The Identification and Long-Term Stability of Polymer Fills in Ceramics and Glass Artifacts: A Retrospective Assessment Involving FTIR Characterisation

ABSTRACT

The potentiality of Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy to identify polymer classes and specific commercial products used for past repairs of glass and ceramics objects is explored for acrylic, polyester, and epoxy resins. FTIR spectra were recorded for samples of polymer fills from objects and from polymer samples prepared in the 1970s and 1980s as accelerated aging test specimens. The results demonstrate that ascribing polymers to a specific class is straight-forward, but that it is difficult and, in most cases, not possible to identify individual commercial products from within these polymer classes. FTIR spectra for the following commercial products exemplify the findings: polyester Vosschemie; acrylic Plastogen G, Technovit 4004a, and Plexiglas; and epoxy Araldite AY103/HY951 or HY956, EPO-TEK 301-2, Fynebond, and HXTAL NYL-1. The degree of yellowing of these polymers, after natural aging spanning 15-45 years, is discussed. The observed yellowing generally matches the predictions of laboratory-based aging studies; however, two troubling discrepancies are highlighted.

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KEYWORDS

FTIR spectroscopy · FTIR-ATR · Acrylic · Polyester · Epoxy · Glass · Ceramics · Yellowing

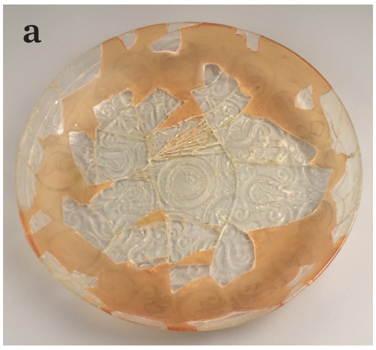
INTRODUCTION

Polymer fills from past conservation treatments of glass and ceramics are a valuable storehouse of information about the aging behaviour, particularly the propensity to yellow, of different polymer classes and specific commercial products within these classes. The evaluation of past polymer repairs can therefore provide important information on polymer stability and degradation, which complements the results of accelerated aging tests. Despite this, few reports have been published that compare the 'real-life' aging behaviour of conservation polymers with the predictions of laboratory aging evaluations. Reports that testify to the value of polymer yellowing assessments based on the examination of restored glass and ceramic objects provided the motivation for the present investigation (Wight 2008; Tennent and Koob 2010; Tennent 2011).

Figure 1. *Undocumented yellow polymer coating identified by FTIR as epoxy. Louis Comfort Tiffany, Window from Rochroanne Castle, 1905 CE, lead cames, H 346.2 cm × W 330.1 cm × D 21.2 cm. Corning Museum of Glass, 76.4.22 · Courtesy of Corning Museum of Glass*

In order to draw useful conclusions on the long-term behaviour of polymers pertaining to past treatments, it is self-evident that the identity of the polymer must be known. However, conservation documentation is often inadequate or completely absent. In some conservation reports, the type of polymer is documented, but the commercial product is not designated. In other instances, the repairs may pre-date the most recent acquisition of the object, and so no treatment records exist. In some treatment documentation, brand names of the specific polymer used may have been recorded without any specification of the chemical nature of the product or the manufacturer or supplier. When such products are no longer commercially available, this is especially problematic for researchers seeking comprehensive information on the chemical composition of the polymer formulation used.

Accordingly, the goal of the research presented herein was to assess the potentiality of Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy to identify unknown polymers from past conservation treatments with sufficient specificity to allow conclusions to be drawn on the product's natural aging, ideally



