

## **Short scientific report FoU 2013-06-11 (Kortfattad vetenskaplig slutrapport)**

Thea Winther

### **Project title**

Foga samman plast – vad händer på lång sikt? En jämförande studie av limning av styrenplast och dess långtidspåverkan.

Joining plastic together – what happens over time? A comparative study of seven adhesives and their long-term effect.

Dnr 353-03471-2011

Riksantikvarieämbetet  
Förvaltningsavdelningen  
621 22Visby

### **Collaborating organisations**

Department of polymer technology, KTH, Royal Institute of Technology  
Swerea KIMAB

### **Project leader**

Judith Bannerman, engineer, PhD, born 1975, Severn Grange Farm Cottage, Northwick Road, Bevere, Worcester. WR37RE England [Judith.bannerman@gmail.com](mailto:Judith.bannerman@gmail.com),  
Thea Winther, conservator, MSc, born 1970, Riksantikvarieämbetet, [thea.winther@raa.se](mailto:thea.winther@raa.se)

### **Project members**

Hilde Skogstad, Conservator, MA, 1984  
Mats KG Johansson, Professor of polymer technology, KTH, 1961  
Karin Jacobsson, Senior researcher, Swerea KIMAB, 1970  
Johan Samuelsson, Researcher, Swerea KIMAB, 1973

### **Summery**

In order to contribute with further knowledge to guide conservators in their decisions in active conservation of polystyrene seven adhesives have been tested for their effect on the plastic material before and after light aging. The main aim of this investigation has been to investigate the stability of the adhesives that are used by conservators and how the join will age by studying the effect of the adhesives on the original material and what chemical and mechanical changes that occur. Furthermore, the question of reversibility has been considered.

Methods applied were assessment of working properties, appearance, colour measurement, tensile testing, hardness measurement, assessment of break type, SEM-imaging, ATR FTIR-imaging and assessment of reversibility. Ageing has been performed by light ageing with a UVA component.

The chosen adhesives were three acrylates in solvent (Paraloid B72 in acetone:ethanol, or in only ethanol, Paraloid B67 in isopropanol and Acrifix 116), one acrylate dispersion (Primal AC-35), two epoxies (Hxtal NYL-1, Araldite 2020) and one cyanoacrylate (Loctite Super Attak Precision (SAP)). They have been tested on extruded sheet material of transparent general purpose (GPPS) and white high impact polystyrene (HIPS) applied on edge joints (of

butt joint type) and as an open layer. Polystyrene is a polymer of styrene monomer, and HIPS is a two-phase system with some part rubber particles, most often *cis*-polybutadiene 5-10%, grafted into the polystyrene matrix to make the plastic less brittle.

A damaging effect to the plastic could be seen for Acrifix 116 and Loctite SAP as cracks visible in the SEM imaging. In addition, an effect on the plastic by these adhesives and for the Paraloid B72 in acetone:ethanol could be seen in the FTIR-imaging. The effect of solvents on the plastic is noticeable and more so for the two-phase system of HIPS. Stress-cracking of the plastic on the plastic edge joints were not visible by human eye or in the stereomicroscope. For the cyanoacrylate a surface effect on the plastic was visible in the SEM.

The tensile strength of the adhesive joins was not severely affected during ageing for most of the tested adhesives. The cyanoacrylate was weakened and for Acrifix 116 and Primal AC-35 on HIPS the bond was strengthened. In general the cyanoacrylate was the strongest and Paraloid B67 the weakest and most bonds stronger for HIPS compared to GPPS. None of the adhesives resulted in a cohesive break in the plastic. Adhesive breaks could be seen for the epoxies.

Most adhesives showed yellowing, apart from Acrifix 116 and only to a minor extent Hxtal NYL-1 on the open layer samples, seen through both visual inspection and in the spectrophotometer measurements. None of the tested adhesives matched the refractive index of the polystyrene and this resulted in the bonds being visible. The bonds of the edge joins for the cyanoacrylate and Araldite 2020 showed visible yellowing. Deformation of the samples with an open layer of adhesive could be seen for Acrifix 116 and to a lesser extent for Loctite SAP. Reversibility was possible for the Paraloids and the dispersion Primal AC-35. The epoxies and Acrifix 116 was possible to remove manually. The cyanoacrylate was not possible to remove.

During this investigation none of the tested adhesives proved to be ideal for polystyrene. If a weak bond is acceptable Hxtal NYL-1 or the acrylate dispersion could be chosen as it was observed to have the least damage to the plastic material. Possible disadvantages for these adhesives could be difficulty in application for the epoxy and a slightly yellow colour for the dispersion. The greatest potential for damage was indicated by Acrifix 116 and the cyanoacrylate.

Ideally an adhesive should be able to hold pieces together for the intended usage, and within conservation it should be able to be separated without damage. When choosing an adhesive for an object in a heritage collection one needs to consider aesthetic aspects, the history of the object, its condition as well as future use with expected stresses. Knowing the behavior of the investigated adhesives and how they age together with polystyrene will guide conservators in making informed choices for polystyrene materials.

### **Background and aim**

During 2011 a review with the aim to identify a relevant research area within the field of preservation of plastic materials was performed at The Swedish National Heritage Board (Dnr 351-949-2011 Probleminventering och förstudie inom vård och konservering av plastmaterial). The starting point for this review was the prior FoU-project *Morgondagens kulturobjekt* performed at The Swedish National Heritage Board 2005-2008. The project concerned damages, degradation and analysis of plastic materials in Swedish museum collections. A survey including fifty-one Swedish museums and a more extensive damage

assessment at nine museums were performed. The museums have collections of art, design and cultural history objects.

The survey showed that 10% of the objects were damaged and 3% were in such a state that they were regarded as a loss. The most usual damages are cracks, discolouration, dirt accumulation and abrasion. The project concluded that there is a need for research of active conservation methods for the preservation of plastics materials.

The review 2011 included a literary survey, a research overview, and contacts with conservators and researchers. The area of adhesive joining was chosen. An application for FoU-funding was submitted and accepted for this project. The preservation of plastic materials is in congruence with the focus theme of modern materials stated in Riksantikvarieämbetets FoU-program 2012-2016 (Riksantikvarieämbetets FoU-program 2012-2016 för kulturmiljöområdet).

The aim of the project is to contribute with knowledge within the field of active conservation of plastic materials and to provide guidance in choosing the best method and material for the preservation of polystyrene objects of our cultural heritage. The investigation has focused these questions:

- How stable are the adhesives that are used by conservators? What will happen to the join upon ageing?
- What effect do the adhesives have on the original material? What chemical and mechanical changes will take place?
- How suitable and compatible are the adhesives with this kind of plastic?

Furthermore, the question of reversibility has been considered.

### **Theory and Methods**

Research on plastic materials from a heritage perspective has been performed since the 1980s and the activities within this field have been steadily rising as the problems of these materials have been observed. To a large extent the research has been investigating identification, damage assessment, deterioration and preventive measures. The need for research on active conservation measures has been recognized.

