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BACK TO TRANSPARENCY, BACK TO LIFE: RESEARCH INTO THE RESTORATION OF BROKEN TRANSPARENT UNSATURATED POLYESTER AND POLY(METHYL METHACRYLATE) WORKS OF ART

Keywords: unsaturated polyester (UP), poly(methyl methacrylate) (PMMA), adhering, cracks, transparent plastics, stress-strain viewer, refractive index (RI), filling

ABSTRACT

The conservation of transparent plastic works of art is not a simple matter for conservators of modern and contemporary art. There is a lack of publications in the conservation field, especially on the topic of adhering, crack filling and loss compensation of transparent plastics. This paper describes a methodology to approach these conservation issues. Two transparent works of art – one made of unsaturated polyester (UP) and the other made of poly(methyl methacrylate) (PMMA) – from the RCE study collection were investigated. The study focused on stress in PMMA and the refractive index of the adhesives used for repairs. Measuring the refractive index of tiny samples from the UP work of art was explored in collaboration with the Netherlands Forensic Institute (NFI). Stress in PMMA could be visualised using a strain viewer and could be released by annealing. Materials and methods for adhering and filling transparent UP and PMMA objects were investigated.

RÉSUMÉ

La conservation-restauration des œuvres d'art en plastique transparent n'est pas une chose aisée pour les restaurateurs d'art moderne et contemporain. Il existe une pénurie de publications dans le domaine de la conservation-restauration, notamment au sujet de l'adhésion, du masticage des craquelures et du comblement des lacunes pour les plastiques transparents. Cet article décrit une méthodologie dédiée à ces problèmes de restauration. Deux œuvres d'art transparentes, l'une en polyester non saturé (UP) et l'autre en polyméthacrylate de méthyle (PMAM), provenant de la collection d'étude du RCE, ont été analysées. L'étude s'est intéressée à l'effet de la contrainte sur le PMAM et à l'indice de réfraction des adhésifs employés

INTRODUCTION

Repairing broken works of art made of transparent plastics is a complex task since many factors must be taken into consideration. Adhesives containing solvents, or producing heat during curing, can dissolve plastics or, in some cases, induce stress crazinc into the material. In addition, repairs must remain invisible, a problem similar to those encountered in glass restoration. However, insufficient knowledge is currently available on adhering, crack-filling and loss compensation of transparent plastics. The aim of this paper is to provide a preliminary methodology to approach these conservation issues through two objects from the study collection of the Cultural Heritage Agency of the Netherlands (RCE): one object made of unsaturated polyester (UP) and the other made of polymethylmethacrylate (PMMA). The RCE study collection consists of de-accessioned objects which can no longer be exhibited but are available for research. Conservation research included selecting appropriate adhesives, materials and techniques for filling cracks and areas of loss in transparent UP and PMMA objects. Due to similarity with repairing broken glass, methods and materials for filling cracks and losses were selected from glass conservation techniques (Davison 2003).

Unsaturated polyester (UP)

Objects made of transparent UP resin can break when subjected to shock or careless handling, due to their low-impact strength. Physical damage may include scratches, cracks, chipped surfaces, broken parts and losses. An earlier study performing adhesion tests on UP showed that a difference in refractive index (RI) of adhesive and UP less than 0.02, resulted in nearly invisible joints (Laganá 2010). Fynebond, a crystal clear epoxy resin, appeared to be the best adhesive due to its transparency, workability, curing time, non-yellowing, high adhesion strength and suitable RI.

This study focuses on the challenging task of loss compensation and filling cracks using Fynebond on dummies and the broken transparent UP sculpture *Untitled* by H.A. de Moor, 1991 (Figure 1). This work was made by pouring layers of polyester resin one after another, in a mould (Figure 2). The determination of the RI of each layer was investigated at the Netherlands Forensic Institute (NFI) due to their experience in measuring tiny samples.

pour les réparations. La mesure de l'indice de réfraction de petits échantillons provenant de l'œuvre d'art en PENS a été explorée en collaboration avec le Netherlands Forensic Institute (NFI). La contrainte sur le PMAM a pu être visualisée à l'aide d'un polariscope et supprimée par recuit. Des matériaux et des méthodes pour le collage et le masticage des objets en PENS et PMAM transparents ont été étudiés.

