PRELIMINARY STUDY ON THE ADHESIVENESS PROPERTIES OF HIDE GLUE

Lucreția MIU*, Mihaela NICULESCU

National Research &Development Institute for Textiles and Leather – Division: Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, 031215, Romania, lucretiamiu@yahoo.com

Received: 13.05.2022 Accepted: 24.06.2022 https://doi.org/10.24264/lfj.22.2.7

PRELIMINARY STUDY ON THE ADHESIVENESS PROPERTIES OF HIDE GLUE

ABSTRACT. Adhesives based on collagen extracted from the skin, tendons, cartilage, bones of animals and fish have been widely used over time as binders and consolidating agents for various organic and inorganic materials. The use of these types of adhesives or glues or gelatins in the restoration activity has been practiced by restorers due to their properties, but also to the special requirements of reversibility of treatments that are stipulated in national and international norms specific to the restoration of heritage objects. For this purpose, the technology of gelatin extraction from bovine hide was studied, and then gelatins were characterized in terms of chemical properties (ash, total nitrogen, amino nitrogen, dermal substance, pH of analytical solution) and gluing experiments were conducted on collagen substrates (leather and parchment, newly made specifically for the restoration activity and some samples of historical parchment, pieces of parchment detached from the back of a heritage object) and characterized in terms of physical-mechanical properties (shear strength and peel strength). Gelatins made from bovine hide were also compared to a commercial product, rabbit glue, a material frequently used in the field of restoration.

KEY WORDS: raw hide, glue/adhesive, gelatin, wood restoration, book restoration, parchment restoration

STUDIU PRELIMINAR PRIVIND PROPRIETĂȚILE DE ADEZIVITATE ALE CLEIULUI DIN PIELE

REZUMAT. Adezivii pe bază de colagen extras din piele, tendoane, cartilagii, oase ale animalelor și peștilor au fost utilizați de-a lungul timpului, pe scară largă, ca lianți și consolidanți pentru diverse materiale organice și anorganice. Folosirea acestor tipuri de adezivi sau cleiuri sau gelatine în activitatea de restaurare a fost și este practicată de către restauratori datorită proprietăților acestora, dar și cerințelor speciale de reversibilitate a tratamentelor care sunt stipulate în normele naționale și internaționale specifice restaurării obiectelor de patrimoniu. În acest scop s-a studiat tehnologia de extracție a gelatinelor din piei bovine, s-au caracterizat din punct de vedere al proprietăților chimice (cenușă, azot total, azot aminic, substanță dermică, pH soluție analitică) și s-au experimentat probe de lipire pe suporturi colagenice (piele și pergament, nou realizate special pentru activitatea de restaurare și niște probe de pergament istoric, bucăți de pergament detașate de pe partea de verso a unui obiect de patrimoniu), apoi s-au caracterizat proprietățile fizico-mecanice (rezistența la forfecare și rezistența la dezlipire). Gelatinele realizate din piele bovină s-au testat comparativ și cu un produs comercial, clei de iepure, material utilizat frecvent în domeniul restaurării.

CUVINTE CHEIE: piele crudă, clei/adeziv, gelatină, restaurare lemn, restaurare carte, restaurare pergament

ÉTUDE PRÉLIMINAIRE SUR LES PROPRIÉTÉS ADHÉSIVES DE LA COLLE DE PEAU

RÉSUMÉ. Les adhésifs à base de collagène extrait de la peau, des tendons, du cartilage, des os d'animaux et de poissons ont été utilisés au fil du temps, à grande échelle, comme liants et consolidants pour divers matériaux organiques et inorganiques. L'utilisation de ces types d'adhésifs ou de colles ou de gélatines dans l'activité de restauration était et est encore pratiquée par les restaurateurs en raison de leurs propriétés, mais aussi des exigences particulières de réversibilité des traitements qui sont stipulées dans les normes nationales et internationales spécifiques à la restauration des objets de patrimoine. À cet effet, la technologie d'extraction des gélatines de peaux de bovins a été étudiée, et on a caractérisé les gélatines en termes de propriétés chimiques (cendres, azote total, azote aminé, substance dermique, pH de la solution analytique) et on a testé leur adhérence sur des substrats en collagène (cuir et parchemin, nouvellement fabriqués spécialement pour l'activité de restauration et quelques échantillons de parchemin historique, morceaux de parchemin détachés du dos d'un objet patrimonial) et on a caractérisé leurs propriétés physico-mécaniques (résistance au cisaillement et au détachement). Les gélatines à base de peau bovine ont également été testées en comparaison avec un produit commercial, la colle de peau de lapin, un matériau fréquemment utilisé dans le domaine de la restauration.

