Title
Testing the Effectiveness of a Novel Treatment for Denatured Leather and Skin Materials

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Testing the Effectiveness of a Novel Treatment for Denatured Leather and Skin Materials

A thesis submitted in partial satisfaction of the requirements for the degree

Master of Arts in Conservation of Archaeological and Ethnographic Materials

by

Mari Elizabeth Guarnieri Hagemeyer

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ABSTRACT OF THE THESIS

Exploratory Investigations into the Effectiveness of a Novel Treatment for Denatured Leather and Skin Materials

by

Mari Elizabeth Guarnieri Hagemeyer

Master of Arts in Conservation of Archaeological and Ethnographic Materials

University of California, Los Angeles, 2018

Professor Ellen J. Pearlstein, Chair

Skin and hide materials such as leather and rawhide are prone to deterioration through a process known as denaturation, which involves the disordering of collagen molecules given sufficient free water and heat. Denaturation has no conservation treatment currently recorded in the literature; therefore, an experimental treatment was devised using catechin. This treatment was compared against other treatments currently in use for deteriorated leather. Samples were aged, treated, and examined using differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, and fiber optic reflective spectroscopy (FORS). Analysis showed that on average, catechin-treated samples had improved properties compared to the control and the other treatments. Furthermore, the catechin treatment was less hazardous to the conservator and caused fewer side effects in the material than the other treatments. Therefore, the experimental treatment is considered a promising candidate for further research and possible future use. However, more study is needed to confirm these preliminary results.

The thesis of Mari Elizabeth Guarnieri Hagemeyer is approved.

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2018

To Rosencrantz and Guildenstern, for keeping me sane.

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I. Introduction

In late 2016, a building housing an extensive collection of Native American ethnographic objects, many composed of leather or skin materials, caught fire. In the aftermath of the fire, the owners were not able to access the collection for several weeks, while the objects remained sitting in stagnant water in the basement, which had no climate control to combat the hot summer weather (J. Claire Dean, personal communication, 2017). In addition to the extensive microbiological growth which flourished in the hot, damp climate, the microbes and the water

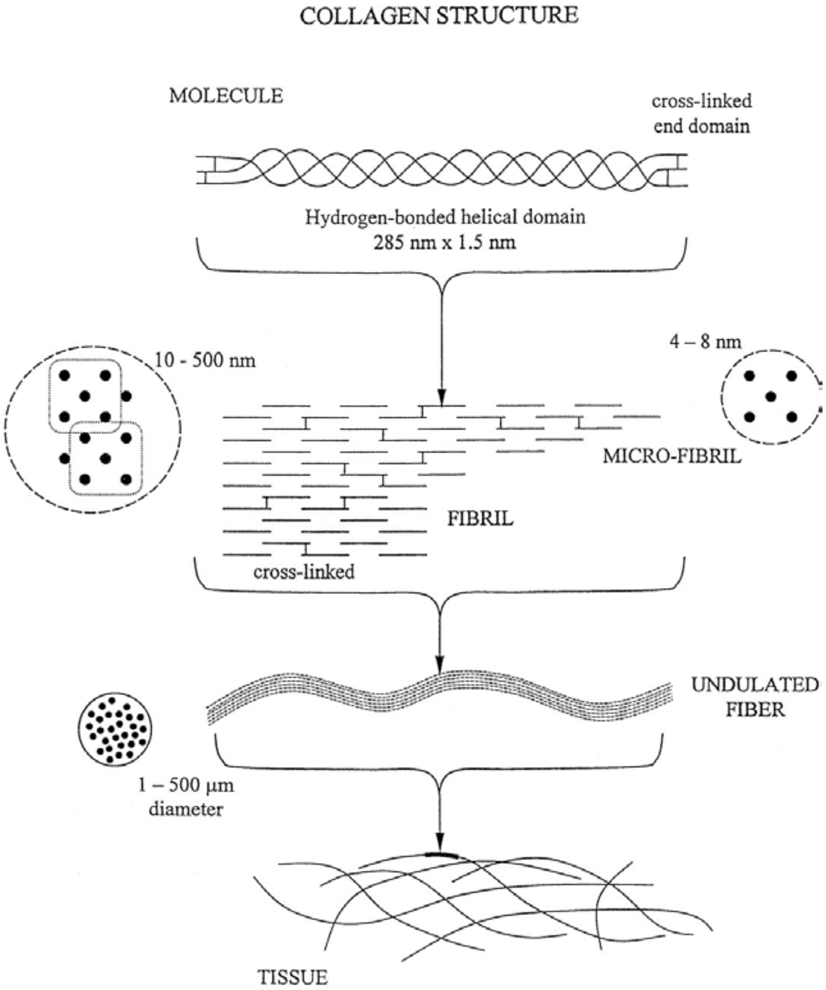


Fig. 1. Structure of native collagen.
From Wright and Humphrey, 2002 (p. 112).

also deteriorated the skin itself. Even after treatment for the microbial growth, the objects remained stiff, discolored, and brittle, unlike their original appearances and properties. The collagen in the skin had experienced a process known as denaturation, where collagen molecules degrade from triple helical fibrils (fig. 1) to an amorphous, glassy solid (Wright and Humphrey, 2002)..

Production of skin and hide materials

Skin and hide materials are ubiquitous around the world for their versatility, favorable properties, and relative ease of manufacture (Covington 1997). Skins and hides may be produced from a vast array of sources, from mammals to birds to reptiles and even fish (Dirksen 1997). These may further be processed by a wide variety of methods, to make materials that are stiff or pliable, delicate or hardy, dark or light, water-resistant or water-absorbent. In all these cases, there is one chief aim: to prevent putrefaction of the material, which is accomplished by making the material inhospitable to microbes through pH adjustment, i.e., through the application of alkali compounds such as quicklime, or drying (Procter 1922, ch. 4). There are three main categories of skin and hide materials, which can be broadly applied to all species and cultures of origin: rawhide, semi-tanned, and tanned.

Rawhide materials require the least amount of processing to create. These materials are created by removing an animal skin, stretching it tightly on some sort of frame, and scraping to remove excess tissue such as fat and blood vessels. This processing must take place very soon after the animal is killed, or putrefaction will begin and weaken the material (Covington 2009, ch.3, pp. 72–76). As with all other preservation methods, rawhide may or may not be scraped of its hair, scales, or feathers. Allowing this skin to dry results in a hard, pale membrane, which may be soaked in water to regain flexibility. Rawhide may be dehaired with an alkali such as lime, which dissolves the hair and other keratinous structures (Danylkovych, Lischuk, and Zhyhotsky 2017). Rawhide is often found in drum heads, shoe soles, and (among Native American Plains tribes) for stiff wallets such as parfleches, but it is a versatile material and may be used for many other applications. Because the collagen of rawhide is not chemically tanned or otherwise altered, rawhide is extremely susceptible to water damage.

Fully tanned leather is on the opposite end of the spectrum of skin and hide materials, being highly processed and chemically changed from its original state. Leather tanning is a lengthy and complicated process. Hides may be salted to preserve them for a short period while they are being transported or stored prior to the actual tanning process. Once tanning begins, the material is soaked to remove the salts from preservation and other unwanted surface materials; dehaired, either chemically or mechanically; limed (treated with alkali) to swell the material, then delimed (washed to remove alkali and correct pH) and bated (treated with dung or enzymes) to soften and remove waste products; pickled (treated with acid and salt) to allow the tanning agent access to the entire thickness of the material while preventing swelling; tanned by the application of chromium salts or vegetable tannins; subjected to post-processing such as re-tanning or dyeing; and fatliquored to replace the water swelling the wet leather structure with non-drying fats and oils (Covington 2009, ch. 3–17). Vegetable tannins were used widely before the introduction of chromium tanning, which is the industry standard today, and are sourced from a variety of vegetable sources (Covington 1997). All vegetable tannins are polyphenols, and may be classed as hydrolyzable (pyrogallol) or condensed (pyrocatecollic) tannins (Covington 2009, ch. 13). Chromium tanning is achieved in a similar way to vegetable tanning, but whereas vegetable tannins react to the collagen fibers and form hydrogen-bonded crosslinks (Covington 209, ch. 13), chromium ions, sourced in tanning from chromium (III) oxide, reversibly adsorb to the material (Wilson and Yu 1941, Gayatri *et al* 1999). This relatively strong bond between the Cr^{3+} ion complexes (which may be of various sizes) and carboxyl sites on the collagen chain may be classified as chemisorption, in contrast to the weaker form of adsorption (physisorption), which is based on van der Waals forces (Everett 1972, pp. 586–587; Gayatri *et al* 1999). After tanning, leather is more resistant to water damage than untanned material, and can take on a variety of characteristics based on post-processing methods.

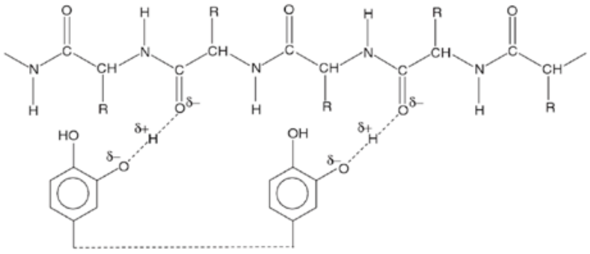


Fig. 2. Vegetable tannin after reaction with collagen molecule.

From Covington 2009, p. 283.

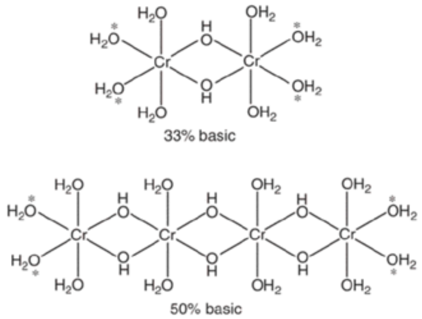


Fig. 3. Chromium (III) complexes, with reaction sites shown with asterisks (*).

From Covington 2009, p. 229.

Semi-tanning describes a variety of methods which provide an intermediate level of preservation between rawhide and fully tanned leather. These methods include tawing, which uses metal salts such as alum which cannot fully tan the material; oil-tanning, which uses drying oils such as cod oil; and brain-tanning, which uses the brain of the source animal along with smoking. As with tanning, semi-tanning processes attempt to eliminate or reduce the amount of collapse between collagen fibers, which in living tissue are kept apart by the body's fluids and which lubricants are designed to separate (Haines 1991). Tawing and oil-tanning may produce similar results, but they are very different on the molecular level. Tawing with salts such as alum causes metal ions to adsorb to side-chain carboxyl sites on the collagen molecule, much like chromium tanning; the only difference between them is the extent to which these ions can bond to the material (Wilson and Yu 1941). While the mechanics of oil-tanning are not fully understood, it is believed that the oil impregnating the hide cross-links and tans the material through a process known as aldehyde tanning (Nurse 2012). The aldehydes used in this process are sourced from smoke, in the case of brain-tanning, or from oxidizing glycerin, in the case of chamois leather (Nurse 2012, Procter 1922). The cross-linked oils form a kind of sheath around the collagen matrix, which can help reverse gelatinization in specific conditions; if oil-tanned leather is exposed to high temperature and moisture, but then quickly cooled before it has been allowed to gelatinize, the interpolated oil matrix allows partially disorganized collagen molecules to return to their original locations (Nurse 2012).

Degradation of skin and hide materials

Unfortunately, as with all organic material, leather degrades under most abandonment and burial conditions, surviving primarily only when waterlogged, frozen, or dried. In extant leather objects, several processes threaten the structural integrity of the material. In objects subjected to sulfur-containing pollutants, red rot is the most common degradation process. Red rot is a complex mechanism that depends on a variety of factors, including manufacturing technique, acid content, and environmental factors. This degradation process manifests as embrittlement, reddening, and eventual crumbling and powdering of the material. Red rot is a serious problem especially in libraries, as it is frequently accompanied by paper degradation in what is known as brittle book syndrome. As it is so well-known, a number of treatments have been developed for red rot, including the so-called “red rot cocktail” (Teper and Straw 2011; Johnson 2013).

In leather materials subjected to high temperature and humidity, a different process occurs. In naturally-occurring materials, unlike gelatin and hide glue which are altered from their original state, collagen molecules self-arrange into a triple-helical structure held together with hydrogen bonds (Engel *et al* 1977). A certain amount of bound water molecules are already included in this triple helix; however, upon heating, the helices incorporate more water, which destroys the ordered structure (Nomura *et al* 1977). Given sufficient heat, moisture, and time, this process, known as denaturation, can convert collagen materials such as skin from a set of ordered fibrils to a completely amorphous material (Chen *et al* 2014). This property of collagen has long been known, and deliberately denatured collagen has been used as an adhesive since at least the 6th century BCE (Bleicher *et al* 2015).

