4.3. On-going studies in consolidation of polyurethane (PUR) foams

PUR encompasses a very large family of polymers which are widely used today for such applications as building insulation, filling for mattresses, flexible fibres and surface coatings. Their flexibility and diverse chemistries allow the synthesis of products that exhibit different physical and mechanical properties, from hard plastics to soft elastomers. This variety is due to the many types of isocyanates and polyols available, which are the fundamental building blocks used to synthesise these polymers.

The first PUR fibre was developed by Professor Otto Bayer in 1937, and it became commercially available in the 1950's. Because of their many forms and applications, PURs have been used by artists and designers for sculptures, paintings, design furniture, textiles and accessories since the 1960's (Quye and Williamson 1999; Waentig 2008).

PUR foams deteriorate rapidly within 20 to 30 years under ambient conditions. The main degradation symptoms are discolouration, yellowing, loss of flexibility, brittleness and crumbling, caused by exposure to moisture, heat and light (Szycher 1999). Museum artefacts made of PUR foam often exhibit loss of their mechanical properties.

During degradation, PUR undergoes both chain scission and cross linking phenomena. For the two main families of PUR (ester and ether) several studies show that PUR esters degrade by hydrolysis (water) while PUR ethers degrade by oxidation, particularly photo-oxidation (Kerr 1993; Wilhelm 1997; Wilhelm 1998; Szycher 1999). The two degradation pathways should be considered when developing a storage strategy for PUR objects in museums. PUR esters will degrade more rapidly in high relative humidity conditions than in a dry store. The lifetime of PUR ethers will be

shortened by illuminating them with ultraviolet or sunlight. The large number of studies concerning degradation and conservation strategies regarding PUR foam artworks reflect the importance of research in this area (Waentig 2008, 305).

A PUR dispersion in water (Impranil DLV) applied by spray or nebuliser has been successfully used for the stabilisation of PUR ether foam (Winkelmeyer 2002; van Oosten 2004; Rava *et al.* 2004). However, for PUR ester foams, when the physical structure is seriously damaged, crumbling or permanently deformed, the most common treatment is the replacement of the degraded foam or the lacunae with new PUR foam.

No convenient consolidation treatment exists at the moment for PUR ester foams, and conservators of modern and contemporary art are still seeking solutions to extend the lifetime of works of art made of this material. When objects are in an advanced state of degradation, consolidation treatments need to be applied to the entire surface. Based on this need, several consolidation routes such as impregnation and coating for both PUR ether and ester foams were investigated within the framework of this POPART study. This work is described in the rest of this chapter.

Various PUR industrial foams were selected as test substrates for consolidants. Since the composition of PUR foam depends on the types of isocyanate and polyol used in the manufacturing process, many PUR foams with various chemical compositions are commercially available.

Six consolidation agents have been selected and tested by project partners ARC, CRCC and SolMates:

- Paraloid B72 (copolymer of ethylmethacrylate and methyl acrylate), supplied by Rohm &Hass (www.rohmhaas.com)
- Plextol B500 (copolymer of ethylacrylate and methyl methacrylate, 50% solids in water dispersion), supplied by Synthomer Deutschland GmbH (www.synthomer.com)
- Poppy seed oil, supplied by Dalbe (www.dalbe.fr)
- 3-Aminopropylmethyldiethoxysilane, supplied by ABCR GmbH & Co. (www.abcr.de)
- N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane supplied by ABCR GmbH & Co. (www.abcr.de)
- Beminguard MC (silicon polymer water based dispersion), supplied by Schmits Chemical Solutions (www.schmits.nl)

Acrylic resins used for conservation and restoration of other materials were tested. Formulations with different solvents and concentrations were carried out using the standard resin Paraloid B72 and the water based acrylic Plextol B500. To enhance their

resistance against photo-oxidation, an inorganic UV absorber in the form of nanoparticular zinc oxide was incorporated added and evaluated for its efficiency and long-term stability.

Poppy seed oil was selected for evaluation as a consolidant for PUR foam. The aim was to create a flexible skeleton in the open pores of the foam via polymerisation of poppy seed oil under ambient conditions.

Aminoalkylalkoxysilanes have been used successfully to deacidify and consolidate paper since 2003 (Cheradame *et al.* 2003; Dupont *et al.* 2010). Two different aminoalkylalkoxysilanes, the 3-aminopropylmethyldiethoxysilane and the (2-aminoethyl) aminopropylmethyldiethoxysilane, were selected for the treatment of PUR ester foam.

A tailor made coating was developed, consisting of a silicone polymer water based dispersion (Beminguard MC), to which different chemicals were added to improve its properties. These chemicals are all commercially available, and their consolidating properties have already shown promise in other applications.

Accelerated thermal and light ageing were applied to foam samples before and after consolidation for two main purposes:

- to induce deterioration in foam samples prior to consolidation treatment in order to evaluate the effectiveness of the treatment on damaged foam
- to induce deterioration of foam samples after consolidation treatment in order to evaluate the long term behaviour of treated samples.

The ageing conditions used were selected to induce real time degradation symptoms found in naturally aged foams based on the experience of POPART partner RCE.

Consolidants were applied using various techniques. Where a homogeneous application that penetrated into the bulk of the sample was required, the consolidant was applied by dipping. In all other cases, spray application was used.

Various analytical techniques were used to evaluate the effects of the treatments on PUR foam samples. The colour of the samples before and after consolidation was monitored to assess the impact on the visual aspect of treated samples. The CIEL*a*b* coordinates were determined using a portable spectrophotometer. Ultraviolet-visible (UV-Vis) spectrophotometry was used to measure the optical transmission of the applied coatings.

Mechanical properties were studied by Compression Force Deflection according to standard ASTM D 3574-03 test C (American Society for Testing and Materials 2003) To investigate the

distribution of the treatment in the thickness of the samples, light microscopy, FTIR spectroscopy and Scanning Electron Microscopy (SEM) were used. Thermogravimetric analysis (TGA) was used to study PUR foam's resistance to thermo-oxidation before and after treatment.

4.3.1. Consolidation by acrylic resins

In conservation, acrylic resins are frequently used because they are known to be resistant to thermal and photo-oxidation. The properties required of a consolidant for application to foam are high fluidity to coat all the interstices of the object and good adhesion between the consolidant and the polyurethane substrate. Acrylic resins satisfy these requirements. Acrylics dissolve readily in ethanol, acetone and ethyl acetate, and adhere well to the urethane groups through acrylate or methacrylate chemical functions by weak Van der Waals forces. Within the foam cell structure, the acrylic forms a film on evaporation of the solvents, which are either organic or water.

Two acrylic systems were selected to consolidate flexible polyurethane foams, of both ester and ether types and with open cell structures. Paraloid B 72 poly(ethylmethyl methacrylate) is soluble in various organic solvents and has been used and tested for decades as a conservation grade adhesive and consolidant for many materials. It has a glass transition temperature (Tg) of 40°C, and is more flexible than Plexiglas (poly(methyl methacrylate), Tg 105°C). This polymer has a long service life, is often used as a standard stable resin and is readily available. The second consolidant system selected was water based, Plextol B 500. It is also a widely used acrylic dispersion in conservation fields containing around 50% solids polymer, and is flexible with a Tg lower than 29°C (Horie 1987).

Paraloid B 72, at concentrations of around 20% is used to varnish pictures by brush while a 10% solution can be applied by spray. For PUR foam consolidation, solutions of Paraloid B 72 of 10% and 20% solids were tested in solution in acetone, ethanol and ethyl acetate.

Aqueous dispersion Plextol B 500 was supplied as 50% solids, and diluted in a mixture of water and ethanol in order to reduce the solids content to around 35%. This dilution reduced the viscosity of the initial dispersion, and in theory enhanced its ability to wet PUR by lowering its surface tension.

To increase the resistance of the consolidants to yellowing by photolysis, UV absorbers were added to the acrylics in proportions from <1 to 5% by weight. Traditionally, absorbers are based on organic chemicals such as benzophenone, benzotriazole and

Formulations	Resin content %	
	PU Ester	PU Ether
10% Paraloid	32	31
10% Paraloid + ZnO	28	28
20% Paraloid	55	55
20% Paraloid + ZnO	56	50
35% Plextol	85	84
35% Plextol + ZnO	89	84
50% Plextol	86	88
50% Plextol + ZnO	84	86

Figure 24. Average resin content of PUR foams determined by weighing samples before impregnation and after drying

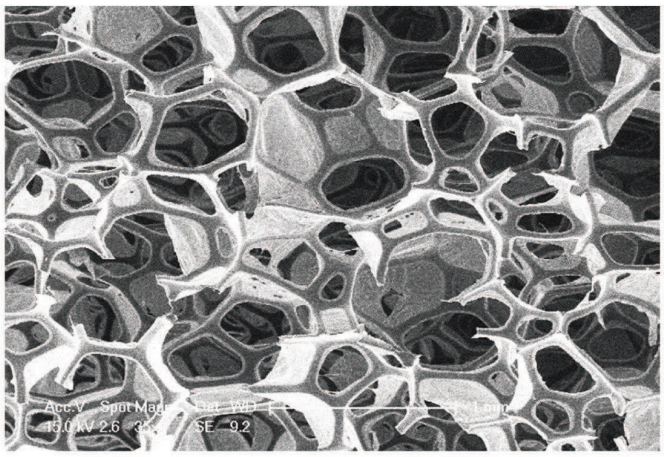
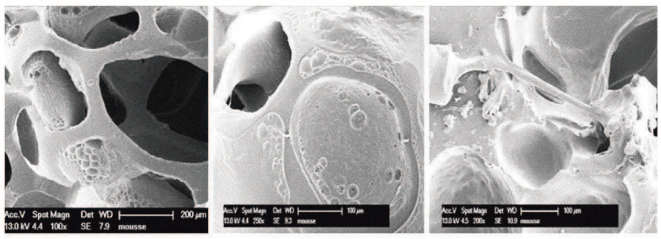


Figure 25. SEM micrograph of untreated PUR foam



30% Paraloid content 50% Paraloid content 80% Plextol content

Figure 26. SEM micrographs of consolidated PUR foam

hindered amine light stabilizers (HALS). For PUR consolidants, inorganic zinc oxide nanoparticles with an average particle size of 35 nanometres were used as powder and dispersions in aqueous solutions with up to 17% solids. Powder was added to solvent-solutions of Paraloid B72, while the dispersion was added to Plextol B 500. The concentration of zinc oxide in the formulations was 5% solid. It was selected to take advantage of its long-term protection properties, heat resistance and resistance to migration (Tigges *et al.* 2012).

