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The creep performance of bio-based and synthetic lining adhesives at different environmental conditions

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ABSTRACT

Canvas paintings are prone to environmental ageing. Hence, the structural conservation of canvas paintings may require lining, a process in which a secondary canvas is adhered to the reverse of the damaged original canvas to provide additional support. Choosing the optimum adhesive in combination with a lining method is crucial and yet challenging, as they should preferably be mechanically and chemically stable and reversible for at least 100 years. Comprehensive data on thermal and long term mechanical behaviour of prevalently used adhesives and their bonded assemblies to canvas is scarce and yet necessary to enable conservators for a proper choice of the materials in terms of durability. In this study, four prevalently used adhesives in the conservation of canvas paintings are investigated and their creep performance is evaluated and benchmarked at three different temperatures and environmental relative humidities (RHs). These adhesives are either bio-based (animal glue-starch paste and beeswax-dammar resin mixtures), or synthetic (BEVA® 371 and an aqueous Plextol™ D540/K360 dispersion mixture). Differential Scanning Calorimetry (DSC) technique is used to study the thermal transitions at different RHs. T-peel and lap shear tests are performed to determine the fracture behaviour and shear strength respectively. An in-house built creep set-up equipped with environmental control is developed which allows investigation of the mechanical creep for different canvas bonded assemblies. The results demonstrate the effects of temperature and relative humidity on the creep behaviour of lined canvases, which are related to their physical response. Moreover, the animal glue-starch paste shows the best creep mechanical performance for this application, while the Plextol™ acrylic dispersion mixture in combination with Mist-Lining is a better alternative when both environment and reversibility are considered.

1. Introduction

Past lining techniques aimed to strengthen, flatten, or consolidate oil, acrylic or tempera paintings on canvas by attaching a new canvas to the reverse of the existing one. Current practice provides individual solutions to separate problems. Lining has been a subject of research due to the rising questions regarding the ethics, impregnation and resulting optical changes of original materials, the stability and durability of the adhesives used, and the extent of the invasiveness of the procedure itself [1–5]. However, there is still a gap of comparable data on the physical and long term mechanical behaviour of prevalently used lining adhesives in different environments. This is important information to investigate in case some relaxations in regulations for the indoor climate of museums all around the world are to be considered in the future [6]. Ashcroft and Briskham noted that creep loading is a primary concern for adhesively bonded load carrying structures along with environmental conditions [7], while Papanicolaou et al. [8] showed that creep is one of the main causes of damage developments in the adhesive joints in composite structures. Generally, high relative humidity (RH) may lead to a reduction in the glass transition temperature (T_g) of hygroscopic polymers, and consequently lead to a decrease in their strength, stiffness values and increase in their creep strain.

Canvas paintings are prone to ageing due to the decay and embrittlement of the original canvas with time. During ageing, canvases often lose their mechanical strength and elasticity and become prone to tears. Degradation can originate from phenomena such as acidification,

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hydrolysis, swelling, or oxidation of canvas cellulose fibres [1]. As a result, many historic paintings on canvas go through a conservation procedure called lining to provide structural support [2,3]. During this procedure an additional canvas layer is adhesively bonded to the back of the original canvas to provide sufficient auxiliary structural support to the original laminate structure which includes ground preparation layers, paint, and (typically, temporarily removed) varnish layers (Fig. 1) [3,4].

A large variety of adhesive products has been adopted for the conservation of paintings on canvas [3,5,9,10]. These can either be natural or synthetic, studio formulated and engineered for the field, or commercially/industrially produced and water or solvent-based materials. From the 17th century onwards, various adhesive combinations have been used and the method adjusted over time according to geographical trends and responses to damages occurring during and after the lining process. Typically, aqueous mixtures of animal glue and flour mixtures (called glue-paste hereafter) were used, especially in the south of Europe. This adhesive and the application process often bring potential problems of shrinkage, mould growth, and reversibility of the procedure [11]. Somewhat later, introduced as an alternative to combat the damages caused by aqueous lining processes, combinations of beeswax and tree resins (e.g. Dammar), with frequent additions of Venice turpentine (called wax-resin hereafter) became popular for lining in Northern Europe and America. Early non-aqueous lining adhesives used solely beeswax, but additions of resins such as dammar were found to improve the mechanical properties [12]. These systems seemed impervious to moisture, though recent research has disputed this [1]. Since the 19th century, the impregnation and lining of the canvas paintings with wax-resin combinations has taken place, with the "Night Watch" in 1851 as one of the best-known examples. The 20th century saw the introduction of synthetic adhesives, such as Polyvinyl Acetate (PVA), though long-term stability issues meant that these fell out of use in the later decades.

The Greenwich lining conference in 1974 was the first major international conference where lining treatments and its consequences were discussed [13]. The adhesives used at the time for this purpose were mainly glue-paste and wax-resin [14]. As a result, Percival-Prescott, campaigned for reconsideration, to escape "*the lining cycle*", by devising non-lining alternatives or using non-impregnating lining adhesives. Such an adhesive formulation was developed by Gustav Berger in the late 1960s – early 1970s, called BEVA® 371 (an ethylene vinyl acetate multi-mixture adhesive) and introduced to the market in 1976 [15]. While designed as a heat-set adhesive, and also available for purchase cast as a film, this adhesive is frequently used above its melt temperature and impregnates both lining canvas and original. Bond strengths are high and reversibility is currently under question. In addition, amongst others, Vishwa Raj Mehra started to research, in the early 1970s, acrylic dispersion lining materials bonded without heat in a process called 'cold lining' [16]. Cold-lining is still practiced in Scandinavian countries. The Mist-Lining system, that evolved at Stichting Restauratie Atelier Limburg (SRAL) in Maastricht, The Netherlands by Jos van Och in the late 1990s, is an adaptation of this cold lining approach. The Mist-Lining technique is one of the application techniques used for this research. It is a minimally invasive cold lining technique by an adhesive nap bond, developed to stabilize paintings on canvas to obtain optimal reversibility. Though the question remains how the bridging adhesive will respond, in time, by changes in its environment.

