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Review: Adhesives for Thread-by-Thread Tear Mending in Torn Fabric-Supported Paintings

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Abstract

This paper presents the results of tests on adhesives that are used in the thread-by-thread tear mending of canvas paintings. Single-linen threads were joined using various natural and synthetic adhesives, and the ultimate tensile strength of these lap joints was tested. In the first series of tests, a mixture of sturgeon glue and natural wheat starch paste proved to be one of the best performers. This mixture offers a high tensile load capacity as well as other positive properties, e.g. neutral pH, reversibility in warm water, good workability, and positive optical appearance (it was nearly invisible). A further series of tests on wheat starch / sturgeon glue mixtures indicated that some industrially manipulated starch products (precooked and swellable in cold water) are an appropriate alternative to the commonly used natural wheat starch. Additional advantages of these precooked products are their quicker preparation and a more consistent paste quality. Some pH-neutral dispersions, based on ethylene vinyl acetate copolymers, also provided promising test results. Dried films produced from these are swellable, even in cold water. Finally, the paper reports on materials for the mending of torn synthetic threads, in this case Polyamide PA 6. The focus of this particular series of tests was the influence of the age of the thread and its sensitivity to light on the choice of adhesive.

Titre et Résumé

Examen des adhésifs utilisés dans la méthode de réparation fil par fil appliquée aux peintures sur toile déchirées

Le présent article traite des résultats d'essais réalisés sur des adhésifs utilisés lors de la réparation fil par fil de déchirures de peintures sur toile. Des fils de lin simples ont été collés au moyen de divers adhésifs naturels et synthétiques et les joints de recouvrement ont été mis à l'épreuve en exécutant des essais de détermination de la résistance à la traction. Les résultats de la première série d'essais indiquent que le mélange de colle d'esturgeon et de colle d'amidon de blé naturel compte parmi les produits les plus efficaces. Le mélange présente en effet une grande résistance à une charge de traction, de même que d'autres propriétés concrètes, par exemple un pH neutre, la réversibilité dans l'eau chaude, une bonne malléabilité et un aspect esthétique satisfaisant (la couche d'adhésif est presque invisible). Une série d'essais supplémentaires ont été exécutés avec différents mélanges de colle d'esturgeon et de colle d'amidon de blé; les résultats indiquent que certains produits d'amidon ayant subi un traitement industriel (notamment ceux qui sont pré-cuits et qui peuvent gonfler dans l'eau froide) constituent des produits de substitution adéquats de l'amidon de blé naturel qui est couramment utilisé. La préparation plus rapide et l'obtention d'une colle de qualité plus uniforme constituent aussi des avantages supplémentaires des produits pré-cuits. Les résultats d'essais de certaines dispersions de pH neutre, à base de copolymère d'acétate de vinyle et d'éthylène, sont aussi prometteurs. Les pellicules séchées, produites à partir de celles-ci, sont solubles, et ce, même dans l'eau froide. En outre, l'article comporte aussi des données sur des matériaux de réparation de fils synthétiques déchirés, particulièrement des fils de polyamide PA-6. Cette série

particulière d'essais ciblait surtout l'étude des effets de l'âge des fils et de leur sensibilité à la lumière sur le choix de l'adhésif.

Introduction

In order to reconstruct the optical and mechanical properties of pre-torn canvas, it is important to copy the shape, color and ultimate tensile strength (UTS) of each thread while mending any given tear. However, substituting the thread's cohesion with an adhesive is a peculiar and possibly problematic concept. The aim, therefore, is to find the most appropriate adhesives according to the general criteria described by Young (2003). To date there are no comprehensive investigations about adhesives suitable for tear mending, which are based on scientific standards and statistical evaluations. The aim of this preliminary study is to determine the stability of over-lapping joints in a single linen thread. A study by Reuber showed the UTS of the joints to be significantly influenced by the adhesive properties, but also by the conservator's dexterity as well as relative humidity (Reuber 2010). In this test series, a highly concentrated sturgeon glue solution, mixed to wheat starch paste (SW-mixture), performed very well. The starch paste only acts as "filler" and increases the viscosity of the sturgeon glue. A further study by Vogel undertook to improve the properties of the SW-mixture by comparing different natural and precooked starch products in mixtures with sturgeon glue (Vogel 2010). Recent pH-neutral dispersions, based on ethylene vinyl acetate copolymers, were tested as well and are still under investigation.

Another focus of the on-going research was the examination of different thread materials and their influence on the choice of adhesive. For instance, no specific adhesive has ever been described for the tear mending of Polyamide 6 (PA 6) in conservation literature. Exemplary tensile tests were carried out by Nägler with this particular synthetic thread, which is frequently used as a textile support in modern art (Nägler 2005).

Methods for Linen-Tests

Thread material

Tests were carried out on single threads, and not on fabric. This was done in order to exclude the influence of parameters such as weave structure and crimp. A relatively uniform, new linen thread was chosen: Linen LEA 20 raw Nm 12, Nr. 115/2007 (average diameter: approx. 0.27 mm; thread size: 83 tex; UTS: 32 cN/tex), sized with a negligible amount of cellulose ether (possibly sodium carboxy methyl cellulose).

Tested adhesives

All the tested adhesives have been compiled in the following table (see Table 1). The test results of the adhesives nos 1-29 are summarized in Test Series 1. Four adhesives (no 11, 16, 17 and 29) were selected to investigate the conservator's dexterity on the UTS in Test Series 2. The influence of humid conditions on the UTS was investigated in Test Series 3 when using the same four adhesives with different hygroscopic properties. The focus of Test Series 4 was SW-mixtures using different wheat starch products (adhesives nos 30-33).

Table 1. Tested adhesives for linen

| No | Product | Polymer name (Abbreviation) | Concentration | pH | Tg (°C) |
|----|---|-------------------------------|-----------------------------------|-----------------|------------|
| 1 | Plextol D360 | MMA/BMA/EMA dispersion | as received (60% polymer) | 7.5 | -8 |
| 2 | Plextol B500 | EA/MMA dispersion | as received (50% polymer) | 9.5 | 9 |
| 3 | Plextol D540 | acrylic dispersion | as received (50% polymer) | 9.0 | 29 |
| 4 | Plextol D498 | acrylic dispersion | as received (50% polymer) | 9.0 | 13 |
| 5 | Lascaux 498HV (stock) | BA/MMA dispersion | as received (approx. 40% polymer) | 8.0-9.0 | 6 |
| 6 | Lascaux 498HV | BA/MMA dispersion | 70% of the stock | | |
| 7 | Mowilith DMC2 | PVAc dispersion | 95% of the stock | 4.0-5.0 | 13 |
| 8 | Mowilith DHS S1 | PVAc dispersion | 85% of the stock | 3.5-5.5 | 38 |
| 9 | Mowilith LD167 | PVAc dispersion | 85% of the stock | 5.0-6.0 | 38 |
| 10 | Mowilith D50 (stock) | PVAc dispersion | as received (50% polymer) | 3.0-4.0 | 38 |
| 11 | Mowilith D50 | PVAc dispersion | 95% of the stock | 3.0-4.0 | 38 |
| 12 | Mowilith D50 | PVAc dispersion | 90% of the stock | 3.0-4.0 | 38 |
| 13 | Paraloid B72 | EMA/MA resin | 100% | - | 40 |
| 14 | Plexigum PQ611 | BMA resin | 100% | - | approx. 32 |
| 15 | Textile Welding Powder Kremer (130-133 °C) | PA 11 | 100% | - | - |
| 16 | Lascaux Polyamide Textile Welding Powder 5065 (80 °C) | PA 11 | 100% | - | - |
| 17 | UHU plus schnellfest | Epoxy resin | - | - | - |
| 18 | BEVA 371, film | EVA, ketone resin N, paraffin | 100% | - | - |
| 19 | BEVA Dispersion D-8 | EVA, ketone resin N, paraffin | as received | 4.0-5.0 | - |
| 20 | BEVA Dispersion D-8-S | EVA, ketone resin N, paraffin | as received | 4.0-5.0 | - |
| 21 | Evacon-R | EVA | as received | approx. 6.0-6.5 | - |
| | | EVA / PVAL* | | | |
| 22 | Neutral pH Adhesive, Lineco | PVAc | as received | approx. 7.0 | - |
| | | EVA | | | |
| | | VAE copolymer / PVAL* | | | |
| 23 | Aquazol 500 | PEOX | 25% | - | - |

