



## UvA-DARE (Digital Academic Repository)

### In search of a perfect bond: An evaluation of potential adhesives to repair transparent poly(methyl methacrylate) objects

Laganà, A.; Doutre, M.; David, M.; Lukomski, M.; Hendriks, E.; van Bommel, M.

**Publication date**

2021

**Document Version**

Final published version

**Published in**

Transcending Boundaries: Integrated Approaches to Conservation

**License**

Other

[Link to publication](#)

**Citation for published version (APA):**

Laganà, A., Doutre, M., David, M., Lukomski, M., Hendriks, E., & van Bommel, M. (2021). In search of a perfect bond: An evaluation of potential adhesives to repair transparent poly(methyl methacrylate) objects. In J. Bridgland (Ed.), *Transcending Boundaries: Integrated Approaches to Conservation: ICOM-CC 19th Triennial Conference preprints : Beijing, 17–21 May 2021* International Council of Museums. <https://www.icom-cc-publications-online.org/4464/In-search-of-a-perfect-bond--An-evaluation-of-potential-adhesives-to-repair-transparent-polymethyl-methacrylate-objects>

**General rights**

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

**Disclaimer/Complaints regulations**

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

# In search of a perfect bond: An evaluation of potential adhesives to repair transparent poly(methyl methacrylate) objects

**Anna Laganà\***

Getty Conservation Institute  
Los Angeles CA, USA  
ALagana@getty.edu

**Michael Doutre**

Getty Conservation Institute  
Los Angeles CA, USA  
MDoutre@getty.edu

**Melissa David**

Independent conservator  
Turin, Italy  
melissa.david@outlook.com

**Michał Łukomski**

Getty Conservation Institute  
Los Angeles CA, USA  
MLukomsky@getty.edu

**Ella Hendriks**

University of Amsterdam  
Amsterdam, The Netherlands  
E.Hendriks@uva.nl

**Maarten van Bommel**

University of Amsterdam  
Amsterdam, The Netherlands  
M.R.vanBommel@uva.nl

\*Author for correspondence

**Keywords**

poly(methyl methacrylate), PMMA, adhesives, bonding, crazing

**Abstract**

This paper presents the results of an extensive research on potential adhesives for the repair of transparent poly(methyl methacrylate) (PMMA) used in art and design. Repairing PMMA sculptures and objects is challenging due to the difficulty of finding adhesives that are able to recover transparency and strength without being harmful to the plastic. Currently, only few adhesives are found to meet these requirements. Therefore, this study aimed to provide conservators with more options to successfully and safely repair PMMA. Thirteen products from different adhesive categories were tested on both cast and extruded transparent PMMA. The suitability of these adhesives was thoroughly assessed in terms of their optical and mechanical properties, aging behavior, and ability to induce stress crazing or cracking in PMMA. The results showed that the following adhesives are suited for the

**INTRODUCTION**

Identifying suitable adhesives to repair transparent poly(methyl methacrylate) (PMMA) objects is one of the biggest challenges in conserving plastic artifacts. A successful adhesive method should bond PMMA without dissolving the material or inducing changes such as crazing and cracking. It should be strong enough to bond, yet weak enough to fail before damaging the PMMA. Furthermore, it should be easy to apply, invisible, chemically stable over time, and preferably removable to allow future retreatment.

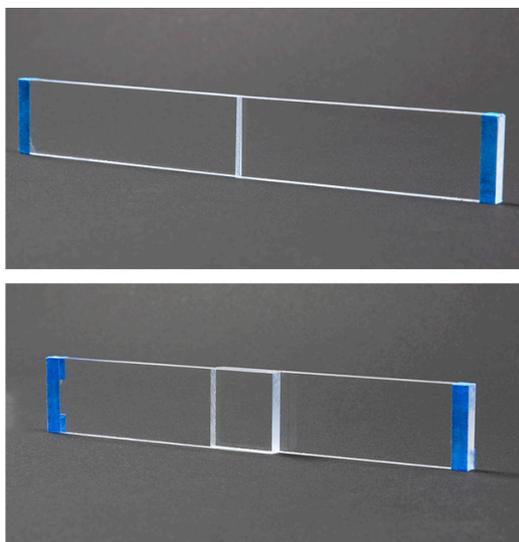
Over the past years, several papers in the conservation literature have focused on the topic of adhesive repair of PMMA objects. However, only a few studies have thoroughly investigated adhesive properties to assist conservators in making an informed selection for repairing PMMA objects, and only a limited number of options have been found to be suitable: the 1:1 mixture of Paraloid F-10 and Paraloid B-67; Plexigum PQ611; and HXTAL NYL-1. In Europe, this range of options is even narrower due to the current unavailability of Paraloid F-10.