This research studies the initial and long-term mechanical performance of four prevalent lining adhesive blends in different temperature and humidity environments in relation to their physical behaviour by Differential Scanning Calorimetry (DSC). The presented test results of this paper should assist conservators to make a more balanced adhesive choice in combination with the application method. It shows the importance of the influence of the environment on the long term mechanical performance of a lining adhesive. In conclusion, the environment, the application method, and ethics should all be considered in the adhesive selection process.

2. Materials and methods

The adhesive mixtures of glue-paste and wax-resin as applied to the canvas test samples were made and provided in the conservation atelier of SRAL based on formulations and methodologies as used in standard practice. All formulations were made during workshops comparing lining techniques given by Paul Ackroyd (National Gallery, London) and Kate Seymour (SRAL, author). The formulations used are studio made, except for BEVA 371, and represent those used at the National Gallery London, except for the acrylic dispersion mixture which is used at SRAL for lining paintings. Other formulations and variations exist, especially of the more traditional lining adhesives, glue-paste and wax-resin. The intention was to compare all four lining systems using the same mechanical-physical instruments, under the same conditions, thus providing a comparable data-set for all four adhesive types.

2.1. Materials

2.1.1. Canvas

The replica simulations of the original paintings consisted of primed artist linen canvases. As a reference canvas, a pre-ground medium rough (pure) linen canvas (Rijn Uni) purchased from Claessens, Belgium, with a density of (18 × 19 weft x warp yarns/cm)), and a height of 0.9 mm, was chosen.

The chosen lining textiles consisted of three different fabrics. All material combinations are listed in Table 1. Two traditional linen canvases were used: one with a closed weave (Libeco, Meulebeke, Begiun, 100% linen 5653 colour: ecru, 25 × 25 weft x warp (yarns/cm) and one with a more open weave (Libeco, Meulebeke, 100% linen P165, colour: ecru, 12 × 13 weft x warp (yarns/cm). Linen was chosen as it is typically/historically used as a lining fabric for the traditional studio adhesive formulations, and is also used for the 'Mist-Lining' Plextol™ adhesive mock-ups. The third canvas was a modern polyester canvas called Clipper (Maritex Europe BV, Mijdrecht, The Netherlands, 24 × 24 weft x warp (yarns/cm). Polyester canvases have been used as a lining

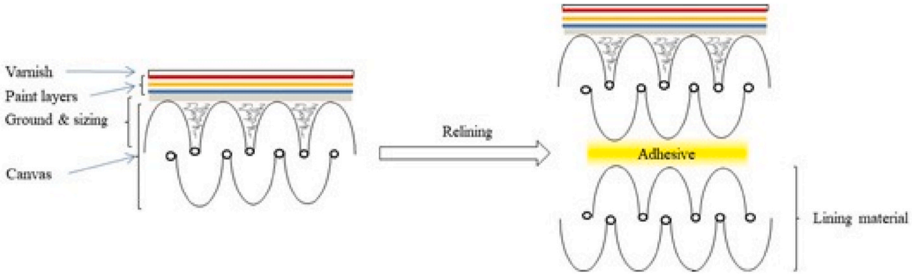

Fig. 1. The lining principle for an easel canvas painting. Left: the original canvas painting; Right: a lining canvas material is adhesively bonded (yellow coloured area) to the original painting.

Table 1
Overview of the researched combinations of plain weaved canvases and adhesives.

Adhesive	Replica painting	Thread count (weft x warp yarns/cm)	Lining canvas	Thread count (weft x warp yarns/cm)
All	Oil-primed, medium rough linen canvas	18 × 19	Oil-primed medium rough linen canvas	18 × 19
Glue paste	Oil-primed linen canvas 5653	25 × 25	Linen canvas 5653	25 × 25
Wax-resin	Oil-primed linen canvas P165	12 × 13	Linen canvas P165	12 × 13
BEVA® 371	Non-oil-primed linen canvas P165	12 × 13	Clipper canvas	24 × 24
Plextol™	Oil-primed linen P165	25 × 25	Linen canvas P165	25 × 25

support since the 1980s, especially when combined with BEVA® 371 O·F.

2.1.2. Adhesive formulations for lining

Four different thermoplastic formulations were used for the lining tests:

Glue-Paste (GP): The procedure followed that practiced at The National Gallery London. This mixture is composed of 2 g animal skin glue (Gosman en Kraan, 400 Bloom, through Peter van Ginkel Art materials, Arnhem, The Netherlands), 12 g wheat flour, and 72 ml water.

Wax-Resin (WR): The recipe used was a reheated version provided by The National Gallery, London conservators made at SRAL (2010). It consists of beeswax (granulate containing yellow flakes of beeswax, melting temp. 60–65 °C), dammar and gum elemi in the ratio: 3:2:1. All materials were sourced late 1990 from Gosman en Kraan, The Netherlands (now known as Gerstaecker, Maastricht, The Netherlands).

BEVA® 371 OF. (purchased 2015, CTS, Italy): This is one of the most established synthetic multi-purpose heat seal adhesives in art conservation, developed by Gustav Berger; a well-balanced multi-component mixture of two ethylene and vinyl acetates (EVA's), a tackifier, a plasticizer and a wax, with an activation temperature of 65 °C, first brought to the market in 1976 [2,13,14]. The content of ethylene in the copolymers amounts to 60–80%. The formulation of this adhesive has shifted due to discontinuation of the ingredients over time [2].

Plextol^{TM} mixtures (manufactured by Synthomer): acrylic based adhesives used in this study were prepared in a mixture of Plextol D540 (an aqueous emulsion of a methacrylic acid ester-/acrylic acid ester-copolymer) and Dispersion K360 (a thermoplastic acrylic aqueous dispersion) with two drops of thickening agent Rohagit SD15 (all materials were purchased at Kremer Pigmente, Germany). The main mixture used in this study consisted of a 30/70 vol ratio (unless stated otherwise). The effect of changes to the mixture content to 50/50 vol ratio can be found in the Supplementary data.