Experimental procedure

New PUR ether and ester foams obtained from Caligen Foam Ltd, UK were cut to size (40 mm x 20 mm x 10 mm), immersed in resin solutions, pressed to absorb the resin, then removed and dried in air to constant weight. The time taken for total evaporation of organic solvents was 24 to 48 hours, while many days were necessary to attain constant weight for water dispersion impregnated samples. The average resin content was determined by weighing samples before impregnation and after drying and the results are shown in Figure 24.

After consolidation, the initial appearance of the samples was largely unchanged except for yellowing of samples treated with Plextol and zinc oxide, due to the initial yellow colour of the zinc oxide dispersion. The foam samples consolidated using solutions of 10% Paraloid, giving a resin content of around 30%, retained their original flexibility. However, consolidation of PUR by impregnation with 20% Paraloid solution and 35% Plextol dispersion reduced the flexibility of PUR foam. Impregnating by other techniques such as by capillarity would preserve the flexibility of the foam but resin content is more difficult to control.

Scanning Electron Microscopy (SEM) of consolidated samples

SEM was used to determine the degree of penetration of the consolidants and to detect the presence of zinc oxide nanoparticles within the open cells of the PUR foam by elemental analysis using energy dispersive X-ray spectroscopy (EDS). Comparing foam before (Figure 25) and after treatment (Figure 26), a thin layer of Paraloid resin (30%) was present after impregnation of the foam with a 10% resin solution. A thicker resin deposit (50%) on the foam cells is obtained with 20% resin solution. Impregnation by Plextol with

Figure 27. Yellowing of PUR foam samples after UV-Visible ageing

either 50% or 35% resin dispersion lead to high resin contents in the foam, with an average of 80%. EDS analysis detected elemental zinc in the resin deposit.

Accelerated ageing of consolidated PUR foam by UV-Visible light irradiation

The main factors of weathering are uv, heat and moisture. Ultraviolet radiation initiates the degradation process and drives it forward, interacting with temperature and humidity to cause adverse effects, such as yellowing in the case of PUR ethers and crumbling of PUR esters. The purpose of artificial weathering is to reproduce real time degradation conditions within a short period. Samples were aged for 64 hours in a Suntest apparatus, model CPS+, fitted with a Xenon lamp, irradiance at 300 – 800 nm, delivering 720 $W.m^{-2}$, and a chamber temperature up to 55°C.

Based on colour measurements, the best protection against yellowing was given by the Plextol 50% with UV absorber zinc oxide at a concentration of 5% (Figure 27). The white areas on the reference and other samples correspond to those that were protected from radiation . Good results were also obtained for Plextol 20% solid containing zinc oxide. Samples treated with solutions of Paraloid 10% solids and containing zinc oxide, yellowed less than untreated samples, while maintaining the original flexibility of the foam. Increasing the Paraloid content to 20% where zinc oxide was present, enhanced the resistance to yellowing when zinc oxide was included, but the foam softness decreased.

PUR ester yellowed more than PUR ether during UV-Visible exposure at 55°C. Polyurethane ethers are known to show less resistance to photo-ageing than polyurethane esters and this was confirmed by FTIR analysis of aged samples, in which the intensity of the peak at 1720 cm^{-1}, attributed to the carbonyl group, increases sharply in the case of untreated ether foam. Neither polyurethane ether nor ester foams treated by the formulations containing zinc oxide showed variation in the peak at 1720 cm^{-1} on ageing, suggesting that good protection against oxidation was imparted by these consolidants.

Thermal analysis of consolidated and aged PUR foams

Light aged samples were characterised by thermogravimetric analysis performed by the partner PISAS Institute in Slovakia. As shown in the thermograms in Figure 28, samples 4 and 8 consolidated using Plextol with zinc oxide, diluted in water and

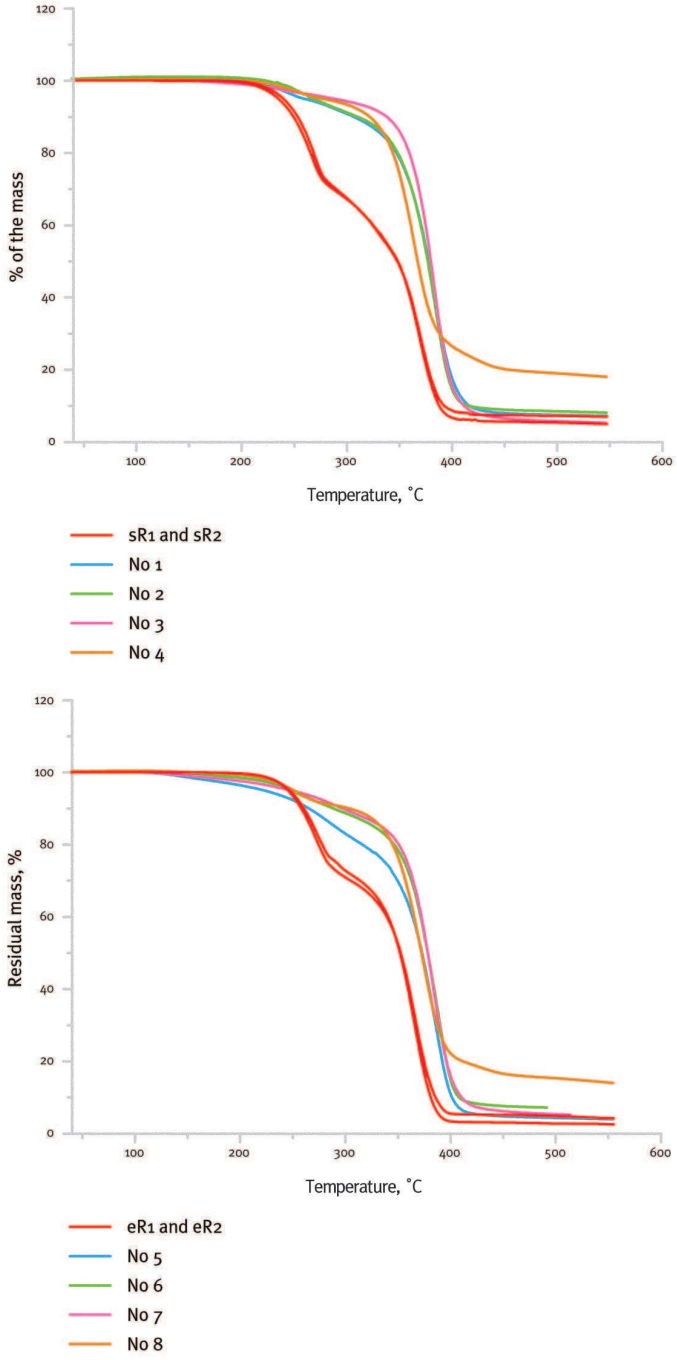


Figure 28. Thermogravimetric analysis of PUR ester (upper graph) and PUR ether (lower graph) foams before and after consolidation. Samples 4 and 8 (consolidated using Plextol with zinc oxide, to a resin content of 35%) exhibited lower total weight loss than samples 1, 2, 3, 5, 6 and 7 (treated using Paraloid B72 with and without zinc oxide and using Plextol without zinc oxide)

ethanol to give a resin content of 35%, exhibited lower total weight loss than the other samples(numbers 1,2,3,5,6 and 7 treated using Paraloid B72 with and without zinc oxide, and using Plextol alone). Both PUR ester and ether foams, when consolidated by these formulations, were more resistant to thermo-oxidation. They also exhibited greater resistance to yellowing, as discussed previously. Samples sR1, sR2, eR1 and eR2, were reference, untreated PUR ester and ether samples and clearly show the benefits of consolidation for PUR foam with an increase in thermal resistance up to around 350°C compared to 250°C in the case of unconsolidated samples.

Conclusion

Two acrylic resin systems have been examined for the consolidation of degraded polyurethane foam objects. The first one was a solvent-based resin, Paraloid B72, dissolved in ethanol or ethyl acetate, with a resin content of between 10 and 20% solids. The second formulation was a water-based resin Plextol B 500, diluted with water and ethanol, giving a resin content of between 20 and 30% solids. Considerable consolidation of the foam structure was obtained with the Plextol solution at 30% solids. For both polyurethane ester and ether based flexible foams, the addition of 5% zinc oxide as UV absorber in the resin formulations undoubtedly enhanced their resistance to yellowing, as well as enhancing stability under thermal ageing. In this study, it was shown that nanoparticle UV-visible stabiliser was effective.