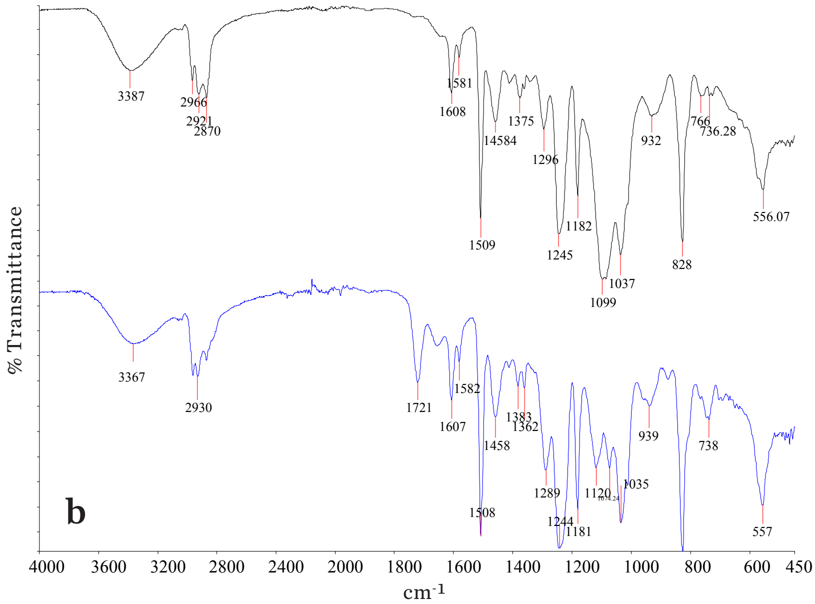


Figure 2. *a) Islamic Bowl, ca. 8th-10th century CE, glass, H 4.1 cm × Diam. 22.2 cm. Corning Museum of Glass, 59.1.436 with documented Araldite AY103/ HY956 epoxy fills, and b) FTIR spectra of epoxy resins from 76.4.22 (above) and 59.1.436 (below) · Courtesy of Corning Museum of Glass*

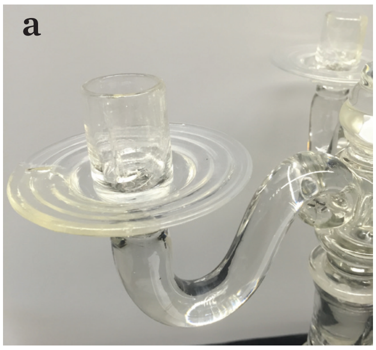
differentiating individual commercial products within the common polymer classes used for gap-filling. For this research, FTIR-ATR was preferred over pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), primarily because it is a less time-consuming method, more readily available to the conservation community, and requires less sample material.

The range of polymers commonly used for gap-filling materials for glass and ceramics in the past half-century has been summarised by Davison (1998) and comprises acrylic, polyester, and epoxy resins. The general chemistry and properties of these polymer classes are extensively covered in numerous polymer textbooks; in the context of conservation, Horie (2010) provides a comprehensive guide to the salient features. For the present research, the range of polymers has been limited to those casting resins that form a hard, glass-like polymer by a reaction cure carried out by conservators, thus excluding polymers that form casts by solvent evaporation from polymer solutions or emulsions, which are increasingly advocated for glass gap-filling (Koob 2006). Amongst commercial acrylic, polyester, and epoxy polymer casting resins, the epoxy resin formulations have the most diverse variety of components. Down (1984) illustrates this diversity in the tabulation of products included in her epoxy light- and dark-aging test programme. The epoxy resin component is most frequently the diglycidyl ether of Bisphenol A (DGEBA), as represented by commercial products such as Araldite AY103, Araldite 20-20, Ablebond 342-1, EPO-TEK 301-2, and Fynebond, all commonly used by conservators. HXTAL NYL-1 is a notable exception, based on an aliphatic epoxy resin rather than the standard aromatic DGEBA epoxy. Amongst the amine hardener compounds, there are many variations (Potter 1970; Down 1984). The incorporation of reactive diluents, as in EPO-TEK 301, plasticisers/ flexibilisers, as in Araldite AY103, and other additives such as accelerators, often present only in low concentrations, adds to the complexity of commercial epoxy products. When present in low concentrations and below their detection limit, additives increase the difficulty of differentiating individual products, even from within the range of brand names supplied by a single company, by their FTIR spectra. Conservators' modification of epoxy resin refractive index for glass repair (Augerson and Messinger II 1993; Messinger II and Lansbury 1989; Tennent and Townsend 1984a) is another situation in which adjustments to a formulation can complicate the identification of a specific product.