The effects of gelatinization are difficult to ameliorate, resulting in permanent damage and loss of functionality, and can only be avoided by controlling the ambient temperature and humidity, which is sometimes impossible. Gelatinization may also affect objects that were subjected to moisture during their use-life, such as clothing, shoes, and other leather goods which remain in prolonged contact with sweaty and moist human bodies. At an extreme level of gelatinization, such objects may become completely unrecognizable, slumping and deforming dramatically. Once the humidity is lowered, water evaporates, leaving the material shiny, hard, and brittle.

Contemporary study of leather degradation

Although significant attention has been given to the recovery and stabilization of waterlogged and red-rotted leather, fully gelatinized or denatured leather has been less studied. As mentioned above, a significant portion of scholarship on degraded leather has been devoted to condition issues typically associated with book materials. This extends to scholarship both on leather bindings and on vellum; indeed, much of the scholarship that deals with gelatinized or denatured skin materials focuses on vellum. Boyatzis, Velivasaki, and Malea (2016) and Cucos, Budrugeac, and Miu (2014) provide two contemporary examples of denaturation research in vellum. Both of these studies used accelerated aging with elevated heat and humidity to produce partially denatured parchment samples, which were studied with differential scanning calorimetry (DSC) along with other methods. Boyatzis, Velivasaki, and Malea (2016) aged parchment samples marked with iron gall ink, examining the influence of the ink on the parchment’s deterioration rate, while Cucos, Budrugeac, and Miu (2014) aged samples of the same parchment skin under the same conditions for a variety of time intervals to determine the rate at which deterioration progressed.

A significant amount of research has also been devoted to archaeological leather, which is typically partially denatured rather than fully denatured, and is affected by material loss due to waterlogging. Elizabeth Peacock describes newly excavated archaeological leather from Trondheim, Norway, as “dark and wet … [but] in good condition: it is relatively strong, flexible, easily handled and with a low percentage of lamination” (2001). She goes on to outline both previous and contemporary treatments for such material, all focusing on mitigating the effects of drying, which causes shrinkage, warping, and disaggregation. Elise van Dienst (1985) studied the differences in pH, moisture content, and fat content between new leather and waterlogged archaeological leather, maintaining that moisture content must be reduced and fat increased to mimic new leather. She also insists that hardening is due to improper lubrication rather than to denaturation of the collagen itself. More recent studies, such as those performed by Bardet *et al* (2009) and Plavan *et al* (2013) acknowledge the role of gelatinization in the degradation of leather, but focus on chemical transformations of the material, such as scissioning or oxidation of the collagen, rather than gelatinization, which is a strictly isochemical process. In all these cases, denaturation was either not acknowledged, or not explored as a treatable condition. To my knowledge, no study has focused specifically on the treatment of denaturation in skin materials.

Given the existence of objects, such as those presented in the introduction, which have been adversely affected by gelatinization, there is a clear need for treatments to improve their physical properties. The present study seeks to provide resources for conservators faced with denatured leather objects by replicating gelatinization in modern skin materials and treating with known techniques as well as an experimental one. The experimental technique repurposes research from bioengineering and medical contexts, among others, by exploring the potential of in-situ polymerization of collagen materials.

II. Treating degraded leather

Contemporary treatments

Leather and skin materials typically receive consolidation treatment in two broad cases: when the material is affected by dry degradation from scissioning and oxidation of the collagen polymer matrix (i.e. red rot), and when the material is waterlogged, which causes a significant amount of the original material to be replaced with free water. In both cases, there is material loss which results in fragmentation, warping, or shrinkage. This loss occurs in a widespread manner on a microscopic scale, unlike breaks or tears, which are localized and on the macroscopic scale. In cases where individual mends or fills are impossible, i.e. where damage exists on the micro- or nano-scale, a consolidant may be used to treat the entire damaged area. Consolidants, in a broad sense, are treatment materials, usually polymeric adhesives, applied to an object in order to reestablish cohesion in the component materials. Consolidants are typically applied as a liquid which will evaporate, cure, or otherwise transform into a solid material which forms bonds between the disaggregated fragments of the material. Consolidants may also be applied to bulk voids in a fragile or friable material.

Denaturation, unlike scissioning and waterlogging, does not involve material loss or chemical change. Rather, denaturation is an isochemical transformation which alters the conformation of the material's component molecules without changing the molecules themselves. Since there is no material loss, denatured material cannot be consolidated. If a consolidant were to be applied to denatured material, it would not fill voids but rather interpenetrate an existing polymer matrix. However, because treatment for denaturation may be applied in an analogous manner to a consolidant, we may create a category such as Teper and Straw's surface treatments to include both consolidants and the similar treatment for denaturation (2011). Such treatments are applied in cases where the material undergoes an area degradation, instead of localized damages such as cracking, rents, or punctures, and involve a treatment material applied over a portion of the object's surface area. The category of surface treatments is naturally broad, and encompasses any non-localized treatment that involves adding material, rather than removing it (as in the case of a cleaning treatment). Therefore, consolidation, coating, and treatment for desalination would all fall into this category.

Red rot cocktail

Waxes and oils have long been applied to leather and skin materials for a variety of purposes. As described above, lubricants are a crucial element of the tanning or curing process of treated skin materials, such as vegetable-tanned or oil-tanned (or tawed) leathers (Haines 1991; Covington 2009, ch. 17, pp. 392–420). Lubricants have also often been used to treat deteriorating leather in the belief that they will behave similarly to the lubricants used in the initial tanning process, although whether this belief is accurate has been under question for some time (Blaschke 2012; Raphael and McCready 1993). Nevertheless, the use of traditional leather dressings as well as more modern blends of waxes and oils persists in conservation laboratories across the world (Teper and Straw 2011). It should be noted, however, that although one survey reports nearly half of respondents used some kind of wax or oil-based leather dressing, over half of these respondents indicated that they do not currently use them on historical leathers (St. John 2000). In addition, it is worth mentioning that both Teper and Straw (2011) and St. John (2000) surveyed book conservators, who treat objects that are often handled and must remain functional, as opposed to conservators who treat leather and skin objects which are rarely handled and do not need to remain flexible and resilient.

Red rot, the dry degradation mechanism described in the Introduction, has long plagued European libraries. Acid hydrolysis of the leather due to historically high levels of sulfur-containing pollutants in the air has resulted in widespread red rot in these collections, which has only been controlled in fairly recent decades. Conservators have used surface treatments such as leather dressings, waxes, and cellulose derivatives have been used for decades to consolidate the powdery and flaky texture of red-rotted leather, and restore their appearance and surface texture to gain more favorable qualities (Teper and Straw 2011, Johnson 2013). One blend of Klucel G (a cellulose derivative, hydroxypropyl cellulose) and SC6000 (a solution of microcrystalline wax in isopropanol) has gained wide popularity, and this standardized blend is known as “red rot cocktail” (Johnson 2013).

Polyethylene glycol (PEG) impregnation

Polyethylene glycol (PEG), a water soluble polymer or oligomer of ethylene oxide (C_2H_4O), has been used for some time as a consolidant for waterlogged wood (Grattan 1982). At lower molecular weights, PEG is an oily liquid, while at higher molecular weights it is a waxy solid. PEG is an ideal consolidant for waterlogged materials because it is soluble in water. However, it has several drawbacks, the most significant one being its molecular weight. PEG is applied as a solution, typically in water which is allowed to gradually evaporate, gradually enriching the solution until it is 100% PEG. As such, longer-chain PEG molecules may experience significant difficulty in penetrating substrates with low porosity or small pores, necessitating protracted treatments which may take months or even years. Examples of such treatments include: consolidation of waterlogged wood, 170 days to 18 months (Grattan 1982); consolidation of Roman-era wood from Pommeroeul, Belgium, 21 months (de Witte, Terfve, and Vynckier 1984); and perhaps the most extreme example, the treatment of the Vasa, which took 17 years (Hocker, Almkvist, and Sahlstedt 2012). Furthermore, PEG impregnation may change the properties of the treated material significantly (Bugani *et al* 2009). From an aesthetic point of view, PEG impregnation may darken the material, and the waxy or oily appearance of various molecular weights of PEG may impart a shininess to the material or alter the material’s texture.

While PEG impregnation as a treatment for replacing material loss was initially applied to waterlogged wood, it has also been successfully used as a treatment for waterlogged leather materials (Van Dienst 1985; Peacock 2001). Such fragile materials cannot be dried through evaporation of the water, as the surface tension of the liquid collapses these materials' delicate internal structures as the liquid evaporates. As with treatments for wood, PEG impregnation treatment for leather may be accompanied by a freeze-drying treatment, which allows safe drying of the material and is thought to assist in drawing the PEG deeper into the material (Jensen and Jensen 2006).

Silicone oil treatment

As an alternative to PEG impregnation, a treatment for waterlogged leather developed and pioneered by Texas A&M University relies on impregnation with silicone oil, which is subsequently crosslinked within the material to form a permanent crosslinked structure interlaced within the existing leather structure (Smith, Hamilton and Klosowski 1998). Information on this technique is frustratingly sparse in the literature, but based on the materials used, the silicone oil treatment appears to be identical to the biological tissue preservation technique known as "plastination" (Raoof *et al* 2007). As with the technique described above, plastination uses a variety of polymers which are impregnated into the object to be preserved and then cross-linked using chemical reagents. Silicones are often used due to their strength and flexibility, but hard epoxies and polyester resins are also used (Von Hagens, Tiedemann, and Kriz 1987). While plastination and the silicone oil treatment are both effective in halting degradation, they both significantly alter the appearance and chemistry of the material. All silicone-based materials have a chemical backbone made up of silicon-oxygen bonds, whereas organic molecules have a carbon or carbon-oxygen backbone (Noll 2012, ch.1)

Experimental treatment

As noted in section I, there has been little research on conservation practices and treatments for denatured leather and skin materials. Further, the existing studies have focused on the mechanisms and parameters by which denaturation occurs, rather than on the effectiveness of treatments. Therefore, a conservator faced with an object affected by denaturation, such as the badly damaged objects introduced at the beginning of this thesis, has one of three options:

1. They can do nothing.
2. They can use passive conservation methods.
3. They can repurpose an existing treatment intended for different circumstances.

All three of these are less than satisfactory. Doing nothing risks further damage, exacerbating the situation. Passive conservation methods such as controlling ambient humidity and temperature are helpful in slowing the process of denaturation, but do nothing to reverse the negative effects of the denaturation which has already occurred. Most risky is the choice to repurpose an existing treatment: as this study's experimental data will show, such treatments may do much more harm than good.

This work explores a fourth option: creating and evaluating a novel treatment. To this end, a literature survey was conducted to investigate processes and materials that are able to address the specific chemical and mechanical changes introduced by denaturation. After this survey was conducted, a study by Madhan *et al.* (2005) on the effect of catechin on aqueous collagen was selected as the most promising treatment for reversing the effects of denaturation in skin and leather materials.

This treatment, which is novel in the field of conservation, is based on the work of Madhan *et al*, who applied 0.01M catechin in solvent to rat tail tendon, which like skin is composed of collagen I (Madhan *et al*. 2005). Catechin, a flavon-3-ol (see fig. 2) found in green tea extract and other plants, is chemically related to condensed tannins (which release catechols upon pyrosis, i.e., burning). In addition to its structural similarity to the tannins used to produce vegetable-tanned leather, this compound was shown by Madhan *et al* to provide some cross-linking to both collagen solutions and cast films, both of which may be considered analogous to fully gelatinized leather as they were composed of fully amorphous collagen molecules. Thus, treatment of collagen with catechin is a type of tanning process itself, albeit less invasive and causing less material change.

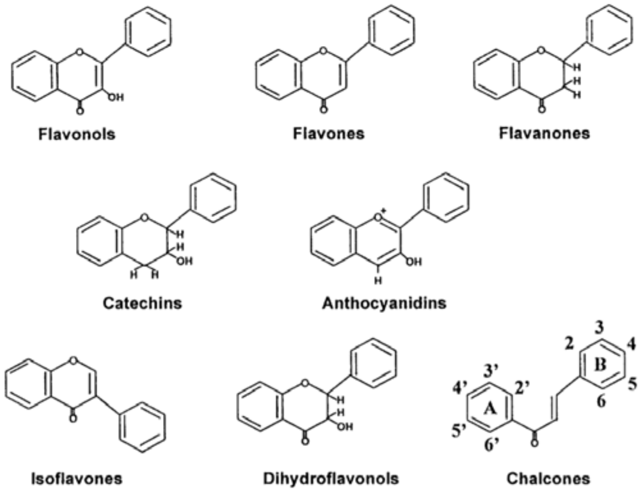


Fig. 4. Comparative structures of different flavonoids.
From Cook and Samman, 1996.

