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Looking through plastics: Investigating options for the treatment of scratches, abrasions, and losses in cast unsaturated polyester works of art

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ABSTRACT

Works of art made of cast polished transparent unsaturated polyester (UP) are typically very challenging to preserve. If the work breaks, scratches, or chips, an inconspicuous repair is very difficult to achieve. As a result, UP works of art often undergo invasive treatments leading to extensive losses of original surfaces and materials, from overall re-sanding to partial or total re-fabrication. The aim of this research is to find alternative, less-invasive repair options to those that are currently used for such works. Building on previous research, a range of methods and materials for filling losses and chips was investigated, including the potential use of 3-D printing technologies. The research especially focused on the challenging task of mitigating the visual impact of scratches and abrasions. The significance of the refractive index of repair materials, and the idea of a threshold of tolerance for variation depending on the intended use, are also discussed.

INTRODUCTION

Objects and works of art made with translucent or transparent plastics are especially challenging to preserve. Their transparency tends to make any damage highly conspicuous, and invisible repairs are extremely difficult to achieve. When these plastics are highly polished, such as in the colorful and pristine-looking works made by a number of artists from Los Angeles in the 1960s and 70s, there is even less tolerance to damage (Rivenc et al. 2011). In order to remove the aesthetic interference of even a few scratches, and since there are no tested and viable alternatives, such works are often submitted to very invasive conservation treatments, including re-sanding and re-polishing, that require the loss of original surfaces in an area much larger than the damage itself, and often over the entire work. Artist De Wain Valentine expressed the dilemma as follows:

> My polyester work needs to be pristine, because if there is a scratch anywhere, all you see is the scratch. The surface needs to disappear as much as possible, so you can look through it to the inside of the piece and out to the other side … With my cast polyester pieces, the interior of the sculpture is so essential. So they get refinished whenever it's needed. Of course when you do that, a small amount of material is always removed from all over the surface, so I guess if you kept doing it, the object would eventually get completely worn away …. (Valentine, cited by Learner et al. 2011, 12)

Besides the aesthetic considerations, the selection of repair materials is further complicated by the fact that plastics can be readily affected or dissolved when some synthetic adhesives and solvents are brought into contact with them. For the same reason, reversibility in solvent is often impossible with such treatments, making the compatibility upon aging between repair resin and the plastic especially crucial.

As part of a broader project exploring alternative conservation treatments for plastics, and building on previous research (Laganà and Van Oosten 2011, Van Oosten and Laganà 2011), this paper reports on preliminary results to find alternative, less invasive, "additive" treatments for mitigating the visual impact of scratches and abrasions, and to repair chips and losses in cast transparent and polished unsaturated polyester (UP). To mitigate the visual appearance of scratches and abrasions, different methods were

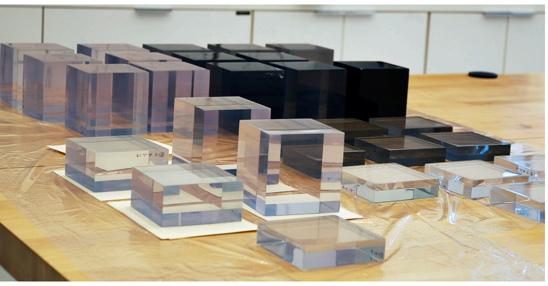


Figure 1
Unsaturated polyester mock-ups

tested to individually fill scratches, as well as the use of coatings to re-saturate entire scratched or abraded areas. To repair chips and losses, casting resins and filling techniques commonly used for the restoration of glass and ceramic objects were tested, as well as the possibility of using novel 3-D printing technologies as a rapid and high-precision technique to produce fills for repairing losses.

Repair materials were selected for their appropriate level of transparency, viscosity, workability, curing time, and compatibility with UP (Table 1). In addition, in order to achieve invisible repairs, their refractive indexes (RI) needed to fall close to or within the range reported for UP, which can vary from ca. 1.54 to 1.57. Since epoxy resins represent the only class of materials matching this RI range as well as the required properties, the investigation has been necessarily restricted so far to these resins, even though they are not reversible in any safe solvent.

