Performance Evaluation of Hybrid Formulations Consisting of Antioxidant and Crosslinking Agents for the Treatment of Acid Degradation in Historic Vegetable-Tanned Leathers

by

Alireza Koochakzaei,[a*] Shadpour Mallakpour[b] and Hossein Ahmadi[c]

[a]*Faculty of Cultural Materials Conservation, Tabriz Islamic Art University*, Tabriz, Iran.

[b]*Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology*, Isfahan, Iran.

[c]*Faculty of Conservation and Restoration, Art University of Isfahan*, Isfahan, Iran.

Abstract

This study investigated the performance of several new formulations for the treatment of acid degradation in historic leathers made with condensed tannins. This investigation was performed for four formulations consisting of collagen-stabilizing agents (oxazolidine E, resorcinol, nano alumina, and nano silica) and an antioxidant agent (Songnox 1010) in the acidic environment. The compounds were applied to 19th-century leathers with a brush. The properties of the leathers before and after treatment and accelerated aging were determined by measuring pH, shrinkage temperature, and color and conducting ATR-FTIR and FORS. For accelerated aging, the samples were exposed to an atmosphere with 95ppm SO_2, 40°C, and 51% relative humidity for 14 days. The results showed that all of the tested formulations slowed down the acid degradation process. The combined use of collagen stabilizing agents provided good treatment properties and adding Songnox 1010 antioxidant agent to this combination further enhanced the effect of treatment. Among the tested formulations, the one containing oxazolidine+resorcinol+nano alumina+S1010 provided the best properties for controlling acid degradation.

Introduction

Leathers and leather products tend to get damaged and degrade as they age. The rate of degradation progress depends on the characteristics of the leather and its surrounding environment. Leather degradation, which has destroyed a significant portion of historic artifacts over time, can have chemical, biological, and physical causes.[1] However, leather degradation is commonly considered a chemical process whose initiation and development are influenced by a variety of factors. In general, the leather-making process and the environment to which it is exposed both play a key role in the formation of complex degradation mechanisms.

Traditional leather-making processes and tanning methods are very diverse. Before the 1850s, common tanning agents were alums, plant-based tanning agents, or a combination of them.[2] The most common method was vegetable tanning with plant materials that contain hydrolysable tannins.[2,3] But starting from the turn of the 19th century and especially after the 1850s, the industrial revolution and rising demand fundamentally changed the traditional vegetable tanning processes. These changes included the widespread use of condensed tannins, sulfur compounds, synthetic dyes, and strong mineral acids (e.g., sulfuric acid) in the leather-making process, which result in the production of less durable leathers.[4-6] Also, the increasing emission of industrial air pollutants, especially SO_2, turned into one of the important causes of leather degradation.[7] The combination of these factors can cause severe chemical degradation in leather products in a short time. The most important cause of this degradation is acidic hydrolysis or in other words, acid degradation, which in its advanced form turns into red rot. It should be noted that similar damage has also been seen in some leathers produced before the 19th century.[8-10]

This aggressive, rapid, and irreversible degradation, which is a combination of oxidation and hydrolysis, is among the greatest concerns in the conservation of leather artifacts.[1,11-13] Acid degradation leads to the decomposition of collagen-tannin complexes, loss of tannins, degradation of collagen structure, and pH and hydrothermal stability reduction, which result in brittleness, poor durability, tearing, discoloration, and appearance of red spots and white deposits on the leather surface.[11,13-15] Considering the severe impacts of acidic degradation, it is important to study this process in order to understand it and determine how it can be prevented. The research on this subject has been ongoing since the early works of Faraday and his colleagues in the mid-nineteenth century and still continues today.[1,12,16] This highlights the importance and necessity of understanding acid degradation and protecting leather artifacts against it. A significant number of studies in this field have been focused on developing and evaluating treatment methods, which could be preventive measures or intervention measures. Over the years, a wide variety of materials have been used for treating leather, including buffer salts, gases, waxes, lubricants, and consolidants, many of which are now considered obsolete because of poor effectiveness.[17] In general, these treatment materials can be classified into three categories based on how they affect leather: stabilizing agents, consolidation agents, and surface coatings.[13] The previously

*Corresponding author email: a.koochakzaei@tabriziau.ac.ir ; alireza.k.1989@gmail.com

Manuscript received October 9, 2021, accepted for publication February 11, 2022.

common treatment materials that are now obsolete include potassium lactate, imidazole, and pliantex, parylene (polyparaxylylene), lankrothane 1304 (polyurethane). Some treatment materials such as ammonia vapor, aluminum alkoxide, klucel g, red-rot cocktail, polyethylene glycol (PEG), renaissance wax, SC6000 and certain leather lubricants and dressings are still occasionally used.[13,17,18] Each of these treatments has its own advantages and disadvantages and there is still no definitive solution to control this degradation. The major drawbacks of existing treatment methods and materials include staining and discoloration, dust absorption, inhibition of future conservation procedures, oxidation and hardening of leather, catalysis of degradation processes, softening of the finishing and decorative layer, creation of a sticky surface, effect on adjacent materials, surface flaking, white spue, biodegradation, problematic solvents, lack of long-term stability, difficult and complex application, flammable, toxic solvents, alkaline decay, and irreversibility.[1,13,17,19-23]