There are occasions when an adhesive bonding of these materials is necessary. Joining of objects can be considered necessary for several reasons such as increasing the understanding and readability of the object or as a measure to prevent further degradation. For preservation purposes it is important to choose an adhesive that will be stable over time and with as little impact as possible on the object. The conservator will need to know what adhesive that can be used for what kind of plastic, how it can affect the object and how it will age. The need for finding appropriate adhesives for polystyrene has been pointed out by conservators (Moomaw et al. 2009). The study is designed to look at the interaction between substrate and adhesive and not only at the performance of the adhesive.

The project is a comparative study of seven adhesives and their effect on polystyrene with both quantitative and qualitative methods before and after light ageing. The project has investigated the effect on substrate and adhesive through comparison before and after ageing and before and after joining. The main impetus for the choice of adhesives was what adhesive would conservators use, or think of using, for polystyrene. A questionnaire was therefore sent

to Swedish conservators likely to come across polystyrene in their work. Replies from approximately 20 conservators formed the basis for a screening test trial of 20 adhesives. After initial testing which included considering working properties, aesthetics and damaging effects seen on visual inspection, and through discussions with the peer review panel, it was narrowed down to seven adhesives for further investigation. The adhesives chosen represent both conservation grade variants commonly used by conservators and some more industrial products. They fall mainly into three categories; acrylates (solvent based or dispersion), epoxies and one cyanoacrylate (see table 1 for a list of the chosen adhesives and data). The solvent based acrylates were Paraloid B72 in acetone:ethanol, Paraloid B72 in only ethanol, Paraloid B67 in isopropanol, and Acrifix 116. The epoxies were Hxtal-Nyl 1 and Araldite 2020. The acrylate in dispersion was Primal AC-35 and the cyanoacrylate was Loctite Super Attak Precision. The projects' emphasis on usage or potential usage of adhesives on polystyrene, might have led the study to include adhesives that theoretically did not meet all requirements from a heritage perspective, e.g. adhesives with solvents dissolving polystyrene or adhesives with a different refractive index than polystyrene. The idea was to investigate empirically, how those adhesives which were selected as potential candidates for polymer adhesion would behave over time and if or to what extent damage would occur. If there was a choice between adhesives that behaved similarly in the screening test then information from the industry and in the literature (Horie 2010, Shashoua 2008) was used for guidance. Those with more compatible qualities with polystyrene in terms of such aspects as glass transition temperature, ageing qualities or reversibility were then chosen.

Degradation processes have been studied quantitatively through the effect on the strength of the bond in tensile testing, effect on hardness of both plastic and adhesive and by the visual changes through comparison of colour values. Qualitatively degradation effects have been studied by molecular characterizing with Fourier Transform Infrared Spectroscopy (FTIR) microscopy imaging and by imaging of the micro scale changes induced by the adhesive joining in the Scanning Electron Microscope (SEM). Moreover, degradation phenomena and type of break have been assessed visually in the stereomicroscope.

Compatibility of adhesive and plastic has been assessed through an appreciation of the type of break of the bond in the tensile testing. Furthermore, compatibility has been indicated through hardness testing, assessment of working properties and reversibility. Based on the results from the above testing some adhesives were chosen and tried on real three-dimensional objects.

### *Experimental*

Accelerated ageing was performed by light ageing with a 430 watt Sol 500 lamp from Hönle UV technology with a metal halide light bulb with radiation efficiency in the ultraviolet and visible range (295-780 nm). The samples were placed flat at a fixed distance from the light source and rotated once a week. Based on average lux levels the ageing period was set to 24 days, which for the visible component corresponds to 60 years with 100 lux 8 hours per day, 7 days a week, 365 days per year (museum exposure) Lux levels, UVA levels, RH and temperature were measured at 22 measuring points once a week. The samples were exposed to an average of 30700 lux and a UVA component of 13 W/m<sup>2</sup> at 26-28°C and 45% RH.

The experiments were conducted in two series. In series 1, 160 samples; 80 GPPS and 80 HIPS, 50x100x1mm in size, were subjected to pull-to-break in the tensile tester before being adhered with the adhesives; 10 GPPS and 10 HIPS for each adhesive. The broken edges of the plastic were after initial break abutted and joined using the different adhesives mentioned above. Working properties and visual appearance were assessed prior to half the unaged

samples being subjected to pull-to-break in the tensile tester. The samples in the other half were subjected to light ageing before a new visual assessment followed by tensile testing. Break force values were compared and the type of break assessed. In the samples with adhered edges all adhesives were applied on break edges with a brush except for Loctite Super Attak Precision (Loctite SAP) which was applied directly from the nozzle of the tube. After application, the adhered pieces were pressed together and laid flat to cure.

In series 2, a 1 mm thick an open adhesive layers of the seven different adhesives were applied with a draw-down technique to cover the centre of 16 samples; 8 GPPS, 8 HIPS, 108x215x1mm. All samples were cut in half, and one half was subjected to light ageing. Visual assessment, hardness testing, colour measurement, SEM-imaging of border area between adhesive and plastic and FTIR-imaging of cross-sections of the interface between adhesive and plastic were conducted and compared on both unaged and aged samples. For colour measuring a set of the adhesives with glass as a substrate was included. One sample was subjected to an elemental analysis in Energy Dispersive X-ray Spectroscopy (EDS).

### *Instrumental*

Spectrophotometer values were taken with a Spectrophotometer CM-2600/2500d (Minolta) to measure the adhesives on both plastics, the adhesives on a glass substrate and on the plastics without adhesive. Measurements were taken with a white A4 paper under the substrates, and three measurement points were taken for each adhesive. For the adhesive measurements, the standards/targets used were unaged transparent GPPS and unaged HIPS. The  $\Delta E^*$  calculations are from the  $\Delta E^*76$  standard.

Hardness testing was done with a Rex Durometer (Rex Gauge Company, INC), Model MSDD-3-A, B, O in accordance with ASTM D-2240.

Tensile testing was conducted with a AGS-x 10N-10kN tensile tester (Shimadzu), data being processed by software Trapezium Lite X. Tensile testing was performed at 100mm/min.

SEM analysis was performed using a LEO 1455VP (Oxford Instruments) with Inca 400 software. Conditions: EHT ranging from 20 kV, iprobe 1.0 nA, backscattering. Magnifications were x18, x100, x250, x1000. Samples were sputtered with gold for 60 seconds at 18mA. SEM-imaging was also done on unsputtered samples. EDS mapping time was 820 seconds.

The FTIR-imaging was performed using a Spotlight 400 microscope (Perkin Elmer) equipped with a geranium ATR-crystal with a resolution of  $16\text{ cm}^{-1}$ , 1 cm/s, pixel size of  $1.56\text{ }\mu\text{m}$  and with a. Microtomed cross-sections of a thickness of  $100\text{ }\mu\text{m}$  where the adhesives were applied to the plastic in the open samples were used and imaging performed with an area of  $200\text{ x }200\text{ }\mu\text{m}$  or  $200\text{ x }100\text{ }\mu\text{m}$  of the cross-section.

