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SCIENTIFIC PAPER

IN-SITU RAMAN SPECTROSCOPIC CHARACTERISATION OF POLYMERS USED IN PAST CONSERVATION TREATMENTS

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This paper reports the successful characterisation of polymers from past conservation treatments using Raman spectroscopy with a fibre-optic probe. It has been demonstrated for the first time that this methodology is well suited to the *in-situ* examination of polymers used as adhesives and gap-fillers for conservation of glass artefacts. By means of a Raman spectroscopic instrument with a fibre-optic probe, conservation polymer spectra were recorded non-destructively, with a spectral resolution of 2 cm^{-1} in the range 200-3200 cm^{-1}. Polymer identification proved straightforward for gap-fillers and, for adhesives, different polymers were also successfully distinguished, even in a glass / adhesive / glass bond less than 100 µm in width. In addition to polymer identification, Fe_2O_3 was identified as the pigment not only in restored areas but also in the original grisaille paint for the grey toning for the glass pictorial scene.

1 Introduction

The evaluation of conservation materials can be aided by an assessment of the current condition of previously conserved artefacts. An important aspect of this is the long-term behaviour of polymers used as adhesives, coatings and gap-fillers. The natural ageing of polymers from past treatments is a valuable guide to the suitability of different products for future use. In particular, the success of future glass conservation methods is dependent on an understanding of the behaviour of materials used for past glass repairs. However, despite numerous laboratory ageing studies which have attempted to predict the long-term durability of adhesives and gap fillers for glass repair[1-5], there have been very few retrospective surveys of the natural ageing of polymers based on their in-service behaviour.

The range of polymers used for bonding broken fragments, for gap-filling or for infusion into cracks is very extensive. Animal glue, shellac and other natural polymers have long been superseded by synthetic polymers; for bonding, cellulose nitrate, acrylics, silicone rubber and epoxy resins have been and continue to be widely employed.

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For gap filling, acrylic casting resins, polyester and epoxy resins have predominated. The properties which polymers should exhibit for optimal results have been elaborated in standard conservation texts.[6-8] Of paramount importance is the stability to photo- and thermal degradation.

Polymer degradation is usually accompanied by yellowing which disfigures the glass artefacts. Sometimes the polymer degradation is partially masked by dyes and/or pigments also used in the restored areas but, mostly, the yellowing is very visible and disturbing. As a result, repaired vessel glass and stained glass frequently require re-restoration but when durable products are used, objects can still be in good condition several decades after restoration. In order to select durable polymers which are stable to degradation, the examination of the current state of past conservation treatments is therefore very instructive. Although retrospective assessments of conservation treatments are not common, past stained glass conservation treatments are, however, currently under investigation by a European consortium of stained glass conservators and conservation scientists from 11 institutions.[9] As part of this concerted approach, the need for the non-destructive, *in-situ* identification of polymers used in previous conservation campaigns is necessary. Records documenting the process of restoration (the polymers, pigments and techniques employed) are often incomplete or totally absent. Up to now, the non-destructive identification of polymers *in situ* has not been possible for objects such as stained glass panels where spectroscopic examination poses severe practical problems. For this reason, the scope of Raman spectroscopy with a fibre-optic probe has been investigated. The preliminary results of the study are reported in this paper.

2 Non-destructive Raman Spectroscopy of Glass Artefacts

Although the use of Raman spectroscopy for the study of objects of art has been the subject of intense activity in recent years,[10,11] this is the first application to this important area of art conservation. The use of micro-Raman (involving removal of a sample from the object) has been the most common technique used for examination of works of art but some research groups have utilised specialised instrumental set-ups for non-destructive examination of artefacts,[10] including the identification of polymer adhesives used for textile conservation.[12] One specific application, involving fibre-optics, is for the inspection of medieval stained glass.[13] This method has, however, never been readily available for use as a conservation tool to work within a building and/or with large objects, such as the stained glass windows in cathedrals or museum installations. Furthermore, the presence in the market in recent years of portable, low resolution systems is not a solution to the problem of non-destructive *in-situ* characterisation of polymers; neither the resolution nor the performance of these instruments is sufficient for detailed studies in which it is important to identify minor components such as plasticisers in polymer formulations.

This paper reports the successful characterisation of polymers, pigments and techniques in a stained glass panel by means of Raman spectroscopy with a fibre-optic probe using the high performance PerkinElmer RamanFlex 400F instrument. This high resolution instrument can be fitted with a fibre-optic probe up to a hundred meters which makes it a useful tool for such applications.

The stained glass roundel shown in Figure 1 was chosen because it presented a range of conservation issues suitable for investigation by Raman spectroscopy with a fibre-optic probe. Figure 2 illustrates the examination of this panel in the laboratory, using the RamanFlex 400F instrument.