| | | | | | |
|----|---|---|-----------|---------|---|
| 24 | 20% Sturgeon glue/ 12.5 % (and 25%) Aquazol 500 | - | ratio 1:1 | - | - |
| 25 | 20% Sturgeon glue/ 1% JunFunori | - | ratio 1:1 | - | - |
| 26 | 20% Sturgeon glue/ 1% Tylose MH1000 | - | ratio 1:1 | - | - |
| 27 | Rice starch paste | - | 10 % | - | - |
| 28 | Wheat starch paste 1 (1: Kumetat product) | - | 10 % | - | - |
| 29 | 20% Sturgeon glue/ 10% Wheat starch paste 1 (1: Kumetat product) | - | ratio 1:1 | 5.0-7.0 | - |
| 30 | 20% Sturgeon glue/ 10% Wheat starch paste 2 (2: Kleindorfer product) | - | ratio 1:1 | 5.0-7.0 | - |
| 31 | 20% Sturgeon glue/ 10% Shin Shofu | - | ratio 1:1 | 5.0-7.0 | - |
| 32 | 20% Sturgeon glue/ 10% precooked wheat starch paste: Gaylord, Crester ff, Kremer Wheat starch | - | ratio 1:1 | 5.0-7.0 | - |
| 33 | 20% Sturgeon glue/ 13% precooked wheat starch paste: Wheat Paste No. 301, Foodgel, Wetgel f | - | ratio 1:1 | 5.0-7.0 | - |

BA/MMA = butyl acrylate/methyl methacrylate

BMA = butyl methacrylate

EA/MMA = ethyl acrylate/ methyl methacrylate

EMA/MA = ethyl methacrylate/ methacrylate

EVA = ethylene vinyl acetate

MMA/BMA/EMA = methyl methacrylate/butyl methacrylate/ethyl methacrylate

PEOX = poly (2-ethyl-2-oxazoline)

PA = polyamide

PVAc = poly(vinyl acetate)

PVAL = polyvinyl alcohol

VAE = vinyl acetate ethylene

(All data collected from technical information sheets, in addition no 21 and 22 *: analysed by Dr. Elisabeth Jägers/CICS 2011; pH test data for no 18-33 by the author Vogel)

Joining procedure

A relatively substantial overlap (1 mm) of thread ends, which were cut beforehand, guaranteed a definite and controllable length of overlap. All steps of the joining procedure were carried out with the help of a stereomicroscope (magnification 20x). Both thread ends were frayed out to a length of 1 mm with Weston dental probes. All sturgeon glue containing adhesives were kept luke warm at 45 °C in a sand bed during mending. In the case of water-and solvent- based adhesives, a small defined droplet of adhesive was applied onto the lower side of the cut with a ball end of an insect pin. Fibers of both thread ends were then intermingled. All joints were dried for approx. 30 seconds at approx. 40-45 °C with the help of a hot needle (transformer

Engelbrecht WZ IV and Minor-hot needle with diagonal tip). The needle was used under gentle pressure and with a constantly sliding motion. Acrylic dispersions were dried at approx. 50 °C. Instruments for joining can be seen in Figures 1 and 2. Hot-melt adhesives were applied with the hot-needle set according to their individual melting temperatures.



Figure 1: Instruments for tear mending: Weston dental probe (top), insect pin (centre) and hot needle (bottom)



Figure 2: Tips of Weston dental probe (top), insect pin (centre) and hot needle (bottom)

In Test Series 1, 10-30 threads per adhesive were joined by one conservator. In Test Series 2, ten joints were carried out by seven conservators. In the Test Series 3, 15 joints were tested per adhesive and humidity condition by one conservator. Seven conservators worked on Test Series 4 (10 joints per conservator).

The joining process and the subsequent drying time (three weeks) occurred at 55 +/- 2% relative humidity (RH) and 20 +/- 2 °C temperature, before tensile testing (Test Series 1, 2, and 4).

Humidification cycles

In order to study the influence of changing humidity during ageing on the tensile strength of the joints in Test Series 3, joint threads were aged with rapid changes of RH. After the first three

weeks, the joint linen samples were exposed to short relative humidity cycles (2.5 hours changes between 30% and 85% RH) under a constant temperature of 30 °C (conditioning cabinet UV 200SB, Weiss Umwelttechnik GmbH) for 43 days (with pre-stressing of 10 g).

Tensile testing

Uniaxial tensile testing was undertaken with the Zwick-universal testing machine (Type Z 2.5/TN1S, 10 N load cell; clamp length 100 mm; speed: 20 mm/min; 1 gram pre-load) at 55 +/- 2% RH and 20 +/- 2 °C. The results were recorded in cN (1 cN = 0.01 N).

The aged samples of Test Series 3 were also tested under a dry condition of 40% RH and 20 +/- 2 °C (after a precondition at 25% RH for 72 hours) and under high humidity of 75% (after preconditioning at 93% for 72 hours).

For the comparative investigation of wheat starch products the SW-joints were tested at 55 +/- 2% RH (Test Series 4). The natural wheat starch 2 and the precooked product Foodgel, mixed with 20% sturgeon glue, were also tested at 72 +/- 2% RH after 3 weeks of drying and after preconditioning at 72% for 72 hours directly before testing.

Methods for PA 6-Tests

Thread material

For bonding tests, new non-contorted Polyamide PA 6 yarn Enkalon 540 T (940dtex) was used. The thread consisted of 132 filaments.

Tested adhesives

All adhesives used to join PA 6 yarns of Test Series 5 are listed in the following table (see Table 2).