MOTS CLÉS : cuir brut, colle / adhésif, gélatine, restauration de bois, restauration de livres, restauration de parchemins

INTRODUCTION

Adhesives or glues of animal origin are the adhesives with the oldest historical record of use [1]. Evidence of their use dates back to at least 1350 BCE and, indeed, animal glue was used to glue wood decorations to the tomb of King Tutankhamun [2]. Animal glues are water-based adhesives that use gelatin protein as an adhesive polymer. Gelatin is the same material used in the food and pharmaceutical industry. It is produced industrially by the chemical treatment (hydrolysis) of collagen protein contained in the skins and bones of mammals [1, 2].

Simple mixtures of gelatin (skin glue) and water have been used in woodworking for thousands of years and in binding books for at least 200 years. Modern animal glues contain not only gelatin and water, but also performance modifiers such as plasticizers, sugars, salts, surfactants, antifoams and biocides. The performance of modern formulations of these

* *Correspondence to: Lucreția MIU, National Research &Development Institute for Textiles and Leather – Division: Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, 031215, Romania, lucretiamiu@yahoo.com*

glues is much improved compared to the simple gelatin/water mixtures of the past [3-5]. The formulations are adapted to each application by changing parameters such as adhesion level, bonding time and viscosity.

In bookbinding, animal glues are used in the manufacture of cardboard cases, covers and flyleaves. The major advantage of animal glues and the reason why they are still used 70 years after the appearance of synthetic adhesives, is that they have an excellent initial wet adhesion. In other words, when applying an adhesive film with animal glue, it is immediately very sticky. This property allows the use of animal glues when a glued turned edge is needed, in bookbinding and in restoration. Animal glues form only mechanical bonds. This means that they adhere well to porous surfaces, but poorly to some coatings and all non-porous substrates, such as metals and plastics. Glues of animal origin are obsolete in certain situations by synthetic adhesives, but persist due to their unique property of excellent moisture adhesion and reversibility of gluing (specific requirement of the restoration-conservation activity), which remains unmatched by any aqueous synthetic adhesive.

EXPERIMENTAL

Materials and Methods

For this study, raw bovine hides were processed to obtain leather tanned with vegetable tannins and raw calfskins and goatskins to obtain parchments. For this, raw materials specific to the leather industry were used, but the special requirements of the restoration field were also taken into account. Bonding tests were also performed on historical parchment samples.

Gelatin or adhesive made and tested in this study was obtained from bovine hide waste.

The investigation methods included chemical methods to characterize the resulting gelatins and physico-mechanical methods to characterize the adhesive strength of these gelatins when gluing leather and parchment.

The technology for gelatin extraction from bovine hide was experimented (protected by patent application) in acid medium, at a pH lower than the isoelectric point:

Stage I: Weighing residual fragments of untanned bovine hide. Dosing the float, water at 70°C, solid/liquid ratio of 1:3, thermostating at 70°C, stirring for 60 min. at 70°C.

pH adjustment with formic acid 25%, to 4.5-5.0, stirring for 4 hours at 70°C.

Quantitative filtration at 70°C, decanting, cooling to 4-6°C for 14-16 hours.

Collection of the first gelatin fraction, with homogenous appearance: GC1

Stage II: Dispersion of residue from the first stage (filtration and decantation residue), in water at 85°C, solid/liquid ratio of 1:2, thermostating at 85°C, stirring for 3 hours.

Quantitative filtration at 85°C, decanting, cooling to 4-6°C for 14-16 hours.

Collection of the second homogenous gelatin fraction: GC2.

Stage III: Dispersion of residue from the second stage (filtration and decantation residue), in water at 95°C, solid/liquid ratio of 1:1, stirring for 3 hours at 95°C. Quantitative filtration at 95°C, decanting, cooling to 4-6°C for 14-16 hours, collection of the third gelatin fraction: GC3.

