Acrylic Barrier Surface Coatings for Epoxy Resin Adhesive Bonds in Glass Conservation: Evaluation of Bond Strength and Reversibility

ABSTRACT

In glass conservation, the requirement of reversibility must often be subordinate when adhering large or decorative arts glasses. Epoxy resin adhesives are still in common use in order to ensure sufficient bond strength or a refractive index matching the glass. To improve reversibility, barrier coatings of PARALOID B-72 or B-44 acrylics can be applied to the adherend surfaces. This approach has already been used with archaeological and historic glasses in conservation practice, but no comparative studies have yet been carried out. The strength and reversibility of three well-established epoxy resins, Araldite 2020, HXTAL NYL-1, and EPO-TEK 301-2, and the ultraviolet-curing adhesive VITRALIT 6164, with and without barrier coatings were investigated and compared. A three-point bending test was carried out to determine the bond strength. Bonded samples were produced by using modern sheet glass of different thicknesses. The results show that the PARALOID B-44 and B-72 acrylic barrier coatings provide reversibility of epoxy resin bonds, while maintaining sufficient strength.

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Epoxy resins · HXTAL NYL-1 · UV-curing adhesive · VITRALIT 6164 · PARALOID B-44 · PARALOID B-72 · Barrier coatings · Bond strength · Reversibility

INTRODUCTION

Considering the current requirements in glass conservation, choosing an adhesive is often a compromise. Rarely does an adhesive fulfil all the ideal requirements. The use of acrylic resins, such as PARALOID B-72 and B-44, as adhesives, especially for archaeological glass objects, is well established. Compared with epoxy resin adhesives, these acrylics have the advantage of remaining soluble after aging. However, this requirement of reversibility must often be sacrificed when strong and structural bonds are required, for example, when joining large and heavy pieces like chandeliers with heavy cantilevered arms, glass vessels with handles, or glass fragments of varying thickness. Thus, the use of epoxy resin adhesives persists. Additionally, epoxy resins remain particularly favored for the repair of clear, colorless glasses, motivated by aesthetical considerations.

In the literature on epoxy resins as adhesives in glass or ceramics conservation, ageing stability

Figure 1. *Bonded with PARALOID B-72 barrier coatings and Araldite 2020 structural adhesive. Roman pitcher, ca. 1st-2nd century CE, glass, H 23.5 cm × Diam. 14 cm. Archäologisches Museum Frankfurt, X 20474 · Courtesy of Archäologisches Museum Frankfurt*

and bond strength are two criteria often addressed and investigated (Coutinho et al. 2009; Down 1996; Down 2001; Fischer et al. 2009; Koob 2006; Tennent 1979; Wanner 2009). The epoxy resin HXTAL NYL-1 is particularly widely used, offering the best light-ageing stability of all epoxy resin adhesives utilized and tested in glass conservation (Down 2001; Coutinho et al. 2009); however, less attention appears to be paid to the reversibility of epoxy resin adhesives by swelling.

In her comprehensive review of prolonged testing of epoxy resin at the Canadian Conservation Institute (CCI), Down (2001, 42) states that no universal solvent for swelling and removing epoxy resin adhesives exists. Solvents such as dichloromethane (DCM), trichloromethane (TCM), dimethylformamide (DMF), and tetrahydrofuran (THF), either pure or in mixtures, are found to be the most effective. Down (2001) refers to two works by Rémillard (1984; 1989), who investigated the ability of a range of solvents to swell different epoxy resin adhesives and noticed that a mixture of equal parts of DMF and THF was the most effective, followed by TCM, DCM, and THF. The least effective solvents were the alcohols and ketones, which is in agreement with the CCI study.[i]

Bradley (1990) performed reversibility tests on HXTAL NYL-1 from 1981-82.[ii] The tests were assessed qualitatively before and after ageing of the resins by immersing fragments of coated microscope slides in acetone, toluene, DCM, and THF for 24 hours. Reversibility was evaluated by the extent to which the adhesive separated from the glass slide. DCM and THF worked well before and after ageing. However, an important remark on this result is that the capacity of solvents to access and penetrate tight adhesive-glass-joints is much less as compared to the surfaces of coated glass slides. According to the experience of the authors of this study, even fragments recently bonded with HXTAL NYL-1 are difficult to separate in DCM.