Appropriateness of catechin treatment for denatured materials

When skin is processed into leather or semi-tanned materials, certain elements are necessary to mimic the properties of living skin. As a living organ, skin is made up of collagen fibers which maintain a specific distance from one another due to the natural fluids present in the skin. Upon removal and drying, these fibers lose water and collapse, making the material stiff and hard. Soaking in water returns flexibility, but the dead skin is vulnerable to over-imbibition of water, which in extreme circumstances leads to the denaturation process described in section I. Tanning and semi-tanning processes introduce lubricants, crosslinks, or both to return the material to its flexible and water-resistant state. Lubricants act in place of the water which maintained distance between collagen fibers, while crosslinks force fibers apart simply by the presence of bonds maintaining a reliable distance (Covington 1997).

When collagen denatures, its properties are once again ruled by the presence of free water. When fully hydrated, the denatured material is pliable, but soft, and deforms easily; when dehydrated, the denatured material is brittle and hard (Nomura *et al* 1977). Therefore, adding water to vulnerable denatured specimens is strongly discouraged, as it can cause further damage, and even completely dissolve and carry material away from the object. In addition, the introduction of water may cause curling and distortion, which upon drying would become permanent. Treatment with catechin in ethanol following Madhan *et al*'s approach addresses both these concerns by increasing flexibility through crosslinking the existing material without the application of water (2005). Furthermore, according to their research, Madhan *et al* were able to improve the water resistance of amorphous collagen samples, which indicates that this treatment should have similar results for degraded leather and skin materials.

III. Materials & methods

Aging

In order to create partially denatured (i.e. “aged”) samples to examine, commercially prepared skin samples were procured and aged as described below. The number and type of samples as well as the extent of the denaturation were limited, in order to be able to fully investigate them during this study’s set period of time. It was decided to restrict skin samples to a single species of animal (cattle) in three different tannages: rawhide, oil-tanned, and vegetable tanned. Although a study including multiple coupons of each tannage would have been more statistically relevant, it was decided to sacrifice wider statistical certainty in order to explore more possible use-cases. In all studied materials, samples were chosen to be as close as possible to their natural color to limit the influence of dyes on their material properties. The sources for these materials are given in Appendix A. Once obtained, these materials were cut into a total of 15 3-cm x 3-cm coupons. Five coupons of each tannage were made in all. Of these coupons, one was retained as a control and was not aged, four were aged, and three of the aged samples were treated with various methods.

The control coupons were kept in dark, relative humidity (RH)-controlled storage (RH=50%), which was achieved by placing silica gel conditioned to the appropriate RH in a custom archival box sealed into a polyethylene bag. The RH was monitored with an Onset model UX100 HOBO datalogger. The remaining twelve coupons were aged for fifteen days in a warm, high-humidity environment. This environment was achieved by creating a closed chamber over a saturated solution of KBr salt in water, which has a reliable RH of 85% at room temperature (Greenspan 1977). This chamber was fashioned from a lab desiccator, which had a convenient lower tray for the saturated solution; hereafter, it is referred to as “the aging chamber”.

After the aging chamber reached equilibrium, the samples were placed within and the aging chamber was placed in an oven heated to 80 °C. Due to the temperature cutoff for the available monitoring equipment (75 °C), it was not possible to monitor the aging chamber’s RH. Instead, a reference chamber was created and held at room temperature, and its RH and temperature were recorded over the aging period. This chamber was conditioned in the same way as the aging chamber, to ascertain that the salt solution placed in each chamber was capable of conditioning the chamber to the desired RH. After 15 days, the oven was slowly cooled and the samples removed once the aging chamber reached room temperature, or 20 °C. The samples were then placed in the same RH-controlled storage container as described above. This container was kept covered to limit light exposure. This RH-controlled storage container is hereafter referred to as RH-controlled storage.

After the samples normalized to the level of the RH-controlled storage (50% RH), four sets of coupons were subjected to treatment. Three sets were taken from the artificially aged samples, while the final set was taken from a naturally deteriorated artifact taken from the collection described in the introduction, described hereafter as an armband. This artifact had been deteriorated by the action of standing water, high humidity, and temperatures exceeding 27 °C. Two of the treatments used were chosen to represent currently-used treatments for degraded leather, while the third is a novel treatment. This treatment was adapted by the author from Madhan *et al*. (2005).

Treatments

The first treatment was impregnation with polyethylene glycol (PEG), which is often used for waterlogged leather (Gregory *et al*. 2012). PEG is chemically similar to glycerol, another material often used to consolidate waterlogged leather (Peacock 1983; Peacock 2005; Ganiaris, Keene, and Starling 1982); however, glycerol is a much shorter-chain compound than commonly-used PEGs, which may have molecular weights of 1000 or greater (Knowles *et al* 2015) Typical treatments for waterlogged leather involve dissolving a consolidant such as glycerol or PEG in water, placing the object to be treated into this solution, and allowing the PEG to impregnate the object over time (Peacock 1983; Ganiaris, Keene, and Starling 1982). The solvent is allowed to evaporate, gradually enriching the PEG solution until no solvent is present. Such treatments may also be accompanied by freeze-drying. However, due to the sensitivity to water introduced by partial denaturation of the samples, this treatment was subjected to several adaptations. The treatment solution, which would ordinarily consist of a 10% solution of high molecular weight PEG in water (Grattan 1982), was changed to a 10% solution of a lower-MW PEG in ethanol. The change to a lower molecular weight was necessitated by PEG's solubility in ethanol, which is extremely low for high-MW PEGs. For this treatment, PEG 400 (that is, PEG with an average molecular weight of 400) was used. Samples were placed directly into the solution; no pre-soaking in solvent was necessary as they were dry at the time of treatment, having come out of RH-controlled storage. Samples were gently heated to 30°C to encourage the evaporation of the solvent, and were left uncovered for three days. At this point, no solvent remained in the system, leaving samples partially submerged in a bath of pure liquid PEG. Samples were removed from the excess PEG and gently tamped off using lens tissue and bibulous paper to remove the excess. After treatment, samples were placed back in RH-controlled storage.

The second treatment was brushing with Dow 1248 fluid, a silicone-based commercial leather treatment marketed as an additive for leather coatings (Dow Corning 2016). The material used for this treatment was generously provided as a sample by Univar. More information is available in Appendix A. This material is described by the manufacturer as follows:

> *DOW CORNING 1248 Fluid is a silicone glycol graft copolymer with secondary hydroxyl functionality. The polymer has a combination of organoreactivity from the glycol group as well as properties typical of a polydimethylsiloxane fluid. The glycol group can be chemically bonded into any system which is reactive towards alcohols to impart durable silicone properties to that system. DOW CORNING 1248 Fluid is used as an additive in polyurethane coating resin systems. Because this polymer can react into the coating, the typical silicone properties imparted are often durable. (Dow Corning 2016)*

This treatment was selected to provide an analogue to the silicone oil/plastination treatment, the chemical components of which proved unobtainable for this study. Dow Corning, the manufacturer, did not provide any recommendations for the application of 1248 fluid to leather materials. Therefore, the treatment was simply applied directly and undiluted to the top surface of each coupon by brush, allowed to cure for 3 days, and then any excess wiped off and the coupons returned to RH-controlled storage.

The final treatment involved the application of catechin to the degraded coupons. For this treatment, Madhan *et al*'s research was adapted to be applicable to the samples in this study. Catechin was sourced as catechin hydrate from Fisher Scientific. It was dehydrated by spreading the material in a shallow watch glass and placing it in a desiccation chamber where the RH was controlled by silica gel. The resulting dehydrated catechin material was dissolved in ethanol to produce a 0.01 M solution. Poultices of Arbocel cellulose powder with Japanese tissue barrier layers were loaded with 5 mL of solution and placed on each coupon; these poultices were left on the coupons for 24 hours and then removed. Glad brand Press'n'Seal® plastic wrap was used to ensure little to no solvent evaporated during this period. After the poultices were removed, the remaining solvent was allowed to evaporate in air. Some white powdery material remained on the surface of the coupons, presumably excess catechin, which did not react with the sample; this was removed by swabbing with ethanol. Thereafter, the coupons were returned to RH-controlled storage.

Analyses

Three different methods were used to analyze the coupons. First, differential scanning calorimetry (DSC) was used to quantify the thermodynamics of the denaturation of each coupon. Denaturation data is often collected by measuring the shrinkage temperature of a given sample of leather or hide; however, shrinkage temperature only indicates at which temperature denaturation begins. DSC provides more complete information, describing the heat needed to cause deterioration (indicating the amount of nondeteriorated material) and the range of temperatures at which material is deteriorating (indicating the range of water-sensitivity). Fourier-transform infrared spectroscopy - attenuated total reflection (FTIR-ATR) was used to understand chemical differences in the base materials and the chemical transformations, if any, caused by the treatment materials following application. UV/Vis/NIR reflectance spectroscopy, also known as fiber-optic reflectance spectroscopy (FORS), was used to corroborate FTIR data. All analysis methods compared results for treated coupons against aged and unaged controls, as described above. Reference spectra were also collected for PEG 400, Dow 1248 fluid, and pure catechin powder, where applicable.

DSC was performed on a PerkinElmer DSC 8000 with a PerkinElmer Intracooler 2 cooling system. This type of analysis is performed by measuring the heat flow into or out of the sample as the temperature is raised. Samples were fully hydrated in DI water and then cut to fit sample pans; care was taken that the entire thickness of the material was represented in each sample. Initial baselines were taken with empty sample pans, and then subtracted from the data from live samples. Samples were heated from 20 °C to 100 °C, at a speed of 5 °C/min.

FTIR-ATR was performed on a PerkinElmer Spectrum Two FTIR spectrometer fitted with an ATR crystal. This type of analysis uses a crystal to excite the sample with infrared light, then measures the amount of light absorbed at different wavelengths. Samples were pressed to the crystal using the minimum pressure needed to produce a signal; therefore, data manipulation through subtraction of spectra was necessary for accurate comparisons. For these manipulations, the spectra of the treated aged samples were subtracted from the spectra of the untreated aged samples, so as to show where the treated samples' spectra were not equivalent to untreated samples.

FORS was performed on an ASD FieldSpec UV/Vis/NIR spectrometer with a 45° angled contact probe. This analysis is similar to FTIR in that light is used to excite the sample and the amount reflected back is measured; however, FORS uses a shorter-wavelength light spectrum, which includes the visible spectrum. Due to the translucency of some of the samples, a matte black substrate was placed below each sample. The contact probe was pressed firmly to the sample until sufficient data was collected. To visualize small deflections in the spectra, data was first transformed from reflectance to absorbance data, using the following function:

$$A = log\left(\frac{1}{R}\right) \qquad \textit{eq. 1}$$

After transforming to absorbance data, the second derivative of the resulting function was taken. Derivation is a useful tactic to take with curves that appear very similar, as small perturbations in slope that are difficult to perceive in the raw data become much more pronounced in the derivative. In the case of this data, a second derivative was needed to make these perturbations pronounced enough to be noticeable. With FORS data, these small deflections in slope can indicate significant differences in the chemical makeup of the samples, especially given the fact that all of the samples of each tannage are chemically equivalent except for the relatively small amounts of treatment materials added to each one. Therefore, these mathematical manipulations were used to analyze what differences could be detected in the source data.

IV. Results & discussion

The effects of the treatments used may be considered in terms of positive effects versus negative effects. In this context, a positive effect of a treatment would include any stabilization or reversal of damage due to denaturation—that is, stabilization or improvement in properties such as shrinkage temperature and flexibility. By contrast, negative effects of a treatment would include any effect that causes unwanted changes, such as change in chemical composition of the original material or change in the appearance or texture of an object. Due to the nature of the investigative methods used, the results of this study can be divided into two broad categories: first, data describing physical properties, and second, data describing chemical properties. First, DSC analysis investigates changes in the response of the samples to heat. This analysis is therefore able to track *physical changes*, that is, changes in the samples' physical properties. In the case of denaturation, the material property being measured by DSC analysis is the shrinkage temperature, that is, the temperature at which denaturation begins, as well as the temperature range over which this transformation occurs. Shrinkage temperature has a direct correlation to the level of denaturation: the lower the T_s, the more denatured (i.e. disordered) the collagen molecules. Second, FTIR and FORS are able to track *chemical changes*, that is, changes in the samples' chemical makeup. It has long been known that while denaturation causes material changes due to differing organization of collagen molecules (i.e. conversion from triple helical structures to an amorphous mass), there is no chemical difference between collagen in its natural state and denatured collagen (Nomura *et al* 1977, Engel *et al* 1977).Therefore, DSC analysis can be used to investigate how the three treatments used affected the samples' material properties, specifically the samples' shrinkage temperatures and the water sensitivity which can be inferred from such data, while FTIR and FORS can be used to investigate the treatments' effect on the samples' chemical makeup. Due to the lack of chemical differences resulting from denaturation, FTIR and FORS data were somewhat difficult to interpret without mathematical manipulation, as the different samples had almost the same spectra with only small perturbations due to the treatment materials added to the sample.

