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Selection of a Hydrophobic Polyurethane Material for the Restoration of a Wayside Shrine

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Abstract

A sandstone (Hildesheimer Rhätsandstein) wayside shrine in Algermissen, Germany, had to be restored. The stone under the painting required both a strengthening and a hydrophobic treatment and two polyurethane-based products, hydrophobic strengtheners, were considered for this purpose. The aim of the research described in this paper was to select the most appropriate product. For this purpose, measurements on treated and untreated samples of the sandstone were carried out. Water related properties, such as water uptake and hydric expansion, as well as mechanical properties like flexural bending strength, were measured on both treated and untreated samples. The paper describes the minimalist approach developed that allowed selecting the suitable product for the conservation of a rather small object with limiting funding.

1 Introduction

The need for conservation of a colourfully painted wayside shrine in Algermissen, a village north of Hildesheim (lower Saxony, Germany) prompted the research described in this paper.

The shrine is about 3.50-m in height and consists of several stone parts. In a round niche it shows the image of the Virgin Mary, so-called „Werler Gnadenbild“. According to an engraving at the back of the shrine it was erected in 1803 by the carver Andreas Brantemaur from Hildesheim.

2 Preliminary Investigations

The first examinations, carried out in December 1997, showed that the shrine was in poor condtion. Although shrine had been re-painted several times, some areas had totally lost their colour because the underlying stone was disaggregating having lost its cohesion and strength.

In February 1998, the shrine was taken apart and moved to the laboratories of Hildesheim University of Applied Sciences for examination and analysis. It was found that the last painting dated from around 1960. Beneath this paint layer, up to 31 previous layers of paint were found [1]. Many of these had been applied with poor workmanship containing sand, dirt and brush-hairs. Parts of the stone surface had been impregnated with oils, probably from oil-based coloured paints.

Hence, the paint coats could not be considered a protection but rather the cause for the damage to the stone. Since the paint coats had not been able to keep water from entering the cracks in the stone, damage from humidity and frost resulted, and in some areas, the stone had totally lost cohesion. Fig. 1 shows the general view and the head of the Virgin Mary in the shrine in 1997.

An analysis of salts showed low concentrations of nitrate and gypsum. The highest concentrations to be detected were 0.005% nitrate and 0.015% gypsum (by weight) near the surface of the stone. These salt concentrations can to be considered as harmless.

The stone was identified in thin-section microscopy. It turned out to be Hildesheimer Rhätsandstein, a small-grained sandstone with clay and silica binders.

3 Selection of the hydrophobic strengtheners

Because of the small, extremely damaged areas of the stone a hydrophobic strengthener with a good adhesive properties was considered necessary. For this purpose, polymeric strengtheners were regarded as more appropriate than silica esters. Two polyurethane formulations were chosen for the preliminary testing.

Figure 1: Algermissen wayside shrine prior to restoration (general view, left; detail, right)

- PU 1:
  A commercial hydrophobic strengthener - widely used by the restorators in the region – based on aromatic polyurethanes with a solid content of 7% by weight. This material is a is a ready reacted polymer dissolved in organic solvents.
- PU 2:
  A prepolymer, with organic solvents, which reacts in the pores of the stone to yield a hydrophobic strengthener. The prepolymer contains an oligosiloxane segment between the two end aliphatic isocyanates and has a solid content of 25% by weight. This polyurethane is a non-commercial laboratory product [4] and was described in detail at a the previous Hydrophobe II conference [2].

4 Experimental

4.1 Sample preparation

The experiments were carried out on sandstone 4 x 4 x 16 cm prisms and with the minimum number of specimens possible given the limited budget available for this small monument.

Given the low number of specimens and to avoid the effects of stone imhomogenities on the measurements, some of these, such as the tests described in 4.3.1 to

4.3.3 were performed twice on the same specimens, once before and then again after treatment and curing. So the effects of the treatment could be observed directly on the same samples. All measurements were carried out on three samples per product tested.

4.2 Capillary Absorption of the Product

For each of the two products, three prisms were impregnated by capillary suction. The stone prisms were placed vertically in a container with the product immersed to a depth of 1-cm into the fluid. A mm-scale was attached to the specimen. The whole setup was placed into an air-tight box to avoid evaporation of the solvent. The height of capillary rise was read every ten minutes up to a total time of four hours.

After treatment, the prisms were stored in a case with high humidity (approx. 90 % r. H.) at room temperature to allow for the curing of the polyurethane prepolymer for 30 days.