Reversing epoxy resin adhesive bonds in glass objects can be a laborious, hazardous, and costly work. Immersion in a solvent may be limited by the size or geometry of an object. This also applies to glass objects combined with sensitive materials or to glass objects with fragile surfaces that may have been previously consolidated. Furthermore, in such cases, the use of solvent vapours may also

Figure 2. *Bonded with PARALOID B-72 barrier coatings and HXTAL NYL-1 structural adhesive. Goblet with lid, 1818 CE, glass, H 26.5 cm × W 11 cm. Private collection, Germany*

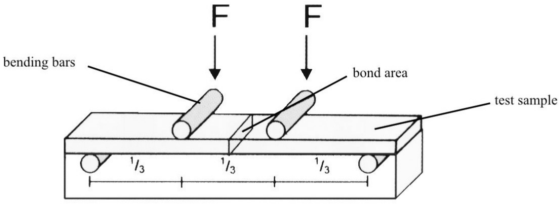


Figure 3. *Diagram of the three-point bending test (Fischer et al. 2009, 101)*

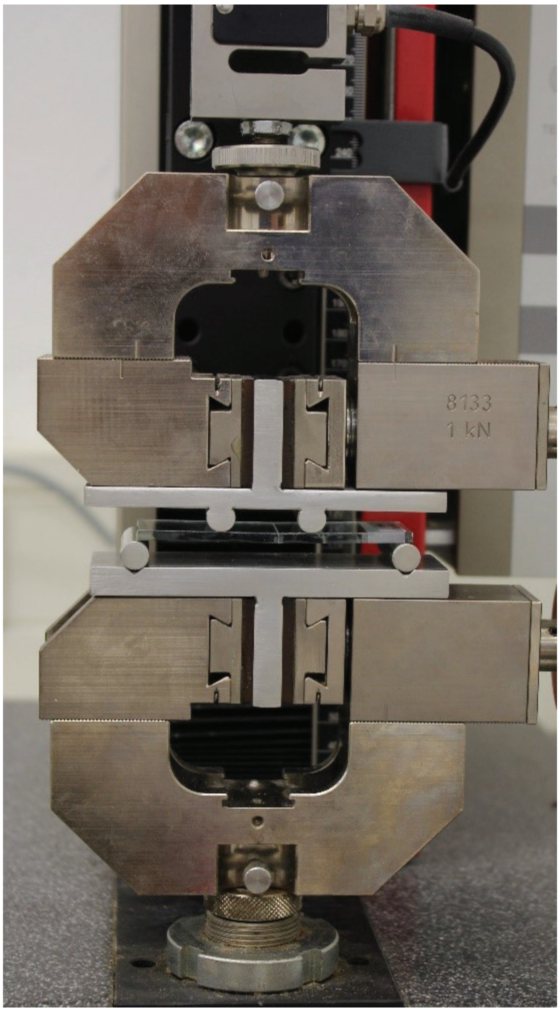


Figure 4. *Experimental set-up of the three-point bending test*

need to be similarly restricted. The use of locally applied solvent gels or poultices may be ineffective when working with more volatile solvents such as DCM, even if evaporation is reduced by foil coverings.

To improve the reversibility of epoxy resin adhesive joints in glass bonds by means of less hazardous solvents and reduced exposure time, the idea of using barrier surface coatings is addressed in this paper. This approach is strongly inspired by Podany et al.'s 2001 publication dealing with PARALOID B-72 as an interface barrier within structural adhesive bonds of epoxy or polyester resins on marble objects.[iii] Interestingly, it was found that differences in bond strength between marble-to-marble bonds made with epoxy or polyester resins compared to those that use additional PARALOID B-72 barrier coatings on the marble surfaces are insignificant, though the reversibility of the latter bonds increased considerably.[iv]

In conservation practice, this approach has already been successfully used with archaeological and historic glass (Figures 1 and 2). Applying this technique in glass conservation, questions that arose are the focus of the research presented here, namely: how do such barrier surface coatings influence the bond strength of epoxy resin adhesive joints, to what extent do they differ from the bond strength of PARALOID resins used as adhesives, and in what way do the barrier coatings influence the reversibility of the epoxy resin joints?