RESUMEN

La conservación de obras de arte de plástico transparente no es una tarea sencilla para los conservadores de arte moderno y contemporáneo. Casi no existen publicaciones relativas a su conservación, especialmente sobre el tema de la adherencia, el resane de grietas y la pérdida de compensación de plásticos transparentes. Este artículo describe una metodología para abordar estos problemas de conservación. Se investigaron dos obras de arte transparentes, una hecha de poliéster no saturado y la otra de polimetilmetacrilato (PMMA), de la colección de estudio RCE. El estudio se centró en la tensión del PMMA y el índice de refracción de los adhesivos empleados para las reparaciones. En colaboración con el Instituto Forense Holandés (NFI, en sus siglas en inglés) se estudiaron las mediciones del índice de refracción de pequeñas muestras de las obras de arte de poliéster no saturado. La tensión del PMMA se pudo visualizar con un medidor de tensión y las tensiones se liberaron con un tratamiento de recocido. Se investigaron los materiales y métodos de adherencia y relleno de objetos de poliéster no saturado y PMMA.

Figure1
H.A. de Moor *Untitled*, 1991, 49 × 39 × 28 cm, RCE study collection

Poly(methyl methacrylate) (PMMA)

Repairing broken transparent PMMA objects is a challenge for conservators due to the fact that most of the effective adhesives are solvent-based and most solvents can dissolve PMMA or cause stress-crazing and cracking. Stress in PMMA is produced by forces, can result in mechanical failure, and may be the result of moulding, or machining and drilling. Crazing in PMMA is either the result of the release of inbuilt stress or can be caused by exposure to solvents and changes in relative high humidity (Sale 1995). Extruded acrylic sheets have a lower stress tolerance than cast sheets. This stress can usually be eliminated by annealing, a heat treatment which relieves internal stress without the risk of crazing. Annealing should be undertaken prior to adhering with solvent based adhesives (Lucite International 2005).

Before any treatment of broken PMMA objects, many questions need to be considered.

What range of RI is usable in order to have a non-visible joint? How much stress is present in an object and how can it be measured? How can extruded and cast PMMA objects be distinguished? Is it possible to conserve both types using the same techniques and materials? Can annealing be an effective method for preventing stress crazing in PMMA before applying the adhesive? The broken PMMA work of art entitled *Nr. III: Geometrische Kompositie* by H.E. Kanmeyer (1978) served as study object. This object consists of a composition of mirrors and cubes made of transparent blue, yellow and pink fluorescent PMMA sheets. The object presents broken parts, cracks, chipped off surfaces and a loss on an edge (Figure 3). Research included identifying the materials using Fourier transform infrared spectroscopy (FTIR), measuring the refractive index, and visualizing stress in PMMA using polarized light and annealing PMMA.

EXPERIMENTAL UP

Samples and materials

UP paperweights from flea markets and private collections served as naturally-aged yellowed dummies to imitate the broken yellowed polyester work of art. All dummies were deliberately damaged by hammer and chisel to imitate cracks, chipped off surfaces and losses. Fynebond was used for filling the cracks, the chipped off surfaces and to compensate the losses. To match the RIs of the various UP layers of the RCE study object, the usability of a mixture of Fynebond and Hxtal NYL-1 was investigated.

Refractive index measurements

The RI of all dummies and adhesives was measured using a Rayner illuminated Dialdex refractometer, while tiny samples of each polyester layer of the RCE study object were measured using a GRIM® 3 (Glass RI Measurement) refractometer.