METHODOLOGY

Polymer samples

The FTIR results discussed in this paper were primarily obtained from tiny scrapings of polymer fill materials, removed using a scalpel, from glass



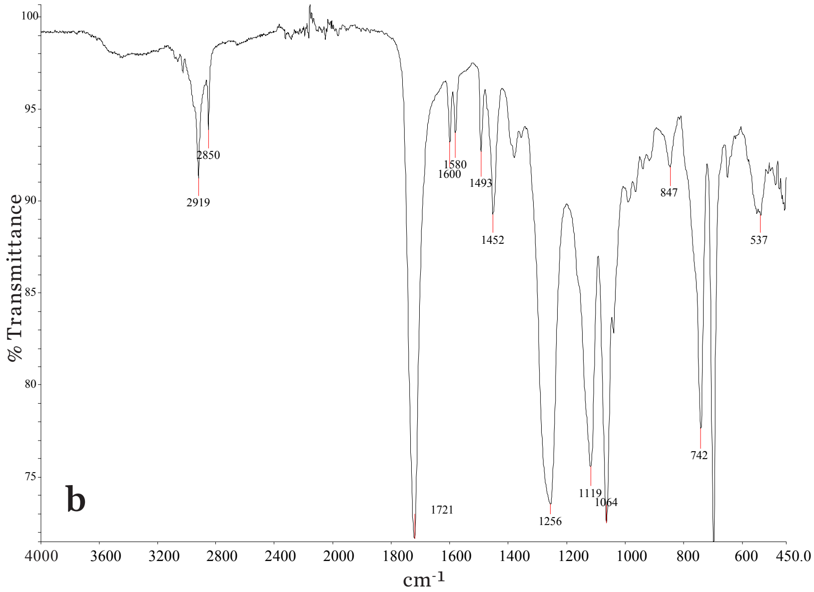


Figure 3. *a) Candelabrum, ca. 1725-1735 CE, glass, H 37.7 cm × Diam. 31.5 cm. Corning Museum of Glass, 91.2.10 with documented Vosschemie polyester fills, and b) FTIR spectrum of associated Vosschemie polyester · Courtesy of Corning Museum of Glass*

objects in the Corning Museum of Glass. The FTIR spectra of polymer samples from many conservation treatments were recorded, of which only a representative subset are illustrated and discussed. The complementarity of ceramic fill materials is illustrated by the polymer reinstatement of missing sections of a blue and white glazed earthenware plate. The objects and polymer fills featured in this paper are illustrated in Figures 1-6. In addition, numerous comparative FTIR spectra, mostly not reproduced in this publication, were obtained from polymer samples archived by Norman Tennent, following accelerated aging testing carried out in the 1970s and 1980s.

FTIR spectroscopy

FTIR spectral data were collected on a Perkin Elmer Spectrum 100 FTIR spectrometer combined with a Specac Golden Gate Single Reflection Diamond attenuated total reflectance (ATR) accessory. Polymer FTIR spectra are illustrated in Figures 2-7.

RESULTS AND DISCUSSION

The selection of polymers with good long-term performance is most often undertaken on the basis of laboratory aging tests, but the extension of the results of accelerated aging to the prediction of ‘real-life’ behaviour can be problematic and unreliable. Feller (1994) underlines this issue in his seminal publication. The polymer repairs illustrated in Figures 1-6 demonstrate the merit of complementing assessment of polymer accelerated aging by natural aging. These acrylic, polyester, and epoxy polymer fills show great variability in their tendency to yellow over a period of several decades of natural aging; they also have the added virtue that the polymer products used have been evaluated in accelerated aging test programmes, thus allowing for comparison between the results of accelerated and natural aging.

The restored Tiffany window with a large area coated with an unknown polymer illustrates the disfiguring polymer yellowing that can occur after a relatively short period, 30 years in this case, of museum display (Figure 1). This window is representative of objects with no treatment documentation stating the polymer used for the restoration. The Corning Museum of Glass treatment records do specify the polymers used for the objects illustrated in Figures 2a, 3a, and 4a, restored in 1974, 1993, and 1974, respectively; but, as is common within museums, object display and storage history is scanty. Even with incomplete documentation, these object fills comprise valuable manifestations of long-term, in-service behaviour of specific polymer products. Furthermore, the polymers’ FTIR spectra can provide a reference standard for aged samples of these products (Figures 2b, 3b, and 4c).