The notion of acceptable deviation for the RI between original material and filling resins was explored, and the Becke test with microscopical immersion method to measure the RI of plastic objects was investigated as an alternative to the use of refractometers, which generally require samples with flat and polished surfaces.

The suitability and stability of the materials and techniques used for such repairs were evaluated before and after accelerated light aging using Fourier transform infrared spectroscopy (FTIR) analysis, refractive index measurements, color measurements, microscopy, and visual observation.

Table 1
Materials tested. Composition and properties

Material	Composition[1]	Colour	Curing time	Viscosity cps	Refractive index
HXTAL NYL-1	Hydrogenated Bisphenol A	Colourless	7 days	200 - 300	1.52
EPO-TEK® 301-2	Epoxy based on Bisphenol A	Colourless	24 hours	225 - 425	1.564
Fynebond	Epoxy based on Bisphenol A	Colourless	36-48 hours	moderately low viscosity	1.565
HXTAL NYL-1 + Fynebond mixture (1:1)	-	Colourless		-	1.55
VeroClear RG810	Styrene-Acrylic Polyurethane	Nearly colourless		-	1.527

[1] Manufacturers data, confirmed by FTIR

EXPERIMENTAL SET-UP

UP samples and damage simulation

A set of UP mock-ups was cast by Eric Johnson, a sculptor working in polyester. They were poured in polyethylene molds, using polyester resin SIL 95BA-42 mixed with 1% MEKP-9 (methyl ethyl ketone) catalyst. Two thicknesses of sample were cast: cubes (10.5 × 10.5 × 10.5 cm) and thinner square plates (2.8 × 10.5 × 10.5 cm) (Figure 1). Four kinds of damage (scratches, chips, areas of abrasion, and losses) were made using a variety of tools (see Table 2 for details).

Table 2
Damages and treatment techniques investigated

Damage	Dimension	Tools used to simulate damage	Treatment technique
Scratches	length 7.5 cm 3 different widths: - 0.1 mm - 0.2 mm - 0.5 mm	sharp metal points	Filling using: A. Mini brush (3 types of mini brushes tested: Monogram; Round; Spotter) PRINCENTON ART & BRUSH Co. series 3050 R made of synthetic sable each with a size of 20/0 B. Tiny insect needle with a size up to 000 C. 1-ml single-use syringe NORM-JECT® Tuberkolin Luer D. 3M Scotch® Clear Packaging Tape applied on the damage. A tiny hole was made into the tape and the resin has been injected through it using a 1-ml single-use syringe NORM-JECT® Tuberkolin Luer
Chips	ca. 8 mm x 4 mm	hammer and a chisel	Filling using: A. Mini brush (3 types of mini brushes tested: Monogram; Round; Spotter) PRINCENTON ART & BRUSH Co. series 3050 R made of synthetic sable each with a size of 20/0 B. Tiny insect needle with a size up to 000 C. 1-ml single-use syringe NORM-JECT® Tuberkolin Luer D. 3M Scotch® Clear Packaging Tape applied on the damage. A tiny hole was made into the tape and the resin has been injected through it using a 1-ml single-use syringe NORM-JECT® Tuberkolin Luer
Area of scratches and abrasions		metal comb and a fiberglass pencil	Coating applied using: A. Flat brush (1/2 BLICK studio synthetic – wash).
Losses	ca. 1 cm x 1 cm x 1.5cm up to ca. 2.5 cm x 2 cm x 1.5 cm	hammer and a sharp chisel	Casting using: A. Direct filling technique (cast from mould taken from the original object) B. Indirect filling technique (cast from a mold taken from an intermediate fill made with a modeling beeswax. The fill can be finished and then joined to the original with an adhesive, preferably matching the RI of polyester of 0.02) 3-D scanning and printing

Repair materials

HXTAL NYL-1, EPO-TEK 301-2, and Fynebond epoxy resins, well established in glass conservation, were tested, as well as a 1:1 mixture of HXTAL NYL-1 and Fynebond (see details in Table 1). EPO-TEK 301-2 and Fynebond have similar chemical compositions and RI; the first is produced in the United States and the second in Europe.