In addition, the zinc oxide nanoparticles selected were heat resistant and, being embedded in the resin, did not migrate. Theoretically, these acrylic resin formulations can also be applied to degraded surfaces of rigid PUR foam, due to the affinity of the two urethane and acrylic organic groups, in spite of the low porosity of this type of foam. Lastly concerns for health and safety when working with nanoparticles were minimised by their initial dispersion in solvent or water.

Figure 29. Comparison of colour of various drying oils

4.3.2. In-situ polymerisation treatment using a drying oil

This section concerns treatment suitable for extremely degraded PUR foams, i.e. material with active powdering. This case is complex because several conflicting objectives must be taken into account:

- high added value in terms of consolidation is expected. It is necessary to reconstitute a polymeric skeleton to ensure overall cohesion of the degraded material and prevent further crumbling.
- no modification of the initial colour of the PUR foam.
- conservation of the initial shape and above all, conservation of the original foam texture and flexibility particularly in the case of soft foam. The material must be kept soft and not transformed into one that is crusty and hard.
- non-intrusive and, if possible, reversible intervention. The treatment must be implemented only in much degraded areas in the artefact, i.e. the areas close to the surface. It is pointless to treat the entire volume of the item.
- the treatment must be easy to apply by non-experts and, if possible, not involve dangerous chemicals.

These objectives are not all mutually consistent. Compromises have to be made in order to reach an acceptable treatment protocol. This was the case with an original method developed in the project, which involved drying oil polymerisation. The aim was to carry out in situ polymerisation of a resin inside the foam pores in order to create a new flexible supporting structure.

Consolidating agents

Drying oils self-polymerise through a slow oxidation process in air (Hatchett *et al.* 2005). This spontaneous and natural polymerisation does not need a chemical catalyst, heating treatment or ionising irradiation. Numerous drying oils are commercially available. At first, four grades were considered in the study, namely linseed oil, walnut oil, poppy seed oil and tung oil (also called china wood oil). The main criteria for the final selection were the polymerisation kinetics and the yellowing induced by oil oxidation.

Since it was not possible to identify a satisfactory compromise, it was decided to select a drying oil with a pale colour, namely poppy seed oil, to preserve the initial PUR foam colour (Figure 29). Unfortunately, this oil also exhibited the slowest polymerisation at

Figure 30. PUR ether foam crumbled after ageing treatment by UV radiation

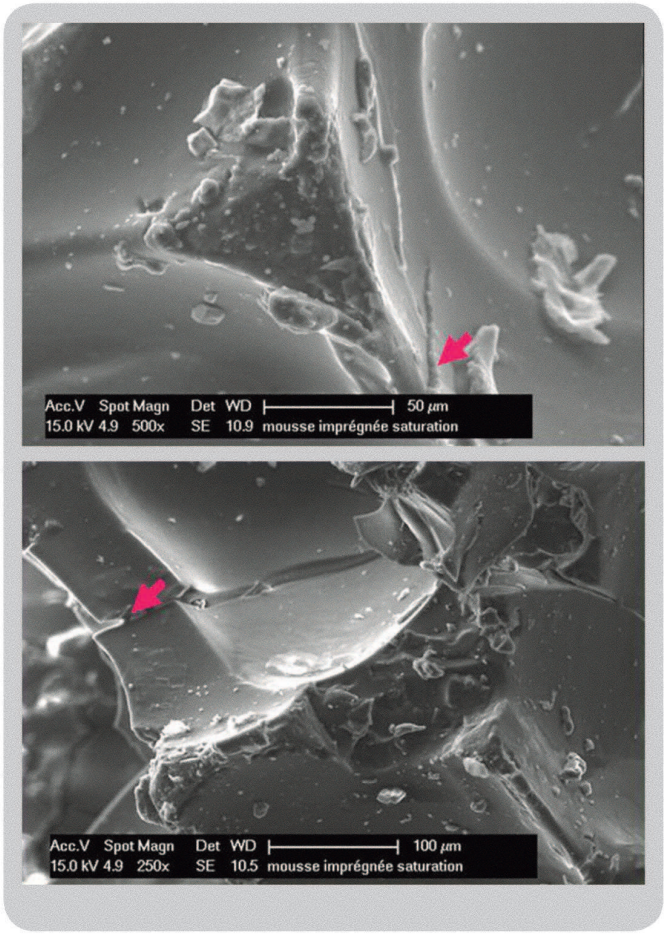


Figure 31. SEM image of poppy seed oil coating and filling PUR foam pores

room temperature. After oil was applied to the foam, it remained liquid for several weeks at room temperature. This was inconvenient and gave a risk of resin running and leaving a sticky surface. To solve this problem, it was decided to initiate self-polymerisation of poppy seed oil before PUR impregnation until an oil gel was obtained. This pre-polymerisation was performed by heating the oil in air at 100°C for 24 hours. Polymerisation was not completed during this operation. Indeed, the gel must be dissolved in a solvent such as acetone for final foam permeation to take place.

To limit the quantity of poppy seed oil in PUR foam, only 5% (w/w) of oil gel was used in the acetone solution. The high wettability of the acetone solution facilitated oil migration into the open foam pores by capillary action to a minimum depth of 1-2 cm. This distance corresponds to the usual limits for photo-oxidation in the case of PUR ether or hydrolysis in the case of PUR ester. After impregnation, no further thermal treatment was necessary to complete oil polymerisation.

Experimental procedure

Sampling and accelerated ageing were conducted with different but chemically similar PUR samples to those consolidated. A climate chamber was used to produce accelerated ageing treatment, with light exposure of 765 $W.m^{-2}$, temperature 60°C and for 64 hours. Following such ageing treatment, the PUR ether foam yellowed considerably and the foam crumbled (Figure 30). This extreme and representative degradation is important to the study of added value of the proposed consolidation treatment.

As stated previously, the treatment solution contained 5% by weight of poppy seed oil in the form of pre-polymerised gel in acetone. The liquid obtained was very low viscosity and therefore showed good wetting of PUR foam.

The PUR samples were immersed for 10 seconds in the solution. Afterwards, the acetone was allowed to evaporate at room temperature in a ventilated chamber for four hours. The surface was slightly sticky, but after 24 hours it had dried and could be handled.

Treatment evaluation

Mechanical properties were assessed by manually handling the PUR foam. Comparison between treated and untreated samples showed that powdering stopped after treatment. The main aim of the treatment was achieved. SEM showed the curing effect of the oil coating in the pores (Figure 31). The flexibility of the foam was

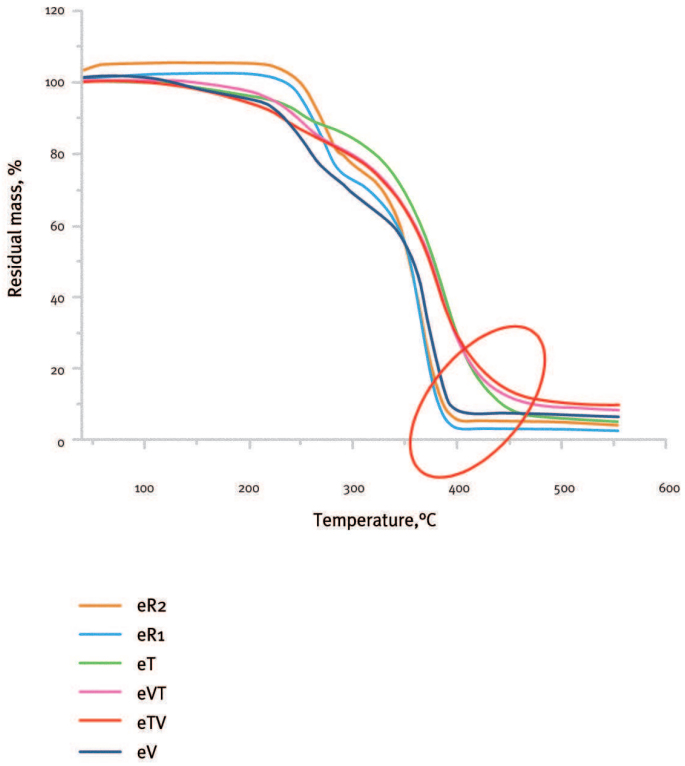


Figure 32. Thermogravimetric curves of untreated (eV, eR1, eR2) and oil-treated (eT, eVT, eTV) PUR foam samples

preserved and there was no crust at surfaces. The initial softness was unchanged by in situ oil polymerisation.

Another important aspect was resistance to chemical ageing. This property was studied using two techniques, namely FTIR spectroscopy and thermogravimetric measurements in air. Both were performed by partner PISAS. Though FTIR analysis of PUR degradation is well established (Gajewski 1990; Rek 1993; Lazzari and Chiantore 1999), the differences before and after ageing treatment were insignificant. Spectral interpretation was complex since the changes were below detection limits. The intensities of the absorption bands characteristic of the urethane group (1533 cm^{-1}) and the ether linkage (1078 cm^{-1}) seemed to decrease with the exposure time, while the carbonyl band (1712 cm^{-1}) increased. No other conclusions could be drawn. It was not possible to use FTIR to reach any conclusion on the efficiency of the oil treatment.

Thermogravimetric results showed that samples not treated with oil (eV, eR1 and eR2) showed a greater overall weight loss than treated samples (eT, eVT and eTV), but that untreated samples were more stable up to 250°C (Figure 32). Application of these findings to real time degradation of PUR foam requires further investigation. The initial colour of the foam was not modified. As expected, oil treatment was unable to restore the initial white colour of the foam prior to degradation. After a couple of days, the foam surface was no longer sticky and the material could be handled without difficulty.