Table 2. Tested adhesives for Polyamide 6

| Product | Polymer name (Abbreviation) | Concentration | pH | T _g (°C) |
|--|-----------------------------|------------------------------|---------|---------------------|
| Araldite AY103/ HY991 | epoxy resin | - | - | 83 |
| Mowilith DMC2 | PVAc dispersion | as received (55% polymer) | 4.0-5.0 | 13 |
| Paraloid B72 (in Toluene) | EMA/MA solution | 33% | - | 40 |
| Alberdink U325 | PUR dispersion | as received (39–41% polymer) | 7.5-9.5 | - |
| Primal AC33 | EA/MMA dispersion | as received (46-47% polymer) | 8.5-9.1 | 16 |
| Lascaux 360HV/ Lascaux 498HV | BA/MMA dispersion | ratio 1:1 | 8.0-9.0 | -8/13 |
| 20% Sturgeon glue/ 13% Wheat starch paste 1 (1: Kumetat product) | - | ratio 1:1 | - | - |

| | | | | |
|---|--------------------------------|------|---|------|
| Regalrez 1094 (2% Tinuvin 292) (in Naphta 60-95 °C) | hydrogenated hydrocarbon resin | 60% | | 33.0 |
| Klucel GF (in Ethanol) | HPC | 3.8% | - | - |
| Methocel A4M (in water) | MC | 2.9% | - | - |

BA/MMA = butyl acrylate/methyl methacrylate

EA/MMA = ethyl acrylate/methyl methacrylate

EMA/MA = ethyl methacrylate/methacrylate

PVAc = poly(vinyl acetate)

PUR = polyurethane

(All data collected from technical information sheets)

Joining procedure

The procedural method conformed to the joining procedure, described above, under methods for linen-tests. Ten joints per adhesive were carried out by one single conservator.

Tensile testing

For the uniaxial tensile test a Zwick-universal testing machine (Type Z 2.5/TN1S, 10N load cell; clamp length 150mm; speed: 20mm/min; 1.5 gram pre-load) was used at 46 +/- 2% RH and 18 +/- 2 °C.

Results

For the discussion of the results of the tensile testing Arithmetic average (AA), Standard deviation (SD) and Coefficient of variation (CV) are used. They are defined as follows:

Arithmetic average (AA): The arithmetic average (arithmetic mean) is a common method to derive the central tendency of a data set (sample space). It is defined as the quotient of the sum of data and the number of data.

Standard deviation (SD): The standard deviation shows the variation from the average (arithmetic mean). A low standard deviation indicates that the data points tend to be very close to the average, whereas high standard deviation indicates that the data are spread out over a large range of values.

Coefficient of variation (CV): The coefficient of variation is defined as the ratio of the standard deviation to the arithmetic average (mean) of the data values. It is expressed as a percentage and therefore used for the comparability of results.

Test Series 1: Linen - Ultimate tensile strength

During the tensile testing, all joined threads tore directly in the joint. Therefore all results can be attributed to the adhesives properties. Overall, the UTS of all joints proved poorer than the test thread itself. The average UTS of the linen thread came out at 2143 cN (coefficient of variation:

19%). There were only a few exceptions to this pattern; all produced by Lineco, which proved significantly stronger in some samples (see Figure 3 and Table 3).

Joints with acrylic dispersions, common Plextol-types, showed a very poor ultimate tensile strength. It would seem that the higher the Tg value, the higher the UTS. Therefore the Plextol D 540 (with its relatively high Tg of 29 °C) proved the best performer in its group.

All PVAc joints have a relatively high UTS, but not all joints have a significantly improved bond strength when compared with SW-mixtures. This tendency has already been observed by Heiber (1996). The best performer was Mowilith D50. The results can be explained with different Tg values. Joints with Mowilith DMC2 had the poorest UTS, due to their low Tg value of 13 °C. The three other test products have a Tg of approx. 38 °C. Furthermore, it is assumed that other parameters have an effect on the joint's UTS: for example solid content, penetration behavior between the fibers, varying drying times of the dispersion and their influence on the workability.

Only one epoxy resin was tested, a product named 'UHU plus schnellfest'. The UTS of the epoxy resin joints was only moderate, even though epoxy resins are generally very strong adhesives. Some sturgeon glue mixtures and PVAc products performed notably better than this resin. Moreover, the joints broke at the interface between the adhesive and the yarn. The relatively low UTS of epoxy resin joints might be explained by the adhesive setting without pressure, leading to a greater distance between the fibers and a reduced fiber intermingling.

The joints of the hot-melt adhesives showed relatively poor UTS values. The best results were achieved using Lascaux Polyamide Welding Powder 5065, which has a melting point of 80 °C. The melting point of the polyamide powder, supplied by Kremer, is approx. 130 °C. It was difficult to reach this high temperature with the hot needle. The result was a low penetration between the fibers and an extremely poor UTS.

The two acrylic resins Paraloid B72 and Plexigum PQ611 gave results comparable to acrylic dispersions.

The modern wax/resin adhesive BEVA 371 was tested as a melted mass. The adhesive appeared to be too weak to be useful in tear mending. Joints with two different BEVA dispersions (D-8 and D-8-S, sold by different suppliers) showed a moderate UTS such as Lascaux Polyamide Textile Welding Powder 5065 (melting point of 80 °C). The pH-neutral dispersions such as Evacon-R and Lineco performed very well in all tests, with extremely high values in the case of the Lineco joints.

The UTS of joints with 10% starch pastes of rice and wheat was too poor for thread-by-thread tear mending. By contrast, joints with 20% sturgeon glue, mixed with 10% wheat starch paste (wheat starch 1: starch sold by Kumetat) in the ratio 1:1, gave a high UTS. This result was significantly higher than those made of other sturgeon glue modifications, e.g. Tylose MH 1000. Interestingly, the values seemed to rise, when no hot needle was used. However, to set the thread ends in the desired position more quickly, an accelerated drying process at a higher temperature of around 40 °C was necessary. This positive result of the Test Series 1 confirms

the findings of Heiber, who recommended this particular mixture of 20% sturgeon glue, mixed with 10% wheat starch paste (no 29) for tear mending (Heiber 2003).