3-D scanning and printing

A portable ROMER Absolute Arm 7525SI (Hexagone Metrology) scanner was used to scan the damaged parts of the UP mock-ups. No surface preparation was done prior to the scan, although in some cases it might be necessary to apply a temporary spray coating to be able to scan transparent objects. To reconstruct missing pieces, surrounding intact areas of objects were also scanned as references. The fills were printed with a PolyJet 3-D printer (GROWit), using VeroClear RGD810, a clear polymer recently introduced for 3-D printing.

Fourier transform infrared spectroscopy (FTIR)

The samples were analyzed using a 15× Cassegrain objective on a Hyperion 3000 FTIR microscope (Bruker Optics) with a mid-band MCT detector and purged with dry air. The spectra were the sum of 64 scans at a resolution of 4 cm^{-1}.

Microscopy

Photographs of the damage before and after treatment were taken using a Spot RT color microscope under 6× and 25× magnification.

Refractive index measurements (Becke test)

Small particles of solid UP and epoxy resins were immersed in a series of refractive index liquids by Cargille and observed with a Leitz DMR microscope (Leica Mikroskopie) at 10×/20× magnification, following the method described by McCrone (1985).

Accelerated light aging

Epoxy resins were cast as films in two thicknesses. Thicker films were prepared from silicone molds measuring 47 mm × 25 mm × 1 mm, and thinner films were applied on Mylar film with an 8-mil drawdown bar (0.2032 mm). Films were exposed in an Atlas Wheater-ometer Ci4000, following the ASTM standard D4459-99 for Xenon-Arc Exposure of Plastics Intended for Indoor Application. The irradiance was controlled at 0.33 W/m^2 at 340 nm and the test pieces were evaluated after 100, 200, 300, and 400 hours of exposure. Four-hundred hours of exposure approximates 40 years of museum lighting at 200 lux (Van Oosten and Laganà 2011). Samples of each epoxy resin were also stored in the dark as references. A circular sample of VeroClear RGD810, provided by GROWit, was also included in the aging tests, measuring c. 50 mm in diameter, with a thickness of 4 mm at the apex and 2 mm at the edges.

Color measurements

Color measurements were performed on the epoxy films before, during, and after accelerated light aging using a Konica Minolta 2600d spectrophotometer, relative to a magnesium oxide white standard (geometry: 0/45°, DRS spectral engine, aperture: 3 mm). Each sample was measured nine times and results for L*, a*, b* and ΔE were averaged using Spectra Magic software.

RESULTS AND DISCUSSION

Evaluation of repair materials and techniques

Different application techniques were tested depending on the type of damage (Davison 2003, Kim and Breitung 2007). They are listed in Table 2.

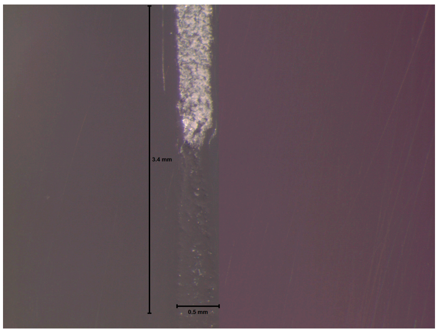
For deep scratches and chips, an important assessment criterion was the ease of applying the adhesive neatly and strictly within the boundaries of the damage, to avoid any later finishing treatment or use of solvents. To fill scratches, the best results were obtained with the round mini-brush 20/0, because the tiny point allowed a very precise application inside the damage (Figure 2). For chips, all the techniques tested proved successful except for the application using 3M tape and a syringe, which created numerous air bubbles (Figure 3). For both scratches and chips, the visual appearance was dramatically improved by all the resins tested. The best results were achieved with Fynebond and EPO-TEK 301-2 whose RI closely matched that of the mock-ups, but even HXTAL NYL-1, whose RI diverges significantly from that of the mock-up, lowered the visual impact of the scratches and chips, making them much less conspicuous.