Conclusion

Overall, an appraisal of poppy seed oil consolidation shows that this method deserves further investigation, particularly because only one oil was evaluated. This should be borne in mind when considering the results. Poppy seed oil treatment was easy to apply. Take up of oil into the open pores of PUR foam occurred readily by capillary action. Immersion or other simple methods such as brushing may be possible. A level of consolidation which slowed crumbling was established. Flexibility and colour were also preserved.

In spite of these advantages, drying oil treatment is not perfect. It is irreversible and involves the use of volatile organic components such as acetone. At least two avenues could be investigated in the future:

- mixing acetone with ethanol to reduce the acetone content in the treatment solution.
- abandoning the pre-polymerisation stage by using catalyst in the form of nanoparticles to accelerate drying. Treatment

may be conducted with a sophisticated solution containing an emulsion of ethanol and oil, mixed with a dispersion of for example TiO2. Ethanol is the best wetting agent for PUR polymer, but the main difficulty is to stabilise an ethanol/oil emulsion and achieve a nano dispersion of catalyst in the emulsion.

4.3.3. Aminoalkylalkoxysilane consolidation

Consolidation agents

Aminoalkylalkoxysilanes (AAAS) give promising results for deacidification and consolidation of paper (Dupont *et al.* 2010) and therefore were chosen to be applied to industrial flexible PUR ester foam samples. For paper conservation the use of AAAS provides an alkaline buffer for the cellulosic network, improves the mechanical resistance of the paper and was effective even after ageing. Two different AAAS, 3-Aminopropylmethyldiethoxysilane (AMDES) and N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane (di-amino), were thus chosen to be tested on a series of aged and unaged PUR ester foam samples to evaluate their consolidation effect on PUR ester. This study was carried out by the CRCC.

Experimental procedure

Accelerated ageing was used to obtain a reference for degraded PUR ester on which to investigate the application of the treatments. Accelerated thermal ageing was conducted at 90°C and 50% RH for a period of 21 days in an environmental chamber Vöstch HC0020. The ageing conditions were chosen to obtain samples closely reproducing common conditions of naturally aged foams. Solutions of AMDES and di-amino in hexamethyldisiloxane (HMDS) solvent were prepared at 2.5%, 5% and 10% vol/vol. Each solution was used to treat aged samples known as AMDES 2.5% aged, AMDES 5% aged, AMDES 10% aged, di-amino 2.5% aged, di-amino 5% aged, di-amino 10% aged and unaged samples known as AMDES 2.5%, AMDES 5%, AMDES 10%, di-amino 2.5%, di-amino 5%, di-amino 10%. HMDS solvent alone was also tested on aged (HMDS aged) and unaged samples (HMDS). The foam samples were weighed and immersed for 24 hours in each solution in closed polypropylene containers. After immersion the samples were dried under vacuum

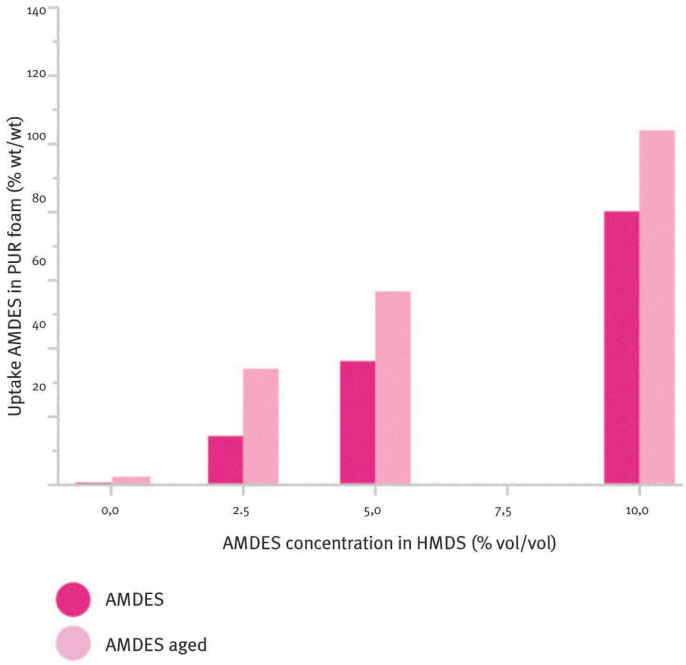


Figure 33. Uptake of AMDES by foam samples (% w/w) as a function of the concentration of AMDES in HMDS (% v/v)

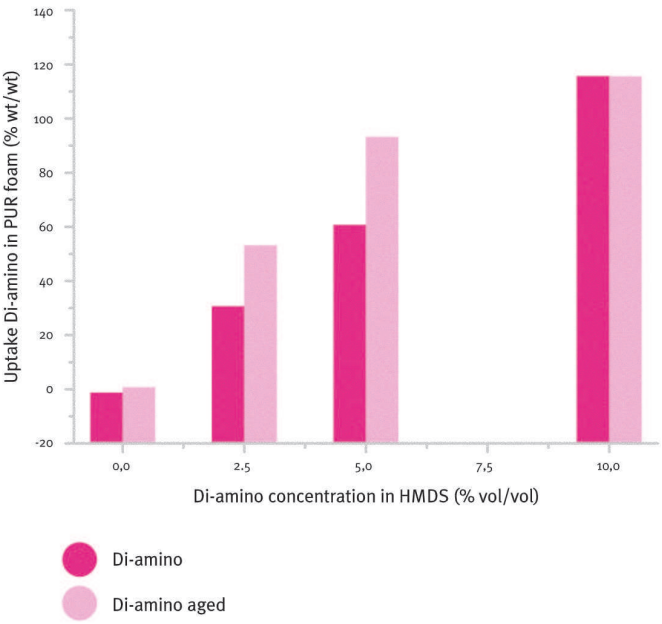


Figure 34. Uptake of di-amino in the foam samples (% w/w) as a function of the concentration of di-amino in HMDS (% vol/vol)

for six hours and weighed in order to determine the mass uptake owing to the treatment.

It is important to note that at this point of the research, dipping was chosen as an application method to achieve reproducible applications and to study the interaction between AAAS and PUR foam. Because the solutions applied have very low viscosities, between 0.50 and 0.55 mPa.s, they could be easily applied by spray or nebuliser.

Treatment evaluation

The mass uptake values obtained after the two treatments are shown in Figures 33 and 34.

They show that higher concentrations of AAAS in solution resulted in greater uptakes and that uptake values are larger for di-amino treatment than AMDES treatment. In addition, aged samples show higher uptakes than unaged samples. Difference in uptake between aged and unaged foams could be explained by AAAS's higher affinity for hydrogen bonding with carboxyl groups (Souguir *et al.* 2011), which are formed by hydrothermal degradation processes.

An important issue of conservation treatments is the impact of the treatment on the original colour of the object treated. For this reason it is important to minimise the colour change due to the addition of a new material. To monitor this property, CIE L*a*b* coordinates were measured with a portable sphere spectrophotometer X-Rite SP64, the measurements were repeated on each sample's upper surface at five different locations and the mean value was used to calculate a ΔE* representing the entire surface. Figure 35 reports the values of L*, a*, b*, the hue difference ΔC* and the colour difference ΔE*. The unaged reference sample had a* and b* values of 15.23 and 31.15 respectively, corresponding to a blue hue. After treatment, unaged samples showed a weak hue variation expressed by ΔC* values between 0.54 and 1.95, while the lightness of the colour rises with the AAAS percentage increasing. The aged reference sample shows yellowing as a consequence of hydrothermal ageing highlighted by a* and b* values respectively of 19.76 and 13.45. Aged samples show a decreasing of the value of b* after treatment, that corresponds to a shift towards bluer values, closer to the original foam colour before ageing. As for unaged samples, the treatment increased lightness.

For polymer foams, mechanical compression is usually tested to evaluate the mechanical features of the material. For this reason, compression force deflection test (American Society for Testing and Materials 2003) was used to evaluate the mechanical properties of

	a*	b*	ΔC*	L*	ΔE*
UNAGED SAMPLES					
Reference	-15.23 ± 0.17	-31.15 ± 0.19	-	47.31 ± 0.61	-
HMDS	-15.7 ± 0.16	-31.53 ± 0.23	-0.54	47.78 ± 0.87	0.98
AMDES 2.5%	-17.09 ± 0.09	-32.02 ± 0.09	-1.62	49.95 ± 0.32	3.34
AMDES 5%	-16.98 ± 0.16	-31.89 ± 0.39	-1.45	50.2 ± 0.61	3.48
AMDES 10%	-17.15 ± 0.16	-31.1 ± 0.32	-0.83	50.96 ± 0.45	4.13
Di-amino 2.5%	-17.24 ± 0.17	-31.02 ± 0.38	-0.81	50.74 ± 0.43	3.99
Di-amino 5%	-17.56 ± 0.15	-32.14 ± 0.30	-1.95	50.44 ± 1.33	4.09
Di-amino 10%	-18.11 ± 0.12	-31.63 ± 0.16	-1.77	51.42 ± 0.48	5.04
AGED SAMPLES					
Reference	-19.76 ± 0.25	-13.45 ± 0.19	-	43.95 ± 0.36	-
HMDS	-20.06 ± 0.25	-15.35 ± 0.62	-1.36	44.01 ± 0.51	1.97
AMDES 2.5%	-20.31 ± 0.32	-19.46 ± 0.5	-4.23	46.49 ± 0.60	6.57
AMDES 5%	-20.92 ± 0.30	-19.76 ± 0.43	-4.87	46.3 ± 0.46	6.83
AMDES 10%	-21.46 ± 0.40	-20.5 ± 0.45	-5.77	47.78 ± 0.99	8.21
Di-amino 2.5%	-21.03 ± 0.39	-17.99 ± 0.46	-3.77	46.72 ± 0.60	5.48
Di-amino 5%	-21.91 ± 0.21	-18.87 ± 0.29	-5.01	47.49 ± 0.46	6.82
Di-amino 10%	-22.86 ± 0.17	-19.11 ± 0.60	-5.89	45.63 ± 0.98	6.70