Figure 1. The extraction process in progress

For this study, leather and parchments were prepared using technologies inspired from ancient recipes at the Leather and Footwear Research Institute (ICPI) of the National Research and Development Institute for Textiles and Leather (INCDTP), Bucharest. In the current technological process of parchment manufacturing, skins preserved by salting [6-8] were used.

Characterisation of Gelatins Extracted from Solid Waste Generated during Wet Hide Processing

Table 1: Chemical characteristics of gelatin from bovine hide

No.	Characteristics, UM	Standard method	GC1
1	Dry substance, %	SR EN ISO 4684 :2006	7.03
2	Total ash, %	SR EN ISO 4047 :2002	1.00
3	Total nitrogen, %	SR EN ISO 5397 :1996	16.22
4	Amino nitrogen, %	ICPI method, not standardized	undetectable
5	Dermal substance, %	SR EN ISO 5397 :1996	98.29
6	pH of analytical solution	STAS 8619/3 :1990	5.86

The lack of amino nitrogen confirms a high average molecular weight, over 40 kDa, specific to gelatins and a high degree of cohesion of gelatin, as suggested by the strength of gelatin.

The better quality of GC1 gelatin as adhesive compared to GC2 and GC3 gelatins was confirmed by the effectiveness of gluing the parchment on wood; the adhesion of the parchment glued with GC1 gelatin compared to GC2 and GC3 gelatins is much better, requiring a greater peel force.

The gelatin strength was determined by a compression test using Texture Analyzer TEX'AN TOUCH 20 N. The gelatin strength is expressed by the maximum force (Fmax. in grams) required for a cylindrical probe (Bloom cylinder) to compress the gel located in a standard glass container with a diameter of 59 mm (+/- 1 mm) and a height of 85 mm, under standard conditions: sensor with a diameter of 0.5 inches, penetration speed 0.5 mm/s, penetration distance 4 mm, Figure 2.

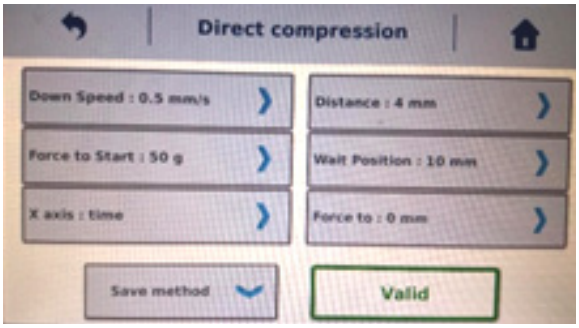
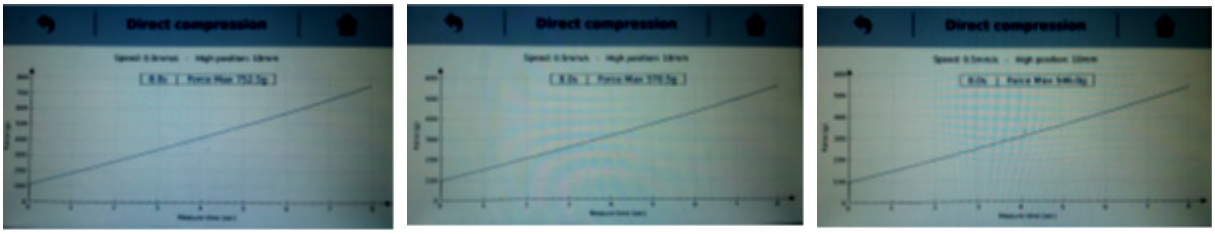


Figure 2. Standard parameters to determine gelatin strength (Bloom test)

Results of tests conducted on raw gelatins are presented in Figure 3.



(a) (b) (c)

Figure 3. Determination of gelatin strength: (a) GC1, (b) GC2, (c) GC3

The analytical data indicate that the strength of GC1 gelatin, extracted at 70°C, expressed in grams, is about 25% higher than GC2 and GC3 gelatins which were extracted at 85°C and 95°C, respectively, which is natural, because at high temperatures, more intense hydrolytic processes take place, leading to the breaking of peptide chains and the appearance of oligopeptides and even free amino acids, which weaken the cohesion of gelatin.