Qualitative examination

After aging, all samples were evaluated qualitatively based on appearance and gross physical properties. Samples appeared to have darkened significantly when compared with the unaged controls, and to have stiffened as well. Unfortunately, it was not possible to quantitatively measure the flexibility of the coupons; all observations regarding flexibility derive from manually flexing the samples before and after treatment. In addition, vegetable tanned samples had all been affected by more aggressive denaturation which partially converted these samples into a dark, brittle glassy solid. Based on these changes, the aging treatment was considered a success. A comparative image of the artificially aged samples are shown in Fig. 3. Samples were also taken from a previously-degraded object from the collection described in section I. Figs. 3 and 4 show this artifact before treatment, along with a collection of related objects which are believed to be a set of beaded regalia.

After treatment, several changes from the aged appearance of the samples were noted. PEG-impregnated samples were the most drastically changed: they were severely darkened in appearance, and some curling during evaporation of the ethanol solvent was noted. Samples also had a greasy feel, due to the PEG which could easily be expressed from the sample by even gentle pressure. The samples treated with either Dow 1248 fluid or catechin, on the other hand, experienced less darkening and change in texture, although some samples had difficulty absorbing all of the Dow 1248 fluid applied during treatment. Treatment with catechin caused a significant increase in flexibility of the samples, although some white powdery material remained on the surface of the samples after the catechin poultice was removed.

Desired results

With regard to the physical and chemical properties of the samples, we may consider a certain set of changes to be favorable or desirable, e.g., increasing stability and durability, while limiting chemical change or change in appearance. Favorable changes monitored by DSC examination would include increased shrinkage temperature T_s, indicating a lower sensitivity to water, with a decreased peak width W_p, indicating more homogeneous material properties. Perfectly homogeneous material will all denature at the same temperature, resulting in a sharp peak with no width at all. By contrast, more heterogeneous material will undergo denaturation over a range of temperatures, resulting in a wide and shallow peak. FTIR and FORS examination are both able to track changes in the chemical properties of a given sample, while manual and visual examination are needed to monitor changes to the sample's flexibility and appearance. FORS analysis is also able to determine the amount of color change experienced by the material. In all cases, it is most desirable that the properties described above conform as closely as possible to those of the nondeteriorated material.

DSC investigation

After collecting DSC data, graphs were made showing the data from the heating stage, as denaturation is an irreversible process; therefore, no useful conclusions can be drawn from data collected during the cooling stage. An overview of the stages of the DSC analysis can be found in section III. The data were analyzed to determine the start and endpoints of the denaturation peak. Given that these peaks were often ambiguous and difficult to perceive, multiple measurements were taken to determine the start and endpoints. Data for one to two samples of each tannage and treatment, including controls, were analyzed in this way.

Sample	F-value	F_{crit}	p-value	α
Rawhide T_s	**11.6**	2.9	**1.8e-05**	0.05
Rawhide W_p	**79.36**	2.9	**6.19e-16**	0.05
Oil-tanned T_s	**736.90**	3.24	**<2e-16**	0.05
Oil-tanned W_p	**46.21**	3.24	**4.18e-08**	0.05
Vegetable-tanned T_s	*3.12*	3.07	*0.05*	0.05
Vegetable-tanned W_p	0.72	3.07	0.55	0.05
Armband T_s	**42.93**	3.24	**7.05e-08**	0.05
Armband W_p	**11.93**	3.24	**0.00024**	0.05

Table I. F-values and p-values for ANOVA analyses of all samples, with regard to shrinkage temperature (T_s) and peak width (W_p).

Where $p \leq \alpha$, the variance is considered significant. If $p > \alpha$, but the F-value exceeds F_{crit}, then the null hypothesis may be rejected. If $p > \alpha$ and $F < F_{crit}$, then the null hypothesis is still valid. The α-value was chosen by myself based on statistical convention; F_{crit} is determined by the degrees of freedom present in the data. Slightly significant results are indicated with italics, while strongly significant results are indicated with bolded text.

To determine whether any of the treatments had had a statistically significant effect on the denaturation temperature (start of peak) or the denaturation range (width of peak), one-way analysis of variance (ANOVA) was performed on these data. Based on this analysis, the treatments had a statistically significant effect on both these properties in all but one case. Where $p \leq 0.05$, a Tukey's honest significant difference (HSD) test was performed to determine which treatment had had a significant effect. This test provided the difference between each variable's effect, as well as the significance of that difference.

While the results for each tannage varied in statistical significance, several trends held through the studied tannages. In all cases, the silicone and PEG treatments did not significantly increase the shrinkage temperature (T_s), therefore indicating no reproducible recovery of water resistance; moreover, in the rawhide and oil-tanned samples, the silicone treatment reduced the T_s, which in turn reduced the materials' water resistance even more. In oil-tanned samples, the

	PEG treatment		Dow 1248 treatment		Catechin treatment	
Tannage	**T_s**	**W_p**	**T_s**	**W_p**	**T_s**	**W_p**
Rawhide	Ø	Ø	↓	↔	Ø	→←
Oil-tanned	↓	→←	↓	Ø	↑	→←
Vegetable	Ø	Ø	Ø	Ø	Ø	Ø
Armband	Ø	→←	Ø	→←	↓	→←

Table II. Summary of significant effects of PEG, silicone, and catechin treatments.

Increase and decrease of shrinkage temperature T_s with respect to the control are indicated with arrows ↑ and ↓.
Increase and decrease of peak width W_p with respect to the control are indicated with double arrows ↔ and →←.
Lack of significant change is indicated with Ø.

effect of the silicone treatment was slightly less severe than the effect of the PEG treatment, which depressed the T_s the most significantly of all three treatments. While neither treatment had a significant effect on the vegetable-tanned samples (compared to the control), the data show that in this case the silicone treatment had a slightly more severe effect than the PEG treatment. However, all the results for vegetable-tanned samples had very high p-values, so only a small significance can be placed on this data. The results from the catechin treatment are somewhat more vague. Although the treatment had a significant, positive effect on the T_s for the oil-tanned sample, it did not have a significant effect on the rawhide or vegetable-tanned samples, and on the armband sample it had a significant but negative effect on the T_s.

However, results regarding the width of the denaturation peak were more consistent. For all samples except the vegetable-tanned sample, in which there was no significant change to peak width (W_p), the catechin treatment caused a reduction in W_p. In terms of the material, a decrease in W_p correlates to a more homogeneous material with regard to water sensitivity. In the rawhide and oil-tanned samples, the silicone treatment caused an increase in W_p, while in the armband sample this treatment caused a decrease. The PEG treatment caused a decrease in W_p for the oil-tanned and armband samples; this effect is less than that of the catechin for the oil-tanned sample, and does not differ significantly from the effect of catechin on the armband sample.

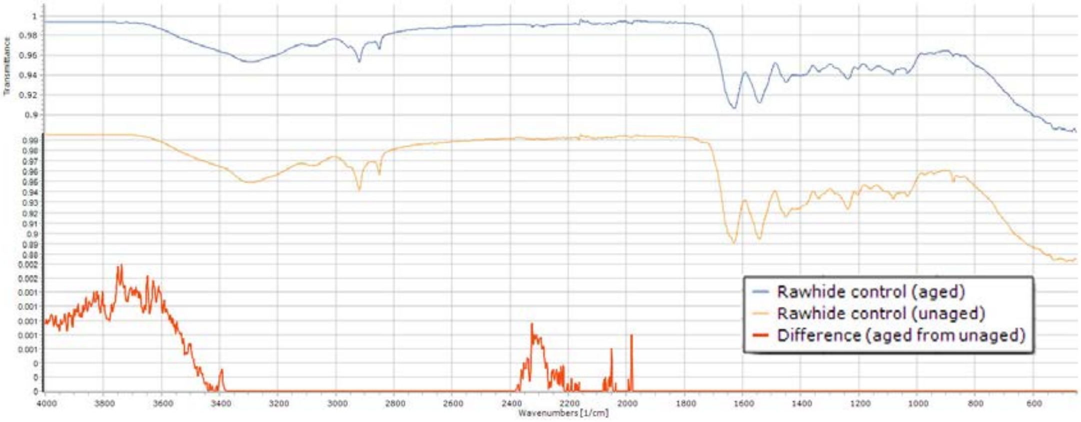
FTIR investigation

After comparing FTIR data of aged and unaged controls, I was unable to detect any chemical difference between the two samples (see Fig. 4). This result conforms to expectations, as the aging was intended to cause denaturation only, which does not change the chemical makeup of the material beyond the amount of free water in the system. Therefore, it may be assumed that all chemical changes in treated samples are due to the treatments applied, not to the aging process. To visualize these chemical changes, FTIR spectra for treated samples were subtracted from the control spectra and plotted together to compare the relative amounts of chemical change due to each treatment. Each of the subtracted graphs is either featureless, indicating perfect similarity between the two compared spectra, or has only small noise peaks (see rawhide sample spectra). These graphs are shown in Fig. 5.

Based on these data, it is clear that the PEG impregnation treatment caused the most obvious compositional alteration. This is not altogether surprising, as PEG is both unreactive with collagen as well as significantly different from collagen with regards to its chemical makeup. Therefore, the signal received from the PEG-impregnated material shows a significant alteration from the untreated state. Chemical change due to the Dow 1248 fluid treatment appeared variable, with oil-tanned samples experiencing the greatest change and vegetable-tanned samples experiencing the least. The greater change in oil-tanned versus rawhide samples may be due to the lower density of oil-tanned leather. Catechin-treated samples also experienced variable change: oil-tanned samples again experienced the most change, while vegetable-tanned and armband samples experienced no discernible change. This variability may be due to different samples’ ability to react with the treatment materials. However, regardless of the

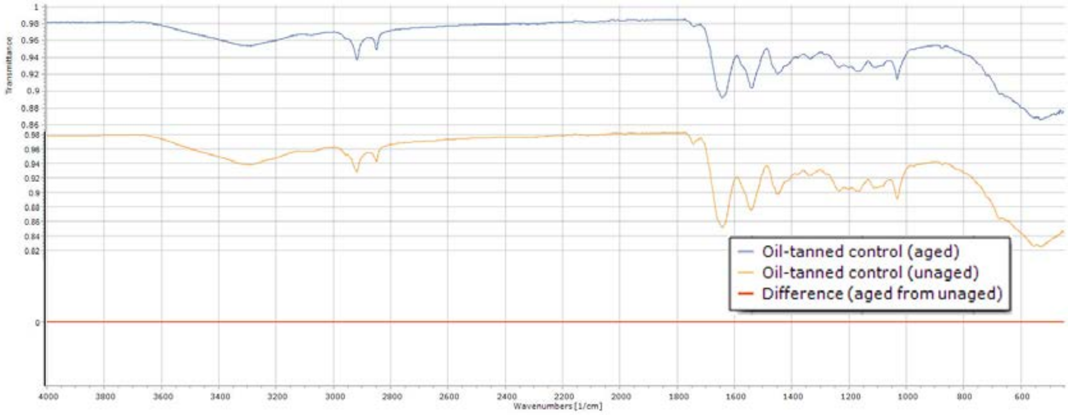
Rawhide Sample

Effect of Ageing



Oil-Tanned Sample

Effect of Ageing



Vegetable-Tanned Sample

Effect of Ageing

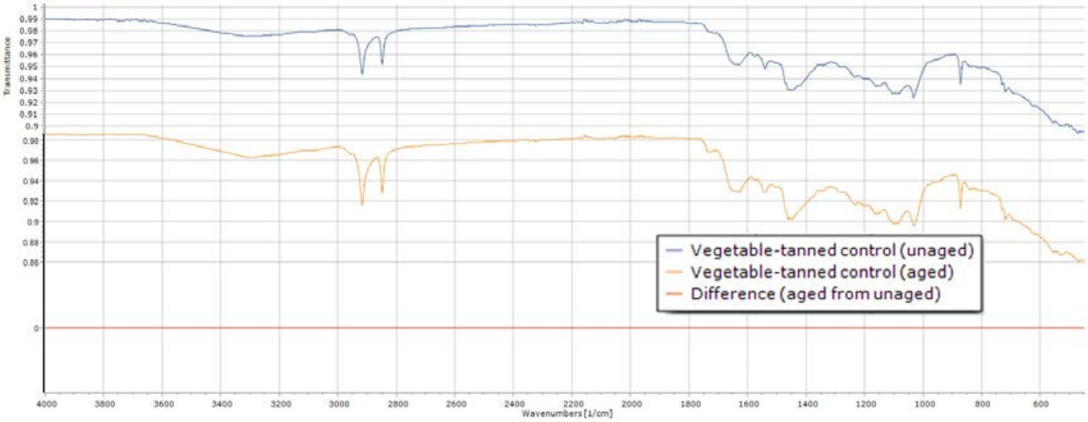
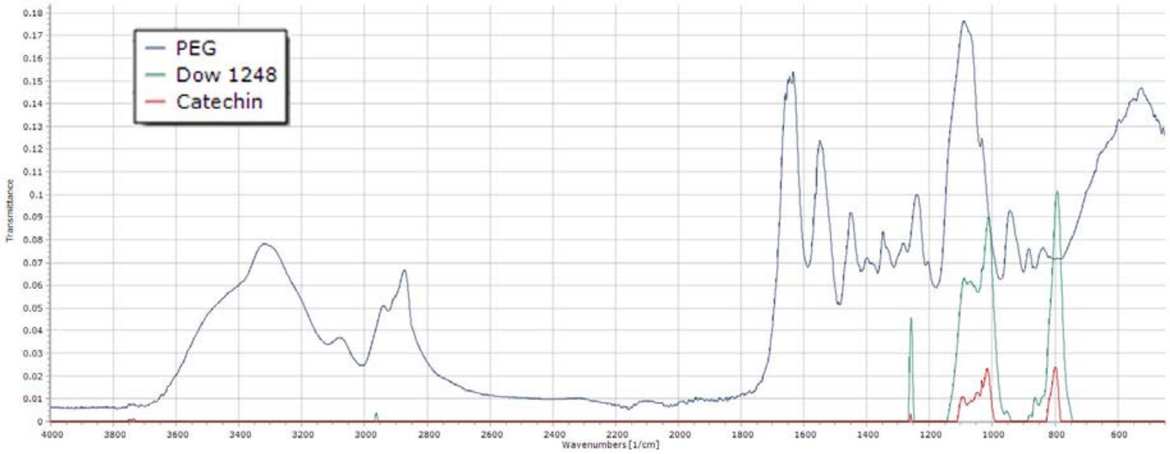