Figure 1: 16th century Flemish stained glass roundel depicting St. Elizabeth of Hungary (Collection J.M.A. Caen).

Figure 2: Analysis of epoxy resin adhesive in the roundel by means of the Perkin Elmer RamanFlex 400F instrument with a fibre-optic probe.

Figure 3: Detail of the reverse of the roundel showing repairs: Raman investigation characterised the unknown polymer (Figure 6) used for edge-to-edge bonding to the left of the head of St. Elizabeth.

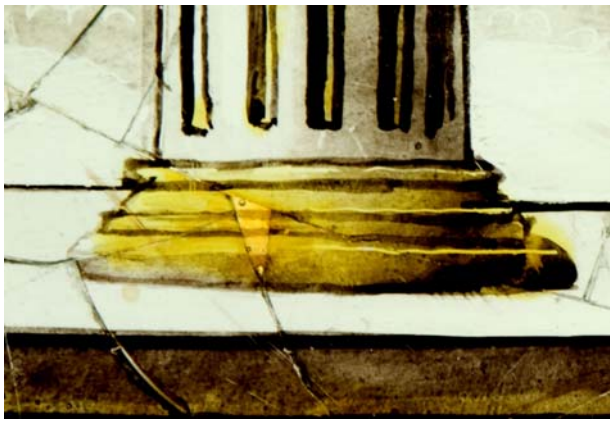

Figure 4: Detail of the reverse of the roundel showing the grey ("grisaille") paint fired on the glass and a yellow dyed triangular area of epoxy resin fill. Raman investigation identified the pigment in the paint as Fe_2O_3 (Figure 8) and the epoxy resin as Araldite 20-20 (Figure 6).

The past conservation treatments in this panel include the use of polymers for edge-to-edge bonding of broken glass and for replacing missing pieces of glass. These are typical examples of polymer identification questions where non-destructive investigation is important for conservation. In addition, the areas of retouching on top of the resin fills and the zones of grisaille shading on the columns offered good opportunities for pigment identification. The areas examined are shown in Figures 3-5.

Figure 5: Detail of the reverse of the roundel showing the restored red area of the robe of St. Elizabeth. Raman investigation identified the pigment in this repainted area as Fe_2O_3 (Figure 8).

3 Experimental

The stained glass roundel (Figure 1) was selected from the collection of one of the authors (JC) as an item representative of glass restored using clear and pigmented polymers as adhesives and gap fillers. The experimental set-up, although in a laboratory context, was intended to reproduce the real challenges that researchers will have to face while carrying out non-destructive, *in-situ* analysis of works of art.

The instrument used was a PerkinElmer Raman Flex 400F provided with a 3 m long standard Fibre-Optic Probe (FOP). The instrument was equipped with a diode laser at 785 nm (maximum output of 300 mW), set up to have a maximum power of *c.* 100 mW at the sample. Prior to recording spectral data, preliminary tests were performed from low (5 mW) to maximum laser power (100 mW) to ensure the integrity of the sample during the experiment, namely to avoid any thermal decomposition. There was no evidence of such degradation on the pigments or polymers present in this artefact. All spectra were recorded with a spectral resolution of 2 cm^{-1} and covering the range 200-3200 RamanShift (cm^{-1}). The instrument is equipped with an Echelle spectrograph that allows the

acquisition of high resolution-full range spectra in a single scan. The instrument and data were controlled and processed using Spectrum® Software. The identification of the polymers was performed by generating a database of different polymers with Compare® Software and comparing the spectra of the unknown adhesives and gap fillers with those in the database. Pigment Raman bands were identified by comparison with data from relevant bibliographic references.

To ensure that the measurements were performed always at the same distance, a contact tip was installed on the FOP; the length of that tip was set up to have a focal point 100 µm below the sample surface. Acquisition times were optimized for each sample (5 to 100 s).

4 Results and Discussion

This exploratory study was entirely successful. The epoxy resins present in the restored Flemish roundel could be easily characterised, not only for large sample areas of gap-filling but also when the polymer acted as a bonding adhesive. In the latter case, the polymer was less than 100 µm in width.

Raman spectroscopy with a fibre-optic probe demonstrated that the unknown epoxy resin used for bonding and gap-filling was the commercial product Araldite 20-20.