CG1 and CG2 gelatins were selected for testing as adhesives for joining collagenous materials in order to promote them in the field of heritage restoration, following the request for gluing pieces of parchment taken from the back of the inventory item titled Original Transylvanian Medieval Shield from the 15th century. The shield is registered as a "Hussar shield" and it is specific to the cavalry, with a characteristic curved shape, and the upper part cut obliquely to protect the shoulder and back. The Hussars were soldiers of the Hungarian cavalry in the Middle Ages. It has been used in Eastern Europe since the first quarter of the 15th century and

has been in use for over 100 years. This type of shield was used by the Ottomans, Poles, Romanians, Croats, Austrians, but especially by Hungarian hussars (riders), a name with which it remained associated. In museums and literature, this shield is called the "Hungarian shield". The shield is a donation from 1926 of the City Hall of Sibiu.

The description of this heritage object from the restoration file is very brief and incomplete due to the impossibility on the part of the restorer to understand the complexity of its composition (materials, form, historical contextualization, technique, etc.).

The wooden shield is covered/glued with calf parchment both on the outside and inside. The outer part, i.e. the convex part, consists of a whole piece of parchment, painted in red and yellow oblique stripes (according to Image 1), and on the concave part (Image 2) the parchment on the front is continued, but because there was not enough material, several pieces were glued which are now totally or partially detached (Images 3 and 4). The technique of assembling the parchment on wood was made with wet parchment by gluing with a gelatin on the wooden substrate. Calf parchment is a compact, dense, lightweight material, very resistant to tearing and breaking, and its use in this assembly (parchment glued to wood) makes it a special object suitable for the purpose created: light, resistant to piercing arrows and spears, resistant to cutting.

Image 1. Front view of the shield

Image 2. Back view of the shield

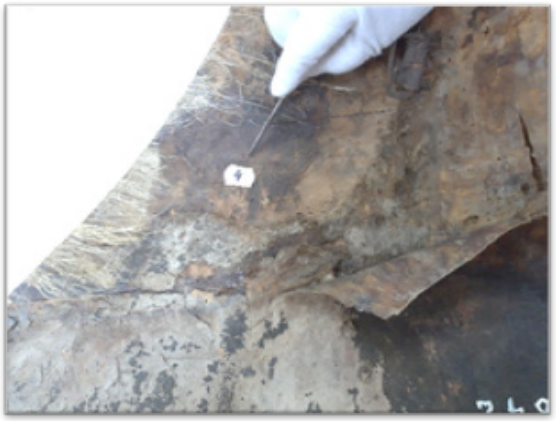


Image 3. Detail from the back side of the shield

Image 4. Detail from the back side of the shield

RESULTS AND DISCUSSIONS

Tests for Adhesiveness

The adhesive capacity of the following gelatins or glues was studied:

- rabbit skin (granules, commercial product of the "Divolo" company) – 5g in 50 mL distilled water was brought into fluid state by heating in a water bath at 40°C;
- GC1 - from bovine hide (70°C);
- GC2 - from bovine hide (85°C).

The materials used were vegetable tanned bovine hide, vegetable tanned sheep hide, dry calf parchment, wet calf parchment, fir wood.

Gluing experiments were prepared in duplicate for each sample: a and b.

The work method involved brushing the glue onto the two contact surfaces (wood and flesh side of parchment) of 3x3 cm^2 and pressing the glued surface using 3 kg weights for 72 h.

Experiment I-1 consisted of gluing wet parchment to wood (fir) (Image 5). After 72 h from gluing, it is noticed that the contact surface of the parchment and wood is consistent (Image 6), which indicates an appropriate behaviour of the parchment, typical for the parchment-wood ensemble from the heritage object: Transylvanian medieval shield.