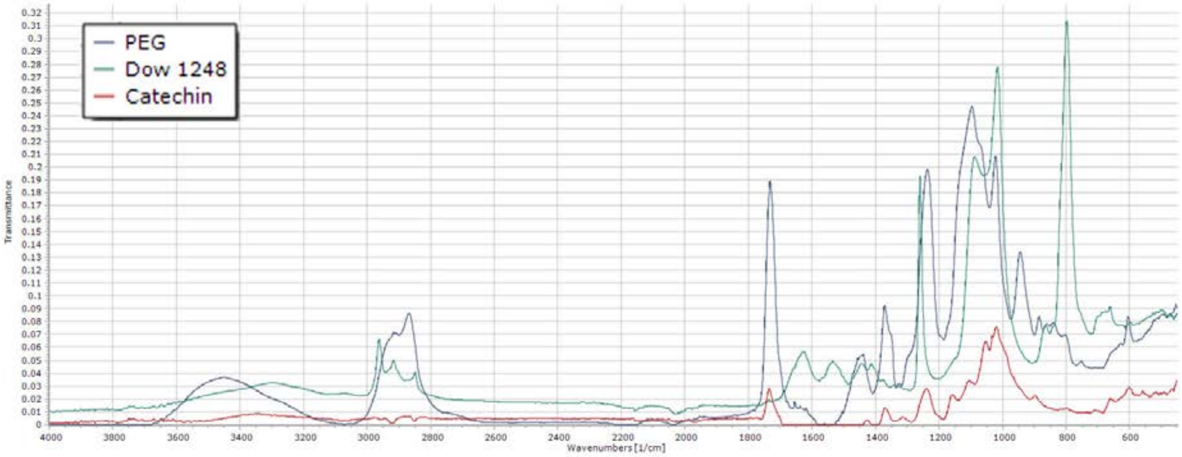
Fig. 5. Subtraction of FTIR spectra from aged and unaged controls.

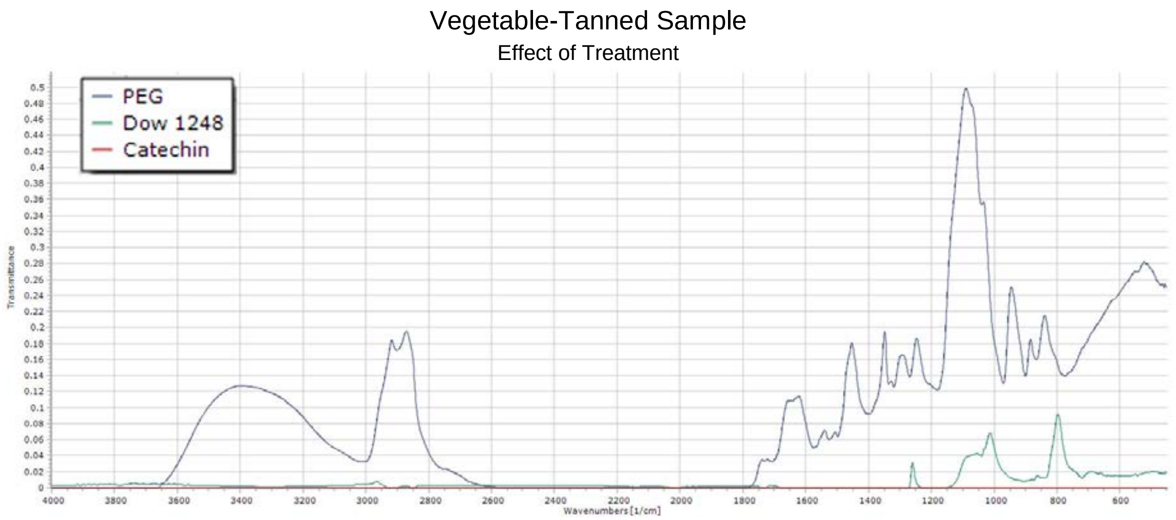
From top: Rawhide, oil-tanned, and vegetable-tanned samples. Rawhide exhibits a small difference between aged and unaged controls, while oil-tanned and vegetable-tanned samples show no change.

Rawhide Sample
Effect of Treatment



Oil-Tanned Sample
Effect of Treatment




Vegetable-Tanned Sample
Effect of Treatment

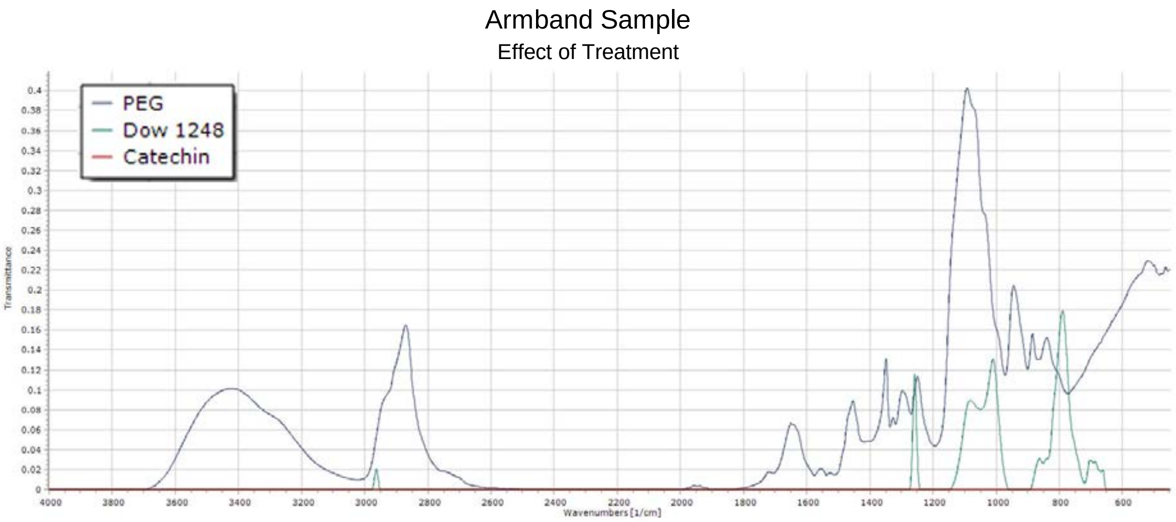

Armband Sample
Effect of Treatment

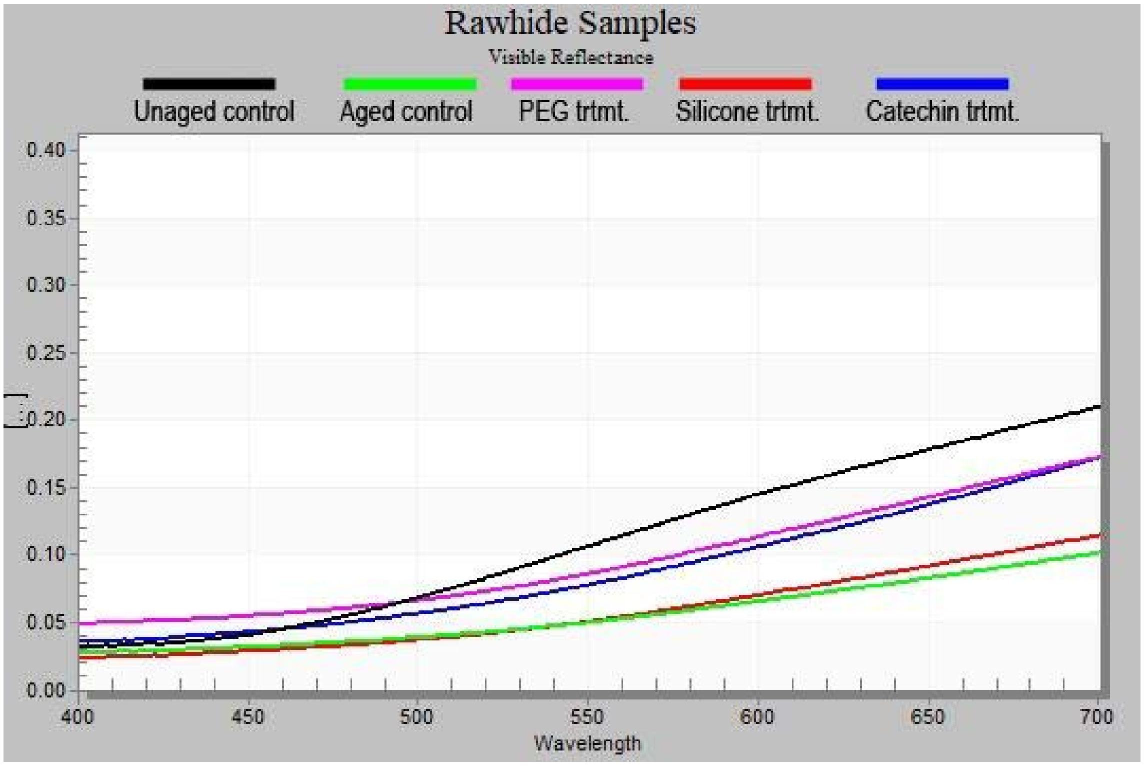
Fig. 6. FTIR spectra showing effects of treatments on samples of different tannages.
From top: Rawhide, oil-tanned, vegetable-tanned, and armband samples.

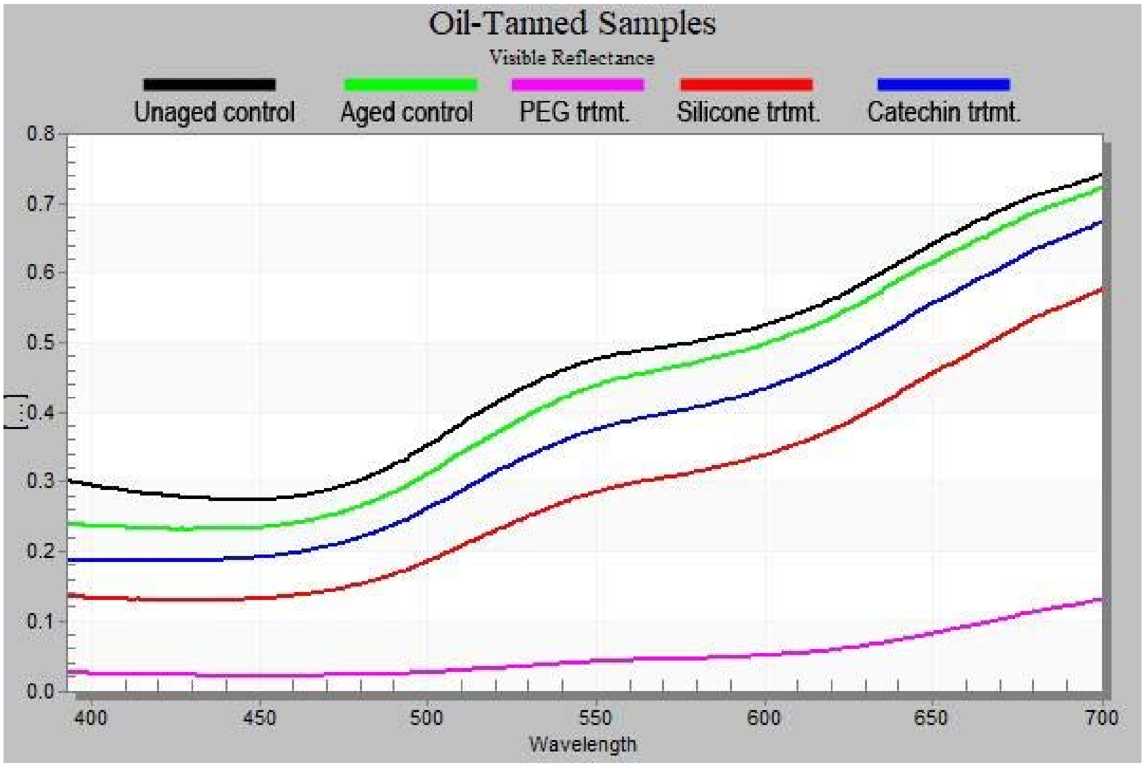
objective change experienced due to each treatment, PEG-treated samples always differed the most from control samples, while catechin-treated samples were always the least chemically changed from the control state.