Based on these considerations, this study had two major aims: first, to increase the adhesive options available and, second, to provide conservators with the data and tools required to select an appropriate adhesive for each specific bonding case. To achieve these objectives, the suitability of a wide range of adhesives was explored by investigating their relevant properties and performance. Bonding tests were performed on PMMA samples with 13 adhesive systems. The chemical composition of the adhesives was investigated using Fourier transform infrared (FTIR) spectroscopy and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis. Their optical properties were evaluated with the naked eye and refractive index measurements, their mechanical properties with tensile tests and shear tests, and their aging behavior with artificial light aging and color measurements. The results are discussed and data displayed in charts to provide easy comparison and help conservators to make better informed choices.

**EXPERIMENTAL****Adhesives**

The selection of the adhesives tested was jointly based on the results of previous studies on bonding PMMA (Comiotto and Egger 2011, Laganà

safe and successful repair of PMMA objects: the water-based adhesive Aquazol 500, the acrylic resins Paraloid B-67, a 1:1 mixture of Paraloid F-10 and Paraloid B-67, a 1:1 mixture of Plexisol P550-40 and Paraloid B-67, Plexigum PQ611, and the epoxy resin HXTAL NYL-1. Results are summarized in an adhesive comparison chart, designed to offer conservators a tool to select appropriate adhesives based on the bonding requirement of the broken PMMA objects to be repaired.



**Figure 1.** Butt and lap joints

and Van Oosten 2011, Sale 2011, Bienefeld 2016), manufacturers' recommendations, and the suitability of the adhesive properties. The following properties were considered the most relevant for a successful and safe bonding of PMMA: optimal transparency with a refractive index (RI) as close as possible to PMMA (RI 1.49) for less visible repairs; appropriate solubility; suitable working and curing time; a curing process without exothermic reaction; and low shrinkage upon curing (<1%).

The selection also considered the sensitivity of PMMA to many solvents (Laganà et al. in press); the choice of adhesives was restricted to those soluble in either water or aliphatic hydrocarbons with low aromatic content, which are considered safe to use on PMMA.

Adhesives with varied viscosity and strength were included in the selection in order to evaluate options for different bonding requirements.

Thirteen products from four adhesive categories were selected and tested:

- Water-based adhesives: the poly(2-ethyl-2-oxazoline) (PEOX) polymer Aquazol 500;
- Solvent-based adhesives: the acrylic resins Paraloid B-67, a 1:1 mixture of Paraloid F-10 and Paraloid B-67, a 1:1 mixture of Plexisol P550-40 and Paraloid B-67, and Plexigum PQ611;
- Two-component adhesives: the epoxy resins HXTAL NYL-1 and EPO-TEK 301-2FL-CX, and Loctite Hysol 9455;
- Single-component UV-curing adhesives, having different proprietary compositions: Dymax 3099, Dymax 431, Dymax 431T, NOA85, and NOA76.

Aquazol 500 was selected especially for its advantage of being soluble and reversible in water. Acrylics were chosen for their solubility in aliphatic hydrocarbons with low aromatic content and reversibility in these solvents, their near-identical RI to that of PMMA, and some for their successful performance in previous studies. The mixture of Plexisol P550-40 and Paraloid B-67 was especially chosen as a possible replacement for the Paraloid F-10 and Paraloid B-67 mixture given the limited availability of Paraloid F-10. Epoxy resins were selected for their very low viscosity and low shrinkage, as well as their potential to create strong bonds. UV-curing adhesives were included for their good optical properties, remarkably fast curing time, and good bonding strength. The chemical composition and properties of the selected adhesives are summarized in Table 1.

### Bonding tests

Bonding tests were carried out using PMMA samples sawn from clear cast sheets, as well as extruded, to evaluate the effect and efficiency of adhesives used on both types of PMMA.

Samples (8.89 × 2.54 × 0.63 cm) were not annealed and their edges were left unpolished.

Two types of joints were made to evaluate appearance and strength performance of the selected adhesives: butt joints and lap joints (Figure 1). These joints were chosen as they are most commonly used to bond PMMA

objects. Moreover, butt joints represent the type of bond generally made when repairing broken objects.

Before bonding, the areas around the joints were protected with a thin layer of Vaseline in order to easily peel off adhesive residues from the PMMA surface once set, especially when these were not reversible in solvents. The adhesives were then applied with a spatula onto the bonding surface. In the butt joints, the PMMA pieces were assembled by placing their short sawn edges together (bond:  $2.54 \times 0.63$  cm), while in the lap joints