BOND STRENGTH EVALUATION

Experimental set-up

Material testing in conservation aims for ensuring reproducibility, as is the case for similar testing in industry. At the same time, it is reasonable to adapt the experimental set-up to reflect common conservation practice. The experimental design used in this study is based on a standard developed for the testing of building materials and has been used successfully in a previous study comparing the bond strength of various glass adhesives (Fischer et al. 2009).[v] The set up consists of a three-point bending test: pressure is applied to a bond via two bars until the bond breaks (Figures 3 and 4).

Choice of materials

PARALOID B-72 and PARALOID B-44 were selected as barrier coatings. The different compositions of these acrylic resins results in a glass transition temperature (Tg) of 40 °C for PARALOID B-72, while PARALOID B-44 is characterized by a higher Tg of 60 °C (Horie 2010; data sheet PARALOID B44). Both resins have the advantages of remaining soluble and having good and well-investigated ageing properties. HXTAL NYL-1, EPO-TEK 301-2, and Araldite 2020 epoxy resins were chosen for testing based on their history of study and continued use in conservation. HXTAL NYL-1 and EPO-TEK 301-2 are recommended by Down (2001) due to their good ageing properties. Conversely, Araldite 2020 tends to yellow but is still in common use in many conservation labs (Wanner 2009).

Ultraviolet- (UV) curing adhesives are less common but have the great advantage of curing during few minutes. VITRALIT 6164 showed good results in aging tests and was exemplarily included in these tests (Sander-Conwell and Schmidt-Ott 1993; Wanner 2009).

The bond strength was evaluated in four series of tests:

- series 1: epoxy resins Araldite 2020, HXTAL NYL-1, EPO-TEK 301-2 and UV-curing acrylic VITRALIT 6164;
- series 2: the epoxy resins and UV-curing acrylic listed above with barrier coatings of PARALOID B-44;
- series 3: epoxy resins and UV-curing acrylic with barrier coatings of PARALOID B-72; and
- series 4: acrylic resin adhesive PARALOID B-72 alone.

Test samples

Samples were produced using modern glass of two different thicknesses. Microscope slides with dimensions of 76 mm × 26 mm × 1 mm thickness were used, as well as sheet glass of the same height and width but 3 mm thickness. The glass samples were broken horizontally in the center and bonded end-to-end. For the investigation, ten samples per series were prepared for each adhesive system.

As barrier coatings, a 3 percent solution of PARALOID B-44 or B-72 (w/v) in acetone:ethanol (9:1) was applied by brush. The ethanol served to slow the solvent evaporation and avoid bubbles, albeit that such thin coatings rarely trap air (Koob 2006, 86). After the barrier coatings had dried for one week, the glass fragments were fixed using adhesive tape. The epoxy resins and UV-curing adhesive were introduced by capillary action. A slightly reduced capillary draw was noted when joining the samples including barrier coatings. For the PARALOID B-72 bonds, a 40 percent solution (w/v) in acetone:ethanol (9:1) was applied by brush, and the bond was allowed to dry for eight weeks before being tested.

REVERSIBILITY EVALUATION

Since increased reversibility of epoxy resin or UV-curing adhesive bonds with barrier coatings is expected to be the major benefit of this method, evaluation of the reversibility is crucial. Test samples with barrier coatings of PARALOID B-72 and bonds of HXTAL NYL-1 were prepared as described above. For comparison, a series of samples bonded with HXTAL NYL-1 without barrier coatings, and another series of samples bonded solely with PARALOID B-72 were prepared. Five samples of each series were tested. All samples were placed in a closed vessel containing a saturated acetone vapour atmosphere. The samples were fixed horizontally so that one part was ‘free-floating’. The bond was considered to be reversed when the ‘free-floating’ part of the bonded sample dropped.

