, much more of those new innovative fabricated plastic objects will occur in museum collections in the near future and it will be become even more difficult to identify an object on the look and feel, touch and sound.

Fortunately, there are many scientific methods for identifying plastics more reliably. The most useful are those that reveal the chemical composition of a material from microscopic sample sizes, or even via non-invasive, in-situ techniques (van Oosten 1999). For this discussion, it is helpful to make a distinction between *identification* (i.e. the class of polymer it is) and *characterisation* (additional information about a polymer's makeup and behaviour, including more quantitative analysis of all the components in a product, molecular weight distribution, polymer size, and physical properties) of plastics.

Identification techniques

Spectroscopic and chromatographic techniques such as Fourier transform infrared spectroscopy (FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) are extremely useful for the identification of plastics. Since the 1990's, spectroscopic techniques have improved significantly in terms of the size of sample required, the speed of analysis, the user interface, and portable/mobile instrumentation. The use of these spectroscopic methods has become widespread in conservation, and is likely to increase further with the recent development of handheld instruments (FTIR, Raman and Near Infrared (NIR)) for rapid, non-invasive, in-situ analysis.

Although Raman spectroscopy has improved on many of the problems it had initially with fluoresce coming from additives in the plastics, and both NIR and Ultra violet-Visible spectroscopy (UV-Vis) have become more sensitive and more useful, the most widely used technique for identifying plastics is still FTIR. The technique is highly versatile, and also permits the analysis of surface deposited degradation products, polymer bond changes, depth-profiling and the monitoring of polymer loss. For the identification of complex mixtures of plastics and additives, however, Py-GCMS offers many advantages over FTIR. The main disadvantage to this technique seems to be the lack of low-cost models and the additional resources needed for its maintenance.

Procedure followed for identification

- To achieve a valid comparison of the various invasive and non-invasive techniques proposed for the identification and characterisation of plastics, a sample collection of plastics artefacts of about 100 standard and reference plastic objects Sample Collection (SamCo) was built (chapter 1.2).

- A Round Robin test for the identification of plastic objects from the reference collection (SamCo) was set up to evaluate all analytical techniques used. The principal techniques for identification were FTIR, Py-GCMS, NIR and Raman.

- The techniques were classified as follows: bench top (in the laboratory), transportable (invasive but can be used outside the laboratory) and handheld (intended to be to be used outside the laboratory).

- To validate the results, a blind test was also implemented. 35 samples of plastics (whose identity was kept hidden from the participating laboratories), were used to compare the accuracy and limitations for identification between the various analytical techniques.

- In order to improve the applicability of NIR spectroscopy, additional reference samples / databases were established building on the SamCo.

- A system for non-invasive microwave dielectric spectroscopy was also tested on the SamCo.

The analytical techniques used to identify the reference standards and reference objects from the SamCo kit, are described. The results of the analyses were used to compare and evaluate the ease and usefulness of the various techniques. Introduction to the various techniques to characterise plastics and for ageing studies and results of the research is given in 1.4.2-1.5.3. Trends in identification and characterisation of plastics are given in 1.6.1-1.6.3 and in 1.7 a comparison of analytical techniques is given.

Results

The identification of plastic artefacts encompasses the evaluation of analytical techniques and methodologies. Analytical techniques, from the non-invasive (no sampling) NIR, UV-Vis, FTIR handheld and Raman handheld to the invasive (micro-sampling 0.6 mm^2 or less) were included. The FTIR bench top and Py-GCMS techniques were also evaluated on their ease of use and the quality of their results.

In general, FTIR was found to be a very adequate technique for most plastics identification. According to the results of the analyses performed by the partners, all were able to conclusively identify all the plastics included in the SamCo, and in some cases partners reporting on seeing features from other components other than the main resins, either inorganic (e.g. fillers, pigments) or organic (e.g. colorants).

Some difficulties of sampling were mentioned, but these were more to do with the specific sampling procedures available. For example, those partners who used a Golden Gate attenuated total reflectance (ATR) accessory could squeeze the more rigid plastics into thin films in order that better contact was made with both diamond surfaces, and hence obtain better resolved spectra.

FTIR was shown not to be ideal for mixed or complex plastics because spectral features that can identify one component might become obscured by a spectral feature of some other component. Thick enough laminates can, however, be cross-sectioned to analyse each layer individually. Additives like fillers, plasticisers, colorants, stabilisers, anti-oxidants, and ultra violet absorbers can therefore only be identified if their concentration is high enough, depending on the nature of the additive, and nature of the polymer (but in some cases is possible for concentrations under 5% w/w). Given that it would be impossible to process most polymers into useful objects without additives, and that additives can affect the long-term stability of the plastic to such a high degree, the inability of FTIR to identify these components in typical situations is clearly a significant limitation, for any kind of study into ageing and/or degradation.