## **Results**

### *Assessment of working properties, appearance and colour measurement*

The viscosity and the work-time of the adhesive were the two most important factors in assessing working properties. The epoxies and the Loctite SAP had very low viscosities which made them difficult to apply in a controlled way. Among the seven adhesives Acrifix 116 was easiest to use and most controllable during application, mainly because it has a relatively high viscosity and long working time. Primal AC 35 was also relatively easy to use.

With both of the epoxies, delamination from the plastic surface occurred when subjected to stress. Delamination was a little more distinct on GPPS than on HIPS. All adhesives except for the epoxies experienced shrinkage after curing. Most shrinkage could be seen for Acrifix 116 and the Paraloids due to the evaporation of solvents.

Acrifix 116 caused visible damage to the plastic in the open layer samples by bending it in a concave shape upon curing (figure 1). HIPS was bent more severely. The bending is caused by a combination of factors. The solvent mixture in the adhesive dissolves the polystyrene and increases the possibility for the polymer chains to move. When the adhesive contracts during evaporation of the solvent with subsequent shrinkage a tension is created giving rise to the deformation. The HIPS is more flexible and thereby more easily affected by this strain. In addition, the greater extent of free volume in the two-phase system of HIPS allows for more efficient dissolution of the plastic. Loctite SAP caused some slight bending of the plastic but less than for Acrifix 116. None of the other adhesives caused any deformation or damage observed during visual inspection.

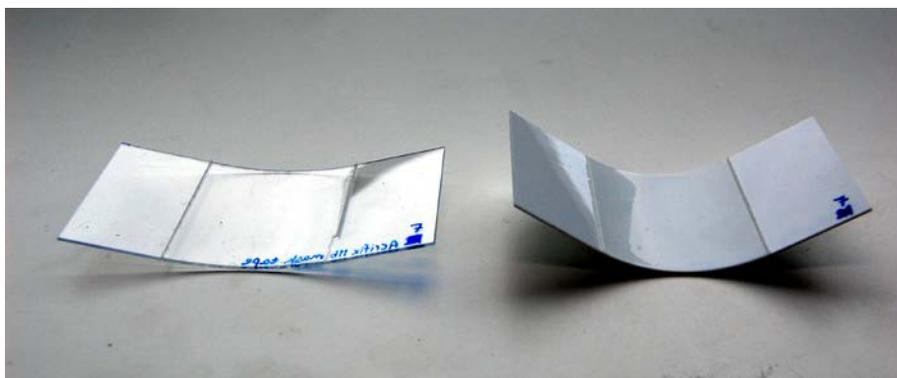


Figure 1. Bending of GPPS (left) and HIPS (right) by Acrifix 116. Photo Hilde Skogstad.

All adhesive bonds were visible after curing, to a greater extent on GPPS than on the HIPS. The visibility of the bond showed that none of the adhesives have the same refractive index as polystyrene. For the HIPS the visibility was related to the amount of excess adhesive around the break edges. A microscopical study of the different adhesive bonds in the samples with adhered edges shows that Acrifix 116 gives the thinnest bond. Stress-cracking of the plastic on the plastic edge joints were not visible at visual inspection or in the stereomicroscope.

All adhesives were transparent in colour before ageing except for Primal AC 35 which was slightly pale yellow and Loctite SAP which was pale white. Loctite SAP also had an uneven, grainy texture. The most apparent visible change in the open layer samples after ageing was colour change. Both the control samples of plastic without adhesive yellowed visibly, the HIPS more than the GPPS. Among the adhesives the Loctite SAP and Araldite 2020 showed the most severe yellowing after ageing for both the open layer samples and the samples of adhered edges. Hxtal Nyl-1 and Acrifix 116 showed no visible colour change. In the samples with the adhered edges Acrifix 116 is more visible after ageing on HIPS; not because of any yellowing/discolouration of the adhesive itself, but rather because the plastic has yellowed while the adhesive has not, thereby creating a visible contrast where the adhesive bond appears lighter than the plastic.

Most yellowing was seen in the open layer samples and not in the adhesive joins of the adhered edges apart from that of Araldite 2020 and Loctite SAP on GPPS. This is not

surprising as the light has more difficulty in reaching the adhesive in these bonds. The Araldite 2020 has been shown to yellow in earlier investigations (Drain, et al. 1985).

The two epoxies showed a difference in colour change where the Hxtal Nyl-1 did not visibly yellow while Araldite 2020 did. The DGEBA\* component of the Araldite 2020 has been noted to yellow in light ageing (Horie, 2010). Severe yellowing for epoxies could be attributed to the amine-structure present as a catalyst (Down, 2001). The two Paraloids experienced the same amount of visible yellowing. In earlier ageing studies, B72 yellows more than B67 during light ageing (Down, 2009).

The spectrophotometer measurements on the open layer samples mirrored the visible colour changes before and after ageing (figures 3 and 4). The curves showing reflectance in the visible wavelength spectrum and the b\* values before and after ageing differ the least for Acrifix 116 and the most for Loctite SAP (b\* scale measures yellowness[+b] –blueness [-b], figure 2). There is a medium amount of difference for the Paraloids and Primal AC 35.

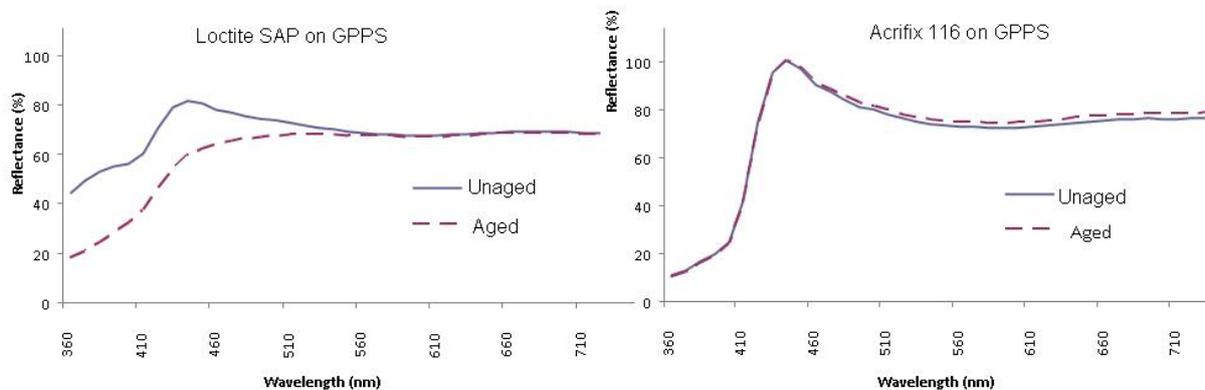


Figure 2. Curves showing % reflectance in the visible spectrum before and after ageing on GPPS. The greatest colour change could be seen for Loctite SAP and the least for Acrifix 116.