EXPERIMENTAL RESULTS

Bond strength (Tables 1 and 2)

All adhesives tested in series 1, without barrier coatings, resulted in strong bonds. HXTAL NYL-1 and EPO-TEK 301-2 showed very high bond strengths, while Araldite 2020 and VITRALIT 6164 displayed lower bond strengths. Substrate failures in the glass were not observed. Similarly grouped results were observed in series 2 and 3, both with barrier coatings.

In series 2, PARALOID B-44 barrier coatings resulted in only slightly lower ultimate load values as compared to series 1. The minimum difference of 0.03 N/mm^2 was observed with HXTAL NYL-1,

SERIES 1: WITHOUT BARRIER COATINGS

	Average bond strength in N/mm²	
Glass thickness	1 mm	3 mm
Araldite 2020	0.48 ± 0.05	1.52 ± 0.15
HXTAL NYL-1	0.47 ± 0.05	1.64 ± 0.27
EPO-TEK 301-2	0.63 ± 0.07	1.67 ± 0.23
VITRALIT 6164	0.56 ± 0.09	1.50 ± 0.21

SERIES 2: WITH PARALOID B-44 BARRIER COATINGS

	Average bond strength in N/mm²	
Glass thickness	1 mm	3 mm
Araldite 2020	0.58 ± 0.09	1.30 ± 0.29
HXTAL NYL-1	0.64 ± 0.04	1.61 ± 0.20
EPO-TEK 301-2	0.58 ± 0.07	1.54 ±0.22
VITRALIT 6164	0.5 ± 0.05	1.20 ± 0.31

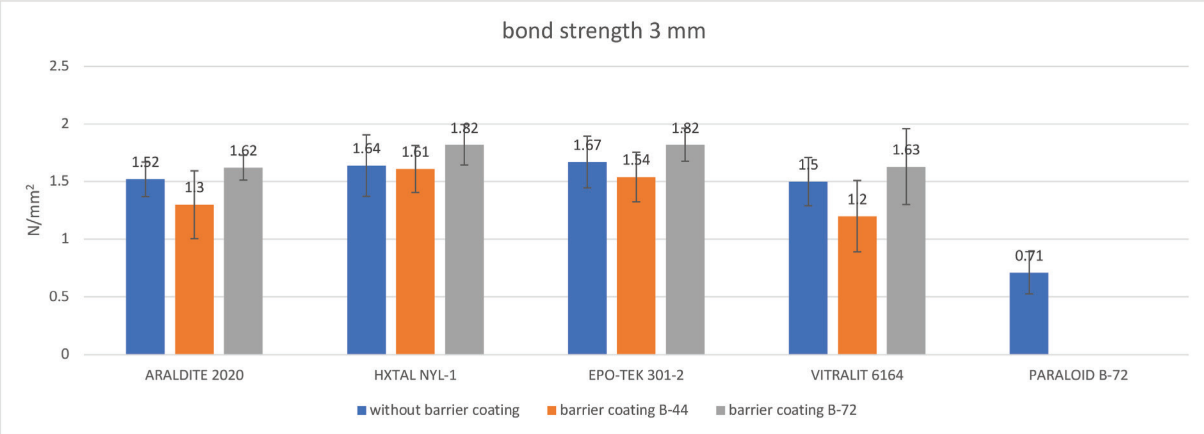
SERIES 3: WITH PARALOID B-72 BARRIER COATINGS

	Average bond strength in N/mm²	
Glass thickness	1 mm	3 mm
Araldite 2020	0.59 ± 0.09	1.62 ± 0.11
HXTAL NYL-1	0.71 ± 0.11	1.82 ± 0.18
EPO-TEK 301-2	0.76 ± 0.11	1.82 ± 0.14
VITRALIT 6164	0.51 ± 0.07	1.63 ± 0.33

SERIES 4: PARALOID B-72 BONDS

	Average bond strength in N/mm²	
Glass thickness	1mm	3 mm
PARALOID B-72	0.20 ± 0.06	0.71 ± 0.18