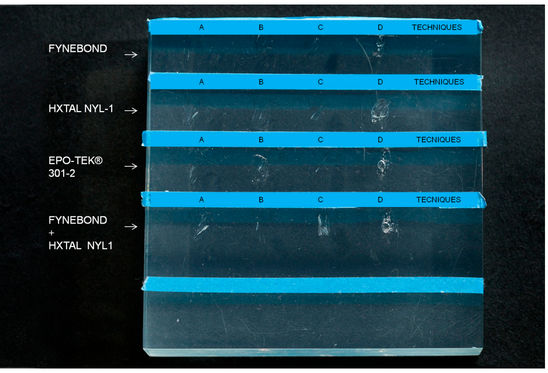
For large areas of scratches and abrasions, where it is difficult to treat each damage individually, the possibility of re-saturating the damage by applying the epoxies resins as coatings was tested (Table 2). The results were promising (Figure 4). All resins tested restored the transparency, but the extent to which the scratches disappeared again depended on the RI value of the specific epoxy. With HXTAL NYL-1, for example, the transparency improved dramatically, but scratches and abrasions remained visible when viewed under certain angles. The gloss of all coatings tested also differed from the gloss of the UP mock-ups, so options to apply the coatings by air brushing, or to treat the coatings surface after application, could also be envisaged.

The techniques evaluated to repair losses were selected based on published literature and adapted from common practices in glass conservation (Koob 2006). For direct fills, a mold was taken with silicone rubber from an intact part of the original object – in this case an intact corner – and repositioned on the area to be filled. The filling material was then poured directly in this mold, on the original object. Finishing was not necessary as the silicone takes a perfect imprint of the surface. The possibility of applying this technique depends on the existence of symmetrical features on the object, or areas identical to the damaged ones, unlike indirect filling techniques.

For indirect fills, the missing piece was reconstructed by modeling beeswax to the shape of the loss. Transparent polypropylene food wrap film was stretched between the wax and the original to remove the wax piece from the mock-ups without touching and deforming it. The wax piece was then used to create a mold in silicone rubber, and the fill was cast out of epoxy resin. Once cured, the resin can be polished as necessary. Indirect filling also offers the advantage that pouring and finishing can be done away from the original object, reducing the opportunities for damage.

Good results were achieved with both direct and indirect filling techniques, although considerable experience and attention to detail are necessary, especially when casting resins directly on the objects. One should keep in mind that shrinkage of the epoxy resins up to approximately 1% can occur, which could cause the fill to not completely match the edges of the loss. Again, the visual performance of epoxy resins ranked depending on how close their RI was to that of the mock-ups. Fynebond seemed to provide the most invisible repair, immediately followed by EPO-TEK 301-2. The 1:1 mixture of HXTAL NYL-1 and Fynebond shrank by more than 1% and was not visually satisfactory, remaining very visible. The fill made with HXTAL, with an RI which differed from that of the mock-ups by 0.048, was the most visible to the naked eye. What is actually disturbing





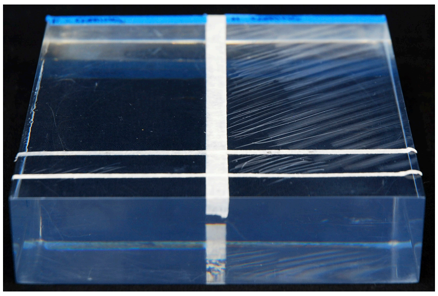


Figure 2
Scratch (25x), lower part treated with Fynebond

Figure 3
Mock-up with chips showing treatments with different materials and techniques (Table 2)

Figure 4
Scratched and abraded surface, left side treated with a Fynebond coating

is not the fill itself, but the damaged surface underneath that remained quite visible through the repair.