The curves and b\* values also differ between the same adhesive on the two different plastics. Paraloid B72, Paraloid B67 and Araldite 2020 demonstrated the largest difference of b\* values between aged and unaged on HIPS, while Primal AC35, Hxtal Nyl-1, Loctite and Acrifix 116 demonstrate the largest difference of b\* values on GPPS. The reason for this can be attributed to the colour change occurring in the underlying plastic interfering with the colour measurements of the adhesives. When the adhesive is close to transparent and very thin, the spectrophotometer most likely also measures the colour of the substrate underneath.

\* DGEBA, diglycidyl ether of bisphenol A

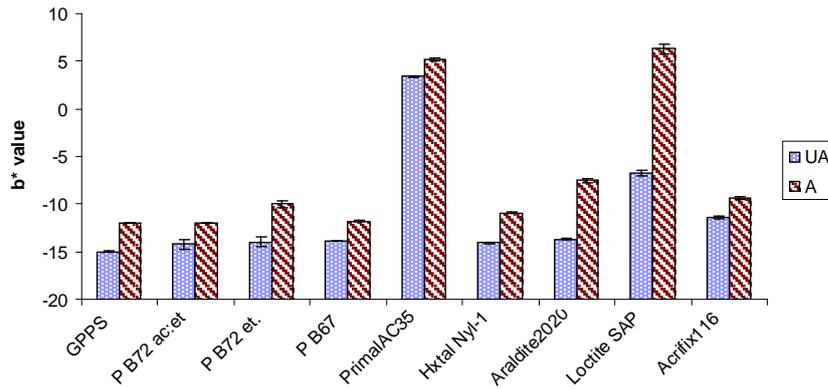


Figure 3. The  $b^*$  values for adhesives on transparent GPPS before and after ageing, UA-unaged, A-aged. GPPS - without adhesive. Loctite SAP and Araldite 2020 show the greatest change and Acrifix 116 the least.

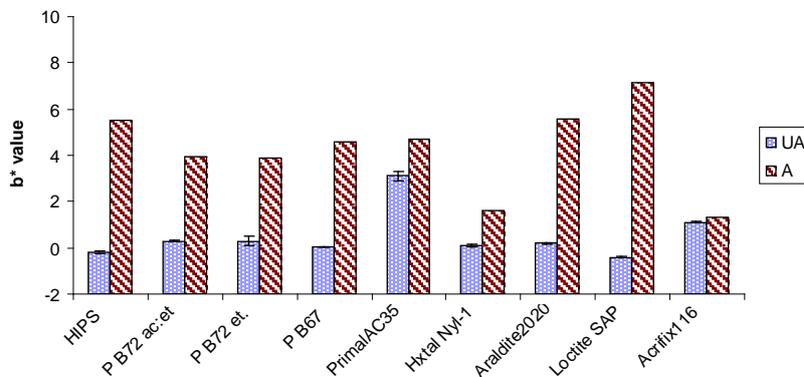


Figure 4. The  $b^*$  values for adhesives on HIPS before and after ageing, UA-unaged, A-aged. H0 HIPS without adhesive. Loctite SAP and Araldite 2020 show the greatest change and Acrifix 116 the least.

To measure colour change of the adhesive only, the adhesives were subjected to ageing with glass as a substrate. Also here the Acrifix 116 shows the least change while Loctite SAP shows the largest in the  $b^*$  value.

#### *Tensile testing, type of break and hardness measurement*

All samples broke in the adhered area with no visible damage to the plastic such as shattering, stress cracks or loss of material. See figures 5 and 6 for average break force sensitivity before and after ageing represented as bar graphs. There is a spread to the values probably introduced as the application of adhesive was performed manually. Tensile strength measurements are also normally associated to a significant data scattering due to occurrence of small defects present in the test specimens. However, taking this uncertainty into account the results are interpreted as applicable in an overall assessment of the general trends.

The adhesives show the same general tendency ranging highest to lowest in break force sensitivity before ageing and after aging; Loctite SAP is the strongest adhesive and Paraloid B67 is the weakest, while Acrifix 116, Araldite 2020, Hxtal Nyl-1 and Paraloid B72, both in ethanol and acetone: ethanol, are relatively close together in the middle range. Both GPPS and HIPS without adhesives have higher values for break force sensitivity than for any of the adhered joints.

Loctite SAP on GPPS has weakened considerably while Acrifix 116 and Primal AC 35 showed increased break force sensitivity after ageing on both plastics. It has been reported that cyanoacrylate adhesives are prone to photo induced ageing with possible chain scissioning which could be in process here as the transparency enables the radiation to reach the adhesive (Horie, 2010). The fact that Acrifix 116 (acrylate in solvent mix) and Primal AC 35 (acrylate dispersion) are getting stronger by light ageing could be due to a prolonged curing process.

The epoxies only have a medium break force sensitivity among the tested adhesives, even though epoxies in general are considered to be very strong adhesives. The epoxies' relatively weak adherence on polystyrene is also seen in a delamination from the plastic observed in the open layer samples when cutting or microtoming. This could be attributed to their lack of affinity with non-polar surfaces. The non-polar surface of polystyrene repels the adhesive upon application which results in low wetting and a weakened bond. This is reflected in the fact that the surface tension value of polystyrene is lower than that of epoxy, 33 mN/m compared to 47 mN/m at 20°C for epoxy. Acrylics have 32 mN/m at 20° C and cyanoacrylates 37 mN/m and should hence wet the substrate more efficiently (Shashoua, 2008). It has been reported that the strength of Araldite 2020 increases during light ageing thought to be a result of cross-linking (Coutinho, et al. 2009), however, this is not reflected in the tensile strength of the bonds. On the other hand the values for hardness measured on open layer samples of Araldite 2020 increase with exposure to light.

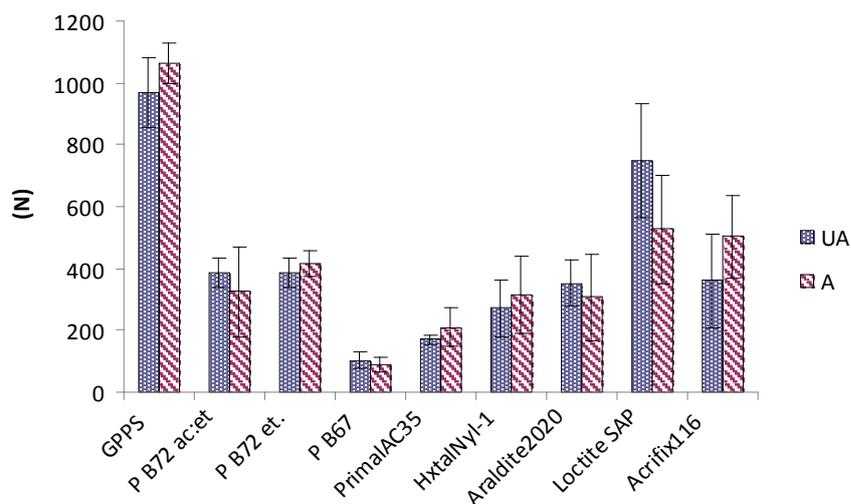


Figure 5. Tensile testing of adhesive joins on transparent GPPS. UA – unaged, A – aged. GPPS is plastic without adhesive.