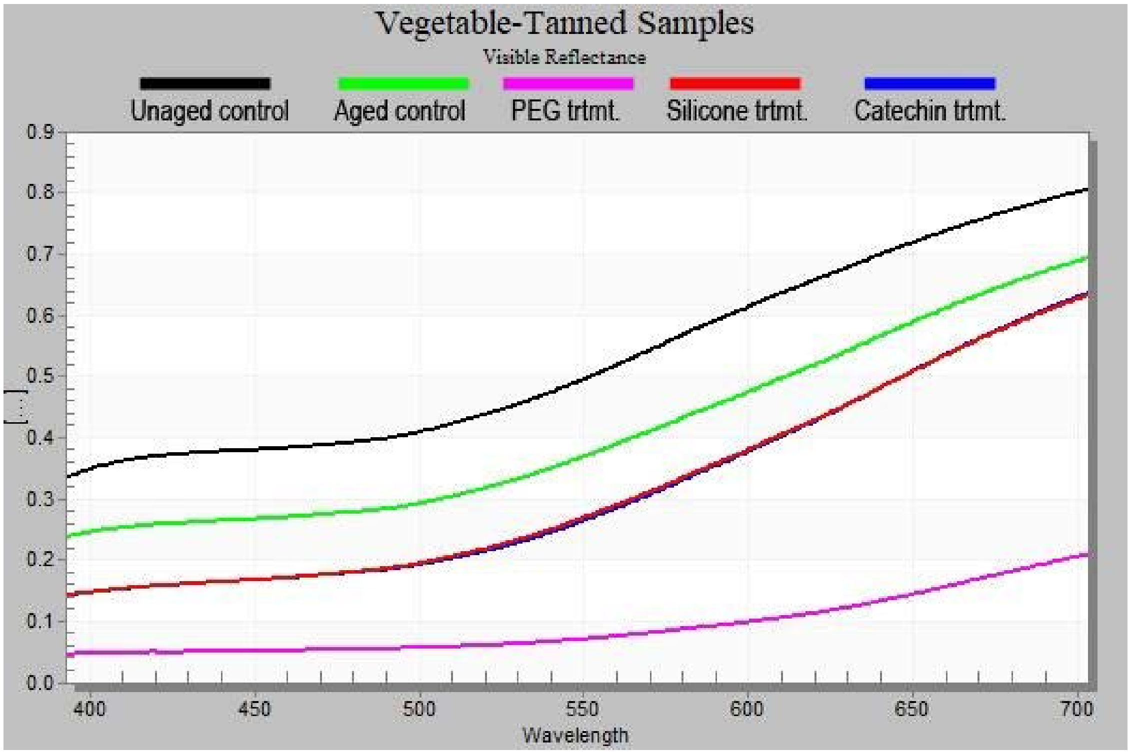
FORS investigation

FORS data was investigated both overall (350 nm ≤ λ ≥ 1800 nm) and in the visible spectrum (nm 400 ≤ λ ≥ 700 nm). Visible-spectrum data revealed that although all samples experienced darkening relative to unaged samples even after treatment, PEG-treated samples always experienced the most darkening, and catechin-treated samples typically experienced the least darkening (Fig. 7). Therefore, it may be concluded that the experimental catechin treatment offers the closest appearance to an object's nondeteriorated state.

When comparing the overall FORS spectra, it was necessary to carry out the manipulations shown in section III to detect what were very slight differences between spectra. As above stated, these manipulations amplify the differences between the spectra, which in the raw data were extremely difficult if not impossible to perceive. Once these transformations were performed, the conclusions drawn from FTIR data were confirmed. Once again, PEG-treated samples experienced the most deviation from the chemistry of control samples, while catechin-treated samples experienced the least deviation. Comparative spectra may be seen in fig. 8.




Oil-Tanned Samples
Visible Reflectance
Unaged control
Aged control
PEG trtmt.
Silicone trtmt.
Catechin trtmt.
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
400
450
500
550
600
650
700
Wavelength


Vegetable-Tanned Samples
Visible Reflectance
Unaged control
Aged control
PEG trtmt.
Silicone trtmt.
Catechin trtmt.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
400
450
500
550
600
650
700
Wavelength

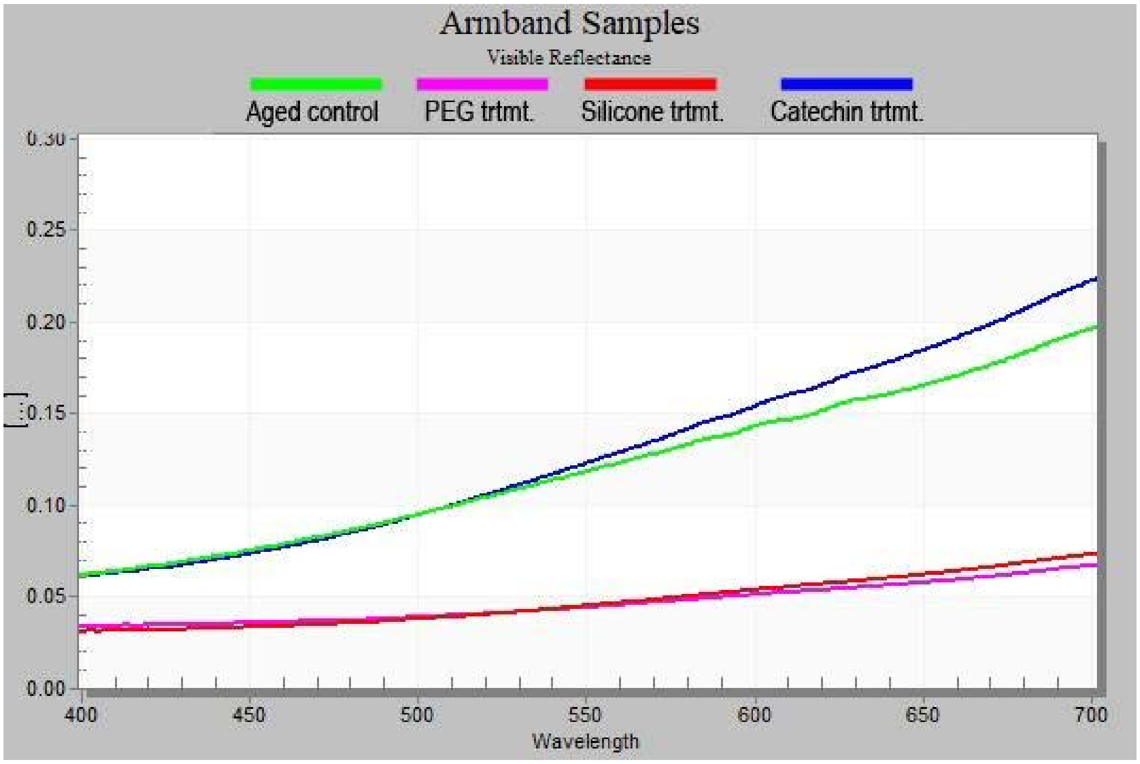
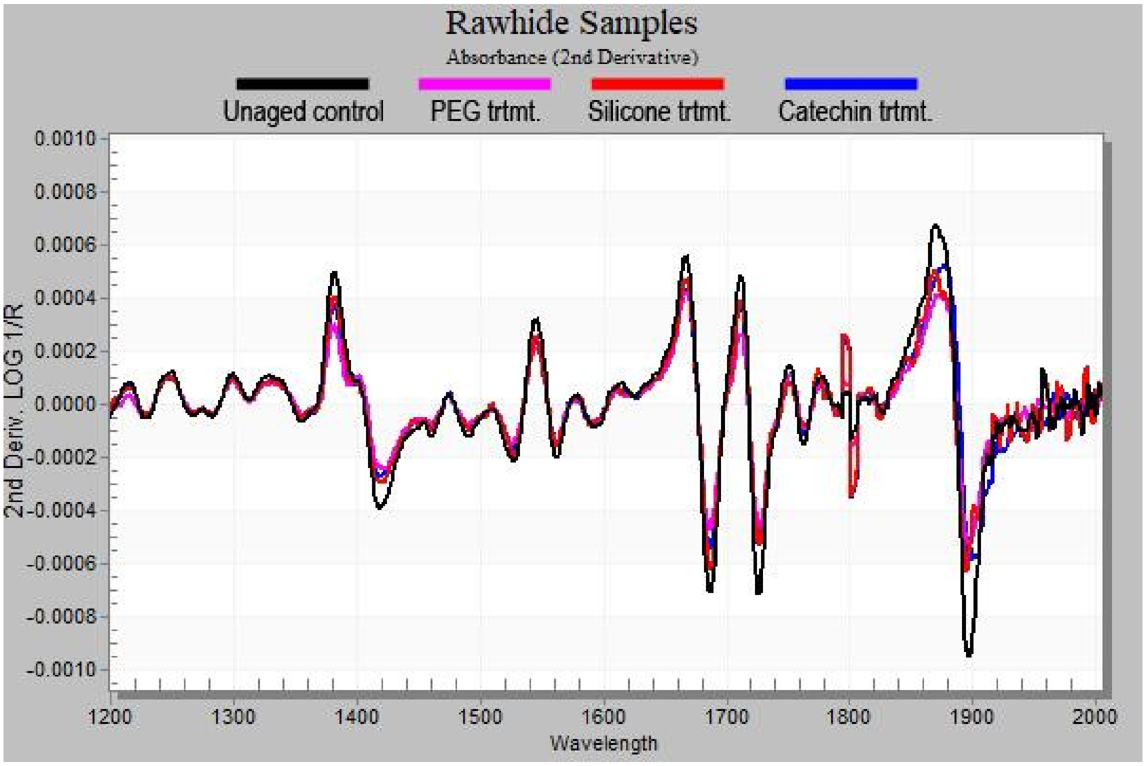
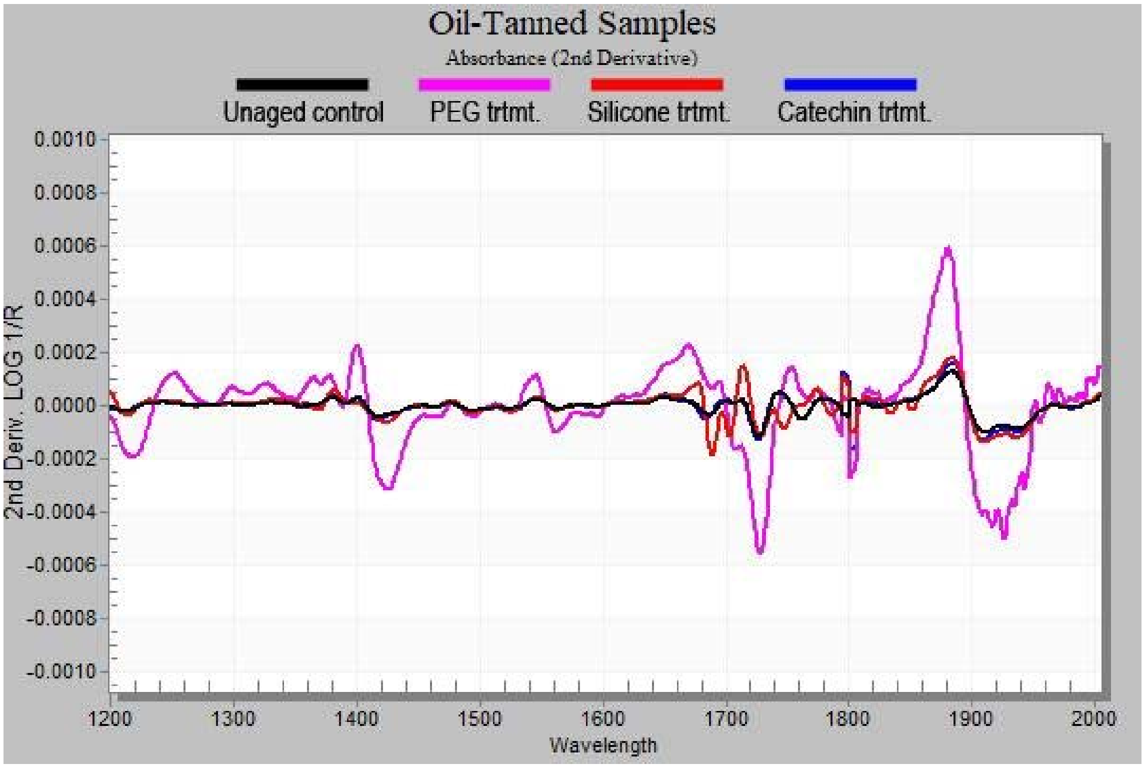
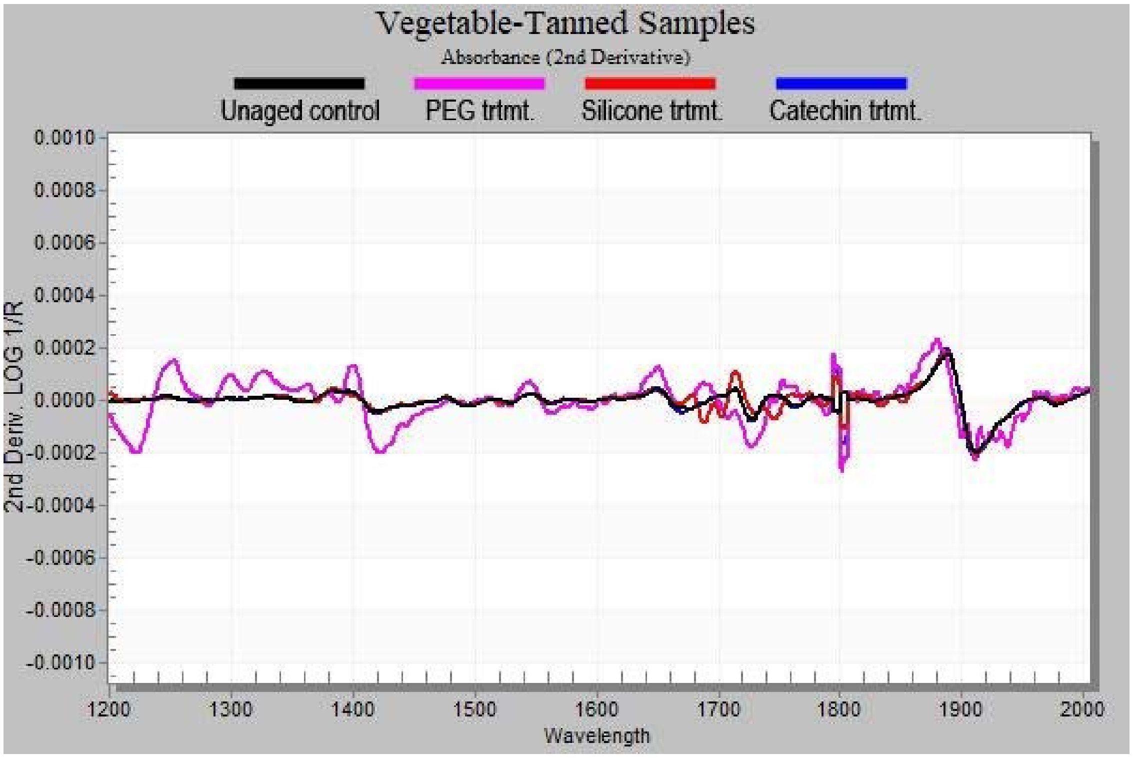