GRIM® 3 is an instrument for high precision RI (standard deviation: 0.00002 RI) measurement and works using the oil immersion temperature variation method. By varying temperature to alter the refractive index of calibrated oil, the RI of an immersed fragment of glass or unsaturated polyester (UP) can be determined at the point of null refraction, the point at which the RIs of the fragment and immersion oil match. Sample size is as small as 50 microns.

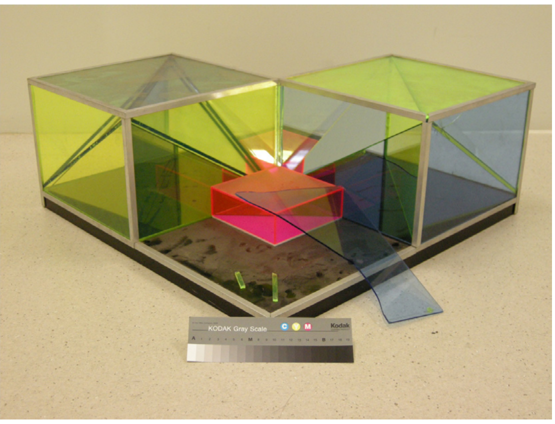


Figure 2
Detail of the polyester layers

Figure 3
H.E. Kanmeyer, *Nr. III: Geometrische Kompositie*, 1978, 60 × 60 × 23 cm, RCE study collection

Artificial light ageing

To investigate yellowing, adhesives and mixtures of adhesives were artificially light aged using a Xenotest, Alpha High Energy (Atlas®), and exposed to the radiation of a filtered (Xenochrome 320) Xenon-Arc-lamp (105 Klx, T 50°C, 40% RH) for up to 160 hours to induce photo-oxidation. 160 hours Xenotest equalizes 40 years museum lighting at 200 lux.

RESULTS AND DISCUSSION UP

Adhering the RCE study object

Measuring the RI of tiny fragments from the various polyester layers of the RCE study object at the NFI indicated that the various layers did indeed have different RIs. Standard calibration oil for polyester was not available at the time, and full measurement of the RI is still ongoing. However, according to literature, a possible refractive index variation between 1.54 and 1.57 can be expected. To match this variation in RI, an adhesive with an average refractive index of about 1.55 is needed, which can be obtained by mixing two epoxies (Augerson 1993).

A 1:1 mixture of Fynebond (RI 1,565) and Hxtal NYL-1 (RI 1,52) was prepared. The measured RI of the 1:1 Fynebond and Hxtal NYL-1 mixture was 1.55. Artificial light ageing of this mixture of epoxies for 160 hours showed a negligible yellowing and no change in the refractive index of the epoxies mixture has been observed. Previous research on glass has shown that the yellowing process can become obstructive when having a significant thickness, but does not affect the RI of the resin in a narrow crack (Tennent 1984).

Filling cracks

Filling tests were carried out on naturally aged dummies. Tiny drops of Fynebond were applied by slowly moving a needle with the adhesive along a crack. The adhesive flowed slowly into the crack due to capillarity, giving a very good filling. Excess adhesive was left until the epoxy resin was in the gel state and then easily removed via mechanical and solvent action using a cotton swab moistened with isopropanol.

Filling chipped surfaces

The best performing method was filling the chipped surfaces in two steps. First Fynebond was applied with a needle until the loss was filled, taking care not to overfill. Due to the expected shrinkage of 1%, a second layer of Fynebond had to be added. After one day, a layer of more viscous, partly cured Fynebond (due to storing in the fridge), was applied and filled the void until the surface was reached. No more shrinkage was shown after curing. This two-step method avoids finishing treatments, such as sanding, which is a risk for the transparent polyester surface.