Table 1. *Results of bond strength evaluation with the three-point bending test (DIN EN 13161)*



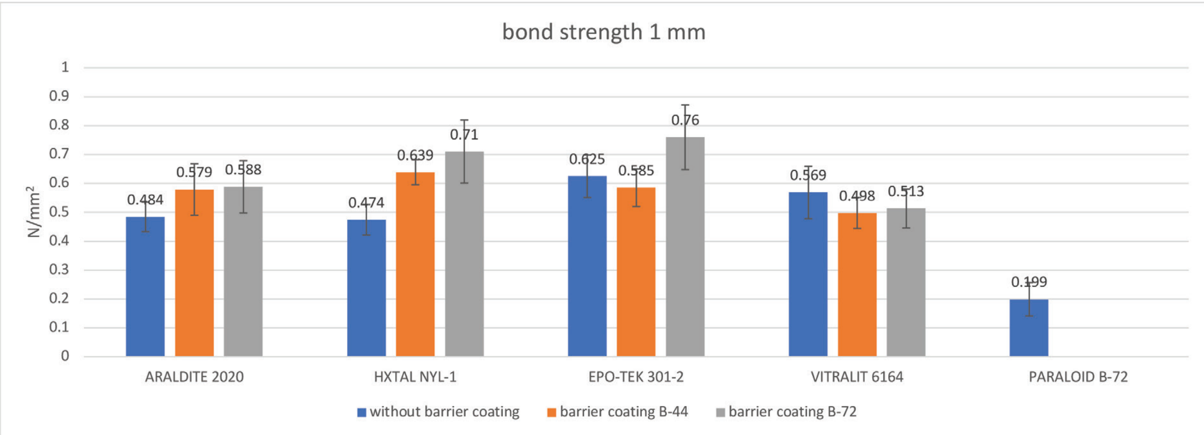


Table 2. *Results presented in Table 1 visualized as a bar chart*

3 mm, and the maximum difference of 0.3 N/mm² was observed with VITRALIT 6164, 3 mm. However, the ultimate recorded bending loads of nearly 1.61 N/mm² for HXTAL NYL-1 and nearly 1.2 N/mm² for VITRALIT 6164 still represent strong bonds between the adherends.

Series 3, with PARALOID B-72 barrier coatings, also showed strong bonds for all adhesives tested. In fact, the measured ultimate load values are significantly higher than those of series 2 using PARALOID B-44 barrier coatings. This observation is most remarkable. It might be assumed that the PARALOID barrier coatings act as a kind of primer. Nevertheless, it remains to be explored to what extent this slight reinforcement or weakening of the bond strength is related to the different properties of the PARALOID resins being used.

The application of barrier coatings results in a slightly higher variation in the recorded ultimate bending force. This can be explained by variations in the thickness of the barrier layers applied with a brush. In general, the results stand in contrast to what might be expected, namely a clear decrease of bond strength due to the presence of the barrier coatings.

The edge-bonded PARALOID B-72 samples investigated in series 4 resulted in rather weak bond strengths, being only half as strong as Araldite 2020. These results differ from values measured by Fischer et al. (2009). However, it should be considered that Fischer et al. (2009) used a higher resin concentration of 50 percent PARALOID B-72 in acetone:ethanol (9:1).[vi] The results clearly show that the bond strength of epoxy resin adhesive bonds with and without acrylic barrier coatings is similar. Such bond strength cannot be achieved by edge bonds of PARALOID B-72.

Reversibility

The results of the reversibility tests show that the edge bonds using PARALOID B-72 alone took an average of 30 minutes at a sample thickness of 1 mm and 100 minutes at a thickness of 3 mm to fail. Joints performed using HXTAL NYL-1 and a PARALOID B-72 barrier coating failed at an average of 24 hours and 26 hours for the 1 mm and 3 mm thicknesses, respectively, while the HXTAL NYL-1 bonds without barrier coatings showed no signs of alteration even after 26 hours.