2.2. Methods

2.2.1. Application methods for lining

Different methodologies were used to come as close as possible to the standard practice for that type of lining, to adhere the secondary canvas to the reverse of the replica paintings.

Glue-Paste Lining: This lining technique was first recorded in the early-to-mid 17th century in France and Italy. It is still widely practiced especially in the South of Europe, although drawbacks are well disseminated [15]. The linen lining canvas was tightly loomed, washed and re-stretched. The front of the replica painting was faced with a sheet of Japanese paper adhered, in this case, with BEVA® 371 diluted with white spirit. The glue-paste was applied thinly, by hand, to the back of the replica painting and to the lining canvas. Subsequently, the lining canvas was placed on top of the replica's verso and the whole package flipped in order to work face-up. An absorbent paper was placed beneath the lining canvas. The front was ironed at about 45 °C, airing the structure at intervals until the adhesive bond was hand-tight solidified. This method is practiced at the National Gallery, London.

Wax-Resin Lining: The wax-resin lining was inspired by the preservation of mummies in the Egyptian tradition [16]. The wax-resin lining system was introduced in The Netherlands in the mid-19th century to combat the drawbacks relating to glue-paste linings, both during lining and as the lined painting aged [17]. It rapidly spread to become one of the most prevalent techniques to treat structural issues and a century later it was widely used throughout Europe, the USA, India, Australia and Far East. The front of the replica painting was faced with a sheet of Japanese paper adhered with, in this case, a diluted solution of wax-resin adhesive. The replica painting was loomed using paper tensioning strips to a working loom. The linen lining canvas was loomed on to a second stretcher larger than the working loom. The mixture was melted in an *au bain-marie* pan, and the warm wax-resin applied with a wide brush to both the reverse of the replica painting and that of the linen canvas (Fig. 2B) independently in small sections as it cools off quickly. Subsequently, each canvas was ironed at 60 °C, again independently to achieve an even layer of the applied adhesive (Fig. 2). The two canvases were then placed together, with the wax-resin applied surfaces facing each other. The painting surface was protected with sheets of paper and ironed until the wax-resin penetrated through to the front of the ground layer on the original canvas. This can be noticed by the darkening of the ground layer on the replica painting. The method employed is typical for wax-resin hand linings.

BEVA® 371 Lining: The polyester lining canvas was stretched on a working loom. The warm un-thinned adhesive was applied to the lining canvas by a roller to ensure an even layer. The reverse of the unstretched replica painting was placed on the BEVA® 371 layer of the lining canvas. The two canvases were placed together and put under vacuum before heat was applied. The lining process occurs on a heated vacuum table (Elkom GmbH) with a pressure of 55 mbar and a temperature of a heated table 68 °C. The pressure was retained until the heat had dissipated. The method employed is typical of working practice as described by Young and Ackroyd [18].

Plextol^{TM} Mist-Lining: which is a lining process where the lining adhesive forms a nap bond with both the lining and original canvases without impregnation of either (Fig. 2A). The spun-yarn lining canvas was stretched on a working loom larger than the replica painting. The size of the replica painting was marked on the lining canvas. The lining canvas was lightly sanded to enhance the nap. The acrylic lining adhesive (74 g/m^2) was sprayed on to the lining canvas in such a way that the adhesive droplets adhere only to the upstanding nap of the lining canvas and do not penetrate the lining canvas weave. The water content of the aqueous dispersion was allowed to evaporate. This procedure ensures an open network of adhesive material which can be regenerated, using appropriate solvent vapors. The lining canvas is placed behind the replica painting in an enclosed envelop. The activation solvent was introduced as a vapour in a controlled manner using a pre-set value (60 ml/m^2) by dampening a delivery cloth with a liquid solvent and placing it behind the lining canvas. In this case xylene was used. The two canvases were then pressed together (20 mbar) in a flexible low-pressure envelope consisting of two plastic sheets from which the air was extracted. This method was developed at SRAL by Jos van Och [19,20]. The result is a lining system in which the minimal amount of adhesive is required to avoid adhesive impregnation of either the original or lining canvases; an excellent starting position for de-lining. Besides this, it causes no shrinkage of the canvases nor resulting in colour changes of decorative layers. Furthermore, minimal weight is added to the lined system.

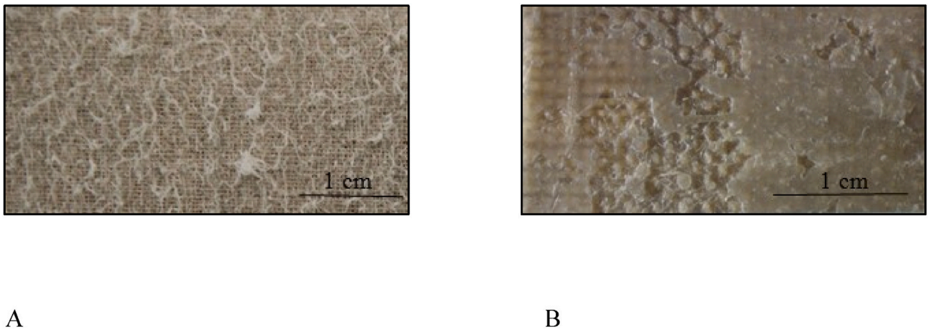

Fig. 2. (2A) Typical examples of the acrylic sprayed adhesive (PlextolTM) used in mist-lining prior to lining, and (2B) the heat-set wax-resin adhesive initially applied by brush.