In general, it can be stated that since acid degradation is a step-by-step process, it can be somewhat controlled by countering each of these steps. One major factor of this process is SO_2 in the atmosphere, which upon oxidization to SO_3, provides a source for the formation of H_2SO_4.[2] Therefore, controlling this oxidation process can be effective in slowing down the degradation process. The formation of H_2SO_4 or its presence in the leather-making process is believed to be one of the most important causes of leather degradation.[14] When exposed to moisture, acids in leather dissolve and form positive hydronium ions, which may cause the pH to drop below the stability level of peptide chains and break the bonds between amino acids.[11] The pH in acid degraded leathers usually drops below 3,[24, 25] which accelerates the degradation process and the breakdown of the collagen-tannin complex.[14] Therefore, another key step in controlling acid degradation is to control acidity. Hydronium ions also weaken the leather structure by breaking the bonds between amino acids in collagen chains,[17] which in some cases causes shrinkage temperature (T_s) to drop to about 30°C [24]. Therefore, another important objective of treatment is to improve hydrothermal stability, which can be considered the best measure of the overall stability of leather.[26]

Treatment of acid degradation has always been an extremely important issue for the conservation of historic leather artifacts. Considering the drawbacks and poor effectiveness of many existing treatment methods, further research is still needed to find better alternatives. Therefore, the present study, which is a continuation of our previous study,[27] evaluated the ability of a number of treatment formulations composed of antioxidant and crosslinking agents to control the acid degradation process, improve the properties of weakened leather structures, and prolong the lifespan of leather.

Materials and Methods

Samples Preparation and Treatment

After applying a total of 17 formulations containing collagen stabilizing agents, antioxidants, and acid scavengers to new mimosa-tanned leathers, four of the formulations that contained collagen stabilizing agents and antioxidants were selected for testing on historical samples.[28] The antioxidant and collagen stabilizing agents used in the formulations were oxazolidine E (Sigma-Aldrich), resorcinol (Merck), nano alumina (US Research Nanomaterials), nano silica (US Research Nanomaterials), and Songnox 1010 (tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] methane; Songwon), which were prepared with concentrations of 10% in isopropanol, 3% in isopropanol, 1% in isopropanol, 2% in isopropanol and 0.5% in white spirit, respectively. The treatments were applied through step-by-step impregnation with a brush (Table I). The historical samples, which were labeled S1, S2, and S3, were 2×10cm pieces of leather collected from the removed and discarded leather bookbinding of antique books belonging to the late Qajar era, from 1789 to 1925.

Accelerated Aging

The accelerated aging was conducted by exposing the samples to a concentration of SO_2 (95±5 ppm) at 40±1°C and 50±1% relative humidity for 2 weeks.

ATR-FTIR Spectroscopy

ATR-FTIR analysis was carried out using a Nicolet 470 FTIR spectrometer and OMNIC 6.1a software (Nicolet instrument corporation, USA) equipped with PIKE MIRacle attenuated total reflectance (ATR) accessory with diamond crystal plate. All Spectra were collected in the range of 1800-525 cm^{-1} at 4 cm^{-1} resolutions with 32 numbers of scan.

Table I

Formulation of hybrid treatments applied on leathers

Treatment	Treatment Formulation (steps and materials)			
	1	2	3	4
T1	Oxazolidine E	Nano alumina	-	-
T2	Oxazolidine E	Nano silica	-	-
T3	Oxazolidine E	Nano alumina	S1010	-
T4	Oxazolidine E	Resorcinol	Nano alumina	S1010

Colorimetry

The colorimetric properties of leather samples were analyzed with Salutron® Colortector Alpha apparatus as a portable colorimeter in terms of CIE Lab color coordinates [L* (brightness), a* (red - green) and b* (yellow - blue)]. Color values were measured five times for each leather sample, and their average was considered as CIE Lab color coordinates.

Fiber-optics Reflectance Spectroscopy (FORS)

The UV-VIS-NIR reflectance spectra were obtained using an AvaSpec-2048 fiber optic spectrometer, an AvaLight-DHc compact deuterium-halogen light source, and a glass fiber reflection probe (Avantes Inc., Netherlands), operating in the 200–1050 nm. Three spectra (with an average of 5 spectra each) were recorded from each sample, taken from different spots on the grain side. The average of reflectance percentage for each wavelength was calculated in Excel and the final spectrum was obtained in the range of 215–915 nm.

Shrinkage Temperature

The shrinkage temperatures of the leather samples were determined according to ASTM D6076-03. The sample specimens, in the form of 12.5 × 76mm strips, were soaked in water tank equipped with a vacuum pump. The wet specimens were inserted into the bath of water at room temperature. The water was heated at 3-4°C/min rate and the temperature at the first definite sign of shrinking was recorded.

pH Measurement

For pH measurement, 0.1g of leather samples were cut into small pieces and soaked in 2ml of distilled water (with 7±0.15 pH) for 12±1 hours. pH of the leather-water mixtures was assessed by using a Metrohm 744 pH meter calibrated between buffers pH 4 and 7.