CONCLUSION AND FUTURE RESEARCH

This investigation addressed the improvement of reversibility of epoxy resin adhesive bonds in glass conservation by using PARALOID barrier surface coatings. The bond strength of samples with and without barrier coatings were measured and compared. In order to evaluate the reversibility of those bonds, samples were exposed to an acetone-saturated atmosphere. The bond strength was tested using modern glass samples of 1 mm and 3 mm thickness. The epoxy resin adhesives Araldite 2020, HXTAL NYL-1, and EPO-TEK 301-2 and the UV-curing acrylic adhesive VITRALIT 6164 were tested with and without barrier coatings of either PARALOID B-44 or PARALOID B-72. The capillary draw was minimally hindered, such that the epoxy resin adhesives and the UV-curing adhesive could be applied via capillary action without any problems. HXTAL NYL-1 and EPO-TEK 301-2 produced the highest bond strengths; Araldite 2020 and VITRALIT 6164 resulted in lower ultimate load values.

Bonds with PARALOID B-44 barrier coatings showed only a slightly lower but still strong bond strength. Samples prepared with PARALOID B-72 barrier coatings actually showed slightly higher bond strengths, as compared to series 1. Reversibility was tested for joints of HXTAL NYL-1 with barrier coatings of PARALOID B-72. These bonds could be reversed within 26 hours in acetone vapour, whereas the epoxy resin bonds with no barrier layer resisted. Hence, the joints with barrier coatings failed and can be considered reversible, while still creating strong bonds with good adhesion to the glass. Using a higher concentration of PARALOID for the barrier coating should increase the reversibility, though it could affect the capillary draw and the epoxy resin bond strength. A concentration up to 5 percent (w/v) may be recommended. In addition, it must be noted that the use of a barrier coating may influence the refractive index of the adhesive, making the joint more visible. This effect was not noticed with the used samples but will be part of future research. The use of barrier coatings in glass conservation is a simple but effective method to increase the reversibility of epoxy resin bonds. PARALOID barrier coatings do not significantly affect the bond strength. The method has been successfully applied in recent conservation treatments of archaeological and decorative arts glasses (Figures 1 and 2).

NOTES

[i] The epoxy resin Ablebond 342 was the most easily removed, followed by EPO-TEK 301-2, EPO-TEK 301-1, Araldite 502\HY956, and finally Epoxyglass. HXTAL NYL-1 was not tested. It was found that different epoxy resin adhesives had different affinities for solvents. For instance, Araldite 502/HY956 swelled more in DMF/THF, whereas EPO-TEK 301-2 swelled more in TCM. This is due to the different chemical properties of the various epoxy resin adhesives, hindering generalization and identification of a universal solvent for epoxies. Down (2001) further reports a study by Scott (1986) who investigated the time it took to swell and separate glass slide epoxy resin adhesive bonds with various chlorinated solvents. He found that mixtures of DCM with methanol and xylene, 90:5:5 or 80:10:10, were the most effective, that ageing increased the time to separation, and that HXTAL NYL-1 was unaffected by many of the chlorinated solvents.

[ii] Two different batches of HXTAL NYL-1 were used. Reversibility tests were performed with HXTAL NYL-1 of the first batch only. The quality of the first batch was not specified; the second batch was a type altered by 'charcoal filtration of both the resin and hardener to improve the colour and reaction of the resin with sodium borohydride' (Bradley 1990, 669).

[iii] The use of PARALOID B-72 as barrier coating for improving reversibility, particularly when using epoxy resin adhesives, namely several Araldites, was also considered by Fiorentino and Borrelli (1975) for archaeological objects and especially for glass. However, detailed information on the solution percentage, solvent, and application of PARALOID B-72 is missing. The reversibility tests were made on copper samples and there is no reference available to which the reversibility results could be compared, i.e. no reversibility tests of bonds without barrier layers are mentioned. Instead of 'barrier coating', Fiorentino and Borrelli used the term 'primer' which, in technical language, refers to adhesion enhancement rather than to reversibility of the bond. Nevertheless, it is noteworthy that the bonding method with barrier coatings, for glass conservation in particular, was addressed by these authors as early as the 1970s.