**Table 1.** Adhesives tested: composition and properties

Type	Adhesive	Composition (datasheet information)	Chemical characterization FTIR (F) – Py-GC/MS (P)	Ratio	Viscosity cP (datasheet)	RI (Becke line test)**
PEOX	Aquazol® 500	Poly(2-ethyl-2-oxazoline)	Poly(2-ethyl-2-oxazoline) (F)	40% w/w in deionized water	-	1.516
	Paraloid™ B-67	Isobutyl methacrylate	Isobutyl methacrylate (F)	40% w/w in Mineral Spirit aromatic free*	-	1.486
Acrylic resins	Paraloid™ F-10 + Paraloid™ B-67	Butyl methacrylate copolymer Supplied at 40% solids in mineral spirits/ Aromatic 150 (90–10) + Isobutyl methacrylate	Butyl methacrylate (F)	1:1 mixture F-10 + B-67 at 40% w/w in Mineral Spirit aromatic free*	-	1.486
	Plexisol® P550-40 + Paraloid® B-67	N-butyl methacrylate Supplied at 40% solids in special mineral spirits 100°/140°C + Isobutyl methacrylate	Butyl methacrylate (F)	1:1 mixture P550-40 + B-67 both at 40% w/w in Mineral Spirit aromatic free*	-	1.487
	Plexigum® PQ611	Iso-butyl methacrylate solution in 2-ethylhexylmethacrylate	Butyl methacrylate (F)	40% w/w in Mineral Spirit aromatic free*	-	1.483
Epoxy resins	HXTAL NYL-1	Hydrogenated bisphenol A. diglycidyl ether	Hydrogenated bisphenol A. diglycidyl ether (F) Hydrogenated bisphenol A (P)	3:1 by weight component A to component B	200–300	1.516
	EPO-TEK® 301-2FL-CX	Bisphenol A diglycidyl ether Polyoxypropylene diamine	Bisphenol A (P)	100:44 by weight component A to component B	150–250	1.484
	Loctite Hysol® 9455	Bisphenol A Epichlorohydrin Benzyl dimethylamine Neopentyl glycol diglycidyl ether	Bisphenol A Di-ethylphthalate Benzyl chloride Isophorone diisocyanate (P)	1:1 by volume Resin to Hardener	-	1.528
UV-curing adhesives	Dymax Ultra Light-Weld® 3099	Mixture of isobornyl acrylate, N,N-dimethylacrylamide photoinitiator (proprietary), silane coupling agent (proprietary), and visible photoinitiator (proprietary)	Urethane, Acrylate (F)/ Norbornanes Isophorone diisocyanate N,N-dimethyl amides (P)	-	150	1.510
	Dymax Ultra Light-Weld® 431	Mixture of methacrylic ester (proprietary), 2-hydroxyethylmethacrylate acrylic acid, and visible photoinitiator (proprietary)	Urethane, Acrylate (F)/ Norbornanes Ethylene dimethacrylate Hydroxyethyl methacrylate (P)	-	500	1.512
	Dymax Ultra Light-Weld® 431T	Mixture of methacrylic ester (proprietary), 2-hydroxyethylmethacrylate acrylic acid, visible photoinitiator (proprietary), and silane coupling agent	Urethane, Acrylate (F)/ Norbornanes Ethylene dimethacrylate Hydroxyethyl methacrylate (P)	-	6000	1.508
	NOA 76	Mixture of aliphatic urethane acrylate (proprietary), methacrylate acid ester 2 (2-thoxyethoxy), and tetrahydrofurfuryl acrylate	Urethane, Methacrylate (F)/ Isophorone diisocyanate Methacrylate (P)	-	3500–5500	1.510
	NOA 85	Mixture of aliphatic urethane acrylate (proprietary), isobornyl acrylate, and 1.6 hexanediol diacrylate Fluorester	Urethane (F) Isophorone diisocyanate Triphenyl phosphate Phthalate (P)	-	200	1.491

\* CAS 64742-49-0: EMPLURA® petroleum benzene, boiling range 100°C–140°C, aromatic content ≤ 0.05%.

\*\* The Becke line test accuracy is ± 0.001.

the pieces were bonded by overlapping a portion of their surfaces (bond:  $2.54 \times 2.54$  cm). After applying the adhesive, pressure was applied using a tailor-made clamping system until the adhesive set. For butt joints, further pressure was applied using weights, and for lap joints pegs were used.

The UV-curing adhesives were cured using a Norland Opticure LED 200 curing system (energy output at full power:  $2.5 \text{ W/cm}^2$  at 365 nm). The intensity needed and curing time varied according to resin composition. The curing time and lamp distance for each UV adhesive were determined according to the manufacturer's instructions, when available, and through preliminary tests. The intensity was measured using an Elsec 765C UV+ logger.

### Chemical characterization

The composition of the adhesives was determined using a  $15\times$  Cassegrain objective attached to a Bruker Optics, Inc. Hyperion 3000 FTIR microscope with an MCT detector, and purged with dry air, collecting 64 scans at a resolution of  $4 \text{ cm}^{-1}$ .