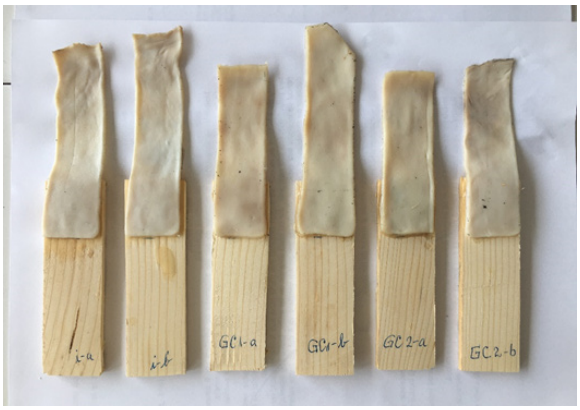


Image 5. Gluing wet parchment to wood

Image 6. Gluing wet parchment to wood after 72 h

Experiment I-2 consisted in gluing leather to leather (bovine and sheep), and experiment I-3 involved gluing bovine leather to wet parchment (Image 7), both following a work method similar to that of experiment I-1.

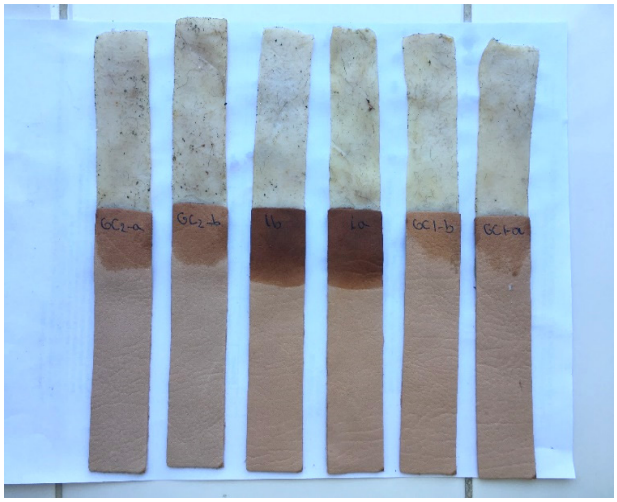


Image 7. Gluing vegetable tanned bovine leather to wet parchment

Image 8 presents samples from experiment I-4, gluing bovine leather to new dry parchment, with a similar work method to that of experiment I-1.

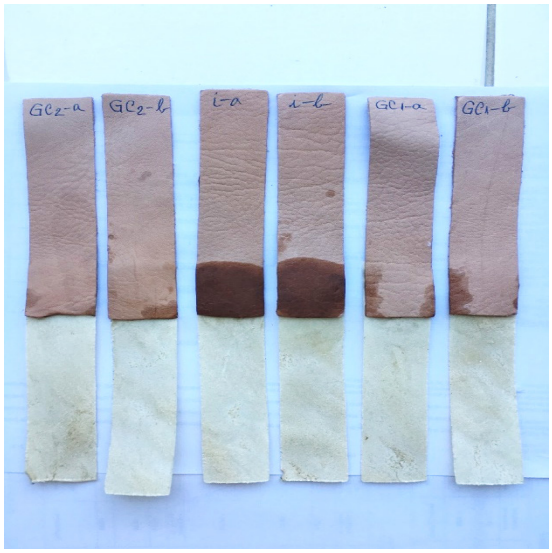


Image 8. Gluing vegetable tanned bovine leather to new dry parchment

In experiments I-3 and I-4 a wetting of the leather samples was noticed on the grain side due to water migration from the rabbit skin gelatin, samples i-a and i-b, compared to leather samples treated with gelatins GC1 and GC2.

In order to determine the rehydration ability of new parchment intended for the restoration activity that involves the gluing operation, rehydration experiments were conducted to study and assess behaviour to various ways of gluing in operations characteristic to restoration such as adding materials, replacing or doubling, experiments I-5 and I-6.

Experiment I-5 consisted of 4 samples of new dry parchment rehydrated by immersion in distilled water and alcohol, 1:1 (2 thin samples: 1-2 and two thick samples: 3, 4, Image 9).

Image 9. New parchment rehydrated in water, after 72 h

Image 10. New parchment rehydrated in urea, after 72 h

Experiment I-6 involved rehydrating 4 samples of new dry parchment by immersion in 2% hydroalcoholic solution, urea and salt (2 thin samples: 1b-2b and two thick samples: 3b-4b, Image 10).