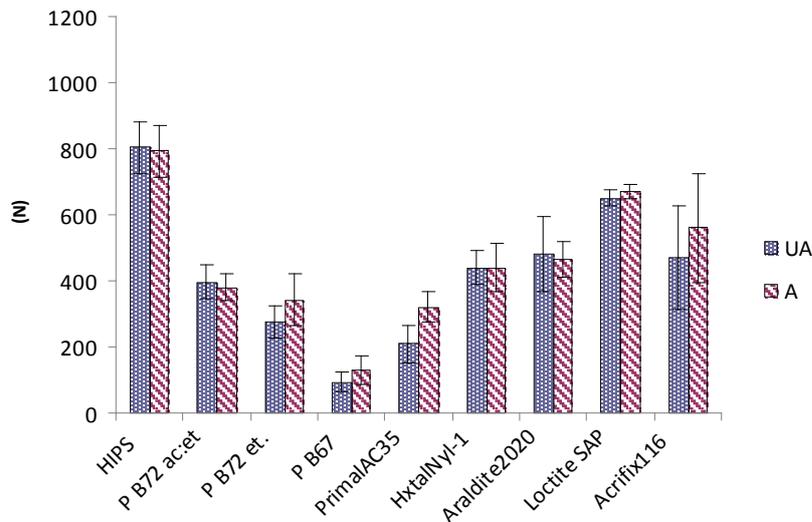


Figure 6. Tensile testing of adhesive joints on HIPS. UA – unaged, A – aged. HIPS is plastic without adhesive.

It is interesting to note the difference in break force sensitivity between the two Paraloids, with Paraloid B72 being clearly much stronger than B67. The brittleness of the B67 observed during hardness testing could be a factor in breakage. Both Paraloids have a lot of bubbles in the adhesive bond but Paraloid B67 have a larger number than Paraloid B72 which is another factor accounting for the weak bond. The brittleness of B67 has been shown in earlier studies (Down, et al. 1996, 2009).

All adhesives are stronger on HIPS than on GPPS after ageing except for Paraloid B72 in ethanol. A contributing factor for this effect can be that the two phase system of HIPS has more free volume in the polymer matrix which could make it more susceptible to interaction by solvents or the small molecules of the cyanoacrylate before curing. The polarity of HIPS could be a contributing factor in regards to the epoxies.

The type of break was studied by SEM and stereomicroscope. None of the samples experienced a break in the plastic. This can be seen in relation to the fact that both of the polystyrenes are stronger than the adhesives, which results in a break either in the adhesive (cohesive break in the adhesive) or between the adhesive and plastic (adhesive break). All acrylates in solvent; the Paraloids and Acrifix 116, experienced a break in the adhesive. Both epoxies experienced breaks between the adhesive and plastic (adhesive break). It is interesting to note that the tendency to delaminate from the plastic as seen in the sample preparation of the open layer samples also occurred on a rough break edge surface and not only on a smooth polystyrene surface. Primal AC 35 and Loctite SAP experienced a combination of break in the adhesive and between adhesive and plastic.

The plastic and adhesives were also tested for hardness before and after ageing on open layer samples. The GPPS is harder than the HIPS and both plastics are harder than most of the adhesives, except for the epoxies. The epoxies are harder than the plastic with the exception of unaged Araldite 2020. The softest adhesives were Primal AC 35 and Paraloid B67. For Paraloid B67 miniature fractures caused by the durometer pencil during hardness testing was visible. The durometer did not cause fractures in any of the other adhesives.

Based on the measurements, a general tendency is that both plastics and all adhesives harden with ageing. Paraloid B72 and Hxtal Nyl-1 changed the least after ageing while Paraloid B67

and Primal AC 35 changed the most. This can be a result of cross-linking in the adhesives caused by light ageing or a continuing process of curing. It has been pointed out by Wolbers (2008) in relation to long term ageing of acrylics that there is a process of loss of retained solvent which will affect their brittleness and  $T_g$ 's. The acrylics have also been shown to become less flexible during dark ageing (Down, et al. 1996).

From a conservators point of view hardness measurement is of interest as a means of understanding how the adhesive and substrate age and function together. The property preferred is that the adhesive should not be harder than the plastic and this is the case for most of the investigated adhesives apart from the epoxies. For the epoxies the type of break were adhesive and should thus not pose a problem for the original plastic material.

#### *Effect and damage on plastic from adhesive seen in SEM and FTIR*

The open layer samples were observed at the edge of the adhesive on the plastic both with and without sputtering with gold. The focus was to determine whether the adhesives caused any damage to the plastic on a micro level, and images of before and after ageing were assessed. Studying the samples using SEM showed damage to the plastic for two adhesives; Loctite SAP and Acrifix 116.

For the samples with Acrifix 116 both unaged and aged showed cracks in the plastic at the border area along the edge of the adhesive (figure 7). This was more prominent in HIPS than in GPPS. The cracks became slightly worse after ageing which could be related to the prolonged drying of the adhesive. The stresses increase as a shrinkage of the adhesive occurs. Also for samples with Loctite SAP cracks could be seen (figure 9).

In the case of Loctite SAP some irregular surface features in the plastic along the edge of the adhesive could be seen (figure 8). This can be interpreted as damage to the polystyrene caused by the adhesive. The phenomenon was also visible in the light microscope.

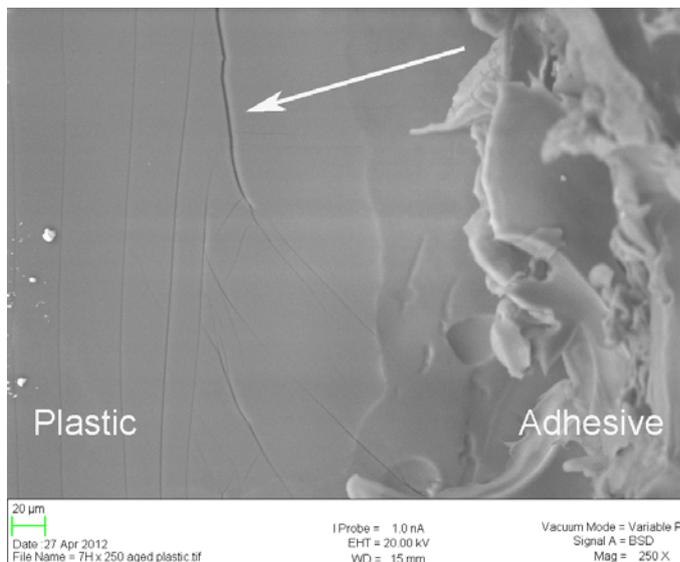


Figure 7. SEM image of sample with Acrifix 116. Adhesive to the right. Stress cracks in plastic along edge of adhesive.