Results and Discussion

The mean pH of the samples is presented in Figure 1. In the control samples, there was no certain pattern in pH changes after accelerated aging. Accelerated aging increased the pH of the untreated (control) S2 sample, but it decreased the pH of the untreated S3 and made no noticeable change in the pH of the untreated S2. This clearly indicates that pH is not a reliable indicator of degradation level. It has already been shown that sometimes the intense degradation of leather leads to increased pH, which is what we observed in S2. However, applying the treatments also raised the pH. This increase was more pronounced in S1 samples, especially S1-T1, where it was about 0.8, and ranged from 0.4 to 0.75 in other samples. An interesting result was the stable pH of the treated samples in the post-aging stage, where we observed only a slight decrease in the pH of S1-T3 and S3-T4 and even a smaller decrease in the pH of S3-T2. Overall, the post-aging pH of all treated samples was higher than that of their untreated (control) counterparts.

In addition to pH, the T_s measurements are also presented in Figure 1. Typically, vegetable tanning raises the shrinkage temperature of collagen to about 75-85°C. However, the shrinkage temperature of all three untreated leathers was around 48°C. This means a more than 30°C reduction in their shrinkage temperature, which is indicative of severe degradation. Accelerated aging further reduced the shrinkage temperature of these samples by 1-2°C. More specifically, T_s decreased from 47°C to 45°C in the S1, from 46°C to 45°C, in the S2, and from 48°C to 46°C in the S3.

Among the treated samples, only S1-T1 and S1-T3 showed a decrease in T_s after treatment (~2°C). In the case of S1-T1, T_s did not change after aging, but in S1-T3, aging decreased T_s from 45°C to 44°C. While these two samples had the lowest T_s values, they also had the highest pH, which again suggests that pH may not be a good indicator of degradation. These two treatments (T1 and T3) had a different impact on S3, where they increased T_s to 52°C and 50°C, respectively. After aging, the T_s of both of these samples increased to 53°C, which could be due to increased cross-linking of treatment agents and collagen during accelerated aging. It has been shown that oxazolidine performs better in reacting with collagen and increasing T_s in higher pH values (alkaline conditions).[29] Therefore, considering the acidic pH of leathers, the reaction of oxazolidine with collagen has been probably slow.

The treatment T2, which was composed of oxazolidine and nano silica, increased the shrinkage temperature of S2 and S3 by 2.5°C (from 46 to 48.5°C) and 3.5°C (from 48 to 51.5°C), respectively. After accelerated aging, the T_s of both of these samples decreased by 0.5°C.

The treatment T2 also increased the shrinkage temperature of these samples by 3°C. After accelerated aging, the shrinkage temperature of S2 and S3 further increased by 5.5°C and 3°C, respectively, most likely because of the treatment-induced cross-linking. The post-aging shrinkage temperatures of S2-T2 and S3-T2 were 54.5°C and 54°C, which were the highest among the tested treatments. In addition to oxazolidine E, this treatment also includes resorcinol, which is a cross-linking agent for collagen. In terms of chemical structure, resorcinol has two hydroxyl groups in the meta position, which is the main cause of its high reactivity.[30] Using resorcinol in combination with oxazolidine E enhances its effectiveness and leads to improved tanning.[31] While using oxazolidine E as the sole tanning agent increases the T_s of collagen to about 85°C, combining it with resorcinol can increase this temperature to over 100°C.[32] This indicates that the combined use of the two agents can offer better outcomes in terms of controlling the acid degradation of leather.

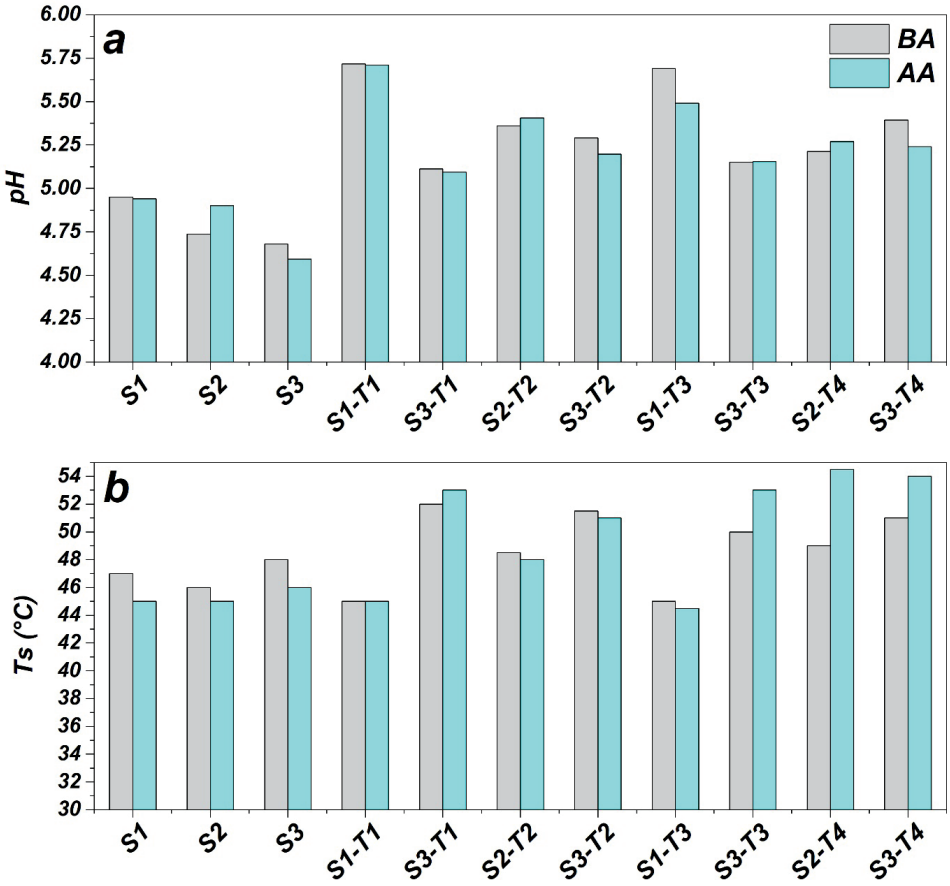

Figure 1. pH **(a)** and Ts **(b)** values of control and treated leather samples, before (BA) and after accelerated aging (AA)