In a previous study (Van Oosten and Laganà 2011) it was shown that for adhering transparent broken UP objects, the most important property for an invisible joint is the RI. Adhesion tests performed showed that a difference in the refractive indices of the adhesive and unsaturated polyester of more than 0.02 resulted in a visible joint, while with a difference less than 0.02, mended breaks and cracks could be nearly invisible under normal viewing conditions. In this study, the applicability of the Becke test with microscopical immersion was investigated and proved a viable option for measuring the RI of very small samples (Table 3). The accuracy of this technique is ordinarily about ± 0.001. The present study confirmed the importance of RI for the visual success of all treatments. However, it also showed that it is more crucial for some applications than others. For the filling of losses, an RI as close as possible to the RI of the object is mandatory. However, for more superficial damage such as scratches, abrasions, and chips, any of the resins provided a visual improvement, and even a 0.04 deviation of the RI, as is the case with HXTAL NYL-1, is less evident in small repairs. So for such applications, the visual performance of the resin might be weighed against its stability upon aging (see below) and in some cases a compromise might be favored.

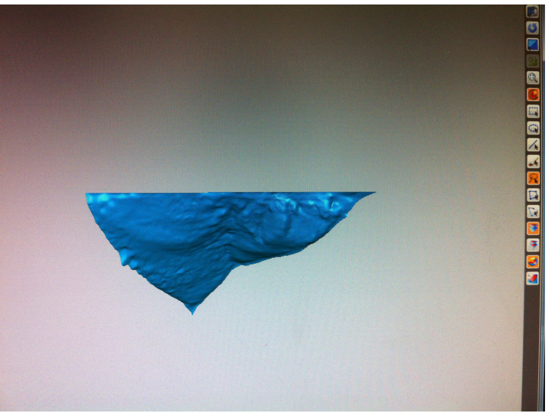


Figure 5
3-D reconstruction of one of the missing UP pieces

Table 3
Comparison of RI measurements of epoxies and UP from data sheets and Becke test method

Products	Refractive index (Datasheets)	Refractive Index (Immersion technique)
HXTAL NYL-1	1.52	1.516
HXTAL NYL-1 + Fynebond (1:1)	1.55	1.55
EPO-TEK® 301-2	1.564	1.565
Fynebond	1.565	1.565
VeroClear RG810	1.527	1.527
UP Mock-ups		
Mock-ups	-	1.568

Evaluation of 3-D scanning and printing materials and technologies

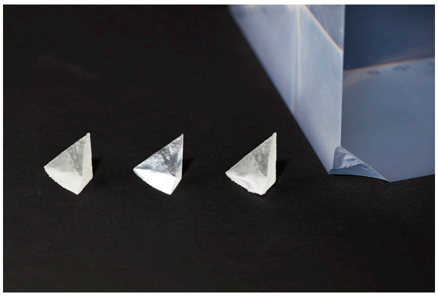
3-D printing technologies are capable of creating three-dimensional solid objects from digital models. The technology offers advantages such as speed, high precision, and the ability to print complex shapes and fine details. Since the 3-D printer does not produce smooth surfaces, it was decided to print two pieces for each fill: one "standard" without additional finishing treatment, to be manually polished, and one polished by GROWit in order to evaluate any eventual change in shape or dimension of the fills due to finishing.

The preliminary results were generally promising. Even a small piece with a complex shape could be reproduced very quickly and precisely (Figure 5). However, it is advisable that a conservator perform the finishing treatment: the pieces finished by GROWit were over-polished and the dimensions slightly altered, so they did not fit perfectly on the original object. In addition, the material used to print, VeroClear RGD810, has a slightly grayish hue that becomes evident on larger and thicker pieces. This, together with its poor aging properties (see below), makes it unsuitable for the filling of losses. However, the 3-D printed fills were used successfully for indirect filling techniques, i.e., to create silicone rubber molds from which epoxy fills could be cast and then glued on the original. In fact, it produced a more precise result than indirect filling with beeswax (Figure 6). This can be a useful solution when direct casting is problematic or when very complex shapes have to be molded.