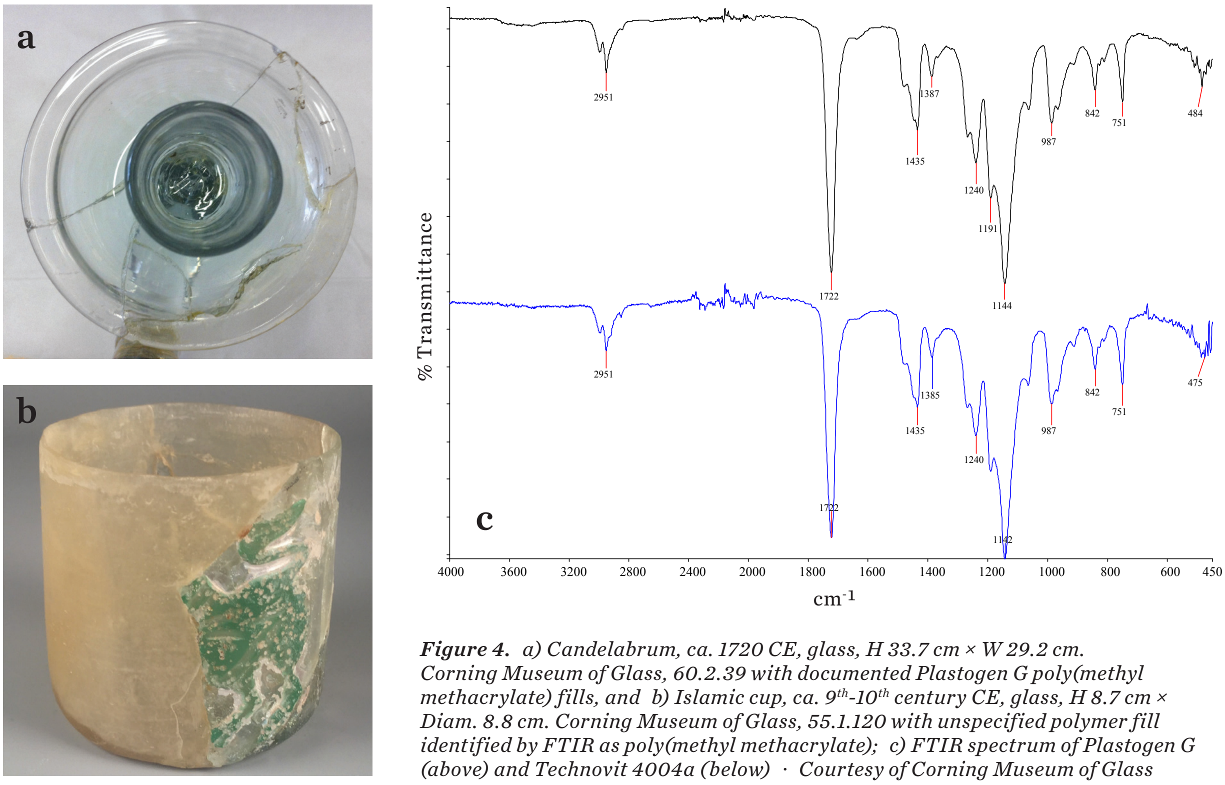


Figure 4. *a) Candelabrum, ca. 1720 CE, glass, H 33.7 cm × W 29.2 cm. Corning Museum of Glass, 60.2.39 with documented Plastogen G poly(methyl methacrylate) fills, and b) Islamic cup, ca. 9th-10th century CE, glass, H 8.7 cm × Diam. 8.8 cm. Corning Museum of Glass, 55.1.120 with unspecified polymer fill identified by FTIR as poly(methyl methacrylate); c) FTIR spectrum of Plastogen G (above) and Technovit 4004a (below) · Courtesy of Corning Museum of Glass*