2.3. *Differential scanning calorimetry (DSC)*

The identification of thermal transitions in relation to the RH is important, as the glass transition temperature (T_g) and softening or melting temperature (T_m) of the adhesives might change with RH. For this reason, differential scanning calorimetry technique (DSC) was used. DSC measurements were done on a TA Instrument DSC 250 equipment. The test samples weighed about 8 mg and were conditioned at 50% RH at 22 °C in a Weiss climate chamber for 72 h before being tested in a hermetically sealed aluminum Tzero pan, while an empty pan was used as reference. All measurements were performed in triplicate.

Samples from each adhesive mixture were prepared from brush-outs cast onto Melinex™ sheets. Each adhesive was subjected to a different temperature range profile depending on where the thermal transitions were expected to occur.

For glue-paste, the cooling cycle started at room temperature and the sample was cooled to −20 °C and held at this temperature for 5 min. Subsequently, the sample was heated up from −20 to 150 °C. The temperature was held at 150 °C for 5 min and cooled down to −20 °C. Subsequently this temperature was held for 5 min. Finally, the sample was heated to room temperature. A ramp of 10 °C/min was chosen for both heating and cooling cycles.

The wax-resin sample was initially cooled from room temperature to −60 °C and held at this temperature for 5 min. Next, it was heated from −60 °C to 150 °C and held at this temperature for 5 min and subsequently cooled down to −60 °C again. Then, the sample was heated up from −60 °C to room temperature. Similar heating and cooling cycles as for the wax resin were performed on BEVA® 371 and the Plextol™.

2.4. *Lap-shear*

Lap-shear tests were done at 20 °C, and 50% RH to determine the initial shear strength of the adhesives when bonded to the reference canvas, according to the ASTM D-1002-10 standard [21] with an overlap of 12.5 mm and a loading speed of 1.3 mm/min on a Zwick 20 kN tensile test machine using a 1 kN load cell for more accuracy. Test results were averaged from at least 3 measurements.

2.5. *Creep test*

The viscoelastic behaviour of polymers used in structural applications, such as lining, makes demands on their long-term physical stability, especially in an environment with variable temperature and RH. A test setup was built to determine the long term mechanical sensitivity of the adhesives in different environments. The design was based on a spring-loaded apparatus as described in the ASTM D2294 standard [22], but with the loading obtained by a variable weight (Fig. 3). The displacement of four sets of three stacked samples (Fig. 4) were measured independently by an Opto NCDT triangulation displacement sensor (Micro-Epsilon, Messtechnik, Germany) in a range of 20 mm with an accuracy of 4 µm. Every minute a data point was supplied to a computer database. The test setup was placed in a Weiss WK111 340 climate chamber (Weiss Technik, The Netherlands).

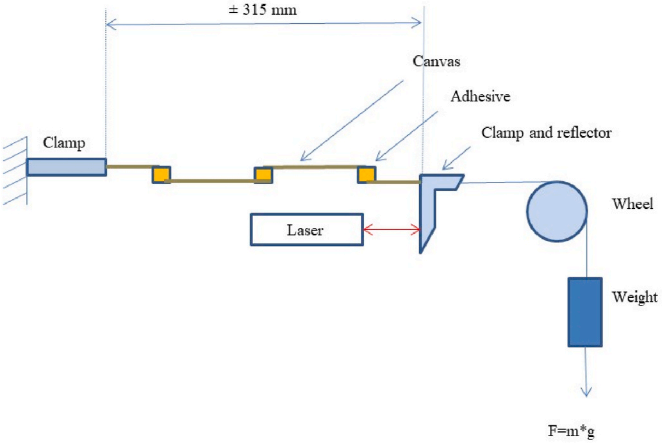

Fig. 3. Schematic representation of the creep test arrangement for the adhesively bonded canvases (Fig. 4). Sketch, not to scale.

The dimensions of the three stacked adhesively bonded samples are shown in Fig. 4. The sample sizes were based on ASTM D1002 [21] and ASTM D5656-04 [23] with an overlap of 5 mm for each of the three lap-shear samples measured in series.

2.6. *Creep measurements*

The long term process in stretched canvases (at constant strain) is primarily a relaxation process, while the mechanical behaviour of continuously loaded polymeric materials at constant stress (static fatigue) is governed by time-dependent rheological effects [24] during which the loading condition of the adhesives was chosen to be 7–10% of the maximum static failure load (Table 1).

A typical creep curve is shown in Fig. 5. It consists of three main stages: the primary creep (ε_0) with a diminishing slope, depending on the magnitude of the applied load either fully elastic or elastic-plastic. In the secondary stage, the strain rate ($\Delta\varepsilon/\Delta t$) or ε' shows a constant creep rate and a linear slope. This steady state creep behaviour is commonly attributed to a state of balance between the rate of generation of dislocations contributing to hardening, and the rate of recovery contributing to softening. Eventually, the tertiary part shows an accelerating creep rate, a strongly increasing strain, leading to micro-cracking, voids, necking and eventually failure, as has been extensively described in literature [24,25].

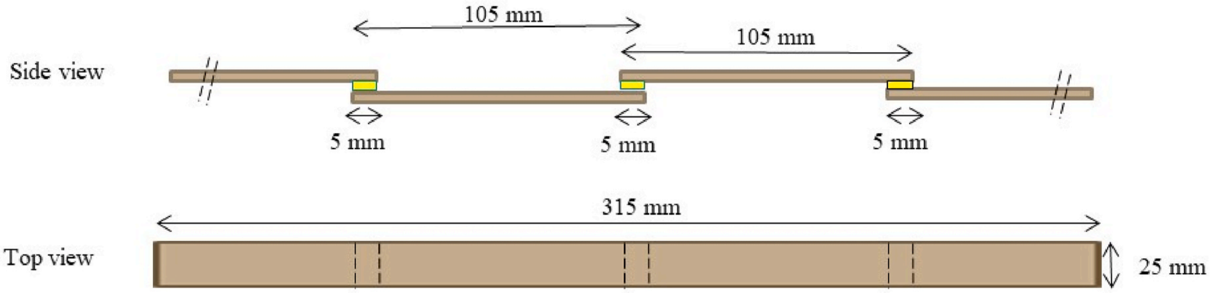

Fig. 4. The adhesively bonded canvases, showing the adhesive in yellow. Sketch, not to scale.

