LEATHER COATED WITH MIXTURES OF HUMECTANT AND ANTIOXIDANTS TO IMPROVE ULTRAVIOLET AND HEAT RESISTANCE

by

CHENG-KUNG LIU,[*] MILA ALDEMA-RAMOS, NICHOLAS P. LATONA, AND RENÉE J LATONA
United States Department of Agriculture,[**] Agricultural Research Service
Eastern Regional Research Center
600 EAST MERMAID LANE,
WYNDMOOR, PA 19038-8598

ABSTRACT

Ultraviolet (UV) and heat resistance are very important qualities for leather products. We recently developed an environmentally friendly finishing process for improving the UV- and heat resistance of chrome-free leather. We previously reported and demonstrated some promising results from coating tocopherol, a natural antioxidant, onto the grain layer of leather. Tocopherol (Vitamin E) is a potent free radical scavenger and highly protective agent for collagen fibers against UV damage. This antioxidant has improved the UV- and heat resistance of the leather product. To help prevent over-drying, glycerol, a humectant, is added to tocopherol to not only maintain proper moisture content, but also to improve the UV and heat resistance of leather. The mixture of glycerol and tocopherol is applied as an emulsion with sodium dodecyl sulfate (SDS), as an emulsifying agent, and coated on the grain layer of leather. Following exposure in a Fade-Ometer, the treated samples were evaluated by colorimetry and mechanical testing for the efficacy of UV- and heat resistance. Data showed that leather coated with glycerol/tocopherol exhibited significant improvement in color fading resistance against UV radiation and heat.

RESUMEN

Las resistencias a la radiación ultravioleta (UV) y al calor son propiedades importantísimas en productos de cuero. Recientemente hemos desarrollado un proceso de acabado ecológicamente amigable para mejorar las resistencias a UV y al calor en cuero exento de cromo. Previamente hemos reportado y demostrado resultados prometedores por recubrimiento del tocoferol, un antioxidante natural, sobre la flor del cuero. Tocoferol, (vitamina E) es un poderoso recolector de radicales libres y un agente altamente protector de las fibras del colágeno contra destrucción por UV. Este antioxidante ha mejorado la resistencia al calor y UV del cuero. Para prevenir **un** excesivo secado, glicerina, un humectante, es añadido al tocoferol, no solo para mantener la apropiada humedad, como para también mejorar las resistencias al calor y UV del cuero. La mezcla de de glicerina y tocoferol se aplica como una emulsión con dodecil sulfato de sodio (SDS), como emulgador y así recubrir la flor de este cuero. Luego de exponer [a la radiación] en un Fadometro, las muestras así tratadas fueron evaluadas por pruebas colorimétricas y físicas por la eficacia de resistencia contra UV y el calor. Las mediciones demostraron que cueros acabados con glicerina/tocoferol demostraron significante mejora en solidez del color contra UV y calor.

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[*] Corresponding author e-mail address: ChengKung.Liu@ars.usda.gov

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INTRODUCTION

In recent years, environmental concerns over the use and disposal of chrome-tanned leather has encouraged the use of chrome-free leather.[1, 2] Among many non-chrome tannages, glutaraldehyde has stood out to be the dominant tanning agent for the preparation of chrome-free leather. Glutaraldehyde tanning was developed in the early 1960's[3-7] by Filachione *et al*. in the Eastern Regional Research Center (ARS, ERRC). Over the years, it has become the most common alternative tanning agent to chrome salts, because it is less expensive, is readily available and is highly soluble in aqueous solution. The chemistry of fixation of glutaraldehyde to collagen may involve crossslinking by the reaction of an aldehyde group with an amino group of lysine or hydroxylysine or an aldol condensation between two adjacent aldehydes.[8] The quality of chrome-free leather such as glutaraldehyde-tanned leather, in some respects is inferior to that of chrome-tanned leather, for example in colorfastness and thermal stability.[9, 10] There is an increasing demand for domestic production of automotive leather tanned with non-chrome tannages such as glutaraldehyde. Leather for car interiors is required to meet exceptionally high quality standards so that leather can withstand exposure to extreme and varying temperatures, light, moisture and mechanical loading conditions over time. If chrome-free leather is used for instrument panels and consoles, the problem of shrinkage due to poor heat resistance is especially acute, when humidity inside the car is high. Moreover, the poor lightfastness of chrome-free leathers prevents the use of light pigments or dyes and, therefore, more natural looking or aniline finishes for leather are difficult to achieve. When using such leather in automotive applications, these inadequacies are important concerns, which need to be studied to find ways of producing lightfast leather with improved thermostability.

Many studies demonstrated the degradation of collagen induced by UV radiation.[11-14] Tocopherol (a natural antioxidant) is a potent free radical scavenger and a highly protective agent against UV skin damage.[15] It is a light yellow colored oil and a fat-soluble vitamin. The principal role of tocopherol as an antioxidant must be to neutralize free radicals that could initiate a chain reaction, resulting in the formation of peroxides and products of their subsequent degradation.[16] Thermal stability of leather may be improved by using antioxidants such as tocopherols to protect against thermal oxidation, thereby improving the stability of the triple helical structure of collagen molecules.