Figure 35. Colour difference before and after consolidation of foams

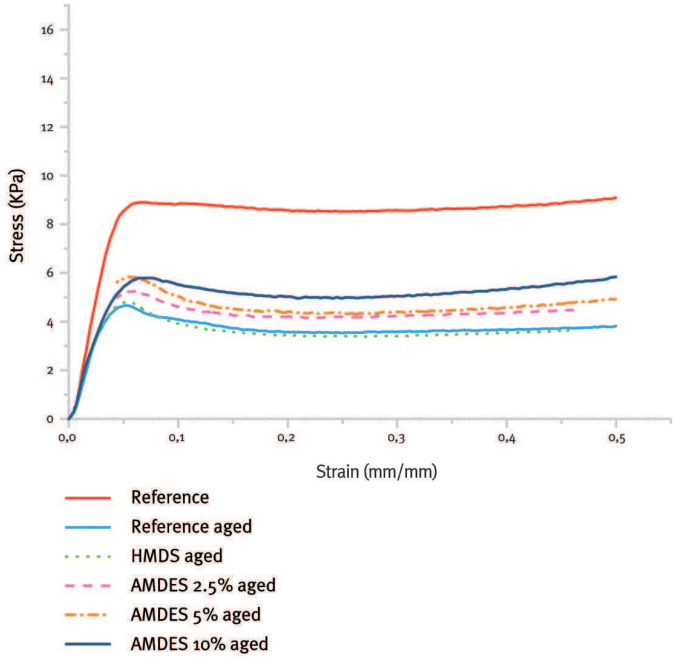


Figure 36. Compression stress/strain curves of samples treated with AMDES

PUR ester foam after AAAS treatments. Mechanical properties were studied using an Adamel Lhomargy DY.20 B traction/compression machine. Two specimens per sample were tested and the value reported is the mean. Every specimen has been compressed by 50% of its thickness (15 mm) at 50 mm.min^{-1} and kept under compression for 60 seconds. The entire stress/strain curve has been recorded and the final force after 60 seconds determined.

Figure 36 shows examples of stress-strain diagrams of treated and untreated foam. All the curves exhibit a first domain with a linear elastic behaviour, which ends with a limit load maximum. This first linear part is followed by a large plateau which involves either plastic deformation or rupture of the cell walls. Rupture of the cell walls occurred on compression of the aged reference sample.

After AAAS treatments, both aged and unaged foams stiffened and this was reflected in the initial modulus and an increase of the maximum load. This results in stiffer materials, which have more resistance to compression. Furthermore, the whole stress plateau moved to higher stress values, corresponding to an increase in toughness. The reinforcement effect was more pronounced for the treatment applied to unaged foams, despite the fact that the uptake values measured were higher for aged samples.

The use of the solvent (HMDS) alone did not affect the compression properties of the aged or unaged foams and therefore

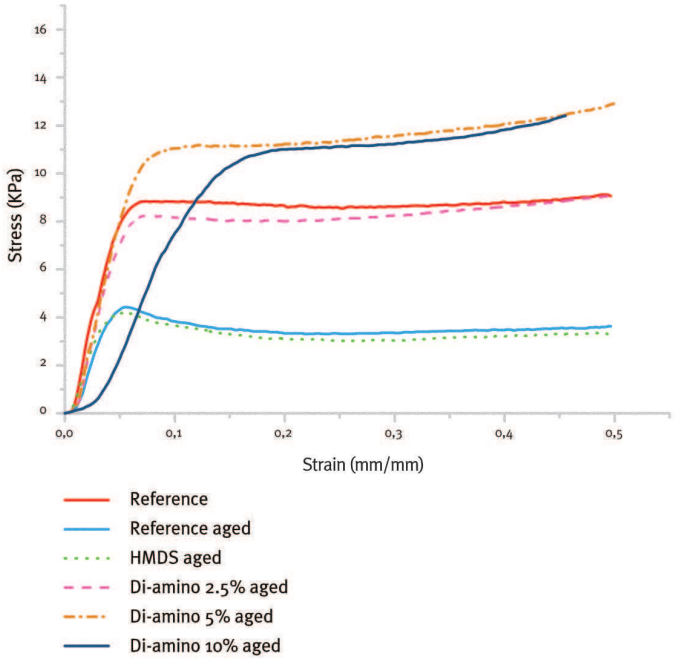


Figure 37. Compression stress/strain curves of aged samples treated with di-amino

it is clear that the resistance to compression is strictly related to the AAAS polymer. Mechanical compression tests on aged foams highlighted essential differences between the two AAAS tested. The use of AMDES reinforced the aged foam, however even when used at higher concentrations (10% v/v) it was not possible to re-establish the original mechanical properties of the foam. By contrast di-amino needs to be applied at lower concentrations to obtain satisfactory results. For example, when it is applied at 10% of concentration, the di-amino polymer network formed in the foam structure is too large and this exerts considerable influence on the mechanical properties of the foam.

In Figure 37 the stress-strain curve of the sample treated with di-amino 10% shows an increase in the stress plateau height corresponding to an increase in toughness, but the initial elastic modulus value decreased suggesting an increase in flexibility. These tests identified the di-amino treatment at a concentration of 2.5% as the one that gave optimal results for consolidation of aged PUR ester foam. This treatment re-establishes in aged foams the same mechanical properties as unaged PUR ester foam. The resistance to compression of the aged sample is around 3.5 kPa. After treatment with di-amino 2.5% , this value rose to 9 kPa, which is identical to the value recorded for the unaged PUR foam.

The sample images recorded after compression by SEM show AAAS interacting with the foam surfaces and the investigation of reinforcement effect at microscopic scale. Secondary backscattered electron images of the foam surfaces before and after treatment have been obtained with a SEM Jeol JSM-5410LV. The samples were adhered with a carbon adhesive on aluminium sample holders and coated with gold to approximately 300 nm. Backscattered electron images highlighted the deposits formed after treatment in the foam structure. AMDES deposits are limited to the surfaces and they do not fill the void of the open cells, which is important with respect to retaining the original structure of the foam.

Figure 38 allows comparison between untreated and treated samples at low magnification (x 100). Unaged and aged reference SEM images are presented on the left. The unaged reference sample, flexible and elastic, keeps its structure intact after compression while, after artificial ageing, cell wall breaking occurs and the material loses its recovery properties. On a macro scale, it is clear that both AAAS treatments inhibit cell wall breaking during compression and enable recovery of the original structure when the load is removed (Figure 39).

To obtain an overall idea of the distribution of AAAS within the samples and therefore verify the homogeneity of the treatment,

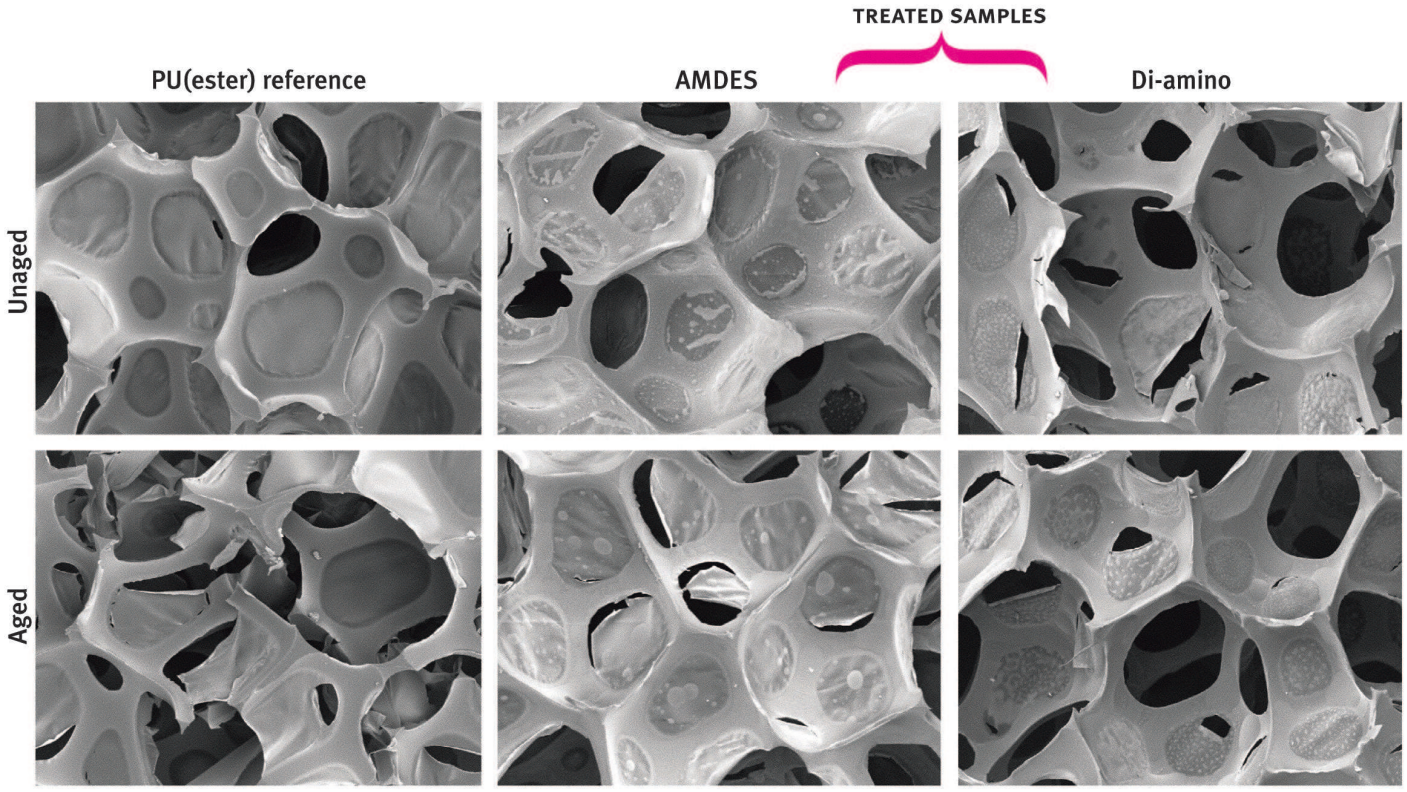


Figure 38. SEM backscattered electron images of foam surfaces of foam samples after compression test