Results of physical-mechanical analyses of gluing samples using the three 3 gelatins/glues [rabbit skin glue (i); bovine hide glue 70°C (GC1); bovine hide glue 85°C (GC2)] are presented in the following tables:

Table 2: Shear strength of samples I-1 when gluing wet parchment to wood

Characteristics	UM	Sample code/ Determined values 148/1			*Uncertainty	Standard method
Shear strength	N/mm^2	i	GC1	GC2	± 0.34	**STAS 6651:1991
		a – 0.52 b – sample detached average: 0.52	a – 1.42 b – 1.35 average: 1.39	Samples detached		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Table 3: Shear strength of samples I-2 when gluing wet parchment to bovine leather

Characteristics	UM	Sample code/ Determined values 148/2			*Uncertainty	Standard method
Shear strength	N/mm^2	i	GC1	GC2	± 0.34	**STAS 6651:1991
		a – 5.74 b – 6.96 average: 6.35	a – 10.06 b – 11.10 average: 10.58	a – 11.00 – leather breaks b – 11.10 average: 11.05		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Table 4: Shear strength of samples I-3 when gluing dry parchment hydrated in distilled water to bovine leather

Characteristics	UM	Sample code/ Determined values			*Uncertainty	Standard method
		148/3				
Shear strength	N/mm^2	i	GC1	GC2	± 0.34	**STAS 6651:1991
		a – 9.77 b – 3.94 average: 6.86	a – 5.72 b – 8.03 average: 6.88	a – 7.34 b – 5.54 average: 6.44		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Table 5: Shear strength of samples I-4 when gluing dry parchment hydrated in urea to bovine leather

Characteristics	UM	Sample code/ Determined values	*Uncertainty	Standard method
		148/4		
Shear strength	N/mm^2	GC1	± 0.34	**STAS 6651:1991
		a – sample detached b – 5.72 c – 6.38 d – 4.97 average: 5.69		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Table 6: Shear strength of samples I-5 when gluing dry parchment samples hydrated in distilled water to bovine leather - code 148/5

Characteristics	UM	Sample code/ Determined values		*Uncertainty	Standard method
		148/5			
Shear strength	N/mm^2	i	GC2	± 0.34	**STAS 6651:1991
		a – 5.50 b – 3.47 c – 4.10 average: 4.36	a – 3.43		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Results of shear strength presented in tables 2-4 show that the best values were obtained for gluing with gelatin GC1.

Historical parchment samples were hydrated for 72h and marked as follows:

- **<u>.</u>, <u>..</u>, <u>...</u>, <u>iv</u>, <u>v</u>, <u>vi</u>** hydrated in hydroalcoholic solution (1:1),
- **., .., ..., iv, v, vi**, hydrated in urea solution

Experiment I-6: Gluing on a surface of 3x3 cm^2, wood (fir)-wet historical parchment

- **<u>.</u>, <u>..</u>, <u>...</u>, <u>iv</u>, <u>v</u>, <u>vi</u>**, hydrated in hydroalcoholic solution

Experiment I-7: Gluing on a surface of 3x3 cm^2, wood (fir)-wet historical parchment

- **., .., ..., iv, v, vi**, hydrated in urea solution

Images of gluing tests for experiments I-6 and I-7 are shown below:

Image 11. Gluing wood and historical parchment hydrated for 72 h in hydroalcoholic solution

Image 12. Gluing wood and historical parchment hydrated for 72 h in urea solution

Table 7: Shear strength of samples I-6 when gluing historical parchment hydrated in ethyl alcohol to wood

Characteristics	UM	Sample code/ Determined values			*Uncertainty	Standard method
		148/6				
Shear strength	N/mm^2	i	GC1	GC2	± 0.34	**STAS 6651:1991
		a – 7.40 – parchment breaks b – 7.24 average: 7.32	a – 7.01 – parchment breaks b – 6.98 – parchment breaks average: 6.99	a – 6.72 b – 6.21 – parchment breaks average: 6.47		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Table 8: Shear strength of samples I-7 when gluing historical parchment hydrated in urea to wood

Characteristics	UM	Sample code/ Determined values			*Uncertainty	Standard method
		148/7				
Shear strength	N/mm^2	i	GC1	GC2	± 0.34	**STAS 6651:1991
		a – 7.14 b – 6.56 average: 6.85	a – 5.41 b – 6.71 average: 6.06	a – 1.53 b – 2.44 average: 1.99		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

In order to study the overall gluing process, experiments were conducted regarding the peel strength of leather samples, as follows: experiment I-8 – gluing two bovine leather samples on a surface of 3x10 cm^2 and experiment I-9 – gluing two lambskin samples on a surface of 3x10 cm^2.