To examine bulk chemical composition, some of the adhesives were investigated with an Agilent Technologies 5975C inert MSD/7890A GC/MS using an Agilent thermal sampling probe and a Frontier Ultra ALLOY-5 capillary column. The helium carrier gas was  $1.2 \text{ mL/min}$ . The injector was ramped up from  $50^\circ\text{C}$  to  $450^\circ\text{C}$  at  $900^\circ\text{C/min}$  followed by a 3-minute hold, then ramped down  $25^\circ\text{C/min}$  to  $250^\circ\text{C}$  and held for 40 minutes. The oven was ramped from  $40^\circ\text{C}$  to  $200^\circ\text{C}$  at  $10^\circ\text{C/min}$ , followed by  $6^\circ\text{C/min}$  to  $300^\circ\text{C}$ .

### Refractive index (RI) measurements

RI measurements using the Becke line test were carried out to determine the match between the RI of the adhesives and that of PMMA. Small particles of the adhesives were immersed in a series of refractive index liquids by Cargille and observed with a Leitz DMR microscope (Leica Mikroskopie) at  $10\times/20\times$  magnification, following the method described by McCrone et al. (1985).

### Photoelastic stress analysis

PMMA samples, before and after bonding, were examined using the Sharples General Purpose Strain Viewer to visualize stresses in the material, which may be a precondition for crazing and crack formation. During measurements, the transparent sample, which has a stress-dependent refractive index, is placed between two polarizing filters and a full wave tint plate and viewed in transmitted light. When polarized light passes through stressed areas, interference patterns are formed. These patterns provide information about the distribution and concentration of stress (see <http://www.sharplestress.com>).

### Mechanical testing

Mechanical tests were performed using an Instron 59444 testing machine with a 2 kN load cell to determine the bond strength of each adhesive. Strength is the maximum measured force divided by area of bonding. Butt



**Figure 2.** Stress crazing test

joint were subjected to tensile tests and lap joints to shear tests following the ASTM standards D3163-01 and D638-14 (ASTM International 2001 and 2014).

The crosshead speed was set at 1 mm/min, and force was applied until bond failure occurred.

Tests were performed in fivefold for butt joints and lap joints with each adhesive using both cast and extruded PMMA. The type of bond failure was determined by examining the de-bonded surfaces of each sample in UV light.

### **Stress crazing and cracking test method**

A test method was designed following two ASTM standards, F791-96 and F484-08 (ASTM International 1996 and 2008), to determine whether the adhesives selected could cause stress crazing or cracking within stressed PMMA objects. These phenomena can occur in areas of high localized stresses introduced during manufacturing of the PMMA or as a result of applied loads. Stresses can be unequally released upon exposure to certain fluids (Wright 1996) contained in adhesives (e.g., solvents, monomers, catalysts, or plasticizers). This results in the development of fine fissures (crazes) or fractures (cracks) in the PMMA.

For this test, samples ( $17.78 \times 2.54 \times 0.31$  cm) were sawn from cast and extruded PMMA sheets. A hole was drilled at the bottom of each sample to hold a weight of 500 g (Sale 1993). Two samples of each type of PMMA were used to evaluate each adhesive, and two as control.

Samples were placed in a tailor-made stress apparatus with a fulcrum that bears on the samples, and then weights were applied to cause bending and induce stress. After 10 minutes under stress, adhesives were applied to the top surface of the PMMA samples held under tension, directly over the fulcrum. Adhesive layers were covered with Melinex to restrict evaporation of any adhesive components as occurs in real joints (Figure 2).

Test duration was 24 hours (h). Samples were inspected using a LED torch after 10 min, 30 min, 1 h, 2 h, 4 h, 8 h, and 24 h.

### **Accelerated light aging**

Films of each adhesive were prepared on Mylar using an 8-mil drawdown bar. UV-curing adhesives were cured between two Mylar sheets to avoid oxygen inhibition. The films were exposed in an Atlas Weather-Ometer Ci4000, following ASTM standard D4459-99 for xenon-arc exposure of plastics intended for indoor application (ASTM International 1999). Irradiance was controlled at  $0.33 \text{ W/m}^2$  at 340 nm; test pieces were aged for 400 hours.

### **Color measurements**

Color measurements were performed on adhesive films before and after artificial light aging using a Konica Minolta 2600d spectrophotometer (D65 illuminant,  $10^\circ$  observer, 3 mm aperture) and a ceramic white standard tile as backing to the films. Each film was measured nine times. Results for  $L^*a^*b^*$  and  $\Delta E_{94}$  were averaged using Spectra Magic software.

## RESULTS AND DISCUSSION

## Visual appearance and working properties

Generally, results proved that the closer the match between the RI of the adhesive and that of the PMMA (less than 0.02), the more invisible the repair will be (Laganà and Van Oosten 2011). Moreover, they showed that low viscosity, allowing adequate wetting of irregular surfaces, also plays a role in improving the visual appearance of bonds.

Bonds performed with Aquazol 500 showed generally good visual results. Although this product appears slightly yellow, this is not perceivable in thin films. The only defect was observed in butt joint interfaces: tiny bubbles developed while drying, primarily along the saw marks.