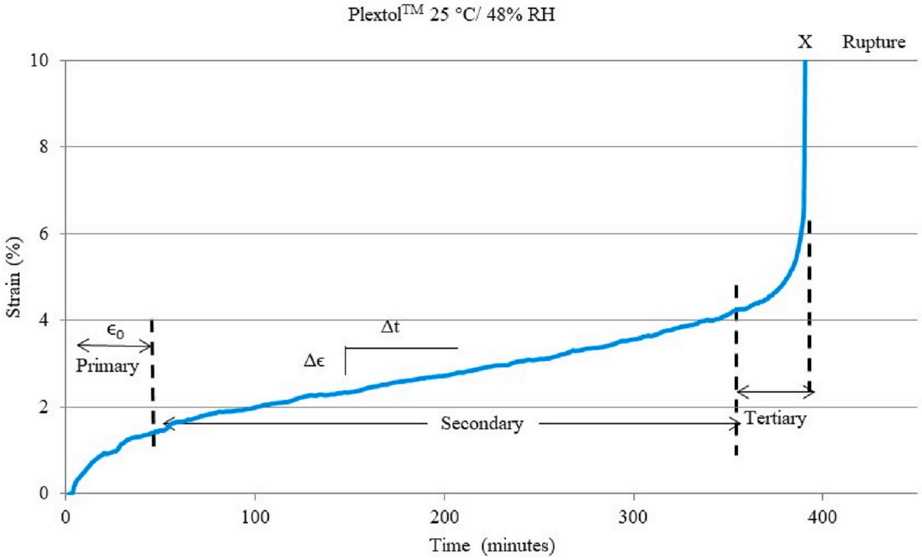

Fig. 5. The three main stages of creep (primary, secondary- and tertiary stage) shown in a typical measurement averaged from three individual canvas samples bonded by Plextol ™ exposed at 25 °C and 50% RH.

3. Experimental results

3.1. Moisture uptake of adhesives

Moisture ingress in polymers leads to plasticising, influencing their mechanical performance. For this reason, reference weight measurements were done. After a pre-exposure in a vacuum oven (4 days, 200 mbar, 30 °C), (Heraeus, The Netherlands) the adhesives were exposed to 6% RH at 25 °C. After weight stabilisation, the moisture ingress during exposure in a Weiss WK111 340 climate chamber at 50% RH and 97% RH (25 °C) was determined by measuring two film samples of each adhesive (approximately 100 mg each) 5 times on a Mettler Toledo AB2024-S weight balance (accuracy 0.1 mg).

The data (Fig. 6) show that wax-resin and (to a lesser extend) BEVA® 371 are hydrophobic, while glue-paste was found to be the most hydrophilic. The average weight increase of the 30/70 v/v Plextol ™

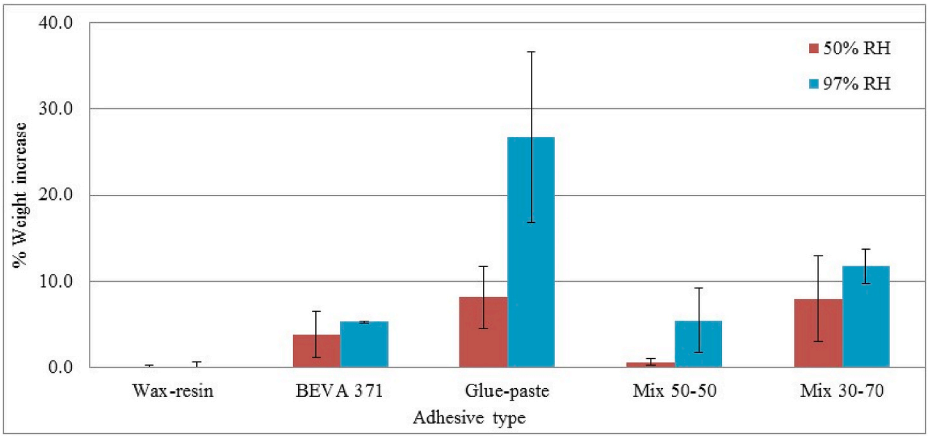

Fig. 6. Percentage of weight increase relative to the exposure at 6% RH, 25 °C.

mixture showed it to be significantly more hydrophilic than the 50/50 v/v mix, showing the large sensitivity of the K360 dispersion with a lower T_g and lower molecular weight to moisture. These results are in line with the mechanical results (Supplementary data).

3.2. *Differential scanning calorimetry (DSC)*

Moisture ingress in the adhesive leads to a decrease of the T_g, and modulus of elasticity, which might result in premature failure during static loading [24]. Hence, DSC analyses were carried out in order to identify the glass transition temperature(s) (T_g), the melting temperature (T_m) including the melting enthalpy of the adhesives after exposure to three different humidity environments.

The DSC data are shown in Table 2. Glue-paste in the dry environment at ambient temperature manifests itself as a glassy state. Hence, it appears as a more brittle material and it contains partially renatured triple helices, originally present in collagen structure before hydrolysis and transforming to gelatine. According to Yakimets et al. [26], the stage with a RH between 10% and 40% is related to the highest triple helix content, and the highest stress and strain at break, as water stabilises the triple helices. Slightly increasing the water content will generate plasticity, resulting in a reduction of T_g and T_m (Table 2). At 80% RH, water molecules are a free water fraction of the dry mass, transferring the skin glue from the glassy into a rubbery state [26,27].

The wax-resin samples being completely amorphous, as a result of its short molecules with little interaction, did not show a T_g. The melting curve showed two peaks instead of one, the lower one being substantially lower than the visually observed melting point at 60 °C, in line with Robert Buchwald's observations [28]. No measurable penetration of water molecules into its wax-resin structure was visible (Fig. 5) and no essential changes in either the melting temperature T_m or melting enthalpy became visible at the DSC measurements.