The changes at the surface of the samples were examined by Fiber Optics Reflectance Spectroscopy (FORS). The mean spectra of the samples are shown in Figure 2. Since FORS is a surface analysis method, the obtained spectrum and its changes after accelerated aging are directly related to the composition and characteristics of the leather's surface layer. In the reference samples, in addition to the peak at 180nm, there is a peak at about 360nm, which can be related to copper or iron acetate and the dye applied to the leather.[33-35] In proteins, absorbance in this range is typically related to $\pi^{®}\pi^{*}$ and $n^{®}\pi^{*}$ transitions in C=O, NH, and CONH groups.[36] It has been reported that absorbance below 250nm can be related to non-aromatic amino acids, but absorbance in the range of 250-350nm is related to aromatic amino acids.[37] It has also been shown that collagen has absorbance in this range because of its triple-helical structure.[38] In

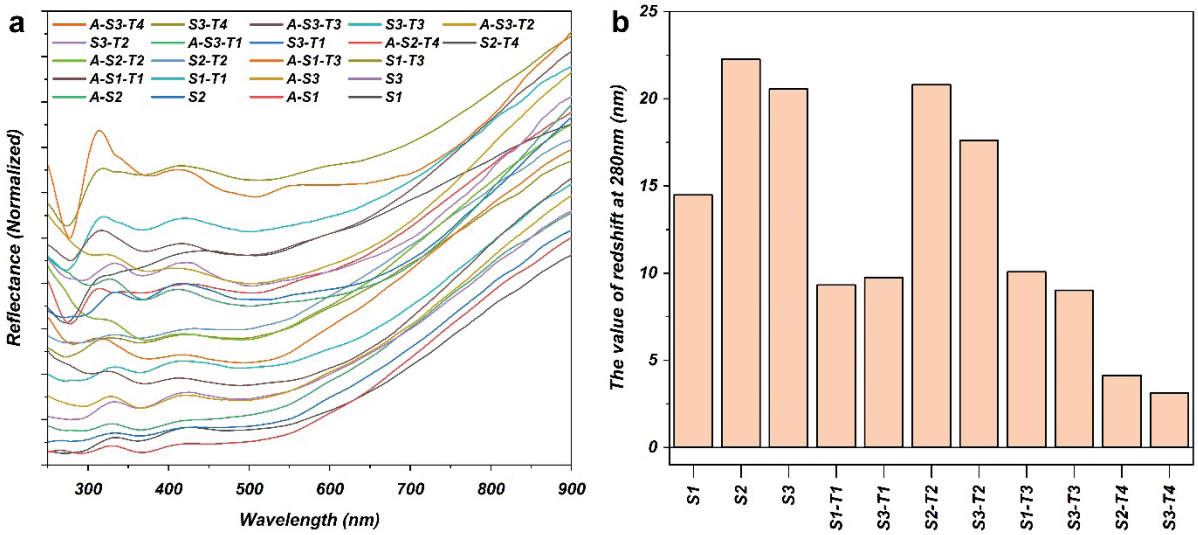

Figure 2. Mean FORS spectra of leathers surface, before and after aging **(a)** and the rate of shift at the peak 280nm after accelerated aging **(b)**

general, changes in structural properties cause peaks to move, and those changes that cause reduced structural consistency tend to shift the peaks to higher wavelengths. Research has shown that red shift occurs when collagen and its triple-helical structure are destroyed and denatured.[39,40] In the reference samples, accelerated aging caused a bathochromic shift in the peak of 280nm, or in other words, moved this peak to higher wavelengths. Therefore, the shift of this particular peak was considered as the measure of surface changes due to accelerated aging.

The shift of the 280nm peak of samples during the aging process is shown in Figure 2. In the untreated S1, S2, and S3 samples, accelerated aging moved the peak by about 14, 22, and 20nm, respectively. However, the applied treatments reduced the magnitude of this shift. Among the tested treatments, T2 had the greatest shift, which was still smaller than the shift in the control sample. In the T1 and T3 samples, the shift was about 9-10nm, but in T4 it was about 3-4nm. These results suggest that all four treatments managed to reduce the surface changes of the samples due to accelerated aging. However, T4 was most successful and T2 was least successful in this area.