All bonds carried out with acrylic resins had a very good appearance due to their close RI match with PMMA. However, these adhesives did show a tendency to form voids/bubbles as the solvent evaporated during curing; this only occurred where bonded pieces did not fit perfectly, or when the pressure applied was not uniform and/or was insufficient to compensate for adhesive shrinkage up to the moment when it had completely set.

Conversely, all bonds made with epoxies were generally bubble free. Very good visual results were also achieved with HXTAL NYL-1 and EPO-TEK 301-2FL-CX for their appropriate optical properties enhanced by their low viscosity. Hysol 9455, however, gave unsatisfactory visual results due a mismatch in the RIs.

Bonds performed with UV-curing adhesives showed very good visual results, especially the ones made with DYMAX 3099, with a RI very close to that of PMMA and the lowest viscosity.

Only NOA 76 did not show consistent results; some bonds appeared perfectly transparent, while others strongly yellowed due to batch-to-batch variation in the clarity of the adhesive.

The majority of the adhesives were easy to work with. An exception was Hysol 9455, due to its short working time and the dual-cartridge system of delivery, which did not allow for precise mixing.

## Mechanical performance

The maximum load at point of failure was measured for both lap and butt joints on cast and extruded PMMA samples to examine the bond strength of the adhesives (Figures 3, 4).

Butt joints of cast PMMA with EPO-TEK 301-2FL-CX demonstrated the highest bond strength, followed by HXTAL NYL-1 and DYMAX 3099 and 431. Conversely, NOA 85, Hysol 9455, and Aquazol 500 exhibited the lowest bond strength. All acrylic resins and DYMAX 431 T showed an intermediate bond strength. For cast PMMA, the butt joints made using EPO-TEK 301-2FL-CX exceeded the capacity of the load cell (2 kN) and therefore these bonds were measured instead with the Instron machine 5885H with a higher-capacity load cell. The maximum load measured when these bonds broke was three times higher than HXTAL (3224 N).

Similar results were obtained with the extruded PMMA, with the exceptions of HXTAL NYL-1 and EPO-TEK 301-2FL-CX, for which the bonds made

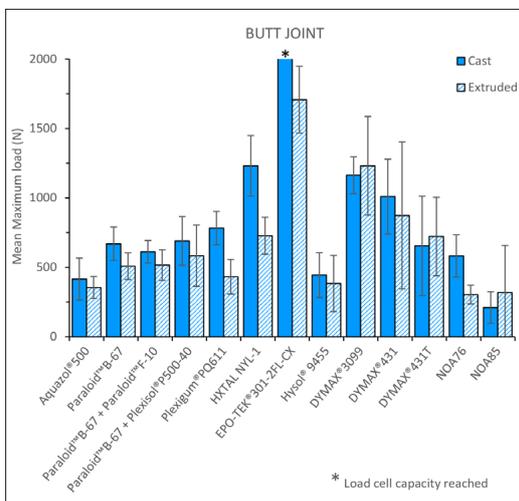


Figure 3. Butt joints, maximum load

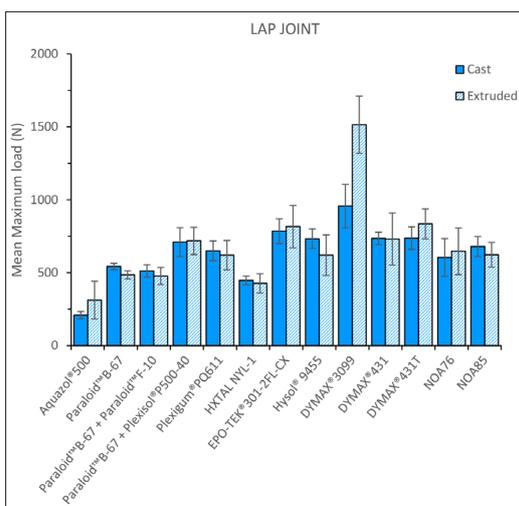


Figure 4. Lap joints, maximum load



**Figure 5.** Cast and extruded PMMA viewed through the Strain Viewer

on cast PMMA exhibited higher strength. In general, small differences between cast and extruded PMMA could be related to a closer fit between the sawn surfaces of the cast pieces bonded, which were slightly less rough than the extruded ones. The UV-cured adhesives were found to produce a less consistent bond strength, likely due to inhomogeneous curing caused by the angled position of the UV lamp, necessary in butt joints for the light to reach and cure the bonding interface.

In the lap joints, the difference in the strength of the adhesives was found to be much smaller. DYMAX 3099 was found to be the strongest. Similar to the butt joints, Aquazol exhibited the lowest bond strength. All of the other materials were found to have similar strengths. The performance of the lap joints on cast versus extruded PMMA was almost identical, other than DYMAX 3099 and Aquazol 500, which exhibited higher strength bonding in extruded PMMA. In the lap joint made with DYMAX 3099 on extruded PMMA, the PMMA itself cracked and broke before the bond failed. Despite the much larger bonding area of the lap compared to butt joints, most of the lap joints were found to fail at a lower load, which suggests that these adhesives may be more sensitive to shear and peel than their tensile loads.