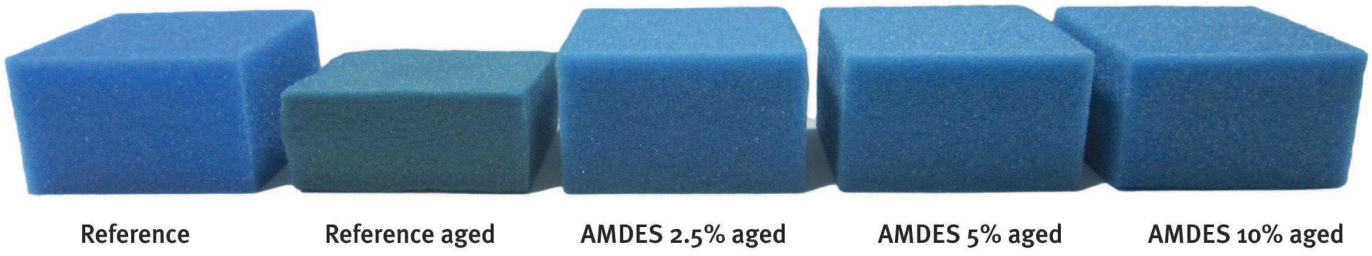


Figure 39. Macro images of untreated and treated samples after compression test (5 x 5 x 3 cm)

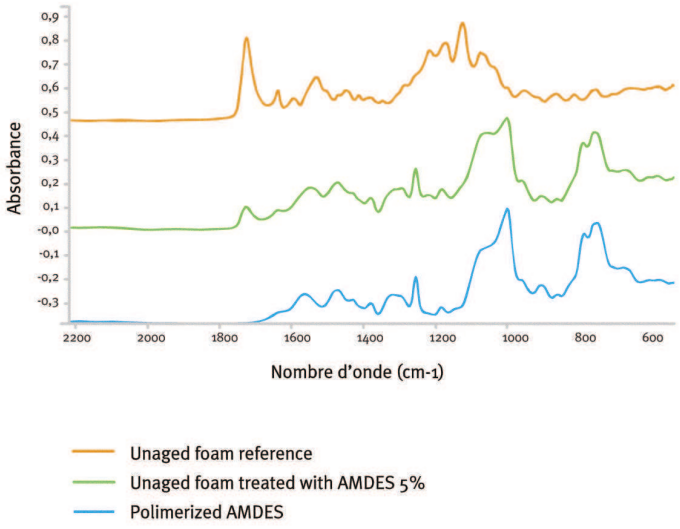


Figure 40. ATR-FTIR spectra of unaged foam, unaged foam treated with AMDES 5% and pure polymerised AMDES

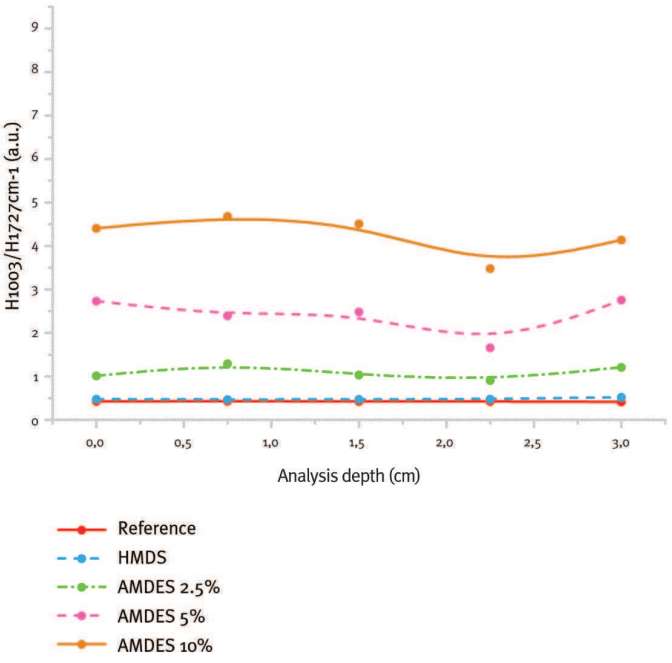


Figure 41. Quantification of AMDES concentration (ratio of AMDES Si-O-Si absorption band to PUR ester C=O absorption band) plotted as a function of depth or thickness of the sample

ATR-FTIR spectroscopy was used. Spectra were recorded on a Nicolet 6700 spectrophotometer, equipped with a diamond ATR macro-system Smart Endurance sensitive from 600 to 4000 cm^{-1}.

Infrared spectra of treated samples (Figure 40) show absorption bands attributed to polymerised AMDES. Absorption bands assigned included 1257 cm^{-1} ($Si-CH_3$ symmetric stretching), 1003 cm^{-1} (Si-O-Si stretching), 907 cm^{-1} (Si-C stretching) and 727 cm^{-1} ($-(CH_2)_3-$ rocking) based on literature (Coates 2000; Szymanski and Erickson 1970). Si-O-Si absorption band at 1003 cm^{-1} confirms polymerisation of AMDES monomers at foam surfaces. SEM images showed the treatment formed a coating on cell walls. For this reason on treated foam spectrum almost all infrared absorption bands due to PUR are hidden by AMDES absorptions and only C=O ester stretching at 1727 cm^{-1} is still visible. ATR accessories have a penetration of 2-4 µm and show only materials within this depth.

The homogeneity of the treatment was examined by cutting treated samples in slices allowing infrared analysis in different points of the sample thickness. Five spectra were collected from each sample, two from the external surfaces and three from the bulk. In Figure 41 the AMDES relative quantification, expressed by the ratio of the area under the Si-O-Si absorption band at 1003 cm^{-1} to the area under the C=O ester absorption band at 1727 cm^{-1}, is plotted as a function of the depth of the points analysed. This ratio is an indicator of the AMDES concentration.

According to uptake values on unaged foams, AMDES seems to be evenly distributed and any differences between values can be attributed to experimental error. By contrast, aged samples highlighted an inhomogeneous distribution of AMDES network. The concentration of AMDES is higher near the external surfaces of the sample and lower in the centre of the foam block. Moreover, the results show that on aged sample foams, a higher concentration of AMDES is observed at each analysis depth point, along with uptake values.

Conclusions

This study shows that, after treatment of aged and unaged PUR ester foams with AAAS, a reinforcement effect is obtained. This effect is a consequence of the formation of a macromolecular network due to AAAS polymerisation at cell wall surfaces.

It was shown that after treatment the AAAS uptake was higher for aged samples than unaged samples. These data allow an interpretation of the interaction between the polymer network and the PUR foam surfaces. Higher uptakes for aged samples are due

to AAAS's higher affinity toward carboxyl groups, resulting from hydrothermal degradation processes.

Beyond its reinforcement effect, the polymeric network formed after treatment has two significant characteristics. Firstly, it does not change the visual appearance of the foam measurably and it reduces the yellowing when applied to aged samples. Secondly it does not fill the void of the open cells preserving the original structure of the foam.

These promising results suggest that AAAS and especially the di-amino treatment could be efficient and a suitable option for consolidation of polyurethane ester foams. However further studies need to be carried out before applying these polymers on real objects. On-going research is geared to establishing the interaction between AAAS and PUR foam and to examine the ageing behaviour of treated samples.

4.3.4. Consolidation by coating

An effective method of consolidation is to apply a surface coating. In general the coating is a thin layer that protects the material underneath from the elements by means of shielding. The most obvious example is the paint on wooden doors, window frames and roof parts. Besides shielding, the coatings impart other properties. Examples of such properties are hydrophobicity, light filtering, electrical conduction and flame retardancy.

Although protective coatings are widely used in automotive, industry and consumer goods, their use in works of art is not so common. The major drawback is that in general the appearance of the coated object is changed in terms of discolouration or texture. Also, once a coating is applied, the process is often irreversible. Because of these reasons the modern art conservation community is reluctant to use them. However, if the drawbacks could be reduced such that the impact on the piece of art is minimal, there would be benefits on the extended lifetime of objects. Therefore, coatings for protection of cultural heritage are researched extensively prior to use (Bescher and Mackenzie 2003).

In this section the work on the protection of polyurethane foam by means of coating is described. The research has been conducted at SolMateS BV. The aim of the research was to develop a coating and application method for the protection of uncoloured polyurethane ester soft foam. This organic material is known to degrade rapidly and no effective method of protection has been

established as yet. Degradation is perceived initially by yellowing of the PUR ester followed by failure of the material resulting in loss of ductility and crumbliness. It is recognised that the degradation of PUR ester is mainly caused by oxidation and hydrolysis. However, the dominant factor of these two mechanisms is still under debate (Lovett and Eastop 2004).