The results of the color examination of the samples after accelerated aging are presented in Figure 3. The untreated S1 and S2 samples, which originally had a brownish color, turned slightly darker and redder after aging, but the untreated S3, which was originally blackish, became slightly brighter after aging. According to the results, all treatments showed an acceptable level of effectiveness in controlling the changes in parameters *L* and *a* during aging. Furthermore, examining the aging-induced total color difference showed substantially limited color changes in the treated samples compared to the control (untreated) samples, which is indicative of the good long-term color stability of the treated leathers.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used to examine structural changes in the leather grain and corium layers. Typically, the interesting absorption bands in the FTIR spectrum of leather are those around 1650cm^{-1} for amide I, 1550cm^{-1} for amide II, 1220 cm^{-1} for amide III, and 1450cm^{-1}.[10] The degree of hydrolysis of polypeptide chains can be assessed semi-quantitatively using the absorption intensity ratio of amide I to II (AI/AII).[36,41-43] This ratio is about 1.25-1.30 for new leathers but increases with degradation. The integrity of the triple-helical structure of collagen can also be studied using the ratio of the absorption intensity of amide III to 1450cm^{-1}.[41] This ratio is equal to or greater than 1 for the intact structure and about 0.5 for denatured collagen. Furthermore, the difference between the absorption bands position of amides I and II can be an indicator of collagen gelatinization.[27, 41] This difference is about 90-100cm^{-1} for new leathers. Occasionally, this difference has also been used to express the extent of collagen denaturation.[36,42,43,44,45] The increased absorption intensity in the range of 2800-3000cm^{-1}, which is related to CH_2 stretching vibrations, can also be used as the measure of collagen denaturation.[11]

In this study, the differences between the positions of peaks of amides I and II and their intensity ratios were used as the measure of denaturation/gelatinization and hydrolysis of collagen at the surface and in the corium, respectively. The data obtained before and after accelerated aging of the samples are presented in Figure 4. The increased Δν in the spectra of the control samples surface indicates

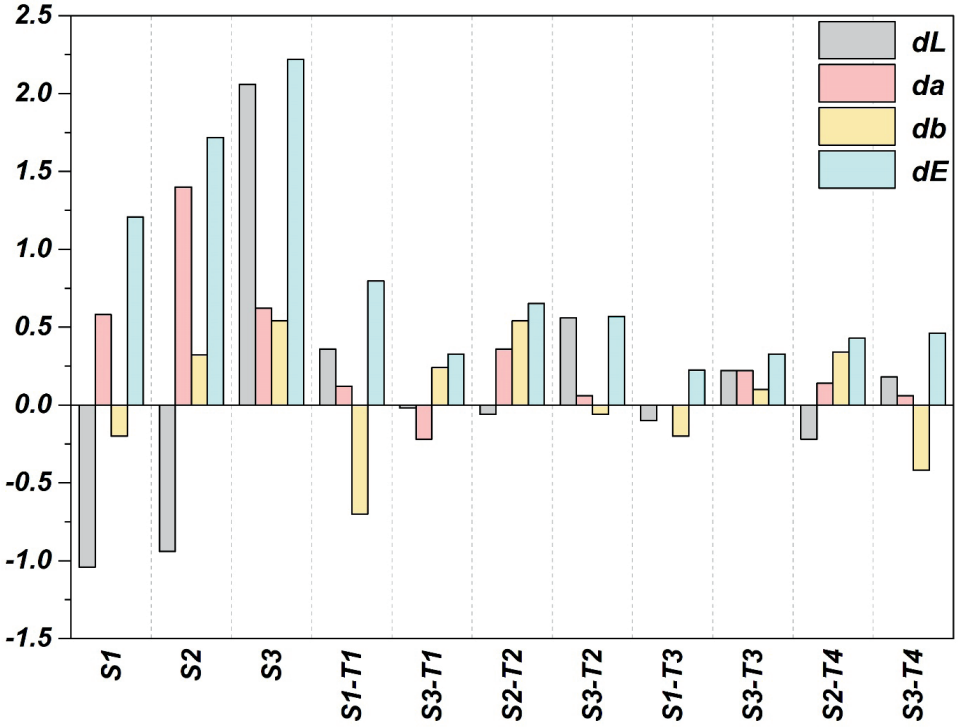

Figure 3. Color difference of leather samples, before and after accelerated aging based on ΔL*, Δa*, Δb* and ΔE