For both lap and butt joints, the majority of the bonding materials failed at the adhesive interface, separating such that residues remained on only one side of the join. An exception were the acrylic materials, which often failed cohesively. This may indicate that the acrylic adhesives had a greater affinity to the surface of the PMMA due to their chemical similarity.

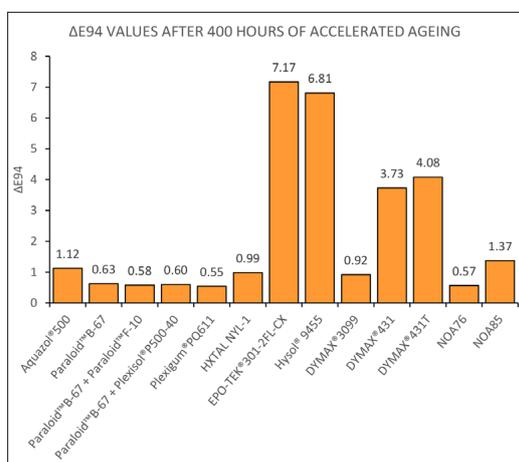
### Stress analysis

Tiny interference patterns, indicating stresses, were observed in the PMMA along some of the bonds carried out with EPO-TEK 301-2FL-CX and the UV adhesives (DYMAX 3099, DYMAX 431 and 431T, NOA 85, and NOA 76). Based on UV adhesives manufacture' sources, stresses can occur with these materials on the bonded surface due to non-uniform curing/UV exposure or to a nonlinear shrinkage in thicker layers (Norland and Martin 2009). However, to fully comprehend the impact of these stresses on the long-term stability of PMMA, future research should be considered.

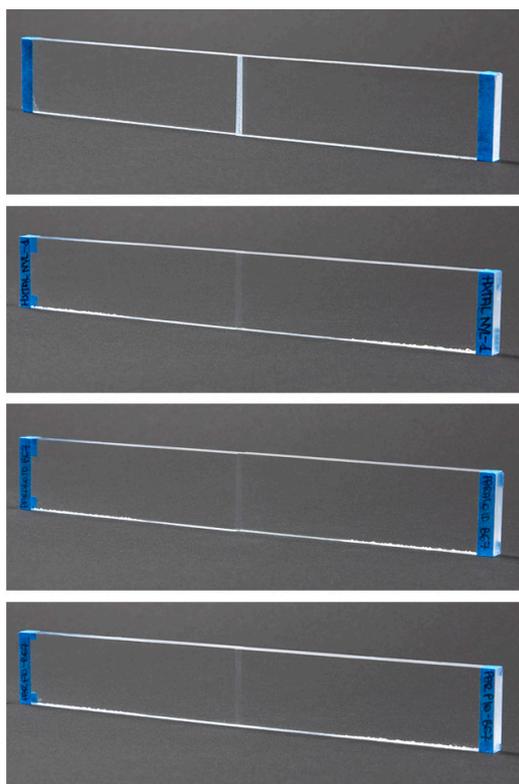
During the study, it was also observed that this type of examination can be used to distinguish cast and extruded PMMA. This distinction is very important for conservators, considering that cast and extruded PMMA are known to have different behaviors. Due to the orientated alignment of the polymer chains in the extruded PMMA, this material interacts with polarized light differently depending on its orientation. Specifically, when polarized light passes through an extruded PMMA piece and this element is rotated in different directions, the color will change, whereas in a cast piece, rotating the material in polarized light will not result in color change as the polymer chains are randomly aligned (Figure 5).

### Craze/crack formation

The formation of crazing and cracking depended on the composition of the adhesives applied and on the type of stressed PMMA; extruded PMMA was affected more than the cast variety.



**Figure 6.** Color change of adhesives after aging



**Figure 7.** Bond appearance (from top to bottom): unbonded, bonded HXTAL NYL-1, Paraloid B-67, mixture of Paraloid F-10 and Paraloid B-67

Specifically, Aquazol 500 and all of the acrylic resins did not cause any visible change. Epoxy resins showed different results, most likely due to their varied composition: EPO-TEK 301-2FL-CX was able to crack and break all extruded samples after only 30 minutes, but did not affect cast samples, while HXTAL NYL-1 and Hysol 9455 did not induce any change in both types of PMMA.

The results obtained with the UV-curing adhesives also differed according to composition. DYMAX 3099 and NOA 76 did not cause any changes, while DYMAX 431 and 431T, as well as NOA 85, caused the formation of crazes on cast PMMA and severe cracks on the extruded samples.