Table 2
DSC data including the Glass transition (T_g), melting temperature (T_m), the melting temperature range and the melting enthalpy for the tested adhesives at three ranges of RH, "—": no thermal transition identified.

Adhesive type	Environment	T_g °C	T_m °C	T_m range °C	T_m enthalpy J/g
Glue-paste	dry	–	–	–	–
	50% RH	47.5 ± 0.5	85.0 ±o	77.0 ± 0–97.0 ± 1	2.6 ± 0.2
	80% RH	–	55.0 ± 1	45.0 ± 0–65.0 ± 3	3.8 ± 0.3
Wax -resin	dry	–	48.0 ± 0 and 60.0 ± 0	26.0 ± 0–65.0 ± 0	144.0 ± 2
	50% RH	–	47.0 ± 0 and 60.0 ± 0	27.0 ± 0–63.0 ± 1	140.0 ± 3.5
	80% RH	–	48.0 ± and 60.0 ± 1	27.0 ± 1–62.0 ± 0	132.0 ± 2
BEVA® 371	dry	−22.0 ± 1	57.0 ± 0 and 65.0 ± 0	29.0 ± 0–97.0 ± 1	82.0 ± 1
	50% RH	−28.0 ± 0.5	56.0 ± 0 and 65.0 ± 1	29.0 ± 0–97.0 ± 1	75.0 ± 2
	80% RH	−28.0 ± 0.6	56.0 ± 0 and 65.0 ± 2	29.0 ± 0–98.0 ± 0	82.0 ± 4
Plextol ™	dry	−29.0 and 30.0 ± 1	55.0 ± 1	48.0 ± 0–62.0 ± 0	2.2 ± 0
	50% RH	−30.0 and 25.0 ± 2	55.0 ± 1	43.0 ± 2–56.0 ± 2	3.0 ± 0.6
	80% RH	−31.0 and 27.0 ± 3	–	–	–

BEVA® 371 showed only one T_g. It hardly absorbs moisture (Fig. 5) and accordingly no essential changes in T_g, T_m or melting enthalpy were found after exposure to high RH at the DSC measurements.

The Plextol™ 50/50 v/v mixture hardly showed any substantial change in its T_g's although some moisture uptake did take place (Fig. 5). Like most immiscible polymer blends, each polymer kept its own individuality, resulting in two T_g's with the T_g of the K360 as the lowest one (Supplementary data). The identified weight increase, due to moisture uptake, and as a result the T_g reduction, was further enlarged with the increase of the K360 component in the Plextol™ mixture and it is expected to reduce the mechanical properties even further.

3.3. *Lap shear tests*

Lap shear tests of the adhesives bonded to the reference canvas were done as a first indication of the apparent shear performance of the adhesives.

The stress-strain curves are presented in Fig. 7, averaged from 3 individual measurements. All adhesives showed a low modulus of elasticity, ranging from 1.5 E−3 MPa (Plextol™ mixture) to 6.3 E−3 MPa (wax-resin). Glue-paste and BEVA® 371 showed the highest deformation capacity and failure strength, but showing a relatively brittle failure, as they tended to penetrate into the canvas textile, leading to mechanical interlocking. This is in contrast with wax-resin, which fully impregnated the canvas (Fig. 2B), but also showed the highest internal polymer toughness. Plextol ™ showed the lowest modulus, plasticity, failure strength, and by far the lowest strain to failure. The yield strength of all adhesives is far below 0.1 MPa. This was expected, as with the mist-lining system, the adhesive does not penetrate into the canvas structure and thus facilitating de-lining. Table 3 shows the ultimate shear stress of the discussed adhesives, and the load (7–10% of the ultimate shear stress) for the creep test.

3.3.1. *Creep measurements as a function of temperature and RH*

All polymers tend to creep upon loading, especially thermoplastic non-*cross* linked ones; polymer chains start uncoiling and begin to slip past each other when a constant load is applied. Continuous stress levels combined with the absorption of moisture (Fig. 8) and/or temperature elevations (Fig. 9) increased creep phenomena [24]. This included an increased instantaneous strain, ε_0 and an increased strain rate, ε' at either a higher RH and/or temperature, (Fig. 10).

The creep performance of Plextol™ (30/70 v/v of D540/K360 respectively) samples at 3 temperatures and two RH's at the same loading condition is shown in Fig. 9. This graph clearly shows the large sensitivity to both variables and is in accordance with the above.

The overall creep data of the adhesives tested at different temperatures and RHs have been combined in Table 4. The presented data are the averaged values from at least 3 separate measurements. Results show the creep resistance at 7–10% of the averaged ultimate shear stress of the lap-shear joints (Table 3) around, and up to "extreme" museum conditions [29]. Showing the deformation of the samples as a function of time up to a limit of 11,200 min, due to practical time restrictions.

Glue-paste joints performed best at museum conditions (25 °C, 50% RH) showing the best failure properties, the highest loading of all and the least strain, even at higher temperatures. Plextol™ and wax-resin performed critical, being the most temperature and moisture sensitive, with wax-resin failing after the shortest time at the higher test temperature, which is not surprising with a T_m of 25 °C. However, it is insufficient to solely use these results as the only selection criterion for a lining adhesive, as reversibility should also be taken into account [9,10,30].