Fig. 7. Color change in samples of different tannages after aging and treatment.




Oil-Tanned Samples
Absorbance (2nd Derivative)
Unaged control
PEG trtmt.
Silicone trtmt.
Catechin trtmt.
2nd Deriv. LOG 1/R
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
-0.0002
-0.0004
-0.0006
-0.0008
-0.0010
1200
1300
1400
1500
1600
1700
1800
1900
2000
Wavelength


Vegetable-Tanned Samples
Absorbance (2nd Derivative)
Unaged control
PEG trtmt.
Silicone trtmt.
Catechin trtmt.
2nd Deriv. LOG 1/R
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
-0.0002
-0.0004
-0.0006
-0.0008
-0.0010
1200
1300
1400
1500
1600
1700
1800
1900
2000
Wavelength

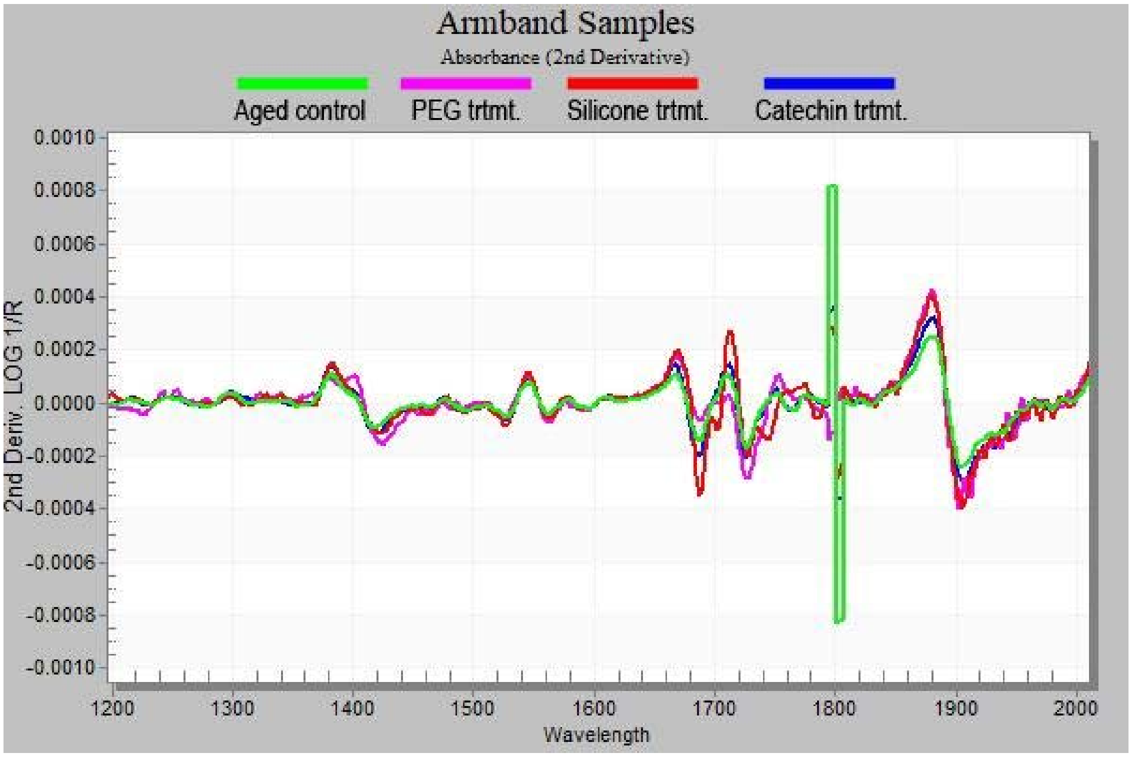


Fig. 8. Chemical change in samples of different tannages after aging and treatment.

V. Conclusions

Successfulness of catechin treatment

While DSC study showed that the effect of the catechin treatment on the samples' material properties varied strongly between the tannages, it was able to show that in most cases, the catechin treatment performed better than the other two treatments studied. In all but one case, the catechin-treated samples performed the same or better than the untreated material with regards to their T_s and W_p. By contrast, neither the silicone nor the PEG treatment were able to improve either property, and in several cases actually performed worse than the control.

FTIR and FORS data both showed that catechin-treated samples experienced the least amount of chemical change of all the treated samples, while PEG-treated samples experienced the most change. Visual examination, corroborated by FORS, also found that catechin and silicone-treated samples experienced the least color change, although some change did occur. Manual examination also showed that catechin-treated samples experienced the most increase in flexibility, while little to no change was experienced in the PEG-treated samples.

To demonstrate the effect of the experimental treatment on an object rather than a sample, the armband from which samples had been harvested for this study was treated with catechin. After treatment, the object's visual appearance was not much changed; however, one significant change was noted. Even after all the ethanol was allowed to evaporate from the poulticed object, it was noticeably more flexible than its twin, which had not been treated. As before, this change was noted after manual manipulation of the object. This result demonstrates the practical usefulness of this experimental treatment.

As has been thoroughly shown above, denaturation endangers objects by embrittling them, making handling impossible for fragile objects. By treatment with catechin, objects which otherwise would be unavailable for study due to their fragility may be handled safely. The collection described in the introduction provides an example. Due to their current extremely stiff and brittle state, research investigating any interior part of the objects (such as investigation of sewing techniques for decorative elements) would be extremely difficult if not impossible. In addition, objects with fringe and other delicate elements are extremely difficult to handle, as the brittle fringes and ties are prone to breakage. If these objects were to be treated with catechin, the flexibility this treatment would allow access to these otherwise inaccessible objects and the information that could be derived from their study.

Ethical concerns

In terms of conservation ethics, the novel treatment developed by this study adheres more closely to this code of ethics than the others studied in several ways. It more fully fulfils the conservation principle of reversibility or retreatability, and it is much more materially compatible with leather and skin materials than PEG or silicone-based treatments. While no surface treatment of a porous substrate can be truly said to be reversible, the introduction of a material which mimics the presumed original state of the material is considered re-treatable – that is, the material may be re-treated with the same treatment in the future with the same results as the first treatment (Smars 1998). Treatment with catechin fulfils this requirement, and to an extent so does PEG impregnation, although retreatment with PEG would require a removal process that may prove extremely stressful for the object. Silicone-based treatments are not reversible or retreatable, given that they bond permanently to the material and do not deteriorate over time.

In terms of material compatibility, PEG is somewhat compatible with collagen materials, being a carbon-based molecule. However, its appearance and chemistry is still extremely different from leather and skin materials. Silicone is even less compatible: not only are its physical properties very different from leather and skin, but its chemistry is also entirely different. Catechin, however, is a chemical very similar to the ones used in the initial treatment of leather and semi-tanned skin materials, and as such is chemically very compatible with leather and skin materials. Such material compatibility might make this treatment favorable in terms of the ethics of treating Native American objects; in my experience, Native communities frequently object to the use of synthetic materials in treatments for their material culture.

Beyond these advantages, the novel catechin treatment is also preferable over the other treatments studied due to the difference in volume of treatment material. While significant amounts of PEG and Dow 1248 fluid were needed to treat the samples, each sample treated with catechin received a minute amount of the chemical – only 15mg per sample. The small amount needed to effect treatment means that the overall materiality of the object is much less changed after catechin treatment than after the other treatments examined. In addition, catechin is non-toxic, making it much safer to use than treatments such as Dow 1248 fluid, which is highly toxic (Dow Corning 2016).

Implication of this study and future study avenues

While the results of this study are promising, more research is needed to quantify the effects of catechin on denatured leather. This study was unable to analyze the changes in the material's flexibility in a quantitative manner; in addition, it did not image the treated samples at high magnification. This study also focused on artificially tanned samples of a single species, cattle. In addition to corroborative studies, studies which focused on quantifying these qualities, which were regrettably outside the scope of this thesis, would provide a more complete picture of the effect of catechin on leather and skin materials, and would aid in understanding whether it is indeed an effective treatment for denaturation. For example, a flexing machine for testing rubber and other similar products could be used to quantify the change in flexibility and durability in treated samples, while SEM investigation could be used to examine changes in microstructure before and after aging and/or treatment. Most importantly, this treatment should be reproduced on a greater number and variety of samples than I was able to encompass with this study. While initial results were very promising, only further testing can show whether those results can be more firmly predicted, and a confident prediction of success is mandatory for a treatment to be applied to an irreplaceable artifact.

Ultimately, it should not be surprising that repurposing treatments for different degradations of leather materials would prove to be ineffective and even harmful to apply to denatured leather and skin materials. Because consolidants are only useful when treating a material that has experienced disaggregation — a phenomenon that does not accompany denaturation — it could be said that applying a consolidant to denatured leather fixes a problem it doesn’t have. Moreover, in applying such a treatment, a conservator may violate the fundamental conservation ideal of reversibility or retreatability. Therefore, the development of a dedicated treatment for denaturation is necessary, so that future conservators have viable options for the treatment of delicate and significant denatured leather and skin objects. While it is important to note that the experimental treatment tested in this thesis is itself more extreme than necessary for some objects affected by denaturation, it is still worth considering for cases where restoration of pre-degradation properties is necessary or valuable; for example, fragile costumes, books, or decorative elements may be treated in this way to allow for movement or manipulation that would destroy the object in its untreated state.