Results of physical-mechanical analyses of gluing samples I-8 and I-9 using the three gelatins/glues [rabbit skin glue (i); bovine hide glue 70°C (GC1); bovine hide glue 85°C (GC2)] are included in the test report and presented in the following tables:

Table 9: Peel strength of samples I-10 when gluing bovine leather

Characteristics	UM	Sample code/ Determined values			*Uncertainty	Standard method
		149/1				
Peel strength	N/mm	Bi	BGC1	BGC2	± 0.14	**STAS 6651:1991
		a – 0.26 b – 0.32 average: 0.29	a – 0.44 b – 0.71 average: 0.58	a – 0.85 b – 0.97 average: 0.91		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

Table 10: Peel strength of samples I-11 when gluing lambskin

Characteristics	UM	Sample code/ Determined values			*Uncertainty	Standard method
		149/2				
Peel strength	N/mm	Ci	CGC1	CGC2	± 0.14	**STAS 6651:1991
		a – 0.24 b – 0.18 average: 0.21	a – 1.14 b – 1.19 average: 1.17	a – 0.69 b – 0,78 average: 0.74		

* Uncertainty for a 95% confidence interval; k=2 and is expressed in the measuring unit of the measured property
** Test not accredited by RENAR

CONCLUSIONS

The gelatins or glues studied were: i - rabbit glue (commercial product), GC1 - bovine hide glue (extracted at 70°C) and GC2 - bovine hide glue (extracted at 85°C).

Gluing tests were performed on vegetable tanned bovine hide, vegetable tanned goatskin, dry calfskin parchment, wet calfskin parchment, fir wood, historical parchment, while gluing experiments were prepared in duplicate for each sample: a and b. The working method for performing the tests was the same for the 3 types of glues studied. The physical-mechanical properties of shear strength and peel strength were characterized, and the bovine hide glue, CG1 extracted at 70°C had the best results, which recommends it for use in the restoration activity.

Acknowledgement

This work was supported by a grant of the Romanian Ministry of Research, Innovation and Digitization, UEFISCDI, project number *PN-III-P3-3.5-EUK-2019-0196)* / no. 253 of 10/08/2021.

REFERENCES

1. Schellmann, N.C., Animal glues: a review of their key properties relevant to conservation, *Stud Conserv*, **2007**, 52, 8, 55-66, https://doi.org/10.1179/sic.2007.52.Supplement-1.55.
2. Kroeger, K., Adhesives in the Bindery: An Overview, February 1, **2010**, available at https://postpressmag.com/articles/2010/adhesives-in-the-bindery-an-overview/.
3. Baglioni, P., Berti, D., Bonini, M., Carretti, E., Dei, L., Fratini, E., Giorg, R., Micelle, microemulsions, and gels for the conservation of cultural heritage, *Adv Colloid Interface Sci*, **2014**, 205, 361–371, https://doi.org/10.1016/j.cis.2013.09.008.
4. Melià-Angulo, A., Fuster-López, L., Vicente-Escuder, A., Study of the mechanical properties of selected animal glues and their implication when designing conservation strategies, *Conservation, Exposition, Restauration d'Objets d'Art*, https://doi.org/10.4000/ceroart.5152.
5. Johlin, J.M., The isoelectric point of gelatin

and its relation to the minimum physical properties of gelatin, Nashville: **1930**, https://doi.org/10.3181/00379727-26-4468.
6. Larsen, R., Microanalysis of Parchment, Archetype Publications, London, England, **2002**.
7. Miu, L., Giurginca, M., Gaidău, C., Bratulescu, V., Meghea, A., Albu, L., Iftimie, N., Bocu, V., Budrugeac, P., Igna, A., Leather and Parchment Heritage Objects, vol. 1: Investigating Deterioration of Heritage Objects (in Romanian), CERTEX Press, Bucharest, **2004**.
8. Dumitrescu, G., Badea, E., Parchment... A Story, the Unseen Face of Parchment Documents Issued by the Royal Chancellery in the Time of Stephen the Great (in Romanian), Excelența prin cultura, Bucharest, **2015**.