The spectrum of the resin used for bonding (Figure 6) was identical to an authentic reference sample of this epoxy resin. Two other epoxies often used for glass repair, Ablebond 342-1 and Hxtal NYL-1, had spectra which were quite distinct from each other (Figure 7). These epoxies are based on the diglycidyl ether of Bisphenol A and a hydrogenated version of this resin, respectively. It is important for conservators to be able to distinguish these two types of epoxy formulation as their stabilities to light are very different.[3]

It was also a straightforward matter to obtain good quality fibre-optic spectra for the pigments in the restoration lacquer and the original grisaille paint; in each case the spectrum was characteristic of Fe_2O_3. The spot diameter (100 µm) of the fibre optic system ensures that the spot area is large enough to minimise the possibility of pigment degradation by the laser. Interestingly, a small shift in the Fe_2O_3 Raman peak positions was observed. We attribute this to the different matrix effects of an organic polymer lacquer and a fired inorganic grisaille paint. Similar small shifts in Raman peak position, dependent on the influence of the substrate, have been observed for SiO_2 supported tungsten oxide catalysts.[14]

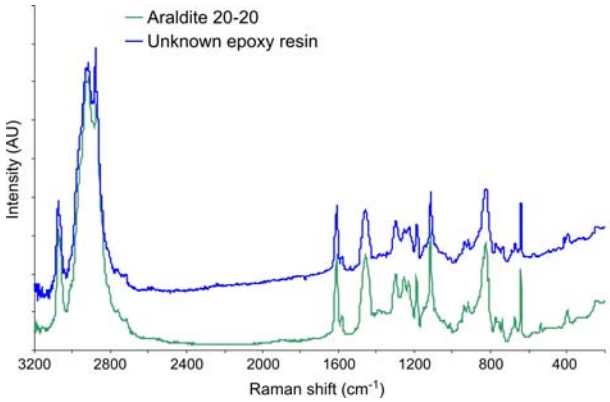

Figure 6: Raman spectra of unknown epoxy resin from roundel and comparative spectrum for Araldite 20-20 epoxy resin.

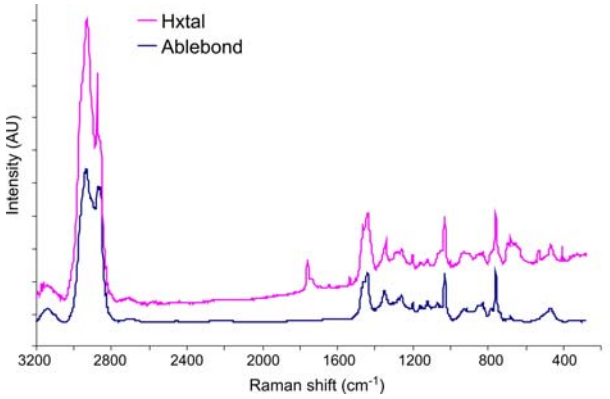

Figure 7: Comparative Raman spectra for Ablebond 342-1 epoxy resin and Hxtal NYL-1 epoxy resin.

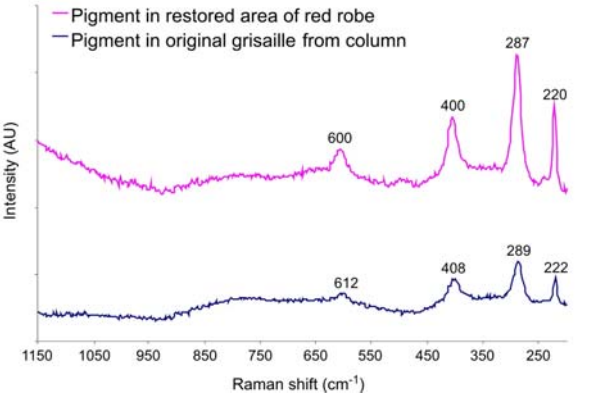

Figure 8: Raman spectrum of grisaille enamel from a shaded area of the column, and the pigmented lacquer from a restored area of the robe. Both spectra are characteristic of iron oxide, Fe_2O_3.

5 Conclusions

Raman spectroscopy with a fibre-optic probe is demonstrated, for the first time, to be well-suited to the examination of polymers used as adhesives and gap fillers for conservation of glass artefacts. Polymer identification is straightforward for gap fillers and for adhesives. We have also successfully distinguished different polymer products, even in a glass/adhesive/glass bond less than 100 µm in width. Finally, we were also able to identify

the pigments used during the restoration and in the original glass grisaille paint.

In this preliminary investigation, we have focused on the potential to characterise epoxy resins and to discriminate between different commercial brands. Future studies will extend this work to the differentiation of different polymer classes and, more challengingly, to the investigation of polymers with similar chemical constitution and to the characterisation of spectral changes in conservation polymers which occur through time, associated with yellowing of epoxy resins, especially at the polymer surface.[15] In unpublished studies, we have demonstrated that Raman spectroscopy has the potential to benefit our understanding of the durability of conservation treatments by probing chemical changes as a result of polymer photodegradation.

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