Loss compensation

Tests were performed on a naturally aged yellowed UP paper weight previously damaged on one edge to simulate the loss of material (Figure 4). According to the size, position and type of loss, it was decided to use the gap filling method known as the two sides moulding technique used in glass conservation for losses on a rim or edge (Koob 2006). The shape of the lost part was copied by making a mould with silicone rubber from a similar not damaged area of the paperweight. The mould was repositioned on the damaged area and filled with Fynebond achieving good results.

Figure 4
Broken naturally aged yellowed dummy

Figure 5
Naturally aged yellowed dummy after loss compensation with Fynebond and Orasol®

Retouching

Two options are available for obtaining a coloured cast or filling: mixing colours with uncured epoxy or retouching a cured epoxy (Davison 2003). In order to match the yellowing of the naturally aged paper weight, both options were performed using Fynebond and Orasol® dyestuff. The best result was achieved using Orasol ® orange G and yellow 2GLN dissolved in a mixture of 80% ethyl alcohol, 5% water and 15% Dowanol PM applied with a brush. The retouching matched the paperweight colour satisfactorily, retaining the transparency of the Fynebond cast (Figure 5).

EXPERIMENTAL PMMA

Samples and materials

Rectangular shaped test samples (12.2 × 4.5 × 0.3 cm) were sawn from cast and extruded PMMA sheet (Altuglas). The RI of all PMMA test sheets was 1.492. The test samples were broken simulating shock by applying an increasing load using a Zwick dynamometer 1474.

Blind cracks and losses on edges were simulated on cast and extruded test samples using a hammer and chisel. Naturally aged PMMA objects from the RCE plastics reference collection, with and without stress crazes, were used as dummies and were also damaged using hammer and chisel. Extensive research has been performed on suitable adhesives for PMMA (Sale 1993, 1995, Lorne 1999, Comiotto 2009). The best performing adhesives from these studies and a few suitable others were selected (Table 1).

Stress-strain viewer

Transparent plastics subject to strain exhibit birefringence properties, lending themselves to photoelastic stress analysis using the Sharples strain

Table 1
Adhesives tested on PMMA. Composition and properties

Product	Composition	Ratio	Tg (°C)	RI	Viscosity mPa.s
Acrifix 192	Acrylic polymer in methyl methacrylate	-	-	1.48	1800 ± 200
Hxtal-NYL-1	4,4-isopropylidenedicylohexanol-Epichlorohydrin	3:1 (resin:hardener)	-	1.52	80
Paraloid B67	Isobutylmethacrylate	40% in mineral spirit (aromatics below 0.1%)	50	1.48	250-375
Paraloid F 10	Copolymer Butylmethacrylate	40% in a mineral spirit and aromatic (9:1)	20	1.49	1400-2800
1:1 Mixture of Paraloid F10 Paraloid B67	Copolymer Butylmethacrylate Isobutyl methacrylate	40% in a mineral spirit and aromatic (9:1) 40% in mineral spirit	-	1.48	-
Plexigum®PQ 611	Isobutylmethacrylate solution in 2-ethylhexylmethacrylate	30% in isooctane	32	1.45	-
Plexisol P 550-40	n-butylmethacrylate	40% in mineral spirit	34	1.47	2800-5400

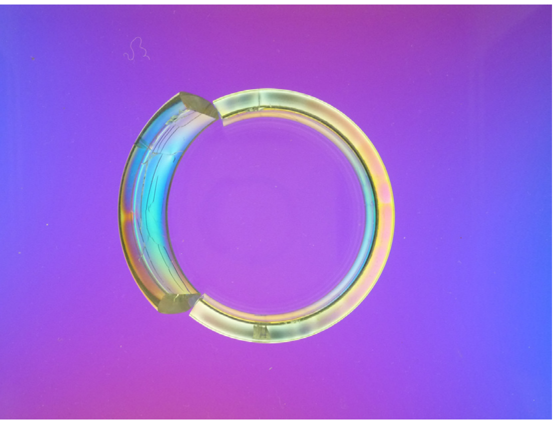


Figure 6
Bracelet viewed under Sharples strain viewer

viewer (Sharples 1970). The level of moulded-in stress or residual stress can be determined by this method.