Several useful conclusions can be drawn from these latter three objects. Firstly, they display a wide range in the extent of polymer yellowing. The Araldite AY103/HY956 epoxy fills to the glass plate have developed an intense dull orange coloration (Figure 2a), whereas the Vosschemie polyester (Figure 3a) and the Plastogen G poly(methyl methacrylate) (Figure 4a) have maintained a visually acceptable appearance without appreciable yellowing. Each of these products has been the subject of laboratory aging evaluations. The good long-term behaviour of Vosschemie (Bradley and Wilthew 1984) and Plastogen G (Tennent and Townsend 1984b) reflect the predictions of accelerated aging tests. In contrast, the extreme colour change of the Araldite AY103/HY956 fills contradicts the assessment from the meticulous epoxy evaluation programme executed by the Canadian Conservation Institute, which concluded that, out of 52 products tested, this epoxy was one of the top five recommended resins for resistance to yellowing (Down 1984; Down 1986).

The corresponding FTIR spectra of these three polymer products are also instructive. The Araldite 103/HY956 FTIR spectrum (Figure 2b) has the typical features deriving from the DGEBA epoxy resin component that renders all epoxy products of this type, i.e. the vast majority of those used by conservators, readily identifiable as a polymer class. Also present in the FTIR spectrum of Bisphenol A itself, a characteristic DGEBA epoxy resin feature is the strong, sharp band at 827 cm^{-1} due to the C-H out-of-plane bending vibration of the aromatic ring. Combined with other FTIR features, this band leads to a straightforward identification of the polymer from the Tiffany window as an epoxy (Figure 2b). However, as discussed further below, the identical comparative spectrum, AY103/HY956, is not unique to this particular brand, thus preventing an unambiguous identification. In the case of Vosschemie and Plastogen G, the FTIR spectra are not only identical to standard spectra from commercial databases for these polymers, but also are indistinguishable from other brand-name polyester and poly(methyl methacrylate) products examined throughout this investigation. For example, the two identical spectra presented in Figure 4c show no FTIR features that differentiate Plastogen G and Technovit 4004a from Plexiglas poly(methyl methacrylate) fills examined in other objects. From its FTIR spectrum, the fill depicted