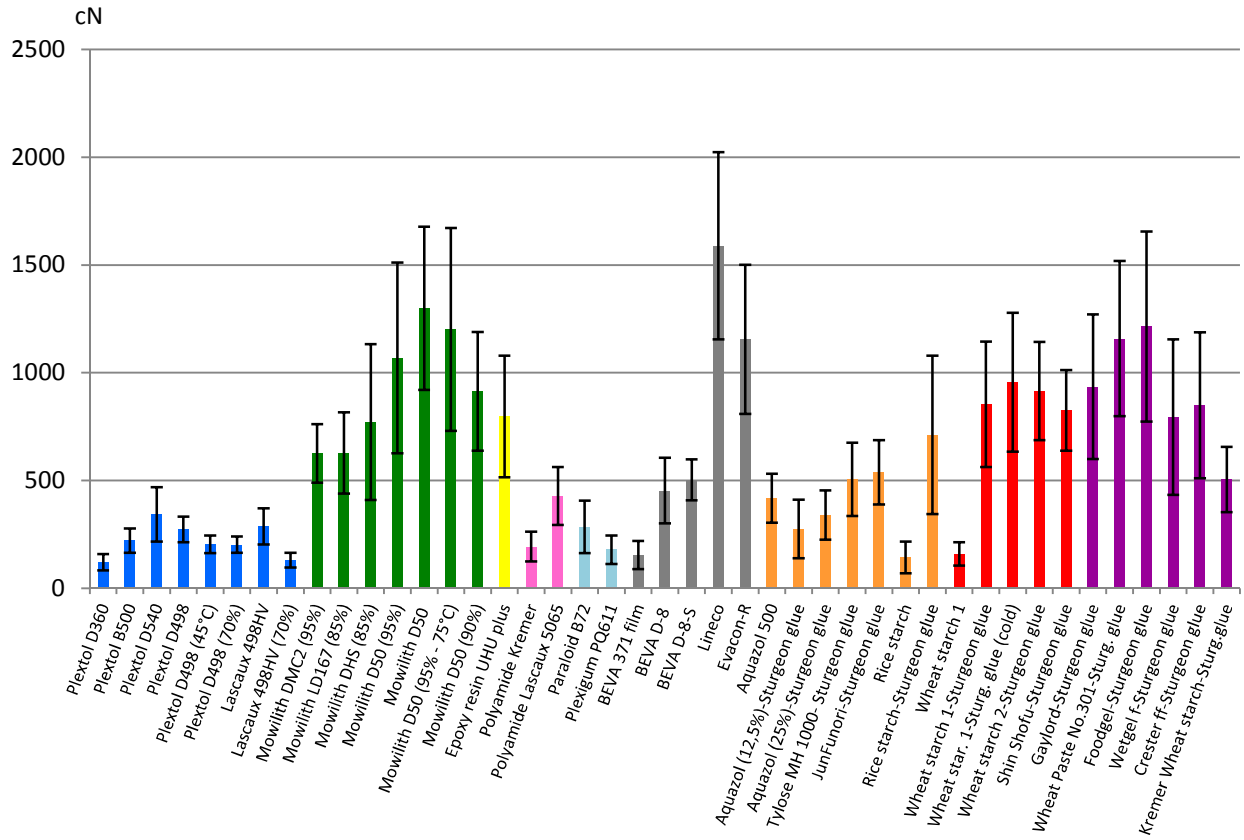


Figure 3. Linen - Ultimate tensile strength (arithmetic average and standard deviation) of different adhesives

Table 3. Linen - Ultimate tensile strength (arithmetic average, standard deviation and coefficient of variation) of different adhesives

| Adhesive | Arithmetic average (cN) | Standard deviation (cN) | Coefficient of variation (%) |
|--------------|-------------------------|-------------------------|------------------------------|
| Plextol D360 | 121 | 38 | 31 |
| Plextol B500 | 221 | 57 | 26 |

| | | | |
|-----------------------------------|------|-----|----|
| Plextol D540 | 343 | 126 | 37 |
| Plextol D498 | 273 | 59 | 22 |
| Plextol D498 (45 °C) | 204 | 41 | 20 |
| Plextol D498 (70%) | 202 | 38 | 19 |
| Lascaux 498HV | 287 | 84 | 29 |
| Lascaux 498HV (70%) | 131 | 34 | 26 |
| Mowilith DMC2 (95%) | 626 | 136 | 22 |
| Mowilith LD167 (85%) | 628 | 188 | 30 |
| Mowilith DHS (85%) | 771 | 362 | 47 |
| Mowilith D50 (95%) | 1069 | 443 | 41 |
| Mowilith D50 | 1299 | 378 | 29 |
| Mowilith D50 (95% - 75 °C) | 1201 | 470 | 39 |
| Mowilith D50 (90%) | 914 | 275 | 30 |
| Epoxy resin UHU plus schnellfest | 797 | 282 | 35 |
| Polyamide Kremer | 193 | 69 | 36 |
| Polyamide Lascaux 5065 | 428 | 134 | 31 |
| Paraloid B72 | 285 | 122 | 43 |
| Plexigum PQ611 | 179 | 66 | 37 |
| BEVA 371 film | 154 | 65 | 42 |
| BEVA D-8 | 453 | 152 | 34 |
| BEVA D-8-S | 503 | 95 | 19 |
| Neutral pH Adhesive, Lineco | 1589 | 434 | 27 |
| Evacon-R | 1155 | 346 | 30 |
| Aquazol 500 | 418 | 114 | 27 |
| Aquazol 500 (12,5%)-Sturgeon glue | 275 | 136 | 50 |
| Aquazol 500 (25%)-Sturgeon glue | 340 | 114 | 32 |
| Tylose MH 1000-Sturgeon glue | 506 | 170 | 34 |
| JunFunori-Sturgeon glue | 538 | 149 | 28 |
| Rice starch | 143 | 73 | 51 |

| | | | |
|-------------------------------------|------|-----|----|
| Rice starch-Sturgeon glue | 712 | 368 | 52 |
| Wheat starch 1 | 159 | 54 | 34 |
| Wheat starch 1-Sturgeon glue | 854 | 291 | 34 |
| Wheat starch 1-Sturgeon glue (cold) | 956 | 322 | 34 |
| Wheat starch 2-Sturgeon glue | 915 | 228 | 31 |
| Shin Shofu-Sturgeon glue | 825 | 187 | 23 |
| Gaylord-Sturgeon glue | 935 | 336 | 36 |
| Wheat Paste No. 301-Sturgeon glue | 1158 | 360 | 31 |
| Foodgel-Sturgeon glue | 1215 | 441 | 36 |
| Wetgel f-Sturgeon glue | 794 | 361 | 45 |
| Crester ff-Sturgeon glue | 849 | 339 | 40 |
| Kremer Wheat starch-Sturgeon glue | 505 | 151 | 30 |

Test Series 2: Linen - Ultimate tensile strength and dexterity

In this Test Series further investigations were carried out on four selected adhesives, which had been the best performers in Test Series 1. At that stage the strong adhesives Lineco and Evacon-R, which are described in Test Series 1, were not taken into account. Seven conservators (P1-P7) joined threads with the SW1-mixture, Mowilith D50, Polyamide 5065 and UHU plus. Notably, the average UTS values of all adhesives vary significantly (see Figure 4). These differences could be explained by the dexterity of the conservator. Despite giving precise instructions about the joining process, e.g. intermingling and handling the material during the drying time, subjective decisions and individual skills are almost impossible to avoid. The influence of the conservator's training and intuition on the UTS became evident. Even small manipulations had a significant influence on the UTS. However, the average UTS values of the joints, done by the seven conservators (P1-P7), were similar to the results of the Test Series 1, carried out by another conservator (P0). This comparison indicates that the values of the First Series (P0) provide an approximation to an average value.