4.3 Test Methods

4.3.1 Thermal Expansion

Metal points were glued on the end faces of the prismatic samples and the distance between them accurately measured. Then the samples were put into an oven at 60° C and after 1 hour the length was measured again. The thermal expansion coefficients α could then be calculated.

$$\alpha = \frac{\Delta l}{l_0 \cdot \Delta T} \qquad (1)$$

Δl	Dilatation
l_0	Length at room temperature
ΔT	Temperature change

4.3.2 Water Uptake

To determine the water uptake, the samples were stored in a container on triangle-shaped spacers. The water level was increased slowly, until the samples were completely covered under a 1-cm layer of water.

The mass of the specimens was determined every 24 h. After 6 days, the samples were taken out of the water and their drying curve obtained by dayly weighings for another six days.

The water uptake (w) was calculated as follows:

$$w = \frac{m(a) - m(0)}{m(0)} \cdot 100\% \qquad (2)$$

m(a) Mass of the completely, pressure-free water-saturated sample

m(o) Mass of the dry sample

4.3.3 Hydric Expansion

The measurement of the expansion-contraction was carried out parallel to the water-uptake measurements using the same measurement points that had been previously attached. The hydric dilatation l was calculated as follows:

$$l = l(a) - l(0) \times \frac{1000 \text{ mm}}{l(0)} \qquad (3)$$

l hygric dilatation

l(0) original length

l(a) measured length after swelling/shrinking

4.3.4 Flexural Bending Strength

The flexural bending strength was measured by putting the samples on two supports separated by a 10-cm distance. The load was applied to the top of the specimen in the middle between the supports. The measurement was conducted with constant force increase. The force at fracture of the sample was used to calculate the flexural bending strength.

5 Results

5.1 Capillary Absorption of the Product

Both materials reached an impregnation depth of over 2-cm after two hours. Agfter 4-hours, the impregnation depths were 12-cm, for PU 1, and 6-cm, for PU 2.

5.2 Thermal Expansion

Both products result in an increase of the thermal expansion coefficient of the treated samples in comparison to the untreated ones. The increases of this coefficient are of 15% for PU 1 and about 19% for PU 2. Both these values fall within the 20% limit suggested by Snethlage and Wendler for stone strengtheners [3].

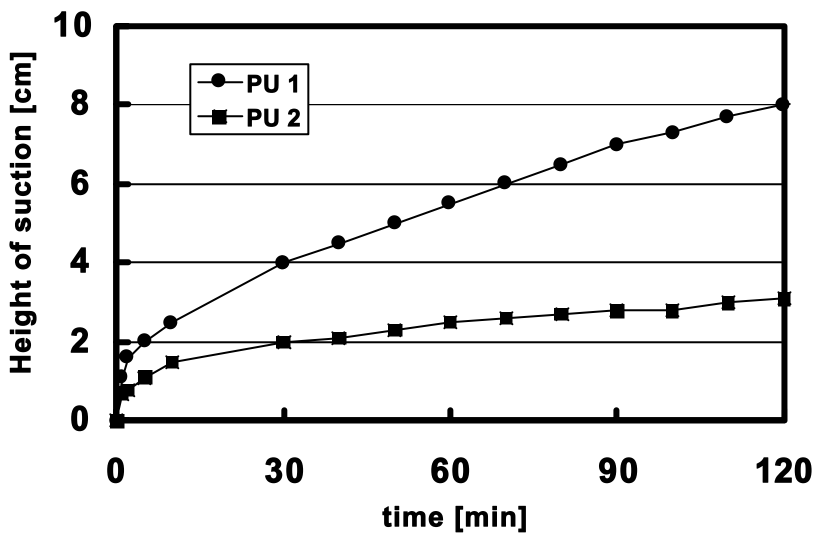

Figure 2: Capillary uptake of the hydrophobic stone strengtheners

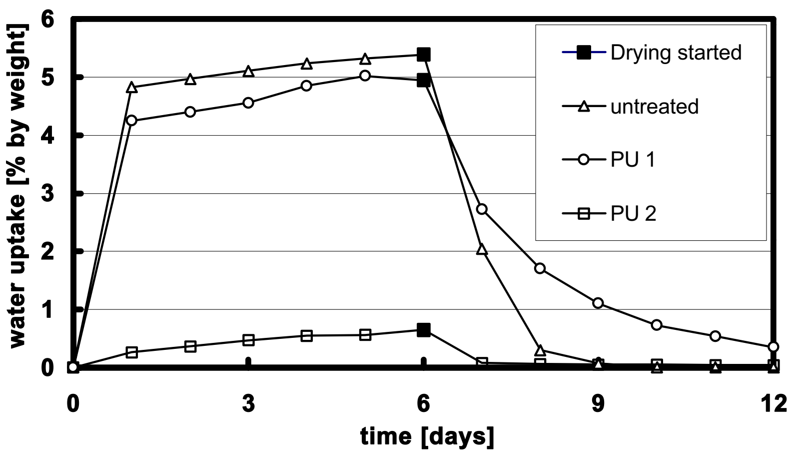

Figure 3: Water uptake and drying of treated and untreated stone samples during a 6 + 6 days wet/dry cycle.