Accelerated light aging results

Color measurements of the repair materials before and after aging are shown in Table 4. All the epoxy resins tested yellowed to a certain extent, but the phenomenon was much less pronounced in thinner layers (Figure 7). HXTAL NYL-1 hardly exhibited any change at all, with a total color change of max 0.5 ΔE in the thin test pieces, while only a color difference greater than 1.5 ΔE is generally considered to be visible to the observer (Ashley-Smith et al. 2002). Fynebond and EPO-TEK 301-2 showed comparable yellowing upon aging. The 1:1 mixture of HXTAL NYL-1 and Fynebond showed a different pattern with a very pronounced yellowing in thick layers, while the thin test pieces exhibited little color change. This might be attributable to experimental error, an irregular distribution of the two adhesives within the mixture while curing, or a possible reaction between the two resins; further tests are needed to confirm whether this is indeed a trend and to suggest an explanation. VeroClear RGD810 was also evaluated, and although the yellowing cannot be compared with the other resins because of the difference in thickness of the test films, considerable discoloration was observed after only 100 hours of artificial aging. However, the degradation process seemed to slow down during further exposure.

When assessing the discoloration, it should be kept in mind that UP also discolors significantly upon aging, possibly mitigating the yellowed



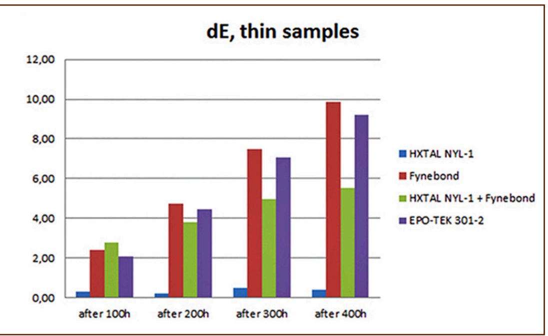


Figure 6
From left to right: two 3-D printed fills (standard and polished) and a fill made with EPO-TEK 301-2 from a mold taken from the 3-D fill

Figure 7
Graph showing changes in ΔE value of the epoxies at aging

Table 4
L*, a*, b* and ΔE values of tested resins before, during, and after artificial light aging

Results of colour measurements on thin test pieces

Time in hours	HXTAL NYL-1				Fynebond				HXTAL NYL-1 + Fynebond				EPO-TEK 301-2			
	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}
0	94.79	1.74	-7.19		95.01	1.90	-7.81		94.90	1.89	-7.77		94.97	1.90	-7.82	
100	95.05	1.70	-7.06	0.30	94.96	1.28	-5.50	2.39	94.85	1.15	-5.07	2.79	95.06	1.31	-5.80	2.10
200	94.97	1.64	-7.15	0.23	94.48	0.69	-3.27	4.73	94.63	0.82	-4.11	3.82	94.59	0.70	-3.54	4.46
300	94.81	1.64	-6.73	0.48	93.84	0.33	-0.57	7.49	94.24	0.73	-2.98	4.97	94.00	0.38	-0.99	7.07
400	94.81	1.47	-6.92	0.39	93.36	-0.16	1.68	9.84	94.17	0.45	-2.48	5.53	93.57	-0.11	1.08	9.23

Results of colour measurements on thick test pieces

Time in hours	HXTAL NYL-1				Fynebond				HXTAL NYL-1 + Fynebond				EPO-TEK 301-2				VeroClear RGD810			
	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}	L*	a*	b*	ΔE_{76}
0	88.68	1.96	-6.02		90.03	2.02	-6.62		90.35	1.95	-6.48		90.45	2.07	-6.94		68.32	-1.09	3.55	
100	90.28	1.50	-4.09	2.56	90.36	1.16	-2.26	4.46	89.79	0.35	1.31	7.98	90.22	1.23	-3.28	3.78	76.50	-0.84	11.01	11.07
200	89.78	1.42	-4.09	2.30	89.89	0.58	0.39	7.15	88.07	-0.19	4.86	11.78	90.23	0.62	-0.91	6.21	72.90	-0.62	14.70	12.06
300	89.38	1.62	-4.47	1.74	88.90	0.36	3.18	10.00	88.16	-0.34	7.56	14.40	89.42	0.41	1.52	8.68	76.27	-0.79	15.04	13.98
400	89.24	1.65	-5.34	0.95	88.52	-0.06	4.96	11.86	87.99	-0.71	9.03	15.92	89.07	-0.03	3.16	10.42	70.38	-0.32	16.71	13.34