In the early phase of this project, we applied *dl*-α-tocopherol (hereafter tocopherol) to the grain layer of leather and also studied the addition of tocopherol to the fatliquoring process.[17-19] Following exposure in a Fade-Ometer, the treated samples were evaluated by colorimetry and mechanical testing for the efficacy of UV- and heat resistance. Data showed that coating leather with tocopherol significantly improves the color fading resistance and strength retention against UV radiation and high temperature. We also studied the addition of tocopherol to the fatliquoring drums, but this treated leather did not have the same beneficial results. More recently, we carried out a study to gain a better understanding of how environmental factors affect the colorfastness and mechanical properties of chrome-free leather.[20] Data showed that an increase in radiation dosage and temperature have a detrimental effect on the colorfastness of dyestuff and mechanical properties of leather. Moreover, observation showed the stiffness decreased steadily with an increase in humidity, whereas the toughness increased slightly with increasing levels of humidity. Using differential scanning calorimetry, we observed a correlation between colorfastness and the denaturation temperature. This finding implies that the factors that break the molecular chains of colorants are also strong enough to break the bonding of the collagen molecules. The knowledge obtained from this research may benefit the leather industry in better understanding the environmental effects on chrome-free leather, thereby tailoring the leather-making process to meet quality specifications. In all these early studies mentioned so far, tocopherol was either coated on naked skin (crust) or added in the fatliquoring bath; the samples were not treated with polymeric coatings. Our objective in doing this was to observe the interaction of tocopherol with leather. We then conducted experiments by adding 1 to 5% tocopherol and mixed-tocopherol to the grain layer finishes (topcoat) of chrome-free leather. Fade-Ometer tests showed a significant improvement in color fading resistance against UV radiation and heat for samples using 5% tocopherol or mixed-tocopherol.[21] We also studied the application of another antioxidant, butylated hydroxytoluene (BHT) to the fatliquoring drums. In addition to being oxidizable, BHT is fat-soluble and is being used to preserve foods, fats and oils in cosmetics and pharmaceuticals.[22] Observation, however, showed BHT has no beneficial effect on the UV and heat resistance of finished leather.

Leather is a collagen material; it can be over-dried to become very brittle and weak. Glycerol is a well-known humectant and a key ingredient in skin care products. One may expect, therefore, that glycerol could improve the moisture retention ability of leather. The possibility of over-drying the leather will be greatly reduced due to the inherent nature of humectants, which is to promote the retention of water. It is worthy to note that glycerol may significantly increase the denaturation temperature of collagen.[23] Consequently, glycerol potentially may function as a heat-resistant agent for leather. We therefore recently explored the use of an aqueous solution of glycerol ($HOCH(CH_2OH)_2$) as a lubricant to leather. Because of its strong hydrophilic property, glycerol easily dissolves in water without the need of surfactants to form a stable solution. Another advantage of glycerol is related to its moisture retention. In a previous study, an aqueous solution of glycerol was applied to leather to evaluate its effects on the physical properties of leather, particularly stiffness. Young's modulus, initial strain energy and acoustic emission methods were used to characterize the stiffness of resultant leather treated with these glycerol solutions. Measurements revealed that glycerol treatment significantly reduced the stiffness of the dried leather, indicating the strong lubrication effect of glycerol to leather.[24]

This current study is to investigate the application of mixtures of glycerol and tocopherol to chrome-free leather. Our objective is not only to maintain proper moisture content, but also to improve the UV and heat resistance of leather. It is critical that emulsification of the oily antioxidants such as tocopherol be made effectively first so that it can be applied more efficiently on any surface. A mixture of glycerol/tocopherol is first emulsified in water by using an emulsifying agent; in this case we used a well known anionic detergent, sodium dodecyl sulfate (SDS). In general, a detergent is amphiphilic in aqueous solution and has a tendency to form micelles above its critical micelle concentration. It is the micellar form that tends to dissolve hydrophobic as well as hydrophilic molecules and anionic SDS also has a negative charge (sulfate) attached to it. Emulsification is done by reducing the oils to a fine state of division and then is uniformly diffused in aqueous liquids by the detergent. Aggregation of the oily antioxidant particles in the aqueous environment is prevented from taking place by the intervention of a viscous micelle of the detergent acting as the emulsifying agent. By using a combination of humectant and antioxidant, one may expect that treated leather could have a better UV and heat resistance and moisture retention property.

Experimental

Materials and Procedures

Commercial wet-white was retanned, colored and fatliquored as previously reported for the preparation of leather samples.[19] The samples were then wet back and passed twice through a Molissa staking machine (model 16370, Strojosuit, Czechoslovakia) at a medium setting (1.6 meters/min). Rectangular pieces, 21.6- x 26.6-cm, were cut out near the standard butt test area (ASTM D2813-97).