The transparent plastic object is placed between a light source, an analyzer and a polarising element both with quarter wave plate. The interference pattern is made up of colours fringes. Colours correspond to stress levels. Areas with higher density of colour fringes have higher stress inside. Many plastic objects show stress cracking, for example the bracelet seen in Figure 6.

Annealing

PMMA objects were placed on a metal plate covered with Melinex and annealed in an air circulation oven at 75°C (extruded PMMA) and 85°C (cast PMMA). The oven temperature was raised at a rate not exceeding 18°C per hour. Annealing time was depending on thickness and in general the following is recommended: 1 hour for up to 3 mm thickness, 2 hours for up to 6 mm, 4 hours up to 12 mm and 6 hours up to 20 mm. The cool down to ambient was at a rate not greater than 12°C per hour.

FTIR

Spectra of objects, dummies and adhesives were recorded from 4000 to 600 cm^{-1}, over 40 scans at a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum 1000 FTIR spectrometer combined with a Golden Gate, Single Reflection Diamond ATR unit (sample size 0.6 mm^2).

RESULTS AND DISCUSSION – PMMA

Adhering broken parts

To evaluate the behaviour of the selected adhesives, adhesion tests were performed by joining broken cast and extruded PMMA sheet test strips (Table 2). The joints performed with Acrifix 192 show a very good appearance, but under polarized light some stress on the joints was observed on cast as well as on extruded PMMA sheets. More stress was observed in the adhered cast than in the adhered extruded test strips. Hxtal NYL-1 and Plexigum®PQ 611 – according to their RIs – should not be as good a match with PMMA than the other adhesives. However, they show overall good visual results, as did Plexisol P550-40. However, the best result was achieved with a 1:1 mixture of Paraloid F10 and Paraloid B67 (with a close RI match to PMMA).

Table 2

Adhering and filling tests on PMMA

	Acrifix 192	Hxtal-NYL-1	Paraloid B67	1:1 Mixture of Paraloid F10 - Paraloid B67	Plexigum®PQ 611	Plexisol P 550-40
Adhering broken parts	±	+	n.s.	++	+	+
Filling blind cracks	n.s	++	-	-	-	-
Filling chipped off material	-	+	-	-	-	-
Loss compensation	-	±	n.t.	n.s.	n.s.	n.s.

++ = very good
\+ = good
± = moderate
\- = bad
n.t. = not tested
n.s. = not suitable for the specific treatment

Stress-strain viewer

Difference in colour between cast and extruded PMMA sheets was observed under polarized light using the stress-strain viewer. When positioned parallel to the full weight plate, both sheets show the same pink; while tilted at 45° to the polarized light, they differ in colour. The cast PMMA appears to be darker blue, while the extruded PMMA sheet appears to remain pink. The same change in colour was observed in some cast and extruded PMMA objects in the RCE reference collection and in the broken PMMA sheets of *Nr. III: Geometrische Kompositie*. Difference in colour under polarized light is the result of the difference in entanglement of PMMA polymer chains in cast and extruded PMMA sheets.

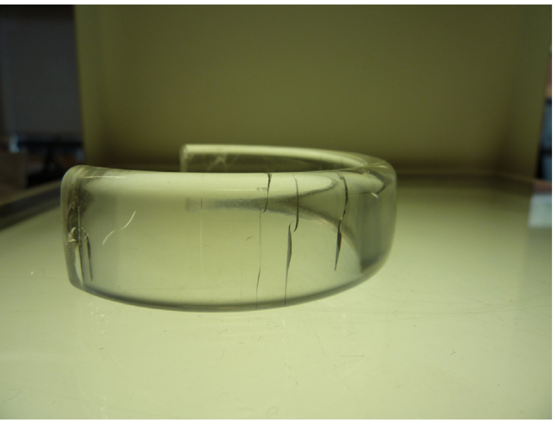
Test samples of cast and extruded PMMA sheets were observed under polarised light before and after breaking. After breaking and chiselling, cast and extruded PMMA test sheets showed stress. Cast test sheets showed more stress after breaking than extruded test sheets. Stress was only visible at the broken side of the sheets when positioned perpendicular to the polarized light.