Figure 8. SEM image of Loctite Super Attack Precision on HIPS. Adhesive to the right and possible damage to the plastic to the left. Goldsputtered.

One sample of Loctite SAP was subjected to elemental analysis by EDS to determine whether the irregularities observed on the plastic surface in the SEM images could be adhesive spill rather than damage to the plastic (figure 9). It was expected to observe more nitrogen in the adhesive than in the plastic. The nitrogen mapping however gave inconclusive results. The carbon-mapping on the other hand, gave indications that the irregularities observed are in the plastic itself and not adhesive spill. The line between the carbon rich area in the carbon mapping corresponds to the line between the adhesive and the plastic in the electron image. Had the pattern and bands of darker and lighter areas seen in the upper right hand area of the SEM image been a spill of cyanoacrylate the same pattern would have been visible as less carbon in the mapping, and possibly as more oxygen.

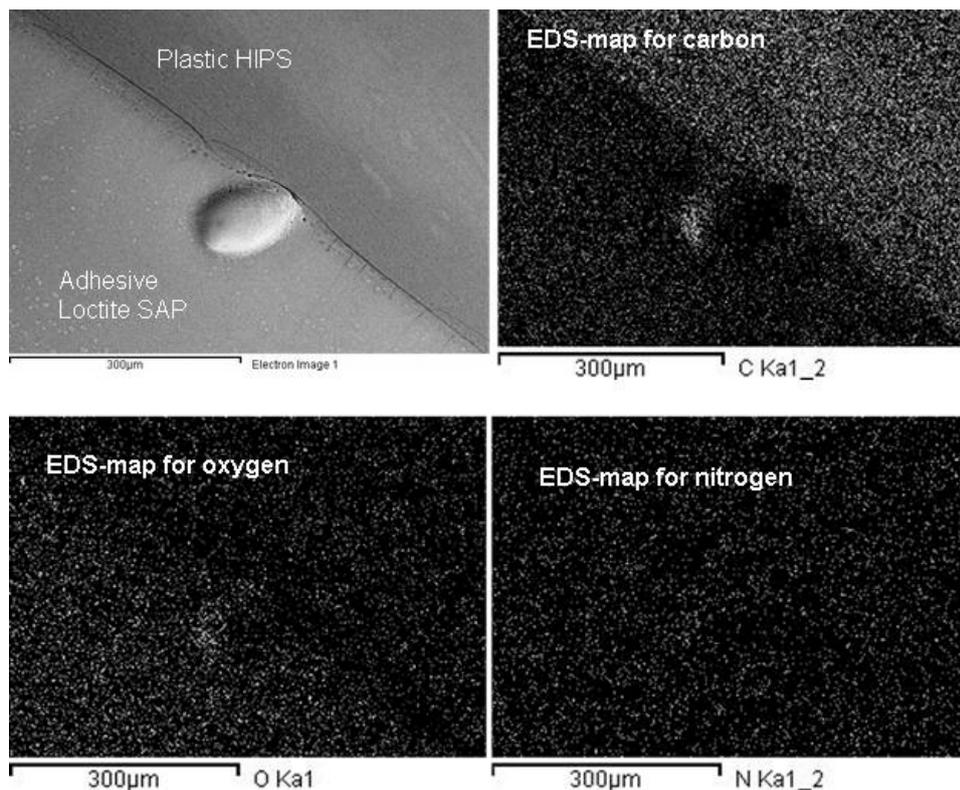


Figure 9. Sample with Loctite SAP on HIPS in EDS-mapping for carbon, oxygen and nitrogen. Corresponding SEM image in upper left hand corner (the centre shape is a conglomeration of adhesive). Adhesive layer in lower left hand corner on all four images. Had the pattern and bands of darker and lighter areas seen in the upper right hand area of the SEM image been a spill of cyanoacrylate the same pattern would have been visible as less carbon in the mapping, and possibly as more oxygen. Cracks in the plastic visible in the SEM image.

The samples were also studied by ATR-FTIR microscope imaging. Microtomed cross-sections from the open layer samples were used. The area of interest was where the plastic meets the adhesive. For the samples with the dispersion, and the epoxies the adhesive layer delaminated during the microtoming process. This also occurred for Paraloid B67 on HIPS before ageing. In case of delamination, the area where the plastic had been in contact with the adhesive was studied. Control samples of plastic without adhesive were also included.

The plastic area in the mapping of the sample was examined to identify significant peak changes compared to reference spectra of plastic. A comparative image comparing every single spectra of the mapped area to that of a reference spectrum of plastic without adhesive was studied. The degree of similarity to the reference spectrum is depicted represented by various colours (figure 10). The size of the zone of change in  $\mu\text{m}$  ( $\Delta\text{zone}$ ) was measured. The size of the zone is assumed to reflect the impact of the adhesive into the plastic.

It was possible to see that all plastics were affected in the contact zone between plastic and adhesive. Viewing the comparative images the Paraloids, Loctite SAP and Acrifix showed the largest change before ageing. Acrifix 116 had less change for GPPS and more change for HIPS. After ageing Loctite SAP, the acrylates and Araldite 2020 showed the largest  $\Delta\text{zone}$  for HIPS. For GPPS they were at a fairly equal level with the exception of the cyanoacrylate which had a slightly larger  $\Delta\text{zone}$ .

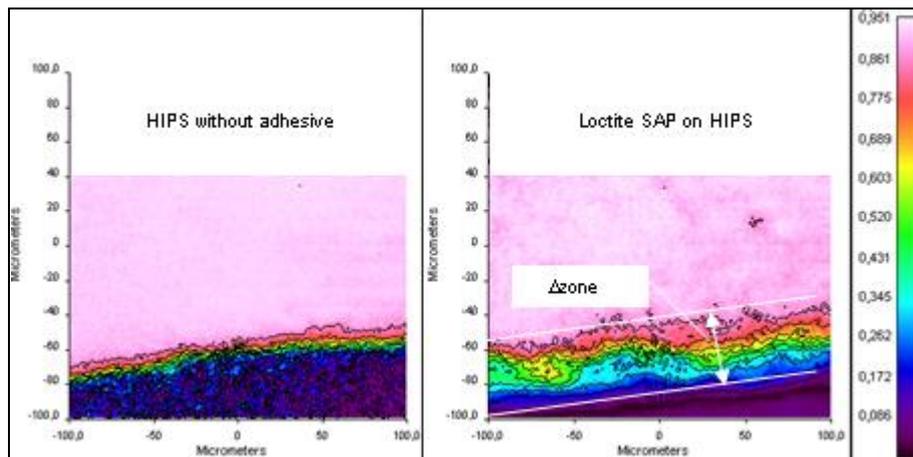


Figure 10. Comparative FTIR images of cross-sections of HIPS without adhesive (left) and HIPS with Loctite SAP (right). Top is plastic (pink indicates a match with spectrum for HIPS reference, correspondence scale in percent to the right) and bottom is adhesive. Arrows indicate the change zone ( $\Delta$ zone).