The influence of the temperature and RH on the mechanical performance of the adhesives was found to be strongly related to the

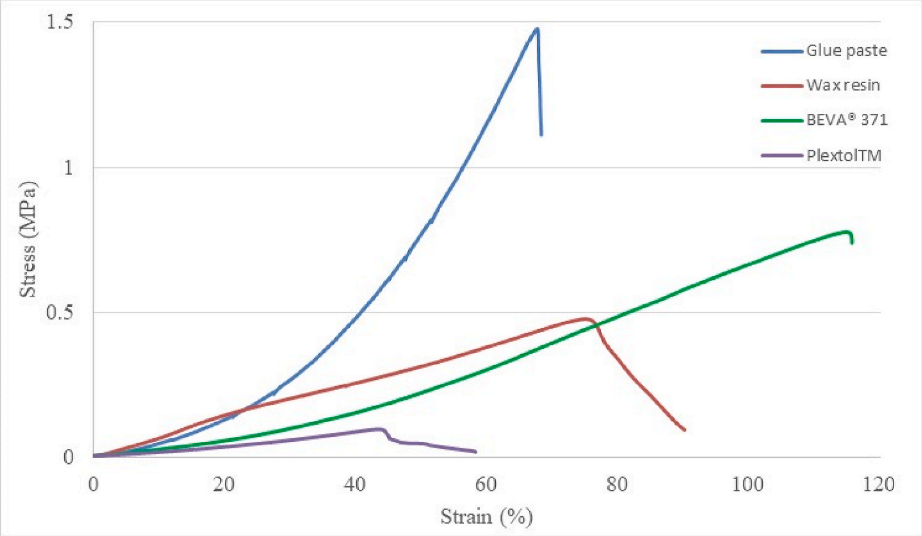

Fig. 7. Averaged stress – strain curves of canvas lap shear joints (20 °C, 50% RH).

Table 3
Lap shear test values, including standard deviation (STD).

Adhesive	Ultimate Stress (Mpa)	STD	Creep load (N)	Failure type
Glue-paste	1.42	0.22	40.0	100% Cohesive in adhesive
Wax-resin	0.39	0.17	16.0	100% Cohesive in adhesive
BEVA® 371	0.62	0.23	20.0	75% Cohesive in adhesive/ 25% Interfacial
Plextol™	0.20	0.03	6.0	100% Interfacial

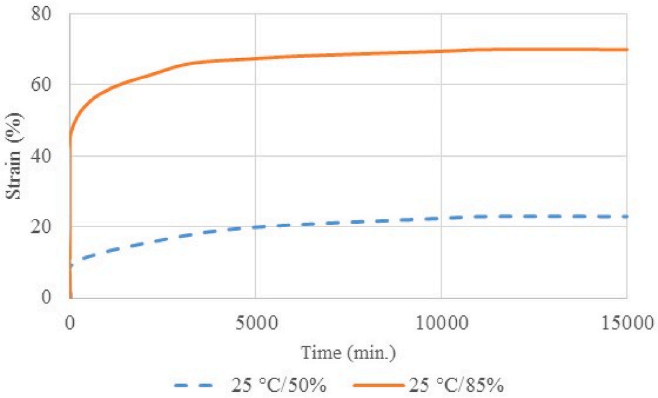

Fig. 8. Two typical measurements of BEVA 371® at 50 and 85% RH, at the same temperature (25 °C) and loading conditions.

polymer type (Fig. 10). Increased molecular weight, crystallinity (such as glue-paste) and/or bulky side groups tend to restrict the chain flexibility and movement, hence resulting in increased viscosity, T_g, elastic modulus, and creep resistance (BEVA® 371). The sensitivity in the secondary creep rate with an increased RH from 50 to 85% at 25 °C was limited for all adhesives (except Plextol™), showing the limited sensitivity to plasticisation with water. However, a temperature increase of 10 °C at 50% RH significantly increased the average secondary creep rate of the adhesives (except glue-paste) leading to an intermediate failure of the wax-resin samples as a result of approaching the melting temperature due to a loss of cohesive strength (or denaturation temperature as in the case of glue-paste). Aggravated even more when both temperature and RH were increased. The results showed that BEVA® 371 is the least effected when both moisture and temperature were increased.

The obtained effects are in-line with the DSC data and moisture uptake measurements (Fig. 6); BEVA® 371 and wax-resin, being hardly sensitive for moisture ingress, and wax-resin being sensitive to higher temperatures.

3.3.2. *Failure types*

The percentage and types of failures of the creep tests were very much the same to those found at the lap shear tests (Table 3). This implicates, that only the mist-lined samples failed 100% adhesively near to the canvas interface, as a direct result of this type of application method. All the other application methods lead to a (more) cohesive type of failure.

4. Conclusions

The aim of this study was to understand and benchmark the physical and long term mechanical creep performance of four prevalently used adhesives in canvas lining for preservation of cultural heritage. For this reason, the physical response (moisture uptake, T_g,T_m and melting enthalpy) and creep performance of these four adhesives at combinations of environmental conditions (temps: 25, 35 and 45 °C and 6%, 50% and 85% RHs) were investigated.

Glue-paste demonstrated the best creep performance at the measured environmental combinations. DSC measurements confirmed this temperature sensitivity, with the T_g for glue-paste being above 48 °C, whilst all other adhesives show lower thermal transitions. Mechanical sensitivity increases at high temperature in combination with high RH.

The mechanical performance of wax-resin was found to show a rather high ductility and to be rather independent of the RH, but to be the most sensitive to temperature increase.

BEVA® 371 showed the highest ductility at room temperature and the least influence of moisture ingress and temperature changes up to 35 °C after which temperature it quickly starts to lose its mechanical strength.

The amorphous low molecular weight acrylic co-polymer Plextol™ mixtures showed the lowest ductility and a low modulus of elasticity during static tests. It had a rather high, but rather stable viscous creep up to higher temperatures, independent of the RH, but with adhesive failure as a result of the application technique.