Bench top instruments and/or transmission mode of operation might offer a better resolution than portable instruments used in ATR/transmission mode, which might help when similar polymers can be discriminated only by very small absorption bands. By comparison bench instruments such as the bench Perkin Elmer at L-C2RMF and the bench Bruker Hyperion 3000 at GCI and the bench Perkin Elmer at RCE all institutions reported subtle differences between the three types of polystyrene and between Nylon 6 and 6,6 measured in standards. However, these small differences can only be clearly observed in standard reference materials and not always obvious in compounded objects. The absorption bands of the compounding materials such as fillers, stabilisers and pigments can obscure the small differences in the fingerprint region absorptions in the FTIR spectrum between different polymers of the same family. Therefore compounded objects can be equally identified using portable and bench top instruments.

The transportable FTIR using invasive sampling used by RCE was not able to distinguish between samples of polystyrene general purpose, high and medium impact, or between different polymers belonging to the same family, like Nylon 6 and Nylon 6,6.

Furthermore, identification using FTIR (either bench top, handheld or transportable) is based on comparing data of the spectra by a library search on the computer. Depending on the amount of reference standards in the database and the skills of the scientist, better results will be obtained (see section 1.3.1.)

For the identification of complex mixtures and additives Py-GCMS has to be used.

Though not all partners have access to or could perform Py-GCMS, this technique provided complete and detailed identification of all plastics analysed. Evolved Gas Analysis (EGA) proved to be a valuable complementary technique to Py-GCMS. For results and more detailed information about identification and the used equipment see sections 1.4.1-1.4.2.

Raman spectroscopy is an efficient tool for the identification of plastics, but bench equipment is much more efficient than the portable instruments tested. Most polymers could be successfully distinguished and identified.

The two portable instruments tested were found to be promising but not yet as reliable as the bench instrument with almost half of the samples yielding illegible spectra. The shape and colour of the samples were also found to have a significant influence on the quality of the spectra. As the Raman technique has only been used by GCI and RCE, no inter-laboratory comparison could be made. Initial findings indicate this approach to be good. With a reliance of the production of a good and extended reference database. The more reference spectra, the more reliable the result. For results and detailed information about Raman spectroscopy see section 1.3.3.

To fully exploit NIR spectroscopy for identification purposes, establishment of a library of spectra of plastic materials with known composition is necessary. A NIR spectral library was built using the SamCo and a collection of plastics objects at the partners institute's – see chapter 1.3.4.

All data of the plastic objects after identification were submitted to the SamCo Filemaker Pro database. Photographs and general information about the reference standards and reference objects of SamCo were registered. Data of the FTIR spectra of the plastics were submitted to the database as Microsoft Word files and results of the Py-GCMS analyses were submitted as chromatographic bitmaps – see chapter 1.2.

Characterisation techniques

Several additional analytical techniques were utilised to provide additional information for characterising many of the polymers, and which would be used to monitor changes in chemical, mechanical and physical properties on ageing and/or after cleaning treatments. These include ultra violet-visible spectroscopy (UV-Vis), thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile-stress strain analyser (TSS) and dielectric spectroscopy (DS).

FTIR imaging and NIR hyper spectral camera-imaging, useful for surface characterisation, size exclusion chromatography (SEC), solid phase micro extraction (SPME-GCMS) and chemiluminescence (CL) were all used for the characterising the chemical changes in plastics on ageing. These techniques are described in more detail in the sections 1.5 and 1.6.

NIR spectroscopy has a significant potential in the field of organic material characterisation and greatly enhances heritage collection management replacing destructive and micro-destructive methods. One aspect of NIR spectroscopy is the use of this technique for quantitative imaging of chemical properties and damage mapping on plastic objects and this is introduced in section 1.6.2. As with NIR imaging, the technique of FTIR imaging can be used to quantify change of chemical properties in the polymer structure. It can used to measure and locate oxidation products on the surface of degraded plastic objects.

DSC was found to be useful to differentiate samples by their melting temperatures, and temperatures of decomposition. Samples from the commercially available ResinKit™, were measured by PISAS using DSC and it was found to be useful to differentiate samples by melting temperatures. DSC is likely to prove more useful for characterisation and ageing studies than identification. RCE performed DSC analysis on the eight SamCo samples that were not identified using FTIR and Py-GCMS. The eight samples (polyethylene HDPE, MDPE and LDPE), polystyrene (HIPS, MIPS and PS general purpose) and polypropylene (copolymer and general purpose) could be characterised by their melting points.

DS is another tool for characterising plastics by measuring their dielectric constants. A system for non-invasive microwave dielectric spectroscopy has been used on the SamCo. The available bench instrumentation (a LF Impedance Analyzer Agilent 4192A/text fixture Agilent 16451B) allows characterisation in the 5 Hz–10 MHz range of samples with standardised shape and thickness. Nevertheless, these preliminary results could be used to single out the most promising spectral interval for characterisation of plastics on the basis of their dielectric properties.

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