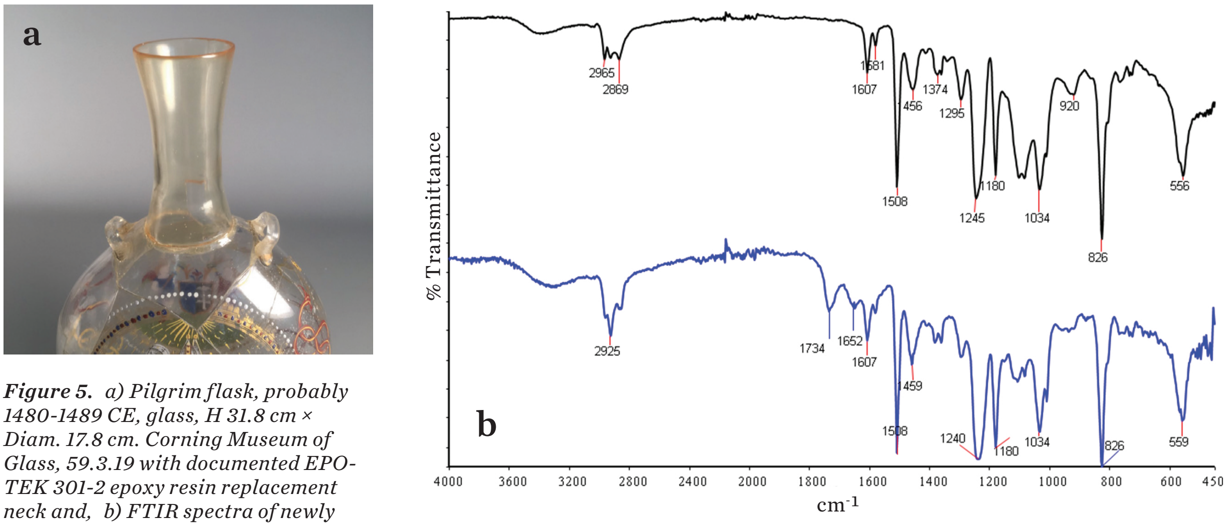


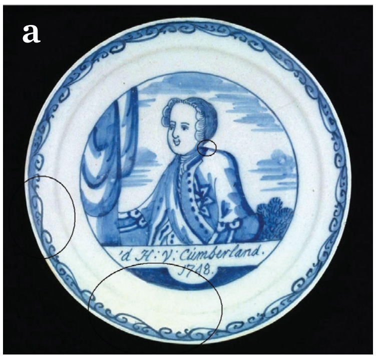
Figure 5. *a) Pilgrim flask, probably 1480-1489 CE, glass, H 31.8 cm × Diam. 17.8 cm. Corning Museum of Glass, 59.3.19 with documented EPO-TEK 301-2 epoxy resin replacement neck and, b) FTIR spectra of newly cast, non-yellowed EPO-TEK 301-2 (above) and from 59.3.19 (below) · Courtesy of Corning Museum of Glass*

in Figure 4b indubitably comprises a poly(methyl methacrylate) casting resin. In this case, a reliable attribution to the product Technovit 4004a is possible on the basis of its typical opaque appearance and its use by glass conservators as the sole acrylic casting polymer (Davison 1998; Errett 1977; Jackson 1983) when the treatment was undertaken.

The behaviour of the EPO-TEK 302-1 epoxy resin replacement neck for the Pilgrim flask (Figure 5a) is a further example where the observed in-service behaviour has failed to match the predicted time span before the onset of yellowing, based on artificial aging tests (Down 1986). This restoration, involving the removal of a previous, unsympathetic replacement neck made from Plexiglas, was carried out in 2004. Since then, the object has been on display in a case with a combination of flood and spot illuminants. A stable case temperature of 24.5 °C was maintained throughout the 15-year duration of the display. The development of yellowing is therefore surprising, given that EPO-TEK 301-2 and HXTAL NYL-1 were Down's (1986) top recommendations with respect to their non-yellowing behaviour. The FTIR spectra show the development of carbonyl bands at 1734 cm^{-1} and 1652 cm^{-1}, typical of photo-oxidative degradation, in addition to diminution of the band intensities at 1103 cm^{-1} and 1085 cm^{-1} as compared to a fresh, newly-cured sample of EPO-TEK 301-2 (Figure 5b).

The complementary nature of the investigation of ceramic fill polymers is illustrated by the Delft blue and white glazed plate, in which three large, approximately triangular fills within the delineated areas were completed in 2001 with Fynebond epoxy resin (Figure 6a). In this example, the fill consists of Fynebond pigmented to match the background colour of the plate. Fynebond was formulated as a successor to Ablebond 342-1, which had good aging behaviour (Tennent 1979; Down 1986), but whose quality control resulted in product variability and the discontinuation of the brand in 1989. After display for 18 years at low illuminant levels, no appreciable yellowing is detectable in the Fynebond fill areas of this plate. The FTIR of Fynebond (Figure 6b) indicates that this epoxy formulation corresponds not only to the spectrum of Ablebond 342-1 (Tennent 1979), but also to that of EPO-TEK 301-2 (Figure 5b). This non-specificity is in contrast to that of HXTAL NYL-1, whose resin component has, unusually, an aliphatic rather than an aromatic ring structure and is thus readily distinguished from all DGEBA-type epoxies on the basis of its FTIR spectrum (Figure 6b).

The difficulty in distinguishing similar epoxy products on the basis of their FTIR spectra is also demonstrated in Figure 7. The spectra of AY103/HY951 and AY103/HY956 are so similar that an unambiguous attribution of an unknown sample to one or the other would not be possible.