Regardless of the specific mechanism, the changes in the chemistry and structure of the polymer molecule are initiated by the absorbance of energy. The energy is induced either by heat or light. Under normal circumstances the influence of light will be more important. The high energy ultraviolet (UV) part of the light spectrum is the most damaging.

Consolidating agents

A coating suitable for PUR ester foam has the following requirements:

- the coating should be flexible enough to withstand possible deformations of a soft foam
- the PUR ester foam exhibits an open structure of closely packed polymer cells. The coating should therefore conform to the rough foam surface, but also penetrate the gaps between the cells to allow maximum coverage of the polymer material
- the coating should be transparent to visible light to prevent unwanted change of appearance of the art object
- the coating should be easy to apply without the need for post-treatment

The coating that best meets these requirements is the commercially available product Bemiguard MC. The coating mainly consists of a water-based polymer dispersion. It can be readily applied by means of impregnating, spraying or knife over air techniques. The viscosity of the coating can be adjusted by dilution with water to allow tuning of the depth to which the coating can penetrate the open PUR ester structure. Drying in air for 24 hours is sufficient to give a hard surface. This organic coating follows the contours of the specimen surface, is highly flexible and provides strong adherence. A thick Bemiguard coating results in a white opaque layer. However, if the thickness is controlled to several microns, the layer is to more transparent. After the coating has dried, it is water repellent which enhances resistance to moisture or dirt.

Although Bemiguard MC is suitable as a coating it does not protect against photo degradation. For this purpose specific

additives should be mixed into the base coating dispersion before it is applied to the specimen.

The first way to prevent photo-degradation would be to shield objects from UV and light. Radiation should be absorbed within the coating before it reaches the specimen. However, not all UV photons will be absorbed, and some will eventually interact with the polymer molecule which results in the formation of free radicals. These radicals will start the chemical breakdown chain reaction. The second way to prevent photo-degradation therefore is to trap these radicals before the subsequent reactions lead to degradation.

Chemical components that have the two properties described above are already commercially used on a large scale in the automotive industry. Although many UV-absorbers are available, for the purpose of this type of work benzotriazole (BTZ) is the absorber of choice and is widely used in organic coatings. BTZ's solubility in water is good and it shows high absorbance over a broad range in the UV spectrum. The specific BTZ selected was UV292, bis(1,2,2,6,6-pentamethyl-4-piperidyl), molecular formula ($C_{30}H_{56}N_2O_4$).

Hindered amine light stabilisers (HALS) were selected to trap free radicals. The molecule used was methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate, formula $C_{21}H_{39}NO_4$.

All chemicals were obtained from Schmits International BV, The Netherlands (www.schmits.nl). The commercial name of the base coating was Bemiguard MC. The ultraviolet absorber and HALS additives were X10-151 and X10-152 respectively.

Several experiments were conducted on sample specimens using the base coating and the ultraviolet absorber and HALS additives, The specimens are pieces of uncoloured PUR ester soft foam around 7 cm x 7 cm x 4 cm obtained from UXEM BV, The Netherlands (http://www.uxem.com/).

The coating was prepared and tested for the following:

- influence of additives. Specimens were coated with the base coating only, and with BTZ or HALS only, and a combination of both
- concentration of additives. The concentration of the additives in combination with the base coating is tested to find optimal coating performance
- solubility. The amount of water in the coating dispersions varied. The viscosity of the coating dispersion changed and influenced the penetration depth of the coating in the soft foam

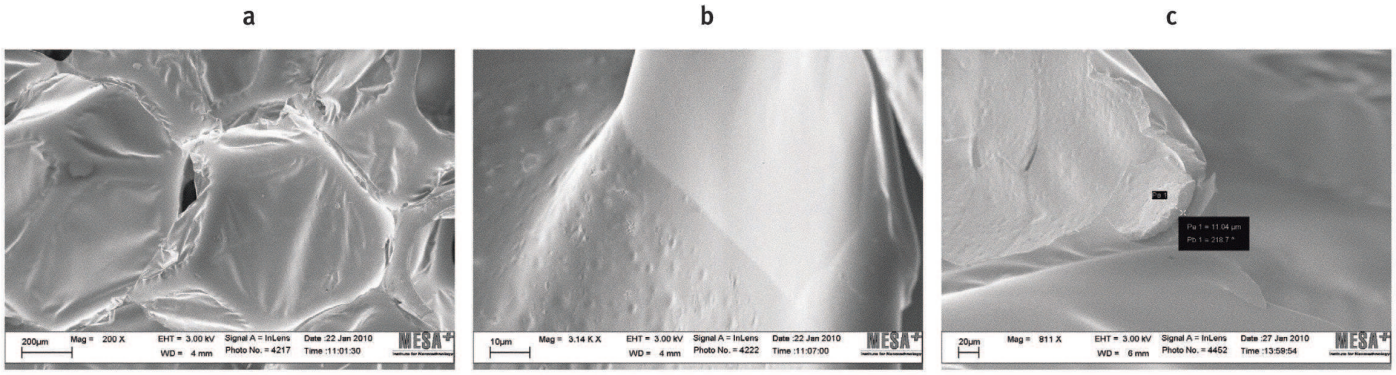


Figure 42. SEM image of the coating covering the cell-structure of PUR-ester foam (a) and expanded image of a single cell being partially coated (b). Cross section of the coating at around 10 microns thick (c)

Experimental procedure

Coatings were applied by dip coating and spray coating. To test the coatings' performance with time specimens were subjected to accelerated ageing in an Atlas suntester CPS+. In all experiments the daylight filter was used. The setup delivered a total radiant exposure of 200 Watt.hours.m^{-2} in the ultraviolet region and a total luminous exposure of 1.2 million lux hours in the visible (400-800 nm). A total of 12 specimens were exposed at the same time. The exposed coated specimens were compared to uncoated reference samples that underwent accelerated light ageing simultaneously. During accelerated light ageing, the specimens were partly covered to create reference data for unexposed surface area.

To test the coating properties and performance several test methods were used. For surface inspection a light microscope was used, whereas scanning electron microscopy was used for detailed examination. A UV-Vis spectrophotometer was used for transmission measurements. Scotch tape tests and ductility experiments are performed to test the coating adhesion and flexibility respectively.

An important requirement was that the coating matrix could uniformly cover the PUR ester foam and adhere well to it. To evaluate adhesion of the polymer matrices, several specimens were coated by means of dip and spray coating, and the resulting coating was investigated using SEM. The results indicated that the use of a polymer base coating material with similar mechanical properties as the sample showed good results in terms of adhesion and film formation. Figure 42 shows cross sections of the sample using different magnification. The low magnification image (a) shows that the coating covered the foam cells very well. It followed the contours of the cell-structure so it could be concluded that the coverage is conformal. The middle of the image shows a cell that was at the boundary of the penetrated coating, which ended up being partly covered (b). The coated lower part shows that the coating

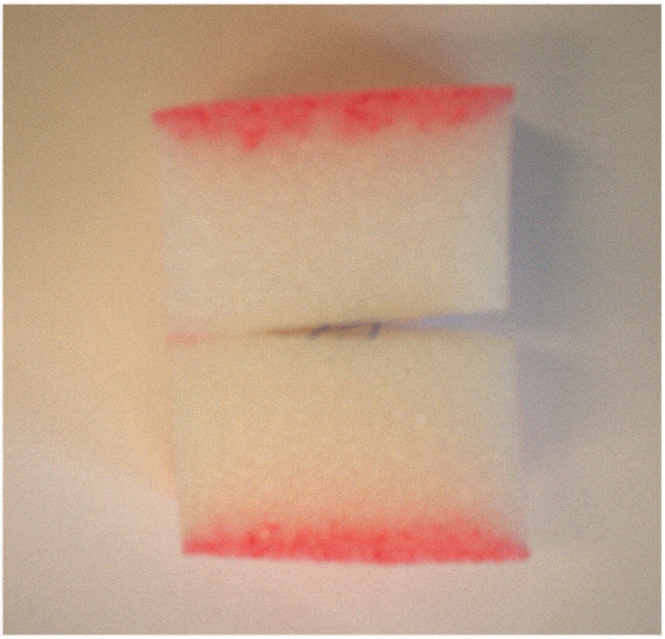


Figure 43. Cross section of a sample being sprayed with coating containing red pigment

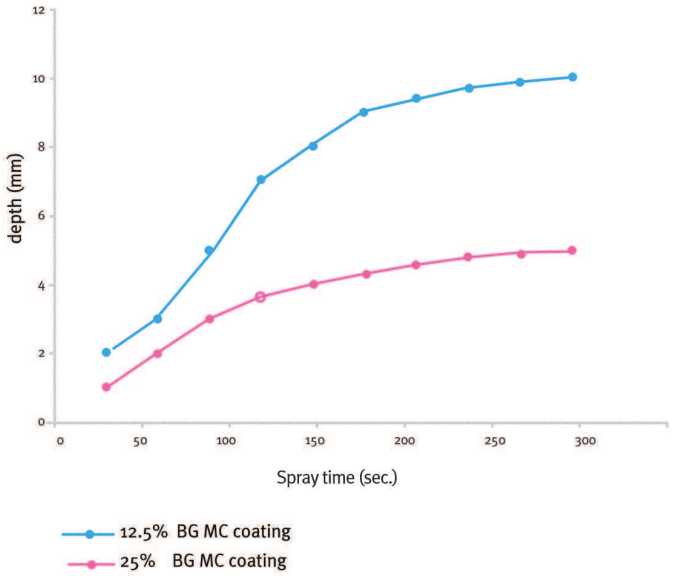


Figure 44. Spray time versus penetration depth of the coating diluted in water. The blue line represents the data for 12.5% coating content in the dispersion, whereas the red line represents a mix with 25% coating content

was smooth and does not affect the PUR ester cell compared to the uncoated upper part. A high resolution cross section image of a single cell is shown in Figure 42c. The coating thickness is measured, at several samples. A coating thickness of about 10 µm was highly reproducible.