Annealing

When viewed under the strain viewer, the observed stress in a PMMA spoon disappeared after annealing for 3 hours at 85°C and cooling to ambient temperature.

Filling cracks

Some of the adhesives were selected to fill blind cracks and applied using capillary action. Acrylics were used as a 20% solution in low evaporating solvents in order to let the adhesive flow into the cracks. Due to the high viscosity of the acrylics, it was difficult to induce flow into cracks. Lower concentrations increased the contact with solvents and PMMA, which is not advisable, due to stress crazing. Introduction of adhesives by capillary action was more effective using Hxtal NYL-1 because of its low viscosity. The best performing adhesive for filling blind cracks was Hxtal NYL-1 and was used on the naturally aged PMMA bracelet with excellent results (Figure 7). After filling, cracks are only visible as hairlines (Figure 8).



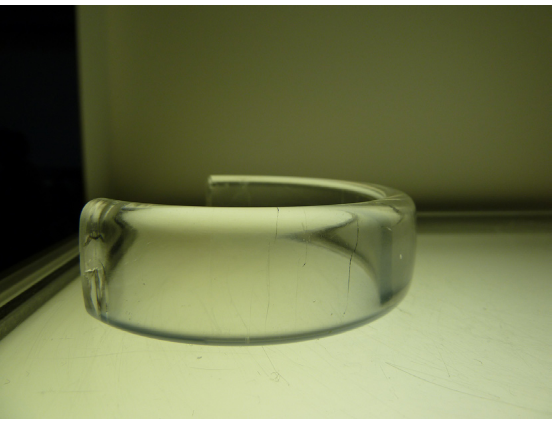


Figure 7
Stress cracked bracelet from RCE reference collection

Figure 8
Bracelet after the treatment with Hxtal NYL-1

Filling chipped surfaces

Acrifix 192 was applied for filling chipped surfaces, but due to its high viscosity it did not perform well in filling tiny losses, whereas Hxtal NYL-1 was applied with good results, despite the not perfect match in RI (difference of about 0.028). Matching RIs becomes more important when filling wider cracks and filling bigger chipped off surfaces.

Loss compensation

Considering the damaged edge of the broken object of the RCE study collection, it was decided to use the direct filling technique (Table 2). Other possibilities that will be further investigated are transparent mould techniques and detachable fills in the form of inlays using a laser and rapid prototyping.

CONCLUSION

Measuring the RI of small unsaturated (UP) samples using forensic science equipment will enable a better choice of matching the RI of adhesives in order to bring back a restored object to transparency and hence to life. The mixture of epoxies (1:1 Fynebond and Hxtal NYL-1) investigated, showed to be a promising option.

Experiments in filling blind cracks and chipped surfaces and compensating loss in UP dummies were successful using Fynebond, as was adapting techniques which are normally used in glass conservation.

The strain viewer gave good insight in the inbuilt stress of PMMA objects. After breaking both cast and extruded PMMA, a higher stress was noticed in cast PMMA than in extruded. Moreover, cast and extruded sheets of PMMA could be discriminated under the strain viewer.

The 1:1 mixture of Paraloid F10 and Paraloid B67 gave the best results in adhering PMMA. The use of Hxtal NYL-1for filling blind cracks and chipped surfaces was successful. However, filling big losses using Hxtal NYL-1 was not successful due to a difference in refractive index, which is more visible when having a significant thickness. Further research is ongoing using acrylics with matching RIs.

Annealing PMMA objects showed promising results and future experiments will involve adhering PMMA before and after annealing. Research will also include artificial light ageing.

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