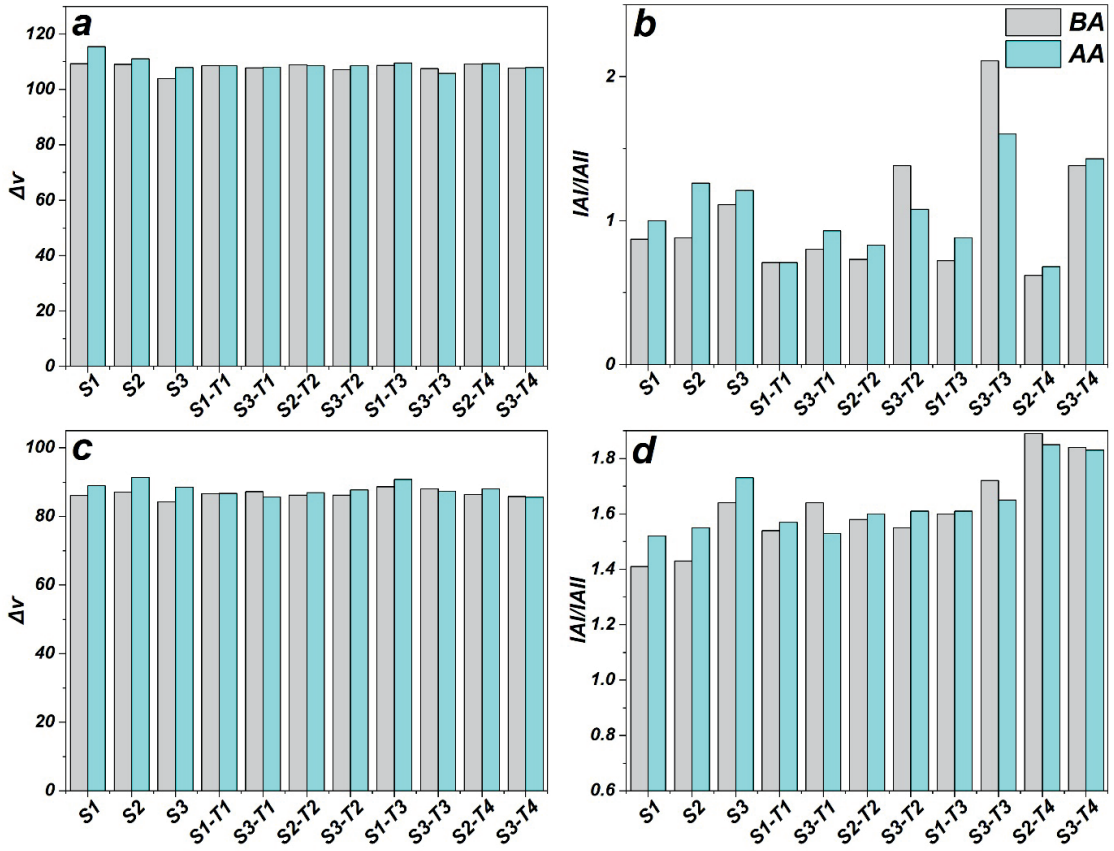

Figure 4. Data obtained from ATR-FTIR spectra of leathers, before (BA) and after accelerated aging (AA); **a:** difference in position of amide I and II (Δv) in the spectra of grain; **b:** Amide I to II intensity ratio (IAI/IAII) in spectra of grain; **c:** difference in position of amide I and II (Δv) in the spectra of the corium layer; **d:** Amide I to II intensity ratio (IAI/IAII) in the spectra of the corium layer

increased collagen denaturation/gelatinization due to accelerated aging. In comparison, the treated samples showed much smaller Δv changes. Among these samples, T4 and T1 had the lowest Δv changes, which reflect their ability to control collagen denaturation/gelatinization on the leather surface. Similar to the grain layer, the corium of the untreated leathers showed an increase in Δv after accelerated aging, which is indicative of intensified collagen denaturation/gelatinization. As before, applying the treatments significantly reduced this denaturation/gelatinization, leading to substantially smaller Δv changes in the treated samples compared to their untreated counterparts.

In all control samples, the hydrolysis index of the leather surface increased after accelerated aging. In S3-T2 and S3-T3, accelerated aging reduced this ratio. All other treated samples also showed signs of reduced hydrolysis at the surface. Among the treated samples, S1-T3 showed the highest increase in the AI/AII intensity ratio, which was almost the same as in the untreated S1. As with Δv, the samples treated with T1 and T4 showed the least change in the AI/AII intensity ratio of the surface layer after aging. As for the corium, accelerated aging also intensified hydrolysis in this layer of the untreated samples, leading to an increased AI/AII ratio. In S3-T1, S3-T2, and S2-T4, however, this ratio decreased after accelerated aging. The change in the AI/AII ratio of S3-T2 was particularly remarkable compared to the untreated samples. In S1-T1, S2-T2, S1-T3, and S3-T4, the aging-induced changes in this ratio were very small, which indicates more inhibited collagen hydrolysis. Overall, the results of ATR-FTIR showed that the treatments significantly reduced collagen denaturation, gelatinization and hydrolysis both on the surface and in the corium. Furthermore, using resorcinol in combination with oxazolidine E appears to increase leather stability.

Conclusion

This study investigated the combined performance of cross-linking and antioxidant agents in controlling acid degradation in historic leather artifacts. The studied compounds included oxazolidine, resorcinol, nano alumina, nano silica, and S1010 in four formulations, which were applied to the leathers with a brush. The leathers used in the experiments were selected from discarded bookbindings related to the 19th century.

Our pH assessments showed that, in general, pH cannot be considered a reliable measure of degradation severity. However, the treated samples showed a slight increase in pH compared to the control samples. T_s values measurements showed that resorcinol enhanced the effect of oxazolidine in improving the shrinkage temperature of

leather. When resorcinol and oxazolidine were used together, the increase in T_s continued even after aging; an effect that can probably be attributed to increased crosslinking during accelerated aging. The results of Fiber Optics Reflectance Spectroscopy (FORS) showed that it is a suitable tool for studying the surface changes of leather in the UV range. These results also showed that while aging led to structural degradation and loss of structural consistency as indicated by the bathochromic shift of the peak positioned around 280nm, all treatments except T2 were effective in inhibiting this effect. Among the tested treatments, the combination of oxazolidine, resorcinol, nano alumina, and S1010 provided the highest level of stability in leather, as was also the case with T_s. The comparison of color changes of treated and untreated samples before and after aging showed the effectiveness of all tested treatments in controlling color changes. Using the position shift and intensity ratio of amide I and II absorption bands in the FTIR spectra of the surface and corium, it was concluded that all treatments reduced collagen denaturation/gelatinization and hydrolysis in the acidic condition.