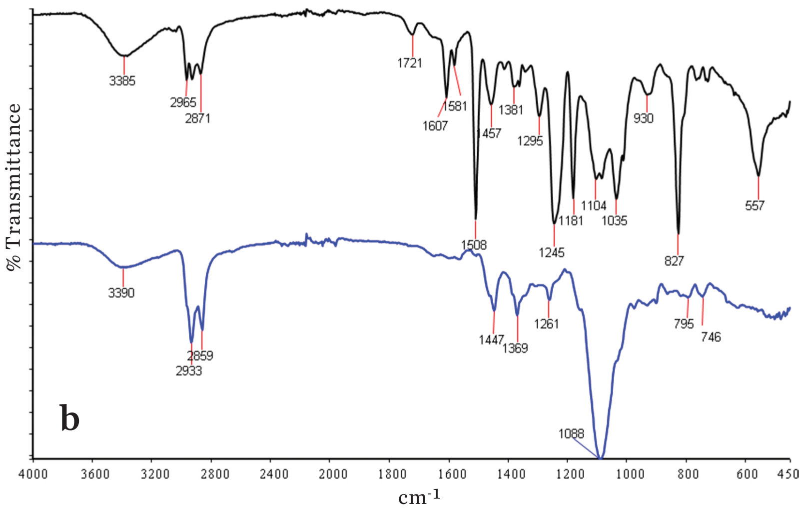


Figure 6. a) Delft blue and white plate, 1748 CE, with documented Fynebond replacement glaze in the three areas delineated, b) FTIR spectra of Fynebond (above) and HXTAL NYL-1 (below) Private collection · Courtesy of Norman H. Tennent

CONCLUSIONS

Study of a subset of polymers used during the past 50 years for gap-filling of glass and ceramics has revealed that identification of specific commercial acrylic, polyester, and epoxy casting resins by means of FTIR spectroscopy is often a forlorn endeavour. It is a straight-forward task to specify the overall chemical class of a polymer, but it is extremely challenging to identify individual commercial products with any certainty based on FTIR analysis. For the various poly(methyl methacrylate) and polyester polymer products investigated, variations in the molecular make-up of the polymer casts were found to be so minor that no differentiation between commercial variants could be achieved by FTIR-ATR spectroscopy.

In contrast, the compositional dissimilarity of many of the commercial epoxy formulations used by conservators means that there is a greater scope for FTIR identification of the precise epoxy resin products used in past conservation treatments than is the case with, especially, polyester fills. Commercial epoxy resin products have greater individuality than acrylic or polyester polymer casting resins. Consequently, FTIR spectral characteristics that arise from a specific epoxy resin, hardener, additive combination make it feasible, in principle, to identify individual commercial products. Despite that potentiality, this study has revealed the practical difficulties that can arise without an extensive database comprising FTIR spectra of the various commercial epoxy brands used by conservators.

As with acrylics and polyesters, epoxies can be readily recognised as a polymer class. The FTIR bands corresponding to the most common resin component, DGEBA, are clearly visible in the resin/hardener cross-linked structure. The differences between commercial products arising from a wide range of possible hardeners, generally amine compounds, and additives can help characterise manufacturers' various products on the basis of spectral variations attributable to these components. However, it has become clear there are two main reasons that it is very difficult to specify a precise manufacturer's product based on FTIR. Firstly, the components of different commercial epoxy products may be the same and give rise to identical FTIR spectra, as with Fynebond and EPO-TEK 301-2. Secondly, the FTIR spectral bands arising from different hardeners may be too similar to reliably distinguish them from one another, as exemplified in this paper by Araldite AY103 cured with hardeners HY951 and HY956.

For conservators, the ability to pinpoint these small formulation differences is important as the nature of the hardener or the presence of additives can have a very significant influence on the overall epoxy aging behaviour. The presence of dibutyl phthalate plasticiser has, for example, previously