### Aging behaviors

Color measurements performed on adhesive films after accelerated aging mainly revealed alterations in the  $b^*$  value that corresponded to yellowing (increased  $b^*$ ), with minor alterations in the  $L^*$  value that represented darkening (decreased  $L^*$ ).

Changes in  $\Delta E_{94}$  values are shown in Figure 6. No color changes were visible to the naked eye on aged films, which had a  $\Delta E_{94}$  value below 2.

Aquazol 500 proved to have good stability with  $\Delta E_{94}$  below 2. All of the acrylic resins performed very well during accelerated light aging with values below 1. Epoxy resins performed differently on aging. The hydrogenated epoxy HXTAL NYL-1 showed very good stability ( $<1 \Delta E_{94}$ ), while EPO-TEK 301-2 FL-CX and Hysol 4955 yellowed noticeably (7.17–6.81  $\Delta E_{94}$ ). The aging performances of the UV-curing materials also varied widely depending on composition. DYMAX 3099 and NOA 76 appeared very stable with less than 1  $\Delta E$  values, followed by NOA 85 (1.37  $\Delta E_{94}$ ), while DYMAX 431 and 431T exhibited yellowing (3.73–4.08  $\Delta E_{94}$ ).

### Summary and application of results

Based on the results obtained, six adhesives were shown to meet all the evaluation criteria and were considered suitable for repairing PMMA objects: Aquazol 500, Paraloid B-67, the 1:1 mixture of Paraloid F-10 and Paraloid B-67, the 1:1 mixture of Plexisol P550-40 and Paraloid B-67, Plexigum PQ611, and HXTAL NYL-1. All of these adhesives proved to be stable upon aging, gave visually satisfactory bonds, and, most importantly, were not harmful for the PMMA. However, they also exhibited different properties and performances that can be used to meet specific bonding requirements. For instance, depending on the bond strength required, one could choose between Aquazol 500 (low bond strength), the acrylic resins (medium bond strength), or HXTAL NYL-1 (medium to high bond strength). Similarly, if reversibility is key, Aquazol 500 and the acrylic resins might be suited as they can be safely removed and allow future retreatments. If appearance of the bond is the primary concern, one might opt for an acrylic resin, or otherwise HXTAL (Figure 7).

Given that there can be multiple and varied requirements for repairs, the main properties and bond performances of the adhesives are summarized here in an Adhesive Comparison/Selection Chart (Table 2)

to help conservators make a quick comparison and easily select the most appropriate options.

**Table 2.** Adhesive comparison/Selection chart

	<b>Aquazol® 500</b>	<b>Paraloid™ B-67</b>	<b>Paraloid™ F-10 + Paraloid™ B-67 (1:1)</b>	<b>Plexisol® P550-40 + Paraloid® B-67 (1:1)</b>	<b>Plexigum® PQ611</b>	<b>Hxtal NYL-1</b>
<b>Type and ratio</b>	PEOX 40% in d. water	Acrylic resin 40% in solvent *	Acrylic resins 40% in solvent *	Acrylic resins 40% in solvent *	Acrylic resins 40% in solvent *	Two-component epoxy resin (3:1)
<b>Color (product)</b>	Light yellow	Clear	Clear	Clear	Clear	Clear
<b>Color (bond film)</b>	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
<b>Viscosity cP (datasheet)</b>	-	-	-	-	-	200-300
<b>Viscosity (based on observations)</b>	High viscosity	Medium viscosity	Medium viscosity	Medium viscosity	Medium viscosity	Low viscosity
<b>Tg (°C)</b>	55	50	20 (F-10) / 50 (B-67)	25 (P550-40) / 50 (B-67)	ca. 32	-
<b>RI (Becke line test)</b>	1.516	1.486	1.486	1.487	1.483	1.516
<b>Appearance of bond</b>	Good	Very good	Very good	Very good	Very good	Very good
<b>Possible defects</b>	Bubbles	Bubbles	Bubbles	Bubbles	Bubbles	-
<b>Bond type</b>	Nonstructural	Nonstructural	Nonstructural	Nonstructural	Nonstructural	Structural
<b>Bond strength (butt joint)</b>	Low	Medium	Medium	Medium	Medium	High
<b>Bond strength (lap joint)</b>	Low	Medium	Medium	Medium	Medium	Medium
<b>Reversibility</b>	In water	In solvent *	In solvent *	In solvent *	In solvent *	Mechanical

\* CAS# 64742-49-0: White spirit, boiling range 100°C–140°C, aromatics-free (≤ 0.1%), or EMPLURA® petroleum benzine, boiling range 100°C–140°C, aromatic content ≤ 0.05%.