Appendix A: Materials and Suppliers

CATECHIN HYDRATE — polyphenolic flavonoid isolated from plant matter with a chemical formula of $C_{15}H_{14}O_6 \cdot H_2O$, supplied as a powdered solid. Manufactured by Cayman Chemical and supplied by Fisher Scientific, www.fishersci.com.

DOW 1248 FLUID — proprietary organoreactive polydimethylsiloxane fluid, described by the manufacturer as a “silicone glycol graft copolymer”. Manufactured by Dow Corning and generously supplied as a free sample by Univar USA, 305 N Henry Ford Ave, Long Beach, CA 90802, (310) 833-1540, www.univar.com/us.

ETHANOL — short-chain alcohol with a chemical formula of C_2H_5OH. Supplied by J.T. Baker through Fisher Scientific, www.fishersci.com.

OIL-TANNED LEATHER — split cow’s hide treated with drying oils and dyed a light cream color. Supplied by The Leather Guy, 149 West Circle Drive, St. Charles, MN 55972, 507-932-3795, www.theleatherguy.org.

POLYETHYLENE GLYCOL (PEG) 400 — Oligomer (short-chain polymer) with a chemical formula of $HO[CH_2CH_2]_nH$, where $n \approx 400$. Supplied by Sigma-Aldrich, www.sigmaaldrich.com.

RAWHIDE — scraped and dried full-thickness cow’s hide. Supplied by Centralia Fur and Hide, 2012 Gallagher Road, Centralia, WA 98531, 360-736-3663, www.furandhide.com

SILICA GEL — porous silica pellets with cobalt hydration indicator, used to absorb free humidity in the air. Conditioned to maintain local RH at 50%. Supplied by TALAS, http://www.talasonline.com.

VEGETABLE TANNED LEATHER — undyed, full-thickness cow’s hide treated with vegetable tannins. Supplied by The Leather Guy, 149 West Circle Drive, St. Charles, MN 55972, 507-932-3795, www.theleatherguy.org.

Appendix B: Tables & Figures

Table I: Analysis of variance (ANOVA) of shrinkage temperature (T_s) and peak width (W_p) for all samples.

Df: degrees of freedom
Sum Sq: Sum of the squares due to the source of variance
Mean Sq: Mean sum of the squares due to the source of variance
F value: F-statistic
P: P-value

Where p≤0.05, the variance is considered statistically significant.

Rawhide

		T_s			
	Df	Sum Sq	Mean Sq	F value	P
Treatment	3	526.60	175.54	11.62	1.8e-05 ***
Residuals	36	544.10	15.11		

		W_p			
	Df	Sum Sq	Mean Sq	F value	P
Treatment	3	4210	140.35	79.36	6.19e-16 ***
Residuals	36	63.70	1.77		

Oil-tanned

		T_s			
	Df	Sum Sq	Mean Sq	F value	P
Treatment	3	128.27	42.76	736.90	<2e-16 ***
Residuals	16	0.93	0.06		

		W_p			
	Df	Sum Sq	Mean Sq	F value	P
Treatment	3	13.83	4.61	46.21	4.18e-08 ***
Residuals	16	1.60	0.10		

Vegetable

		T_s			
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Treatment	3	362.70	120.91	3.12	0.05 *
Residuals	21	815.20	38.82		

		W_p			
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Treatment	3	21.05	7.02	0.72	0.55
Residuals	21	203.95	9.71		

Armband

		T_s			
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Treatment	3	52.14	17.38	42.93	7.05e-08 ***
Residuals	16	6.48	0.41		

		W_p			
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Treatment	3	18.40	6.13	11.93	0.00024 ***
Residuals	16	8.22	0.51		

Table II. Tukey's honestly significant difference (HSD) of all significant ANOVA analyses.

Diff: difference
Lwr: lower limit
Upr: upper limit
p_{adj}: Adjusted p-value

Where $p_{adj} \leq 0.05$, the variance is considered statistically significant.

Rawhide

		T_s		
	diff	lwr	upr	p_{adj}
P-R-C-R	0.92	-3.76	5.61	0.95
S-R-C-R	-8.20	-12.90	-3.52	0.0002
TAR-C-R	-0.72	-5.41	3.96	0.98
S-R-P-R	-9.13	-13.81	-4.44	0.00004
TAR-P-R	-1.65	-6.33	3.04	0.78
TAR-S-R	7.48	2.80	12.16	0.00069

		W_p		
	diff	lwr	upr	p_{adj}
P-R-C-R	6.96	5.36	8.56	0
S-R-C-R	8.41	6.81	10.01	0
TAR-C-R	6.61	5.01	8.21	0
S-R-P-R	1.45	-0.15	3.05	0.088
TAR-P-R	-0.35	-1.95	1.25	0.93
TAR-S-R	-1.8	-3.40	-0.20	0.023

Oil-tanned

		T_s		
	diff	lwr	upr	p_{adj}
P-O-C-O	-7.09	-7.52	-6.65	0
S-O-C-O	-3.26	-3.70	-2.82	0
TAO-C-O	-2.64	-3.07	-2.20	0
S-O-P-O	3.83	3.39	4.26	0

TAO-P-O	4.45	4.01	4.89	0
TAO-S-O	0.62	0.19	1.06	0.0042

		W_p		
	diff	lwr	upr	p_{adj}
P-O-C-O	1.09	0.52	1.66	0.00028
S-O-C-O	2.21	1.63	2.78	0
TAO-C-O	1.76	1.19	2.34	0.0000008
S-O-P-O	1.12	0.54	1.69	0.00022
TAO-P-O	0.67	0.10	1.25	0.018
TAO-S-O	-0.44	-1.013	0.13	0.16

Vegetable

		T_s		
	diff	lwr	upr	p_{adj}
P-V-C-V	-6.25	-17.23	4.74	0.41
S-V-C-V	4.40	-6.58	15.39	0.68
TAV-C-V	-4.18	-13.70	5.33	0.62
S-V-P-V	10.65	-0.34	21.63	0.060
TAV-P-V	2.062	-7.45	11.57	0.93
TAV-S-V	-8.59	-18.10	0.93	0.086

Armband

		T_s		
	diff	lwr	upr	p_{adj}
P-A-C-A	3.57	2.42	4.72	0.0000008
S-A-C-A	4.18	3.03	5.34	0.0000001
TAR-C-A	3.13	1.98	4.28	0.0000044
S-A-P-A	0.62	-0.54	1.77	0.44
TAR-P-A	-0.44	-1.59	0.71	0.70
TAR-S-A	-1.06	-2.21	0.10	0.078

		W_p		
	diff	lwr	upr	p_{adj}

P-A-C-A	-0.75	-2.05	0.54	0.37
S-A-C-A	0.17	-1.12	1.47	0.98
TAR-C-A	1.87	0.57	3.17	0.0040
S-A-P-A	0.93	-0.37	2.23	0.21
TAR-P-A	2.62	1.33	3.92	0.00015
TAR-S-A	1.70	0.40	2.99	0.0087

Figures

During-Testing Photographs

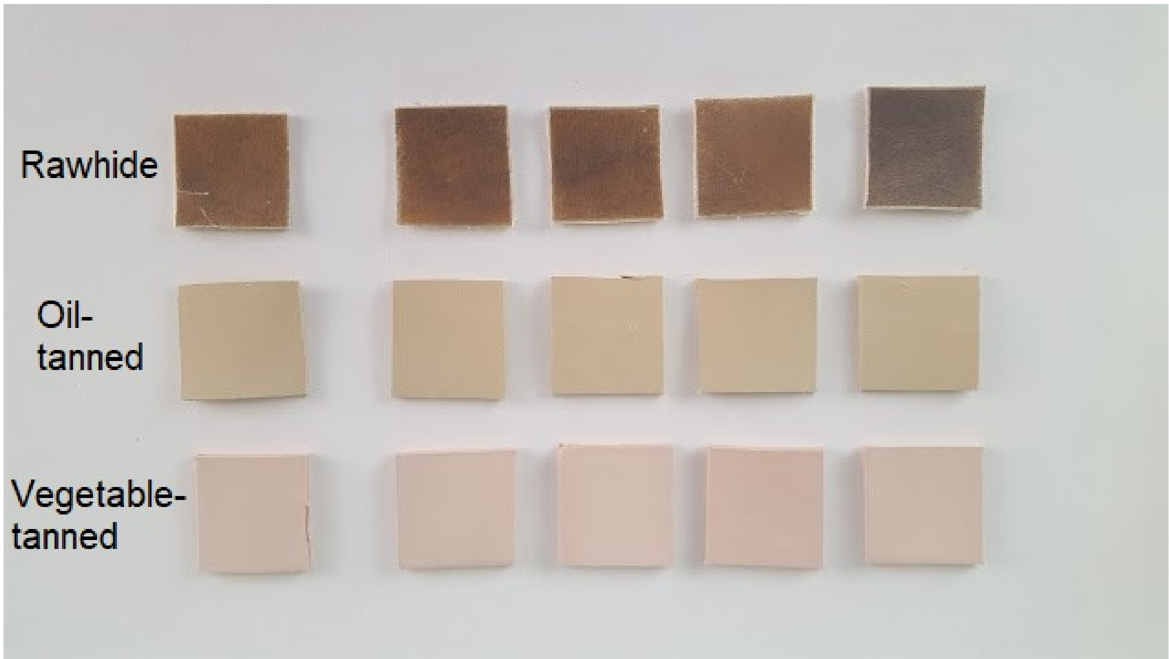


Fig. 1. Appearance of samples prior to aging.

Fig. 2. Appearance of aged samples (pre-treatment) with unaged controls.

Fig. 3. Appearance of aged samples (post-treatment) with aged and unaged controls.

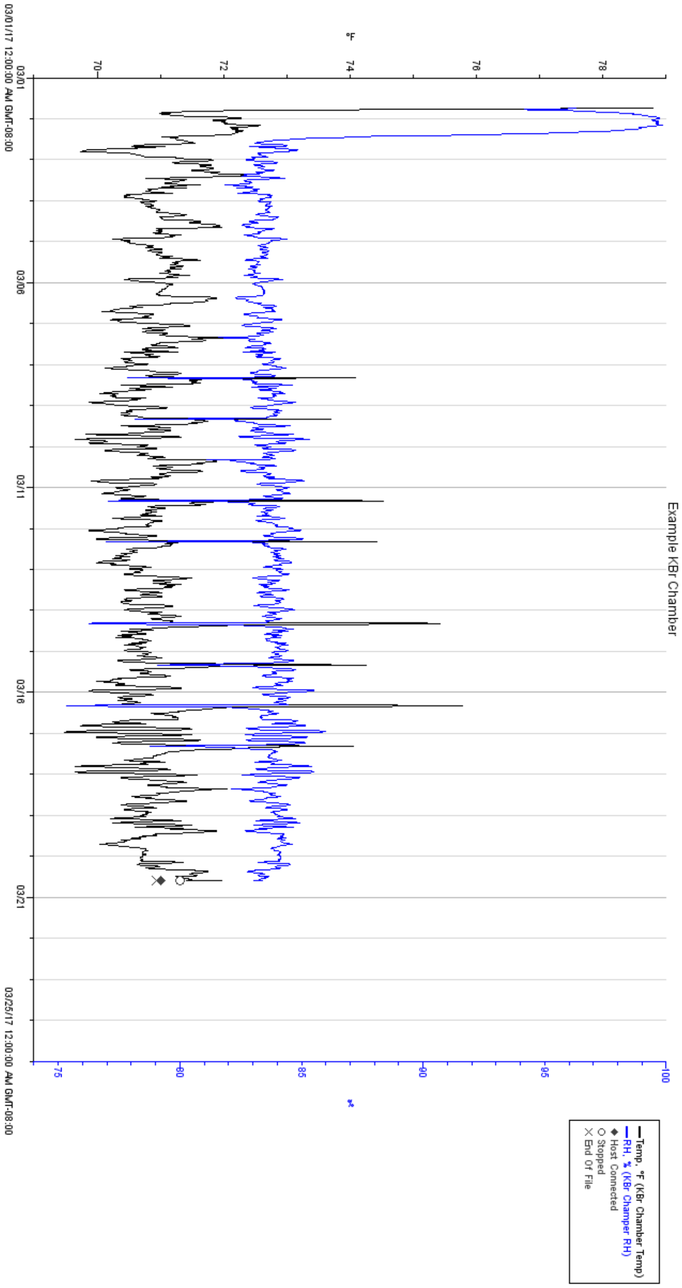
Fig. 3. Initial setup and testing of aging chamber.

Fig. 4. Setup for desiccation of catechin hydrate.

Appendix C: Environmental data

Example KBr-Conditioned Chamber

Environmental data was collected for the example KBr chamber as a proof that the solution was able to condition the interior. This data is provided below.



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