Although both dip and spray coating were tested to apply the coating, the latter seemed to be the most practical. It is easier to use a spray gun on real art objects rather than dipping large objects in coating baths. A spray setup is cheap and easy to use. In the experiments described here a Conrad Airbrush-pistol SP30 with a 0.3 mm nozzle in combination with an Airbrush compressor CE-55 was used.

The coating dispersion was diluted with deionized water. For optimum protection the coating should have a sufficiently low viscosity to penetrate the foam deeply. However, diluting the dispersion too much may result in loss of the functionality of the additives. Specimens were coated with different coating to water ratios. The samples were cut in half in order to determine the penetration depth. As the coating is almost transparent, red pigment was added to make the coating clearly visible. Figure 43 shows the cross section of a specimen after it was sprayed with the coating containing the red pigment. The coating penetration depth was carefully measured using a micrometer screw gauge. For dispersions diluted with water to various concentrations, spraying time was varied. In Figure 44, the penetration depth is shown at two different concentrations.

From the data it can be concluded that the foam was saturated, regardless of the coating concentration, after about 300 seconds. It is also clear that as the viscosity increases, penetration depth is reduced. The dispersion with a coating content with respect to water of 25% penetrates only 5 mm, whereas a coating content of about 12.5% penetrates up to 10mm. Dispersions with even lower coating contents did not result in a higher penetration depth. Therefore the optimum coating content was determined to be 12.5% in the water dispersion. It was calculated that the maximum penetration depth and coating coverage was obtained for 0.4 ml dispersion for every square centimetre of surface area.

BTZ and HALS were added at different concentrations to the optimum coating concentration. For both BTZ and HALS the concentrations with respect to the Bemiguard MC base coating varied between 0 and 5%.

Figure 45 shows several specimens after 120 hours of accelerated ageing. Of the twelve specimens, nine were coated with Bemiguard MC. The BTZ and HALS were added to the Bemiguard in different

concentrations. From visible inspection it was clear that the addition of BTZ or HALS alone only protects the PUR esters to a limited extend. However, if the BTZ is used in combination with the HALS, better results are obtained.

The optimum concentration of both BTZ and HALS was found to be 4% with respect to the Bemiguard base coating. Although this coating recipe offers the best protection against photo degradation process, the process can only be slowed down and not stopped. Figure 46 shows microscope images of the cell structure of the coated sample before exposure (a), after 120 hours exposure (b) and an uncoated sample after 120 hours exposure (c). The cell walls are discoloured and thinned. By contrast the exposed sample in Figure 46 (b) shows little discoloration.

Conclusion

In summary, the coating recipe that performed best was 4% BTZ plus Bemiguard MC dispersion with 4% HALS, one part diluted with 7 parts of water (12.5%) to obtain the required viscosity. The coating can be best applied by spray followed by drying for 24 hours. It can be concluded that the optimised coating can significantly increase the lifetime of PUR ester samples by protecting against photodegradation.

Gilles Chaumat, Khôi Tran, Jan Matthijn Dekkers, Eleonora Pellizzi and Agnès Lattuati-Derieux

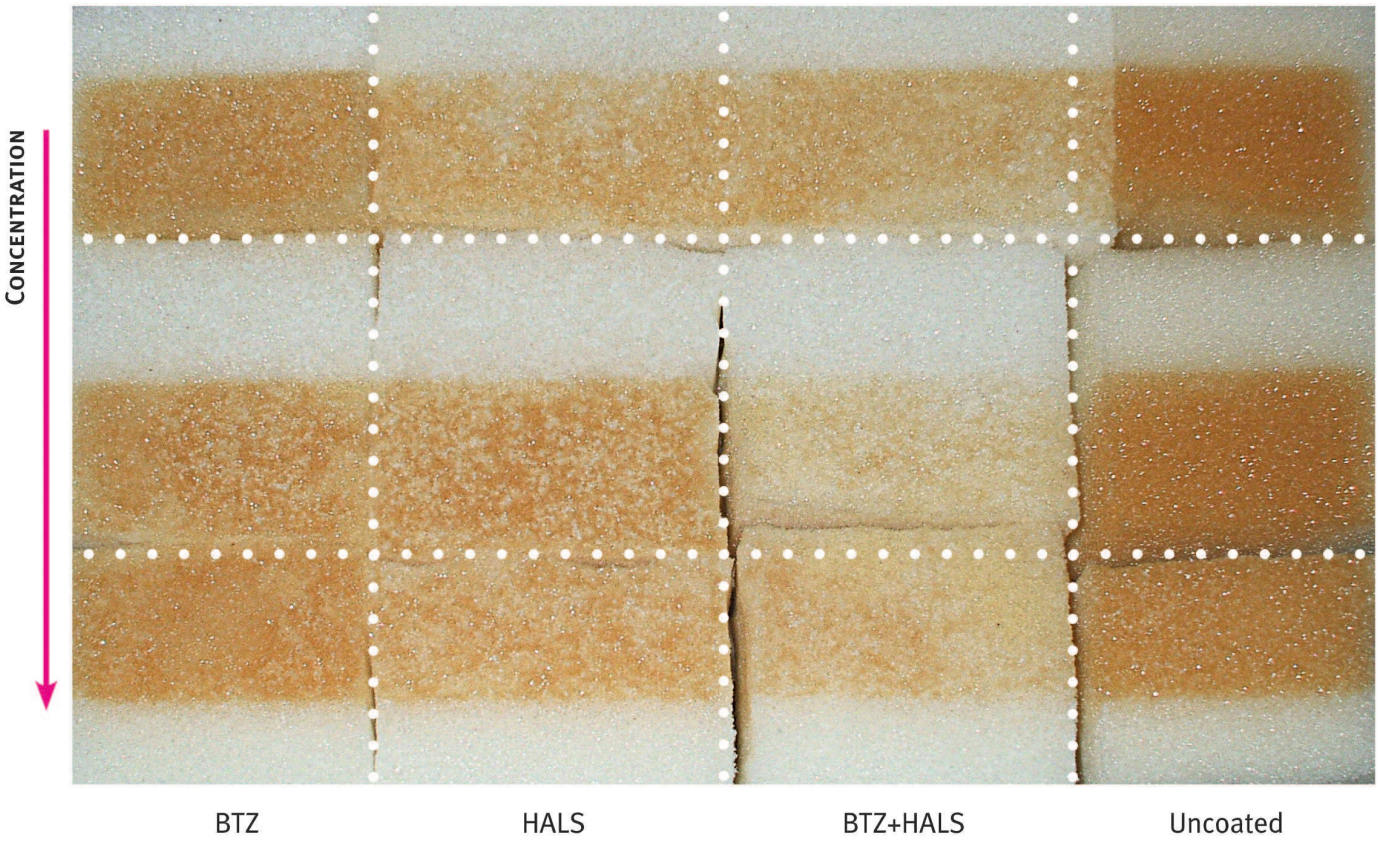


Figure 45. Image of light aged PUR samples where the BEMIGUARD solution and additives are varied

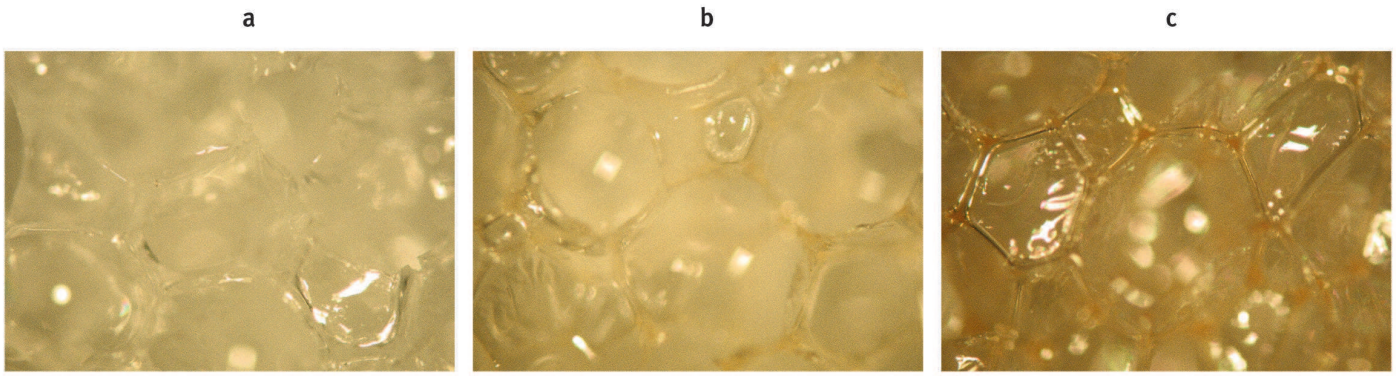


Figure 46. Microscopic images of the coated PUR-ester foam surface before exposure (a), and after 120 hours artificial ageing (b) and the surface of an uncoated reference sample after 120 hours of artificial ageing (c)