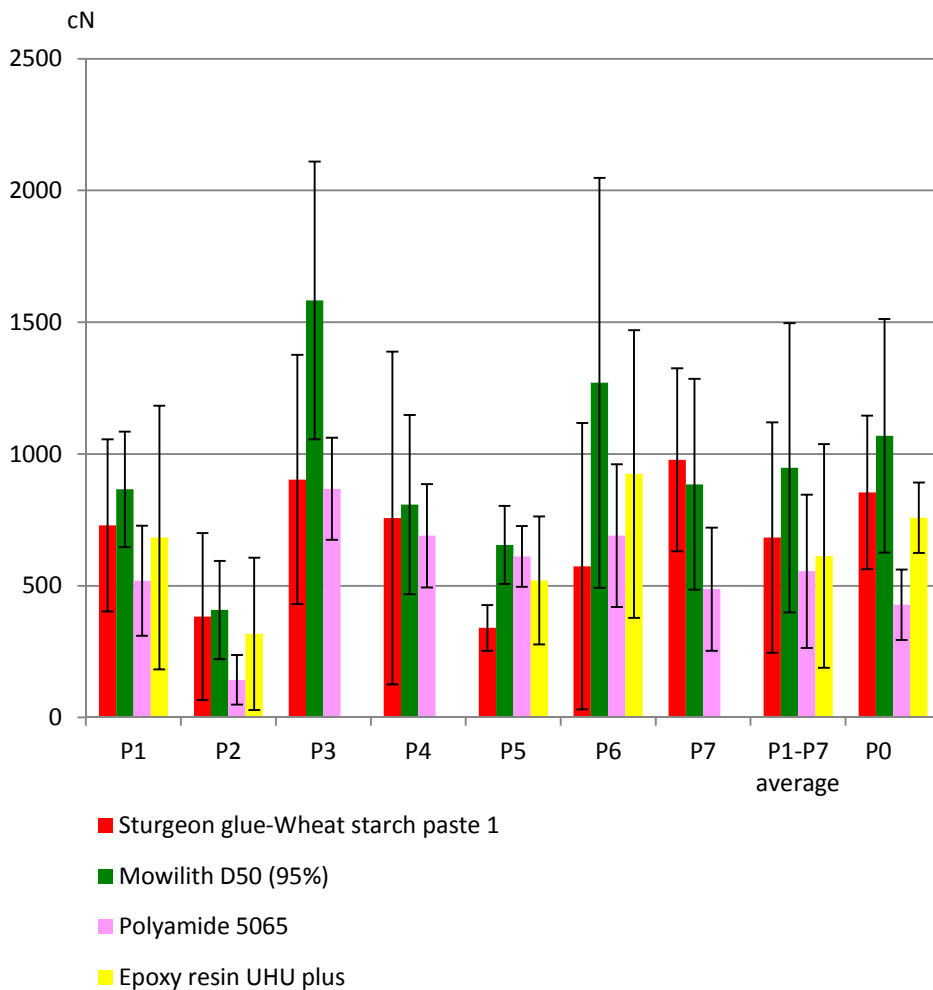


Figure 4. Linen - Ultimate tensile strength (arithmetic average and standard deviation) of four selected adhesives and eight conservators

Test Series 3: Linen - Ultimate tensile strength at different RH after changing humidity exposure

After exposing tensioned joined threads to changing humidity, the values of the SW1-mixture, Mowilith D50 and UHU plus were only slightly lower than those which had not undergone climate exposure (see Figure 5). The decrease of the UTS of the SW1-mixture joints could be explained by a decreasing stiffness of the adhesive: The water absorption causes a reduction in cohesion. PVAc shows similar results. Many parameters such as relaxation, cold flow or surfactants could have an influence on the reduction. Polyamide 5065 showed the opposite behavior and higher values after the climate change exposure. However, more testing is needed to verify this.

Surprisingly the SW1-mixture joints showed the least change in UTS, tested under high humidity. Even though the T_g of animal glue decreases under high RH, the humidity resistance was much higher than expected. PVAc joints showed a significant drop in the ultimate tensile strength. The UTS of polyamide joints was the lowest of all. The epoxy resin joints proved to have an insufficient strength for application in humid environments. In general, the drier test condition led to a considerable increase of the UTS. Polyamide 5065 joints, however, showed a different behavior, as the UTS seemed to decrease under damp and dry conditions.

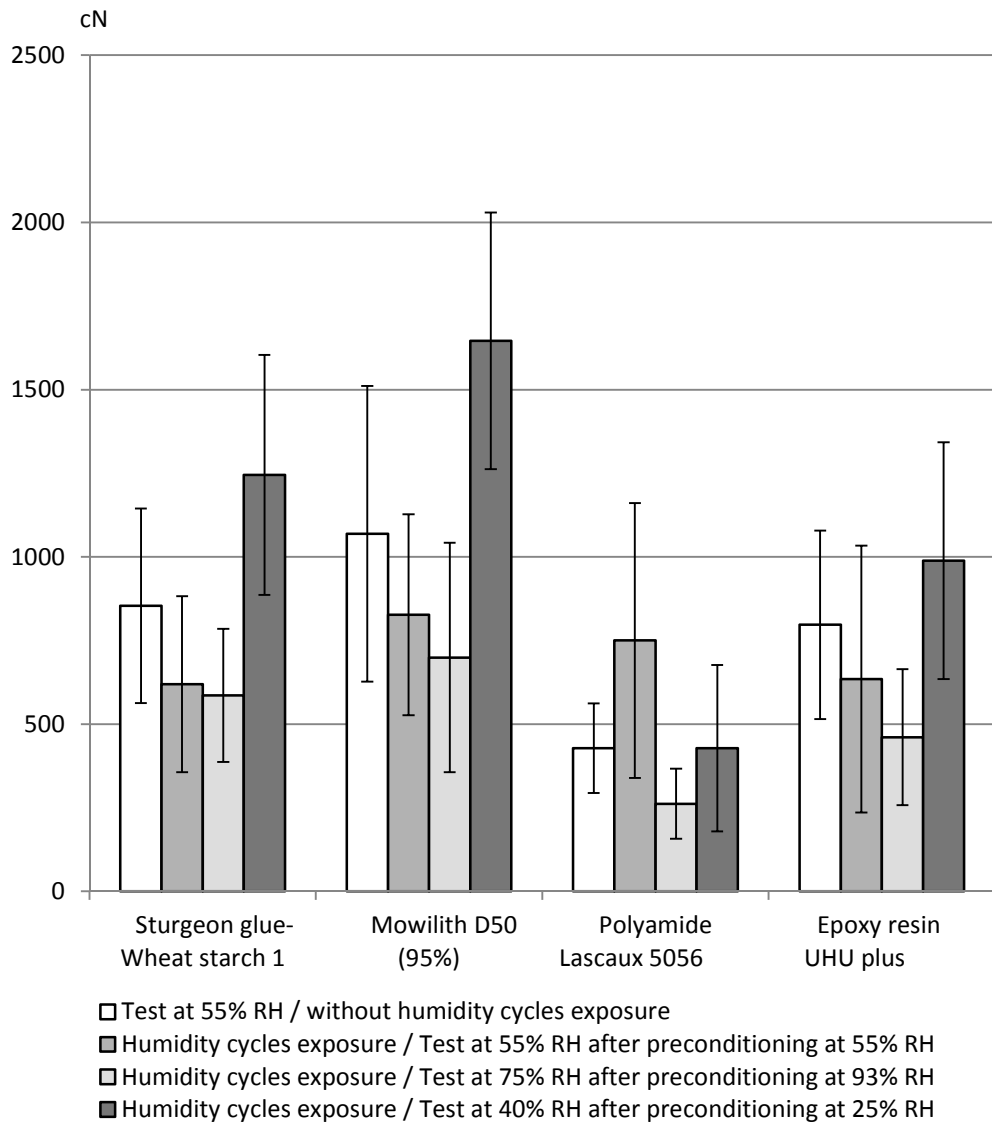


Figure 5. Linen - Ultimate tensile strength (arithmetic average and standard deviation) of four selected adhesives: tested at 55% RH without changing humidity exposure, after changing humidity exposure, tested at normal (55% RH), high humidity (75% RH) and under dry condition (40% RH)