5.3 Water uptake

While the PU 1 treatment induces a small decrease for water uptake and a slower drying, the PU 2 shows a strong hydrophobic effect so that the maximum of water uptake of the treated stones is only 10 % of that of the untreated specimens and the drying is completed within two days.

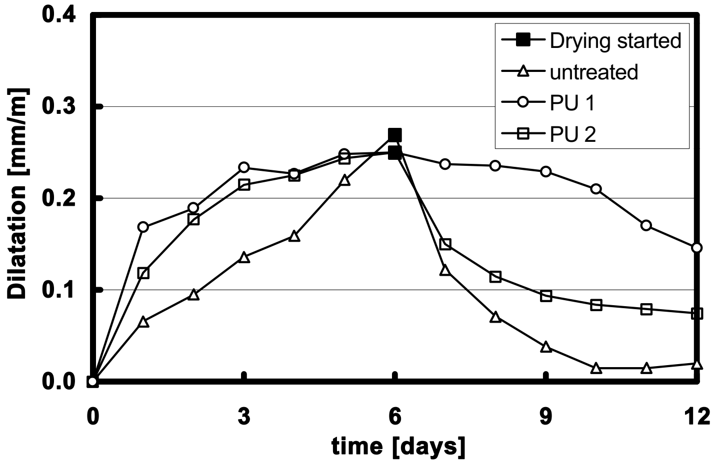

Figure 4: Swelling and shrinking of treated and untreated samples during a 6 + 6 days wet/dry cycle.

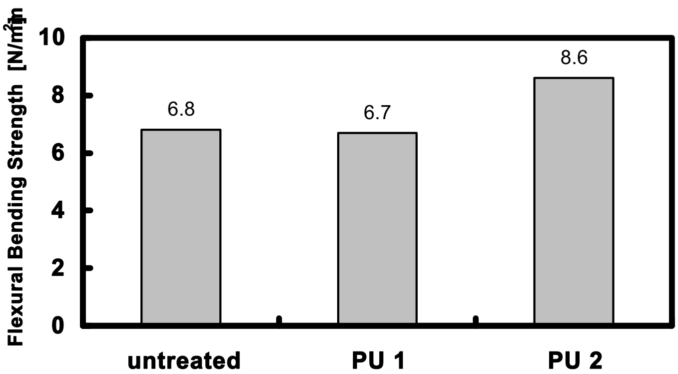

Figure 5: Results of the mesurement of flexural bending strength

5.4 Hydric Expansion

As seen in Fig. 4, the untreated samples have not reached their total expansion after 6-day immersion in water, however, the treated samples have reached their maximum value which is about 0.25 mm/m. However, the swelling of the treated stones is faster while their shrinking is delayed. The difference observed between the treated and the untreated samples can be of 0.2 mm/m for PU 1, while it is smaller for PU 2. The most significant difference between the two products is

Figure 6: Wayside shrine after restoration (detail)

observed in the drying. Samples treated with PU 2 show a very similar behaviour of the untreated specimens.

5.5 Flexural Bending Strength

The bending strength of the stone is practically not affected by treatment with PU 1. The small difference observed can be attributed to measurement uncertainties. On the other hand, treatment with PU 2 leads to a 25% increase in the flexural bending strength of the stone.

6 Conclusions

On the basis of the above results, PU 2 was selected as the strengthening and hydrophobic treatement of the wayside shrine. The deciding points were the improved strengthening and the more neutral expansion-contraction behaviour, both for thermal and hydric conditions, with regards to the PU 1 product. Although only a partial treatment was envisioned, the very high hydrophobicity conferred was not considered a problem, as the whole shrine was to be painted with a hydrophobic silicone paint afterwards. Figure 6 shows a detail of the shrine after complete restoration and re-erection.

The main point of this exercise was to show that a selection of a hydrophobic strengthening product is possible even when keeping the number of specimens and tests to a minimum. The results may not have big scientific significance but they are addressed to restorators to show that unexpensive and relatively fast tests—that provide important data for the selection of restoration materials—are available.

The restoration of the wayside shrine also required repair of broken or missing stone pieces which was done with a polyurethane-modified mortar. As the original colouring could only be detected in small parts, the stone was cleaned and completely re-painted but respecting the previous colour scheme. For this purpose, specific pigments to match these colours were added to the silicone resin emulsion paint used.

The wayside shrine was re-erected in Algermissen and is used again regularly for pilgrimage and devotions.

7 Acknowledgements

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