A large  $\Delta$ zone can be seen for the cyanoacrylate on HIPS (figure 10). The two-phase system of HIPS could give room for an affect of the small cyanoacrylate monomer. The SEM-images of the plastic with Loctite SAP showed a surface pattern on the plastic indicating change induced by the adhesive. The surface phenomenon for the cyanoacrylate is more apparent on HIPS than on GPPS which could indicate that the small molecules of the cyanoacrylate or its additives could diffuse more easily into the HIPS. The polybutadiene phase creates more free volume in comparison to GPPS. It has been shown that cyanoacrylates can mix with polycarbonate while curing (Drain, et al., 1985) and a similar process might be indicated here.

#### *Effect of solvent action*

Looking at Hildebrand solubility parameters the  $18.6 \text{ MPa}^{1/2}$  of the ethyl acetate in Acrifix 116 is very close to that of polystyrene;  $18.7 \text{ MPa}^{1/2}$ . Also that of acetone of  $20.4 \text{ MPa}^{1/2}$  is within the  $2 \text{ MPa}^{1/2}$  difference range of dissolution and the larger  $\Delta$ zone seen for Paraloid B72 in acetone: ethanol in the FTIR-imaging can be attributed to this. Ethanol and water on the other have Hildebrand solubility parameters of  $26.6 \text{ MPa}^{1/2}$  and  $47.7 \text{ MPa}^{1/2}$  respectively (Shashoua, 2008). For the dispersion, no damage has been observed. It has to be remembered that the solubility of the plastic can change with ageing.

To some extent the diffusing effect of solvents can contribute to the strength of the adhesion and more so for HIPS. That Paraloid B72 in acetone:ethanol was stronger than Paraloid B72 in just ethanol on HIPS may be related to dissolution between the HIPS and the acetone as solvent. However, there is no consistent relation between the strength of the solvent borne adhesive bonds compared to chemically cured adhesives. In the case of the cyanoacrylate an element of mixing with the surface could increase its strength. The polar affinity with polystyrene and the materials' flexibility needs to be taken into account.

#### *Assessment of reversibility*

The possibility to remove the adhesive was assessed by attempting to remove or dissolve the adhesive left on the break edge samples with a scalpel, wooden toothpick, water, ethanol, acetone and isopropanol. Results were observed under the microscope and any possible damage or dissolving of the plastics was assessed. There was no apparent difference in reversibility between the same adhesive on the two polystyrenes.

The different adhesives demonstrated the same reversibility results after ageing as before ageing, apart from the fact that a larger amount of solvent was needed and it took a longer time for the adhesives to dissolve after ageing. Reversibility was possible for the Paraloids and the dispersion Primal AC-35. It was possible to remove the epoxies and Acrifix manually with a wooden toothpick with some difficulty. The other adhesives were not possible to remove without the risk of damaging the plastic. The cyanoacrylate was the most difficult to remove.

#### *Overall assessment*

Based on all of the different experiments, no single adhesive appears as clearly superior to the others or to be recommended in general for use on all polystyrene plastics. This is not only because all of the adhesives had some areas where they demonstrated a clear weakness, but also because the choice of adhesive must be seen in relation to the object in question, and depending on what qualities are sought. However, some conclusions can be drawn based on the testing, at least in relation to which adhesives that should not be recommended from a heritage perspective.

Even though Acrifix 116 showed some very good qualities both in relation to ageing, general aesthetics and working properties, it damaged the plastic through severe bending, micro-cracking seen in SEM and noted change in FTIR-imaging. The increased break force sensitivity after ageing might also indicate some unwanted strengthening of the bond.

If choosing an epoxy one should not expect it to be as strongly adhered on polystyrenes as it is generally known to be on other materials. This was observed during testing as delamination. Among the epoxies, Hxtal Nyl-1 yellows far less than Araldite 2020 when aged.

If a very strong bond is needed, a cyanoacrylate might be an alternative among the tested adhesives, but the risk of a break in the plastic rather than in the adhesive bond must be considered. Moreover, the damaging affect seen in SEM-imaging and the affect seen in FTIR-imaging raise questions on its suitability. In addition, the yellowing and non-reversibility need be taken into account.

Both Paraloids showed good ageing qualities, but Paraloid B72 appeared superior to B67. Paraloid B67 showed a very weak bond and great brittleness both before and after ageing. Paraloid B72 should preferably be mixed in ethanol rather than ethanol: acetone due to the risk of acetone damaging the plastic. Testing also demonstrated enhanced working properties of Paraloid B72 when mixed only in ethanol. If choosing a Paraloid, one should be aware of the difficulty in achieving a very clean, thin bond due to the large amount of bubbles in the adhesives. If a relatively weak bond and a white or pale yellow colour is wanted or accepted, Primal AC 35 can be an alternative based on its good working properties, easy reversibility and no detected damaging effects.

It should be noted that none of the tested adhesives match the refractive index of polystyrene and therefore all joins are visible. The difference for a match should be less than 0.02 and such adhesives should be included in future studies.

#### **Results in relation to other research**

Surveys and research on the preservation of plastic materials in the museum context have taken place since the 1980s and their numbers have been rising steadily. Research have

focused issues of identification, damage surveying, degradation, preventive measures and storing. More structured research on active conservation has taken place more recently.

Recent research was presented in the EEC project POPArt, Preservation of plastic artefacts 2009-2012 (Lavedrine et al. 2012). Within this project identification, damage assessment and surveying, assessment of degree of degradation and cleaning of plastics have mainly been studied. In addition, studies of consolidation, mainly for foamed polyester, was included. In Sweden the project Morgondagens kulturobjekt took place 2005-2008 at the Swedish National Heritage Board in collaboration with several museums (Nord et al. 2008). This project looked into damages, degradation and analysis.

Specific research studying adhesive joining of plastics from a preservation perspective have been performed mainly for poly (methyl methacrylate) and unsaturated polyester (Sale 1995, 2011, Roche 2011, Lagana and van Oosten 2011, Comiotto 2009). For work investigating and systemizing synthetic adhesives used within conservation and how they function and age the work of Jane Down, Velson Horie and Stephen Koob should be mentioned. (Down 2001, Down et al. 1996, 2009, Koob 2009, Koob et al. 2010, Horie 2010). Relevant for the adhesives in this investigation are especially Down on cyanoacrylates and epoxy.

Within the conservation community there are several papers describing testing of adhesives in the context of a case study or for a particular kind of object/s. Relevant observations on the adhesives tested in this investigation or for polystyrene in particular can be found in Comiotto et al. 2009 and Moomaw et al 2009).