Test Series 4: Linen - Natural and modified wheat starch

The approach of this test series was seeking to improve the qualities of the commonly-used SW1-mixture, a recipe developed by Heiber (2003). The quality of the wheat starch paste varied significantly depending on the method of preparation. The wheat starch paste should be prepared from scratch and mixed with the sturgeon glue daily. However, it is difficult to produce the necessarily small amounts of a homogeneous paste. Test results of 20% sturgeon glue mixed with 10% wheat starch pastes (except 13% Foodgel) clearly highlighted the importance of using a homogeneous mixture (see Figure 6). Lumps in all wheat starch pastes had a negative effect on the UTS of the tested joints.

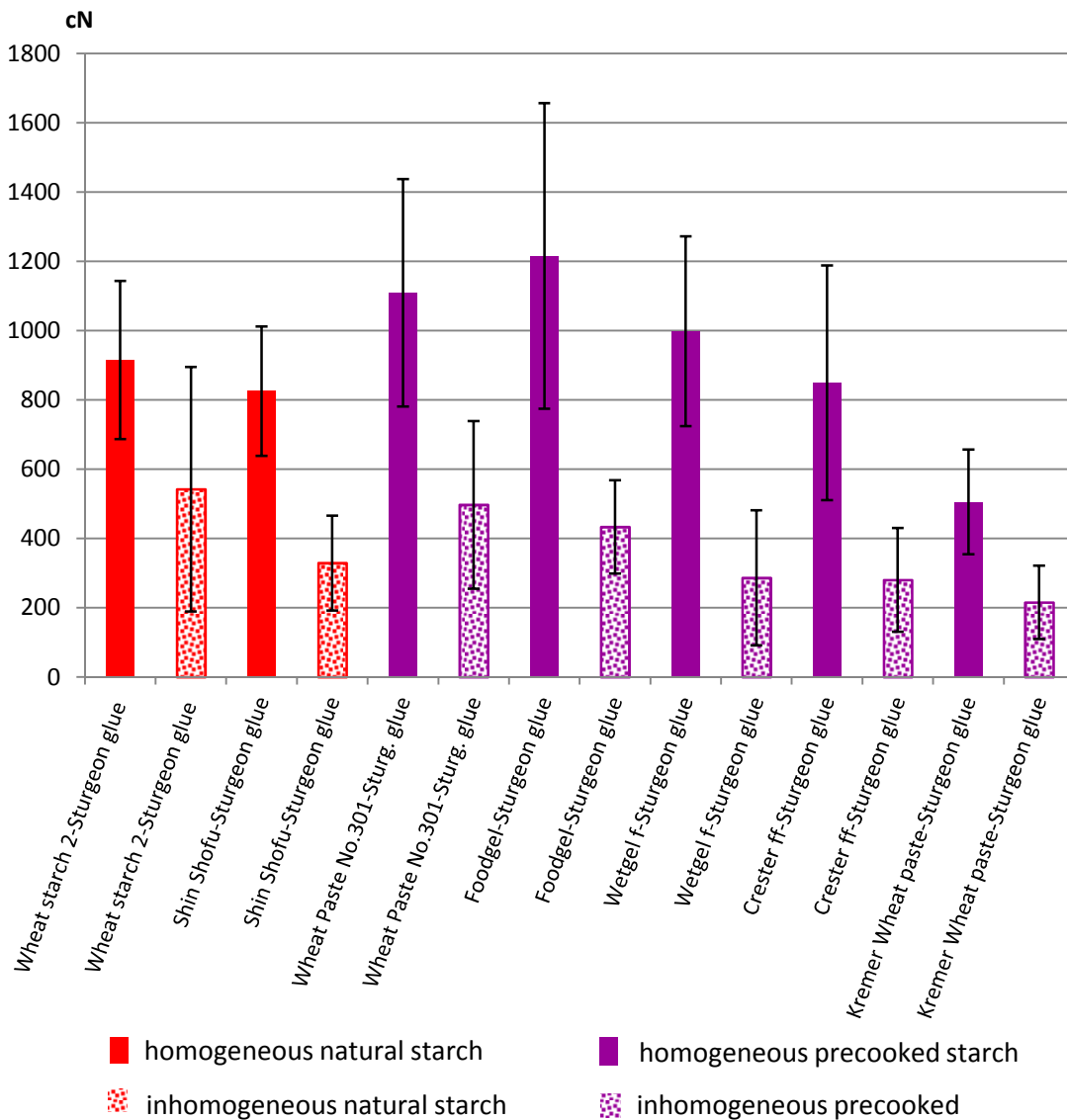


Figure 6. Linen - Ultimate tensile strength (arithmetic average and standard deviation) of homogeneous and inhomogeneous sturgeon glue-wheat starch mixtures (two natural and five precooked products) in comparison

Two natural wheat starches (W2: European product of Kleindorfer and Shin Shofu) and five different precooked wheat starches were investigated. Precooked wheat starches are not chemically changed. During the manufacturing process only the physical shape and condition of the wheat starch granules have been modified. As a result they are swellable in cold-water, in contrast to natural wheat starch (also called native wheat starch). Modified wheat starches have a high level of purity according to references. They also have the advantage of a fast and easy preparation. In Test Series 4 the starch powder was added to the water and stirred thoroughly with a kitchen hand mixer to allow an optimal dispersion. After approx. 2 minutes of swelling (except Foodgel which needed 15 minutes), the paste was passed through a thick nylon stocking (60 denier) twice. The result was a smooth and lumpless consistency.

Apart from tensile testing (see Figure 1), the workability and optical qualities after drying were examined. A survey of the properties indicated two products of precooked starches as appropriate alternatives to the commonly used wheat starches. The joints using Wheat Paste No. 301 or Foodgel, mixed to sturgeon glue, showed similar UTS results to those joined with Mowilith D50. Sturgeon glue mixtures with these two 13% wheat starch pastes were the best performers in test, followed by the 10% Gaylord paste mixture. Despite their relatively high viscosity, these three mixtures led to a sufficient wetting of the fibers. In addition, good initial setting (high tack) in combination with a short drying time enabled an efficient joining process. Only minimal color changes and gloss were observed on the surface of the joints after drying. Heiber had already described the addition of 13% natural wheat starch paste in his initial publication (Heiber 1996). According to the results of Test Series 4, the higher solid content of wheat starch paste seems to improve the UTS of the joints. Due to a low viscosity, long drying time without an initial setting and discoloration the products Wetgel f (13%), Crester ff (10%) and Kremer wheat starch (10%) showed less acceptable results. To a certain extent, it is possible to adjust the speed of drying and the penetration of the mixture to the condition of the threads, thus allowing more precise aligning of the fibers. Small variations of the starch concentration (10-13%) or an increase in the sturgeon glue content (ratio higher than 1:1) might be considered.