[iv] All bonds with barrier coatings reversed within eight hours in an acetone vapour chamber. Polyester resin Akemi Marmorkitt 1000 bonds without barrier coatings reversed within 18 hours in the vapour chamber, while epoxy resin Araldite AY 103/HY 991 bonds without barrier coatings remained unaffected even after two months. (Podany et al. 2001)

[v] DIN EN 13161: Natural stone test methods - Determination of flexural strength under constant moment, German version EN 13161: 2008.

[vi] Podany et al. (2001) aptly point out that 'for a material so prevalent within the field of conservation as B-72, little information is available on the strength of B-72 as an adhesive, particularly tensile and shear evaluations' – a remark very true indeed. In their study, they found that, for tensile bond strength, there is little or no difference between the use of the tested epoxy and polyester resin structural adhesives and PARALOID B-72.

REFERENCES

Anonymous. 2019. Paraloid B-44. Data sheet, Rohm and Haas, United States.

Bradley, S.M. 1990. Evaluation of Hxtal NYL-1 and Loctite 350 as adhesives for glass conservation. In *ICOM-CC 9th Triennial Meeting Preprints, Dresden, 26-31 August 1990*, ed. K. Grimstad, 669-674. Paris: International Council of Museums.

Coutinho, I., A.M. Ramos, A.M. Lima, and F.B. Fernandes. 2009. Studies on degradation of epoxy resins used for conservation of glass. In *Holding it all together: Ancient and modern approaches to joining, repair and consolidation, London, 21-22 February 2008*, eds. J. Ambers, C. Higgitt, L. Harrison, and D. Saunders, 127-133. London: Archetype.

Down, J.L. 1996. Epoxy resin adhesives: Report on shear strength retention on glass substrates. *Journal of the International Institute for Conservation, Canadian Group* 21: 28-35.

Down, J.L. 2001. Review of CCI research on epoxy resin adhesives for glass conservation. *Studies in Conservation* 46(2): 39-46.

Fiorentino, P. and L.V. Borrelli. 1975. A preliminary note on the use of adhesives and fillers in the restoration of ancient materials with special reference to glass. *Studies in Conservation* 20(4): 201-205.

Fischer, A., A. Wollmann, L. Selb, and M. Eska. 2009. Glasklebstoffe in der Restaurierung: Eine vergleichende Untersuchung zur Klebfestigkeit. *VDR Beiträge zur Erhaltung von Kunst- und Kulturgut* 2: 99-103.

Horie, V. 2010. *Materials for conservation: Organic consolidants, adhesives and coatings*. 2nd edition. Oxford: Butterworth-Heinemann.

Koob, S.P. 2006. *Conservation and care of glass objects.* London: Archetype Publications in association with The Corning Museum of Glass.

Podany, J., K.M. Garland, W.R. Freeman, and J. Rogers. 2001. Paraloid B-72 as a structural adhesive and as a barrier within structural adhesive bonds: Evaluations of strength and reversibility. *Journal of the American Institute for Conservation* 40(1): 15-33.

Rémillard, F. 1984. The effect of solvents on epoxy resin adhesives. Unpublished thesis, Queen's University, Canada.

Rémillard, F. 1989. Adhésifs à base de resins epoxy: Étude de solubilisation. *Journal of the International Institute for Conservation, Canadian Group* 14: 12-17.

Sander-Conwell, E. and K. Schmidt-Ott. 1993. Vergleichende Untersuchungen zu UV-härtbaren Klebstoffen. *Arbeitsblätter für Restauratoren* 26(1): 67-71.

Scott, M. 1986. An experimental project aimed at formulating a solvent which will attack a broad range of epoxy resins. Unpublished research report, Canberra College of Advanced Education, Australia.

Tennent, N. 1979. Clear and pigmented epoxy resins for stained glass conservation: Light ageing studies. *Studies in Conservation* 24(4): 153-164.

Wanner, A. 2009. Glasklebstoffe und –ergänzungsmassen für die Hinterglasmalerei. Tests zur Alterungsbeständigkeit, Biegebruchfestigkeit und Schadstoffemission. *Restauro* 115(6): 382-393.