Temperature was found to be the variable that had the highest influence on the mechanical performance of the tested adhesives. The

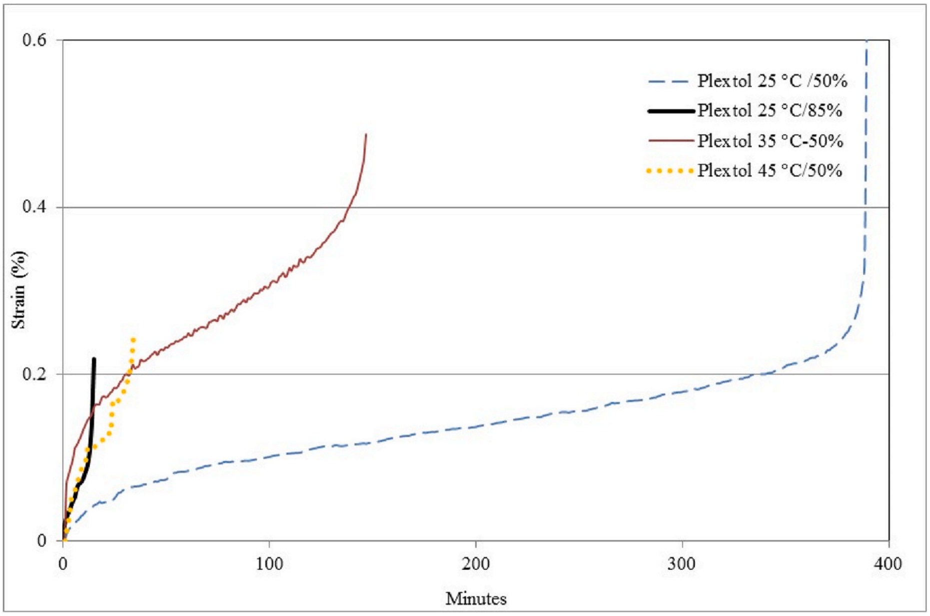

Fig. 9. Typical influence of RH and temperature on the creep performance of Plextol™.

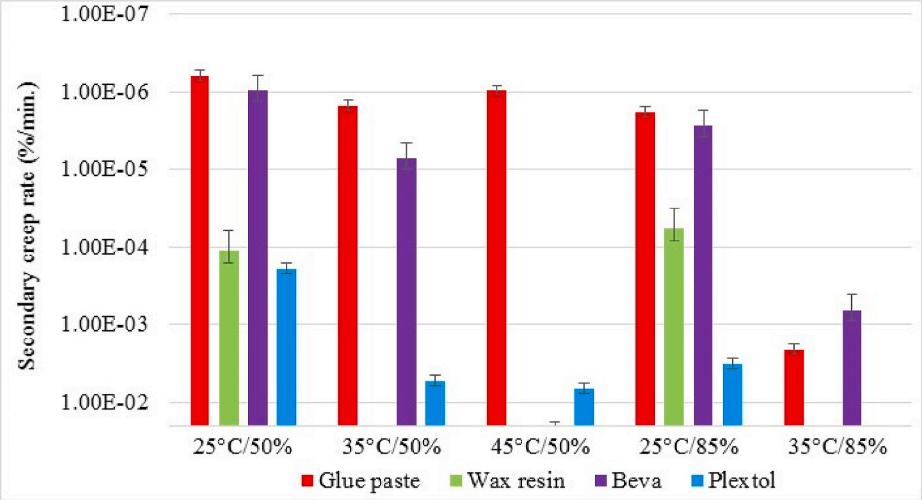

Fig. 10. Comparison of the secondary creep rate, ε' of the tested adhesives in 5 different environments at a loading of 10% of the static failure. Please note the logarithmic scale on the vertical axis.

Table 4
The creep performance (percentage adhesive strain and time to failure) including loading condition at different temperatures and RH. The time to failure is given, if it occurred within 11,200 min. Otherwise, the strain after 11,200 min is presented. The data shown in green belong to non-failed samples, those in red to failed samples. n.a: not applicable.

Adhesive type/Loading	25 °C/50%		35 °C/50%		45 °C/50%		25 °C/85%		35 °C/85%	
Glue-Paste (40 N)	no failure		no failure		no failure		no failure		Cohesive failure in adhesive	
Max. Strain/Time to failure	10.7%	11,200	13.1%	11,200	17.2%	11,200	26.4%	11,200	30.1%	48 min.
Wax-Resin (16 N)	Cohesive failure in adhesive		Cohesive failure in adhesive		Cohesive failure in adhesive		Cohesive failure in adhesive		Cohesive failure in adhesive	
Max. Strain/Time to failure	29.0%	5800 min.	59.0%	1.7 min.	n.a.	0.02 min.	47.5%	3279 min.	29.5%	1.6 min.
Beva ® 371 (20 N)	no failure		Cohesive failure in adhesive		Cohesive failure in adhesive		no failure		Cohesive failure in adhesive	
Max. Strain/Time to failure	22.0%	11,200	43.2%	9124 min.	28.0%	3 min.	71.3%	11,200	17.4%	3000 min.
Plextol™ (6 N)	Adhesive failure		Adhesive failure		Adhesive failure		Adhesive failure		Adhesive failure	
Max. Strain/Time to failure	50.0%	387 min.	38.0%	197 min.	28.0%	34 min	17.0%	15 min.	21.0%	1.5 min.

effect of RH on the mechanical long-term performance is found to be substantial, especially in combination with increasing temperature. Hence, the results allow conservators to make better informed decisions choosing lining adhesives, as their selection criteria can now also include long-term mechanical performance data.

For lining purposes, the mechanical performance of the lining adhesive is not the only selection criterion when choosing an adhesive. Different lining application technologies were applied for this research, which resulted in different failure types. One such technique; mist-lining, makes up for an excellent starting point in terms of reversibility. Combined with the right mechanical behaviour of the adhesive, this would be a potential technique in accordance with reversibility. It is unfortunate that these adhesives are short-lasting on the market as manufacturers frequently change or discontinue acrylic dispersion formulations.

In addition, while it is useful to compare the values obtained in this study directly, it should be noted that the formulations of the adhesives used in practice will vary according to geography and time of the application. Performance related values of lined paintings are thus extremely difficult to equate with each other. This study aimed to present a comparison of a known set of representative formulations using the same testing environments. The data and results can be classified in trends and thus used to relate to real case studies.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijadhadh.2022.103119.

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