Tested under higher humidity (72% RH), the UTS values (arithmetic average values) of joints with sturgeon glue mixed with Wheat starch 2 were 11% lower than the examples tested in a normal climate at 55% RH, and 26 % lower in the case of the Foodgel mixture. A similar tendency was observed in Test Series 3 (Reuber 2010). The decreasing strength of hygroscopic mixtures may be attributed to a decreasing T_g value in high humidity (Horie 2010). The relatively small difference in the UTS between 55% and 72% RH could be explained by an increasing tackiness and a high affinity to the cellulose.

Test Series 5: Polyamide 6

During the testing process, 10 different adhesives were compared (see Figure 7 and Table 4). The choice of adhesives followed industrial recommendations for PA 6 (e.g. epoxy resin, PUR dispersion) and conservation guidelines in relation to the reversibility and aging properties of adhesives. Again, as all threads tore precisely at the joint, the results could be evaluated as properties of the adhesives. The highest UTS was reached with an epoxy resin (Araldite AY 103/HY 991), followed by a PVAc dispersion (Mowilith DMC2). In the middle range, we find the acrylic Paraloid B72, two acrylic dispersions (Primal AC33 and a mixture of Lascaux

360HV + 498HV), and a PUR dispersion (Alberdingk U325). Less stable joints were achieved by a SW1-mixture, Regalrez 1094, Klucel GF and Methocel A4M.

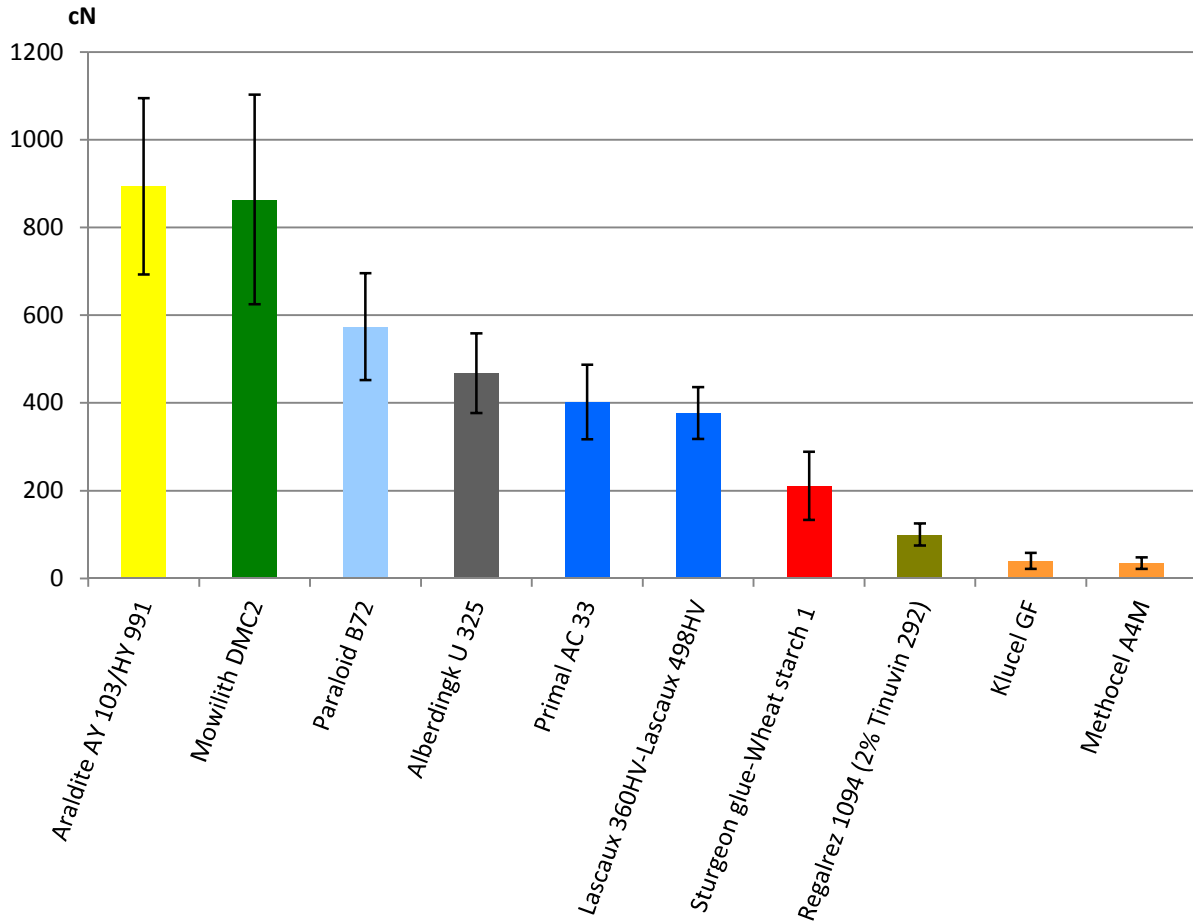


Figure 7. Polyamide 6 - Ultimate tensile strength (arithmetic average and standard deviation) of different adhesives

Table 4. Polyamide 6 - Ultimate tensile strength (arithmetic average, standard deviation and coefficient of variation) of different adhesives

| Adhesive | Arithmetic average (cN) | Standard deviation (cN) | Coefficient of variation (%) |
|------------------------|-------------------------|-------------------------|------------------------------|
| Araldite AY 103/HY 991 | 894 | 201 | 22 |
| Mowilith DMC2 | 864 | 239 | 28 |
| Paraloid B72 | 574 | 122 | 21 |

| | | | |
|------------------------------------|-----|----|----|
| Alberdingk U325 | 468 | 91 | 19 |
| Primal AC33 | 402 | 85 | 21 |
| Lascaux 360HV/Lascaux 498HV | 377 | 59 | 16 |
| Sturgeon glue-Wheat starch paste 1 | 211 | 78 | 37 |
| Regalrez 1094 (2% Tinuvin 292) | 100 | 25 | 25 |
| Klucel GF | 40 | 18 | 45 |
| Methocel A4M | 35 | 13 | 37 |

Discussion

Coefficients of variation (CV) between 19-52% were recorded in the Linen-tests, similar to the Polyamide PA 6-test values. All standard deviations were relatively high. Apart from the varying yarn strength (CV: 19%), the reasons for this can probably be found in minor changes in quantities of adhesive, in the intermingling of fibers as well as to the pressure applied during joining.