appearance of the repair materials, and also that this effect would be of much less significance for colored works.

The visual trends were confirmed by the FTIR measurements performed before and after aging. Fynebond and EPO-TEK 301-2 have identical aging patterns, both displaying evidence of oxidation (increase in carbonyl peak), as does VeroClear RGD810. No significant changes upon aging were detected in the spectra of HXTAL NYL-1. FTIR measurements taken after aging were performed on both sides of the resin films: the one exposed to light showed evidence of changes, while spectra collected from the unexposed side did not display major changes (Figure 8).

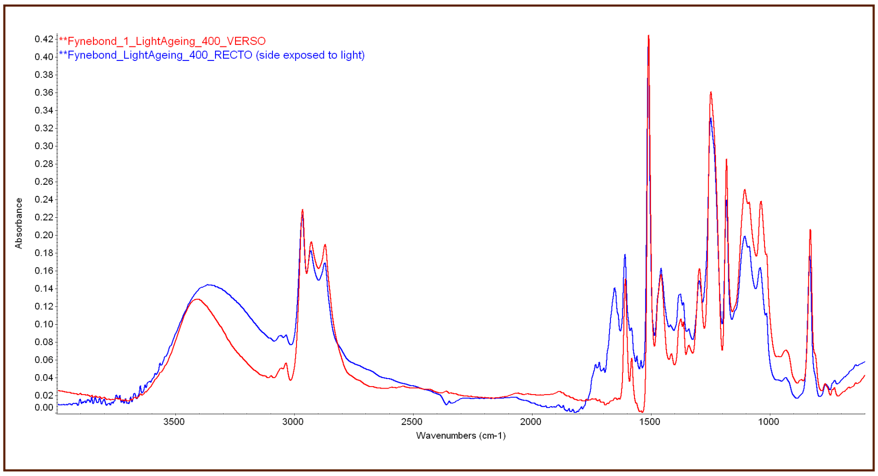


Figure 8
FTIR spectra of Fynebond after 400 hours of aging: side exposed to light (recto) and other side (verso)

CONCLUSION

The preliminary results of this research are especially encouraging, as they showed that mitigating the visual impact of scratches, abrasions, chips, and losses in cast, transparent UP objects using "additive methods" is possible. In line with previous research, the RI of the repair materials proved to be a crucial factor in the visual success of the treatment. In fact, the larger the loss, the greater the impact of the RI. Unfortunately, the most stable material investigated, HXTAL NYL-1, has a very low RI which does not match that of the UP mock-ups tested. Fynebond and EPO-TEK 301-2, although they discolor to some extent upon aging, gave the best results, providing nearly invisible repairs. However, experiments also indicated that all the resins tested can mitigate the visual appearance of more superficial damage such as scratches, abrasions, and chips, since even an RI match that is not close is less visible in smaller repairs. Therefore, in many cases the choice of a suitable repair resin will be a trade-off between different desirable properties. The study also showed that although VeroClear RGD810 is not a suitable material for filling losses, 3-D printing technology can be a useful technique for indirect fills. The project will continue to investigate the repair of other transparent plastics, especially PMMA, as well as to refine some of the techniques discussed here. Non-invasive methods of measuring the RI of real objects will also be explored. It is hoped that, although most repairs on transparent objects are irreversible, exploring less-invasive options than are currently used will open up new possibilities for conservators and help reduce the likelihood of works of art being "worn away."

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