The need for using appropriate adhesives for polystyrene has been pointed out by conservators (Moomaw, *et al.*, 2009). There has been little research into the repair of objects and especially for polystyrene materials. This study is designed to look at the interaction between substrate and adhesive, not only at the performance of the adhesive itself.

### **Relevance and usefulness of project**

During the last 100 years the plastic materials have become an important part of human life and are now a part of our cultural heritage. The objects are represented in the museums' collections to a great extent and within many types of collections. This project meets a need for further research into active conservation methods for the preservation of plastic materials.

There are occasions when an adhesive bonding of these materials is necessary. The conservator will need to know what adhesive that can be used for what kind of plastic, how it can affect the object and how it will age. This project contributes with knowledge of the long-term effects of adhesives on polystyrene objects. Polystyrene is one of the most common plastics. A damage survey of Swedish collections shows it to be one of the most frequent showing breaks and cracks (Nord et al. 2008). The need for finding appropriate adhesives for polystyrene has been pointed out by conservators (Moomaw et al. 2009). Furthermore, there has been little research into repair of these objects. The results of give conservators guidance in choosing adhesives in their work with the preservation of polystyrene artifacts.

### **Remaining efforts**

There will be revisions of the article to perform. A presentation for an international conference will be made; the biannual Future\_talks on the preservation of modern materials is planned, awaiting call for papers for 2013. An evaluation of the project will be done.

## Dissemination

The project has been presented at Samlingsforum 2012.

A manuscript for Studies in Conservation (Maney Publishing) has been submitted 2013-02-04 and a revised manuscript was submitted 2013-05-16.

Texts for the web page will be written and the full-length report will be posted as a pdf on the web-page of Riksantikvarieämbetet. The project has been covered by Swedish radio (Kulturradion, Sveriges Radio) and Gotlandic local press (Gotlands Allehanda 2013-01-09). The project will be presented at an international conference, at Future\_talks, conservation of modern materials, Neue Sammlung, Munich, Germany 2013. A text for Kulturvårdsforum will be written.

## References

Comiotto, A. and M. Egger. 2009. M. Naum Gabo's Sculpture Construction in Space Crystal (1937): Evaluating a Suitable Bonding Strategy for Stress loaded Poly (methyl methacrylate). *Postprints of Papers presented at the Conference FUTURE TALKS 2009: The Conservation Of Modern Materials in Applied Arts and Design*. Munich: Die Neue Sammlung. pp. 32-39

Coutinho, Inês; Ramos, Ana Maria; Lima, Augusta M.; and Braz Fernandes, Francisco. "Studies of the degradation of epoxy resins used for the conservation of glass." In Book. *Holding it all together: ancient and modern approaches to joining, repair and consolidation*. Ambers, Janet; Higgitt, Catherine; Harrison, Lynne; and Saunders, David (Editors). Archetype Publications Ltd. (2009), pp. 127-133

Drain K.F. and J. Guthrie, C.L. Leung, F.R. Martin, M.S. Otterburn. "The effect of moisture on the strength of polycarbonate-cyanoacrylate adhesive" *International Journal of Adhesion and Adhesives*, Volume 5, Issue 3, (1985), pp. 133-136

Down, Jane L. "Adhesive testing at the Canadian Conservation Institute : an evaluation of selected poly(vinyl acetate) and acrylic adhesives : report / by Jane L. Down, Maureen A. MacDonald, Jean Tétreault" *Canadian Conservation Institute* (1994)

Down, Jane L.; MacDonald, Maureen A.; Tétreault, Jean; and Williams, R. Scott  
Adhesive testing at the Canadian Conservation Institute--an evaluation of selected poly(vinyl acetate) and acrylic adhesives. *Studies in conservation* 41, no. 1 (1996), pp. 19-44

Down, Jane L. "Review of CCI research on epoxy resin adhesives for glass conservation." *Reviews in conservation* no. 2 (2001), pp. 39-46

Horie, Velson. "Materials for conservation" *Butterworth-Heinemann*, (2010) pp. 153-179, 289-297

Koob, Stephen P. "Paraloid B-72®: 25 years of use as a consolidant and adhesive for ceramics and glass." In Book. *Holding it all together: ancient and modern approaches to joining, repair and consolidation*. Ambers, Janet; Higgitt, Catherine; Harrison, Lynne; and Saunders, David (Editors). Archetype Publications Ltd. (2009), pp. 113-119

Koob, Stephen P.; Benrubi, Sarah; van Giffen, N. Astrid R.; and Hanna, Nathalie  
An old material, a new technique: casting Paraloid B-72 for filling losses in glass.  
In Book. *Symposium 2011: Adhesives and Consolidants for Conservation: research and applications: proceedings = Adhésifs et consolidants pour la conservation: recherche et applications: les actes*. Canadian Conservation Institute (2011),

Laganá, Anna; and van Oosten, Thea B. "Back to transparency, back to life: research into the restoration of broken transparent unsaturated polyester and poly(methyl methacrylate) works of art." In Book. *ICOM-CC 16th triennial conference Lisbon 19-23 September 2011: preprints*. ICOM Committee for Conservation (2011)

Moomaw, Kate; Weerdenburg, Sandra; and Timmermans, Rebecca. "The conservation of *Colonne* (1959) by Martial Raysse: a case study in plastics treatment." *Zeitschrift für Kunsttechnologie und Konservierung* 23, no. 2 (2009), pp. 297-314

Nord, A. G., Tronner, K., Lampel, K., Björling Olausson, K. Jonsson, Franzon, M., Halldén-Tengnér, C., Mattsson, E. & Johansson, M. "Morgondagens kulturarv – projekt för bevarande av plastföremål". Riksantikvarieämbetet, Stockholm (2008)

[Lavédrine, Bertrand](#), Alban Fournier and Graham Martin, Eds. "Preservation of plastic artefacts in museum collections" CTHS, Paris (2012)

Sale, Donald. "An evaluation of six adhesives for repairing poly(methyl methacrylate) objects and sculpture: changes in tensile strength and colour after accelerated ageing". In book. *Resins: ancient and modern*. Margot M Wright, and Joyce H Townsend, Editors. Scottish Society for Conservation and Restoration (1995), pp. 17-32

Sale, Donald. "Adhesives for Poly (methyl methacrylate) Sculpture: a Reappraisal of 20-year-old Samples" Pre-print symposium *Adhesives and consolidants 2011*, Canadian Conservation Institute, Ottawa (2011)

Shashoua, Yvonne R. "Conservation of plastics: materials science, degradation and preservation" Butterworth-Heinemann, Amsterdam, (2008)

Wolbers, Richard. "Short-term mechanical properties of adhesives: solvent and plasticizer effects." In Book. *The care of painted surfaces: materials and methods for consolidation, and scientific methods to evaluate their effectiveness: proceedings of the conference, Milan, 10-11 November 2006: third international congress on Color and Conservation, Materials and Methods of Restoration of Movable Polychrome Works*. CESMAR7: The Center for the Study of Materials for Restoration (Editor). Il Prato (2008), pp. 111-118