Linen

For linen, the most suitable adhesives, as far as UTS is concerned, were 20% sturgeon glue mixed with 13% starch pastes (Foodgel and Wheat Paste No. 301), Lineco, Evacon-R and Mowilith D50. So far, the two SW-mixtures remain the best performers according to the test results. Their advantages could be summarized as follows: a high UTS of joints caused by a good wetting of the fibers and penetration into the threads. These mixtures have a moderate viscosity, a relatively high solid content, a sufficient adhesion and cohesion and an expected high Tg value of approx. 40 °C at normal room climate (Horie 2010), which avoids creep under continuous load. They also showed a relatively good resistance to climate changes and high humidity. Their reversibility in warm water enables a re-opening of the joint and allows repeated attempts during the joining process and in the future. Other positive properties were their compatibility with other different adhesives, the neutral pH value and their positive visual properties (no darkening or gloss – nearly invisible). Finally their good workability can be attributed to adequate water content and a sufficient working time, which allow for precision work in the aligning of the fibers thread ends. Furthermore, they offer a fast initial setting as well as an appropriate drying time.

Mixtures of precooked starch products and sturgeon glue were able to result in bonds of a consistent high quality. This was due to the easy and reproducible paste preparation as well as their positive working properties in combination with sturgeon glue.

The pH-neutral dispersions Evacon-R and Lineco produced promising test results, due to high UTS of their joints, good handling and adequate working time. Their swellability in cold water is yet another advantage in terms of the reversibility. Their chemical compositions, response to

changing humidity and ageing properties need to be examined in detail, before they can be recommended for the use in tear mending.

For a complete understanding of the results one further fact should be pointed out. The UTS is an important parameter, it is but one among many others. The following underlines this complexity.

Visual appearance: JunFunori might be considered as a useful substitute for wheat starch in the sturgeon glue mixture, even though it may not be the best UTS performer. Joints made with this mixture appear almost invisible, due to its excellent optical properties.

Length and type of joint: Generally, it is rare to find an overlap of 1 mm in torn canvas paintings. An overlap of approx. 0.3-0.5 mm is more realistic (Heiber 1996). Furthermore, the type of joining has an influence on the strength of the joint. Due to the lack of fiber intermingling, epoxy resin UHU plus performed only moderately well in tests, but may well be considered a strong and useful adhesive for butt joints (Heiber 2003).

Thread material: Epoxy resin was the best performer of tensile tests with polyester yarn (Plötz 2002) and wax-impregnated linen threads (Plötz 2003).

Long-term behavior: The testing did not investigate the long-term behavior under a constant load or changing tension.

Tear mending: The UTS of joined single threads cannot be directly transferred onto mended tears. The comparison of joined threads and thread-by-thread mended tears in a fabric still has to be carried out in further tests. This remains the only way to apply the test results to the reality of torn paintings.

Polyamide 6

As a result of the tensile tests, a range of suitable adhesives for new PA 6 thread were revealed. The evaluation of adhesives should also take into consideration the aging of PA 6 and the associated embrittlement. According to its degradation, a PA6 thread sample from the early 1960's had a low UTS of 552 cN. Thus this value presents the maximum ultimate tensile strength for aged PA 6. Considering this maximum limit as well as the working properties and the appearance of the joints, there were just three adhesives of interest: Primal AC33, the Lascaux-mixture and the SW1-mixture. All acrylic dispersions showed a similar performance in tensile testing. The Lascaux mixture with its high butyl acrylate fraction has a high tendency to form cross-links. Adversely, the more stable ethyl methyl methacrylate Primal AC33 guarantees solubility even after longer aging periods and therefore should be preferred in conservation. Adversely Primal AC33 generates an acid pH value of 3.71 (Down et al. 1996) after long light aging. A low pH adhesive is a risk, because PA 6 is soluble in strong acids. The joints with the SW1-mixture had a lower UTS than the acrylic dispersions joints. Therefore this mixture should be used for very brittle PA 6 threads. In addition to a very good solubility, it offers better optical properties than the acrylic dispersions.

Conclusion

The aim of this study is to move towards a consensus about the preferred adhesives for tear mending in linen and PA 6. The investigations have shown that adhesive, original thread and type of joint have to be matched precisely, to optimize tear mending in paintings. No adhesive could reach the UTS of either new linen (except Lineco), nor new PA 6 thread. For linen, the mixtures of 20% sturgeon glue and 13% precooked wheat starch paste - especially Wheat Paste No. 301 and Foodgel - were the best performers in the overall evaluation. The pH-neutral dispersions Lineco and Evacon-R (based on ethylene vinyl acetate copolymers), have a high potential, although further material testing is essential before their introduction in painting conservation. The investigation also revealed two adhesives for aged PA 6 thread with general good tear mending properties. According to the UTS results the use of Primal AC33 was the best compromise.

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Materials and Suppliers

Adhesives

Alberdingk U 325: Alberdingk Boley GmbH, www.alberdingk-boley.de

Aquazol 500, Araldite AY 103/HY 991, Klucel GF, JunFunori, Lascaux 360 HV, Lascaux 498 HV, Lascaux Polyamide Textile Welding Powder 5065, Methocel A4M, Mowilith DMC2, Paraloid B72, Plexigum PG611, Plectol B500, Plectol D498, Primal AC 33, Regalrez 1094, Rice starch, Salianski Sturgeon Glue (isinglass), Tinuvin 292, Textilschweißpulver (Textile Welding Powder): Kremer Pigmente, www.kremer-pigmente.de

Beva D-8, Wheat Paste No. 301: Talas, www.talasonline.com

Beva D-8-S: C.T.S. S.r.l Altavilla Vincentina, www.ctseurope.com

Cresters ff, Foodgel, Wetgel f: Kröner Stärke, Hermann Kröner GmbH, www.kroener-staerke.de

Evacon-R: Conservation By Design, www.conservation-by-design.co.uk

Gaylord: Gaylord, www.gaylord.com (Monochrom, www.monochrom.com)

Shin Shofu, Wheat starch 2: Kleindorfer, www.gmw-gabikleindorfer.de

Mowilith D50, Mowilith DHS S1, Mowilith LD167: Celanese Emulsions GmbH, www.celanese.com

Neutral pH Adhesive: Lineco, www.lineco.com (Preservation Equipment Ltd, www.preservationequipment.com)

Plectol D360, Tylose MH1000: Deffner&Johann, www.deffner-johann.de

Plectol D540: Polymer Latex, www.polymerlatex.com

Wheat starch 1: Kumetat, www.kumetat-rpk.de

UHU plus schnellfest: UHU GmbH, www.uhu.de (Bauhaus, www.bauhaus.de)

Yarn materials

Linen yarn: H.D. Textil Trade GmbH, Volksgartenstrasse 85-89, 41065 Mönchengladbach, Germany

Enkalon 540 T (940dtex): Polyamide High Performance GmbH, www.polyamide-hp.com

Instruments

Insect pin 000 (0.25 mm, "Sphinx", black enamelled): Ehlert & Partner GbR, www.ehlert-partner.de

Weston dental explorer, double ended, cork screw: AF - Medical GmbH, www.af-medical.com

Transformer Engelbrecht WZ IV and Minor-hot needle: Deffner&Johann, www.deffner-johann.de

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