## CONCLUSION

This research confirmed the complexity of finding suitable adhesives for bonding PMMA and highlighted the importance of thoroughly investigating material performance before introducing them into practice. Many of the adhesives tested were shown to be unstable and/or to affect the stability of PMMA. However, the results of this extensive investigation have identified more adhesive systems able to successfully and safely repair PMMA, increasing the number of current options. Moreover, it also provided a selection chart comparing relevant properties and performance aimed to assist conservators in making an informed selection when repairing PMMA objects.

## ACKNOWLEDGMENTS

The authors would like to thank Elena Joulin and Alexandra Bridarolli for their valuable assistance in this study, and David Carson, Anna Flavin, and Odile Madden for their support.

## REFERENCES

- ASTM International. 1996. *ASTM Standard F791-96: Standard test method for stress crazing of transparent plastics*. West Conshohocken, PA: ASTM International. Available at <https://www.astm.org/>
- ASTM International. 1999. *ASTM Standard D4459-99: Standard practice for xenon-arc exposure of plastics intended for indoor applications*. West Conshohocken, PA: ASTM International. Available at <https://www.astm.org/>
- ASTM International. 2001. *ASTM Standard D3163-01: Standard test method for determining strength of adhesively bonded rigid plastic lap-shear joints in shear by tension loading*. West Conshohocken, PA: ASTM International. Available at <https://www.astm.org/>
- ASTM International. 2008. *ASTM Standard F484-08: Standard test method for stress crazing of acrylic plastics in contact with liquid and or semi-liquid compounds*. West Conshohocken, PA: ASTM International. Available at <https://www.astm.org/>
- ASTM International. 2014. *ASTM Standard D638-14: Standard test method for tensile properties of plastics*. West Conshohocken, PA: ASTM International. Available at <https://www.astm.org/>
- Bienefeld, C. 2016. *Untersuchung von physikalisch und chemisch abbindenden Klebstoffen zur Restaurierung von Polymethylmethacrylat*. Diploma and master's thesis. Author's edition.
- Comiotto, A. and M. Egger. 2011. Naum Gabo's sculpture 'Construction in Space: Crystal' (1937): Evaluating a suitable bonding strategy for stress loaded poly(methyl methacrylate). In *Future Talks 009. The Conservation of Modern Materials in Applied Arts and Design. Papers from the Conference Held at the Pinakothek Der Moderne, 22–23 October 2009*, ed. T. Bechthold, 124–31. Munich: Die Neue Sammlung/The International Design Museum.
- Laganà, A. and T. van Oosten. 2011. Back to transparency, back to life: Research into the restoration of broken transparent unsaturated polyester and poly(methyl methacrylate) works of art. In *Cultural Heritage/Cultural Identity: The Role of Conservation. ICOM-CC 16th Triennial Conference Preprints, Lisbon, 19–23 September 2011*, ed. J. Bridgland, art. 1002, 9 pp. Almada: Critério Produção Gráfica, Lda. [for the] ICOM Committee for Conservation. Available at <https://www.icom-cc-publications-online.org/>
- Laganà, A., M. David, M. Doutre, S. de Groot, H. van Keulen, O. Madden, M. Schilling, and M. van Bommel. In press. Reproducing reality. Recreating bonding defects observed in transparent poly(methyl methacrylate) museum objects and assessing defect formation. *Journal of Cultural Heritage*. Available at <https://doi.org/10.1016/j.culher.2020.11.002>
- McCrone, W.C., L.B. McCrone, and J.G. Delly. 1985. *Polarized light microscopy*. Chicago, IL: McCrone Research Institute, Inc.
- Norland, E.A. and F.S. Martin. 2009. Mechanisms relating to reducing stress in curing thick sections of UV adhesives. <https://www.norlandprod.com/techrpts/thick.html> (accessed 21 December 2020).
- Sale, D. 1993. An evaluation of eleven adhesives for repairing poly(methyl methacrylate) objects and sculpture. In *Saving the Twentieth Century: The Conservation of Modern Materials: Proceedings of a Conference Symposium 91*, ed. D.W. Grattan, 325–40. Ottawa, ON: Canadian Conservation Institute.
- Sale, D. 2011. Yellowing and appearance of conservation adhesives for poly(methyl methacrylate): A reappraisal of 20-year-old samples and test methods. In *Proceedings of Symposium 2011 – Adhesives and Consolidants for Conservation: Research and Applications, Ottawa, Canada, 17–21 October 2011*. Ottawa, ON: Canadian Conservation Institute.
- Wright, D.C. 1996. *Environmental stress cracking of plastics*. Shrewsbury: Rapra Technology.

Copyright © 2021 by ICOM-CC and The J. Paul Getty Trust. All rights reserved.

## To cite this article:

Laganà, A., M. Doutre, M. David, M. Lukomski, E. Hendriks, and M. van Bommel. 2021. In search of a perfect bond: An evaluation of potential adhesives to repair transparent poly(methyl methacrylate) objects. In *Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, 17–21 May 2021*, ed. J. Bridgland. Paris: International Council of Museums.