In summing, the results suggest that the combined use of antioxidant and collagen stabilizing agents will be effective in controlling acid degradation in vegetable-tanned leathers. Among the formulations tested in this study, those containing a combination of oxazolidine, resorcinol, nano alumina, and S1010 were the most effective in controlling this degradation.

References

1. Thomson, R., Leather, In May E. and Jones M., Eds. *Conservation Science: Heritage Materials*. Cambridge: The Royal Society of Chemistry, 92-120, 2006.
2. Haines B.M.; Deterioration in leather bookbindings - our present state of knowledge. *The Electronic British Library Journal* **3**(1), 59-70, 1977.
3. Thomson, R., Leather Working Processes, In Cameron, E., Ed. *Leather and Fur, Aspects of Early Medieval Trade and Technology*. London: Archetype, 1-9, 1998.
4. Thomson R., Testing leathers and related materials, In: Kite M. and Thomson R., Eds. *Conservation of leather and related materials*. London: Butterworth-Heinemann, 58-65, 2006.
5. Thomson R.; The Manufacture of Leather, In: Kite M. and Thomson R., Eds. *Conservation of leather and related materials*. London: Butterworth-Heinemann, 66-81, 2006.
6. Bennett H.G.; *The manufacture of leather*. London: Constable, 1909.
7. Puica N.M., Ardelean E.; The industrial pollution impact on religious heritage in Romania. *Eur. J. Sci. Theol.* **4**(2), 51-59, 2008.
8. Larsen R.; *Fundamental Aspects of the Deterioration of Vegetable Tanned Leathers*. Denmark: The Royal Danish Academy of Fine Arts, 1995.
9. Larsen R.; Deterioration and Conservation of Vegetable Tanned Leather, In Larsen R., Ed. *STEP Leather Project*. Copenhagen: Royal Danish Academy of Fine Arts, 165-179, 1994.
10. Koochakzaei A. and Mohammadi Achachluei M.; Red stains on archaeological leather: degradation characteristics of a shoe from the 11th–13th centuries (Seljuk period, Iran). *JAIC* **54**(1), 45-56, 2015.
11. Kozjak I., Igrec I.; Environmental influence on the leather used for book restoration, practical aspects of UV and hydrothermal degradation. In *the International Scientific Conference: Protection of Cultural Heritage from Natural and Man-made Disasters*. Zagreb and Šibenik: National and University Library in Zagreb. 8-10 May, 2014
12. Overell R.; The 'Red-Rot' Problem. *The La Trobe Journal* **73**, 101-107, 2004.
13. Johnson A.; Evaluation of the use of SC6000 in conjunction with Klucel G as a conservation treatment for bookbinding leather: notes on a preliminary study. *Journal of the Institute of Conservation* **36**(2), 125-144, 2013
14. Creangă D.M., Novel aspects in leather covers conservation manuscripts from putna monastery. *Eur. J. Sci. Theol.* **2**(2), 91-97, 2006.
15. Mahony C.C., Pearlstein E.; Evaluation of consolidants for the Treatment of Red Rot on Vegetable Tanned Leather. In *AIC 42nd Annual Meeting*. San Francisco: American Institute for Conservation. 13-17 May, 2014.
16. Caple C.; *Conservation Skills: Judgement, Method, and Decision Making*. London and New York: Routledge. 2000
17. Mahony C.C.; Evaluation of consolidants for the treatment of red rot on vegetable tanned leather: The search for a natural material alternative. M.A. thesis, Department of arts in conservation of archaeological and ethnographic materials, University of California: Los Angeles, 2014.
18. Lama A., Antunes A.P.M., Covington A.D., Guthrie-Strachan J. and Fletcher Y.; Use of aluminium alkoxide and oxazolidine II to treat acid-deteriorated historic leather. *Journal of the Institute of Conservation* **38**(2), 172-187, 2015.
19. Kite M., Thomson R., Angus A.; Materials and Techniques: Past and Present. In: Kite M. and Thomson R., Eds. *Conservation of leather and related materials*. London: Butterworth-Heinemann, 121-129, 2006.
20. Blaschke K.; Lubricants on Vegetable Tanned Leather: Effects and Chemical Changes. *Restaurator* **33**(1), 76-99, 2012.
21. Waterer J.W.; A novel method for the conservation of fragile leather. *Stud. Conserv.* **17**(3), 126-130, 1972.
22. Larsen R., Vest M., Poulsen D.V., Kejser U.B.; Fibre Assessment, In: Larsen R., Ed. *Environment Leather Project*, Copenhagen: Royal Danish Academy of Fine Arts, 113 -120, 1996.
23. Parker J.; *Re-evaluation of the condition of a previously conserved Mexican saddle and anquera (Am.913) FR2003/22*, London: British Museum, Department of Conservation and Scientific Research, 2003.
24. Lama A., Antunes A.P.M., Fletcher Y., Guthrie-Strachan J., Vidler K.; Investigation of acid deterioration in leather. In: Proceedings of the Joint Interim Conference. *Multidisciplinary Conservation: A Holistic View for Historic Interiors*. Rome: ICOM-CC. 23-26 March, 2010.