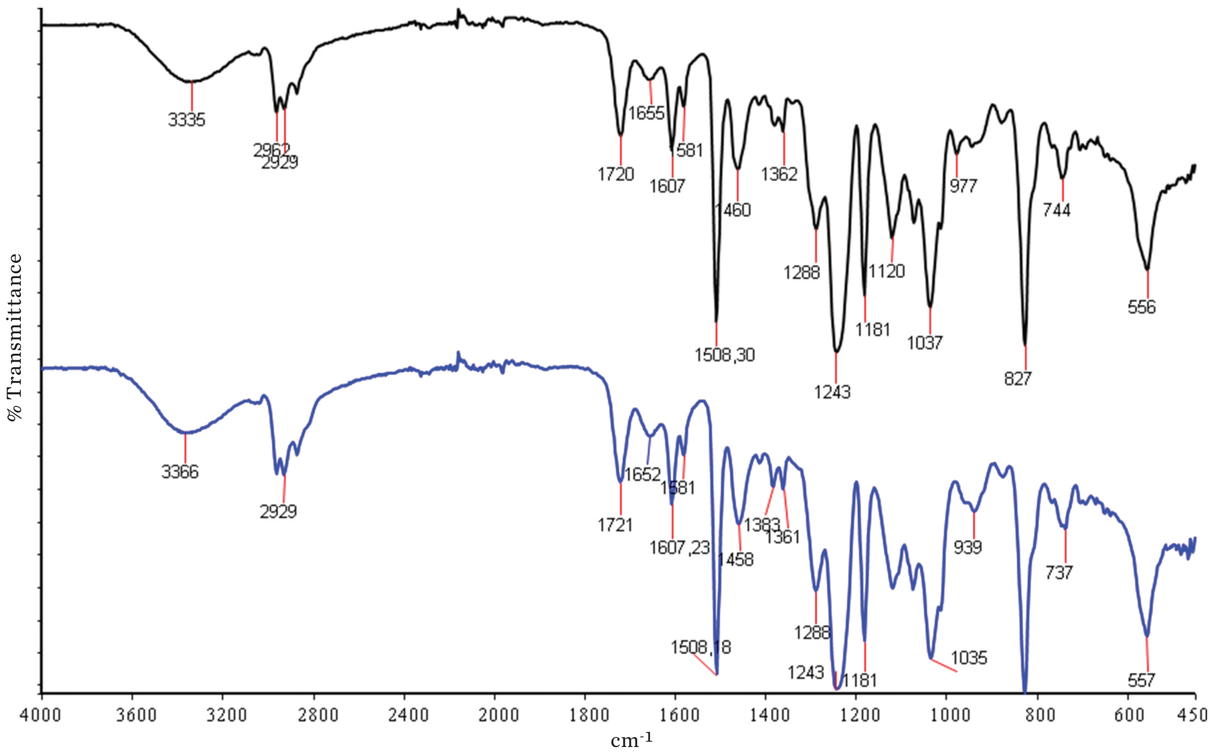


Figure 7. *FTIR spectra of Araldite AY103/ HY951 (above) and of Araldite AY103/ HY956 (below)*

been shown to promote yellowing (Tennent 1979). Fortunately, the presence of dibutyl phthalate plasticiser, present in Araldite AY103, is easily distinguished by its distinctive carbonyl band at 1720 cm^{-1}.

In considering the scope of FTIR spectroscopy for a complete characterisation of the chemical make-up of a polymer, it should not be forgotten that it would be extremely difficult to detect tiny quantities of minor impurities that may be responsible for variations in yellowing behaviour between different brand-name products. Likewise, it is beyond the scope of FTIR to distinguish different batches of a single product as a result of poor quality control. By the same token, it is unlikely that FTIR could pinpoint the traces of a blue dye added to a formulation in order to mask a slight yellow tint. Both these situations are known to occur in practice and complicate an understanding of the explanation of variations between different products' aging behaviour.

The full potentiality of FTIR as a means of precisely identifying undocumented epoxy fill materials from past conservation treatments can only be realised by the establishment of a comprehensive database of authenticated commercial products used by conservators. Currently, a single epoxy resin spectrum is present in the database of the Infrared and Raman User's Group (2019), and so it is the ambition of the authors to continue this research in the hope of further realising the potentiality of FTIR spectroscopy to assist in enabling definitive conclusions to be reached on polymer stability, based on the evidence of 'real-life' natural aging in restored objects.

It is envisaged that future research may include the use of FTIR microscopy in combination with the diamond cell for measuring transmittance spectra of certain samples in order to investigate the scope for greater differentiation between different brands of epoxy resins. However, in a homogeneous mixture, the detection limit for additives will still be 3-5 percent. It is also anticipated that Py-GC-MS, as an adjunct to FTIR, will be explored.

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