25. Lama A., Antunes A.P.M., Fletcher Y., Guthrie-Strachan J., Vidler K.; Investigation of acid-deterioration in leather leading towards finding a suitable product for treatment. In: *114th Society of Leather Technologists and Chemists (SLTC) Conferenc*e. Northampton (UK): University of Northampton. 7 May, 2011.
26. Larsen R., Wouters J., Juchauld F., Blüher A.; Bookbinding Leather in the Paper Deacidification Process. Part 1: Analytical Investigation of the Leather. In: *ICOM Committee for Conservation 14th Triennial Meeting*, The Hague. London: James & James. 2005
27. Koochakzaei A., Ahmadi H., Mallakpour S.; An experimental comparative study of the effect of skin type on the stability of vegetable leather under acidic condition. *JALCA* **113**(11), 345-351, 2018.
28. Koochakzaei A.; *Treatment of Acid Deterioration in Historic Leathers Tanned with Condensed Tannins using Collagen Stabilizing, Antioxidant and Acid Scavenger Agents*, Ph.D. thesis in Conservation and Restoration of Historic and Cultural Property. Iran, Isfahan: Art University of Isfahan. 2018.
29. Covington T.; *Tanning Chemistry*. Cambridge: The Royal Society of Chemistry. 2009.
30. Durairaj R.B.; *Resorcinol- Chemistry, Technology and Applications*. Germany: Springer-Verlag Berlin Heidelberg. 2005.
31. MaidmentC.;*Effectofresorcinolonoxazolidinetanning*.LASRA:Online. 2015. Available from: https://www.lasra.co.nz/wp-content/themes /LASRA/uploads/Catherine-Maidment-Effect-of-Resorcinol-on -Oxazolidin-Tanning.pdf. (Date accessed: 05/6/2018)
32. Chen H., Shana Z.-h.; Stabilization of collagen by cross-linking with oxazolidine E-resorcinol. *Int. J. Biol. Macromol.* **46**(5), 535-539, 2010.
33. Ishibashi M., Shigematsu T., Yamamoto Y., Tabushi, M. Kitayama M.; Ultraviolet Spectrophotometric Determination of Iron (III) as Acetato-complex. *Bull. inst. chem. res., Kyoto univ.* **35**(6), 6-15, 1957.
34. Kamnev A.A., Shchelochkov A.G., Tarantilis P.A., Polissiou M.G., Perfiliev Y.D.; Complexation of Indole-3-acetic Acid with Iron(III): Influence of Coordination on the π-Electronic System of the Ligand. *Monatshefte für Chemie / Chemical* Monthly **132**(6), 675-681, 2001.
35. Seguel G.V., Rivas B.L., Paredes C.; Study of the interactions between copper(II) acetate monohydrate and orotic acid and orotate ligands. *J. Chil. Chem. Soc.* **55**(3), 355-358, 2010.
36. Badea E., Miu L., Budrugeac P., Giurginca M., Mašić A., Badea N. and Della Gatta G.; Study of deterioration of historical parchments by various thermal analysis techniques complemented by SEM, FTIR, UV-Vis-NIR and unilateral NMR investigations. *J. Therm. Anal. Calorim.* **91**(1), 17-27, 2008.
37. Oujja M., Rebollar E., Abrusci C., Amo A.D., Catalina F., Castillejo M.; UV, visible and IR laser interaction with gelatine. *J. Phys. Conf. Ser.* **59**(1), 571, 2007.
38. Na G.C.; UV Spectroscopic Characterization of Type I Collagen. *Collagen and Related Research* **8**(4), 315-330, 1988.
39. Rasheeda K., Bharathy H., Nishad Fathima, N.; Vanillic acid and syringic acid: Exceptionally robust aromatic moieties for inhibiting in vitro self-assembly of type I collagen. *Int. J. Biol. Macromol.* **113**, 952-960, 2018.
40. Khan M.Y., Jaikaria N.S., Frenz D.A., Villanueva G., Newman S.A.; Structural changes in the NH2-terminal domain of fibronectin upon interaction with heparin. *J. Biol. Chem.* **263**(23), 11314-11318, 1988.
41. Petroviciu I., Carsote C., Wetter W., Miu L., Schreiner M.; Artificially aged parchment investigated by FTIR. In: *3rd International Congress "Chemistry for Cultural Heritage" (ChemCH 2014)*. Vienna, Austria: Academy of Fine Arts. 1-5 Jul, 2014.
42. Plavan V., Giurginca M., Budrugeac P., Vilsan M., Miu L.; Evaluation of the physico – chemical characteristics of leather samples of some historical objects from Kiev. *Revista de Chimie* **61**(7), 627-631, 2010.
43. Koochakzaei A., Ahmadi H., Mohammadi Achachlouei M.; Performance Evaluation of Dimethyl Silicone Oil as Archaeological Dry Leather Lubricant. *JALCA* **115**(4), 140-144, 2020.
44. Derrick M.; Evaluation of the State of Degradation of Dead Sea Scroll Samples Using FTIR Spectroscopy. *The book and paper annual* 10, 49-65, 1991.
45. Vetter W., Pöllnitz G., Schreiner M.; Examination of Historic Parchment Manuscripts by Non-invasive Reflection-FTIR - Possibilities and Limitations. In: *3rd International Congress "Chemistry for Cultural Heritage" (ChemCH 2014)*. Vienna, Austria: Academy of Fine Arts. 1-5 Jul, 2014.