Mixture of Glycerol and Tocopherol Coating

The leather grain was coated twice with mixtures of glycerol/*dl*-α-tocopherol/SDS. The *dl*-α-tocopherol (noted as tocopherol) was purchased from Sigma (St. Louis, MO). The earlier experiment consisted of coating the leather with the spray gun as received and mixing with a stir bar. The tocopherol could be seen separating out from the emulsion right away after the stir bar stopped mixing. Therefore the later experiments employed the same coating that was refrigerated after the earlier experiment and mixed with a high speed shear mixer at a shear rate of 13,600 sec^{-1}. The tocopherol remained in the emulsion for a minute or 2 longer than the stir bar mixed samples. We experimented with several mixture compositions. They included (a) 10% glycerol + 0.30%SDS; (b) 5g tocopherol/250ml water + 10% glycerol + 0.30% SDS; (c) 12.5g tocopherol/250 ml water + 10% glycerol + 0.50% SDS; (d) 25g tocopherol/250 ml water + 10% glycerol + 1.5% SDS. The coated leather samples were then air dried and conditioned in a conditioning room at 23°C and 50% RH. Figure 1 shows the relationship between the tocopherol concentration in the mixed solutions with compositions described above and the amount of coating measured gravimetrically on the leather. This figure demonstrates that the amount of coating on the leather is closely related to the content of tocopherol in the coating solution, therefore the increase of weight in coated leather is largely due to the increase in the amount of tocopherol added to the leather.

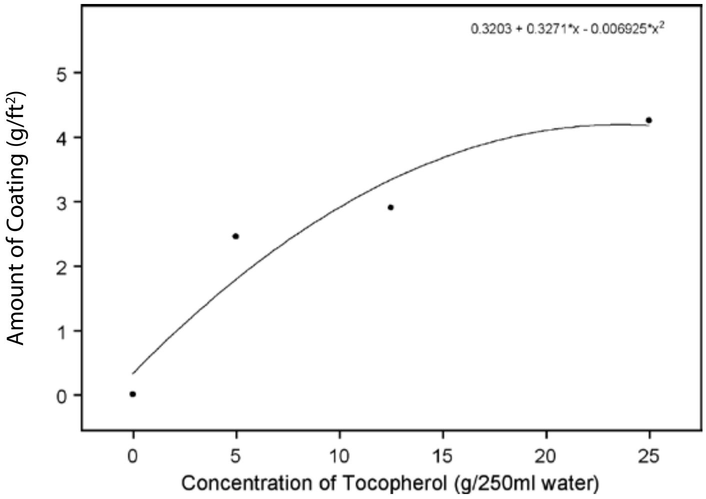

Figure 1. - Tocopherol concentration in the mixed solutions versus amount of coating on the leather.

Measurements

Before physical property testing, the samples were stored in a conditioned room at 23 °C and 50% RH according to ASTM D1610-96. Mechanical property measurements included tensile strength, elongation, and fracture energy. Tensile strength is the stress in tension at which the leather breaks. Elongation is defined as the strain at which the leather breaks. Rectangular shaped leather samples (1- × 10-cm) were cut near the standard test area as described in ASTM D2813-97 with the long dimension parallel to the backbone. These properties were measured with a sample length of 5 cm between the two grips. The strain rate (crosshead speed) was set at 5 cm/min. An upgraded Instron mechanical property tester, model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on four samples to obtain an average value. We used an Atlas Ci3000F, Xenon Arc Fade-Ometer (Oxford, PA), to evaluate the UV- and heat resistance of the leather samples. The samples were put inside the Fade-Ometer that calibrated at 420nm, for total radiation dosage of 225.6 kJ/m^2 (about 72 h exposure). The settings for the Fade-Ometer were as follows: black panel temperature 125 °C, dry bulb temperature 25 °C, radiation intensity 0.7 Watts/m^2 and RH 30%. The colorfastness to light of the specimen is evaluated by measuring the color change (ΔE) between the exposed samples and the unexposed original samples, using the color-insights® QC Manager System (BYK-Gardner, Inc., Silver Spring, MD), which is an absorptiometric colorimeter often used for fabrics. We followed the CIELAB colorimetric method; ΔE was calculated using the following equation:[25]

$$\Delta E = (\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2} \qquad \textbf{(1)}$$

where ΔL* represents the Euclidean distance between white and black, Δa* represents the Euclidean distance between green (-a*) and red (+a*), and Δb* represents the Euclidean distance between yellow (+b*) and blue (-b*). Measurements were conducted four times to obtain an average value.

Acoustic Emission Studies

In this study, we used acoustic emission methods to investigate the effects of the coating liquids that we applied to the grain surface of the samples on the lubrication of leather. As reported previously, the deformation of leather (as the leather is squeezed, torn or stretched) caused by an external force is accompanied by a rapid movement, relocation, or breaking of structural elements such as fibrils, fibers and/or fiber bundles.[26] As a result, sound waves are produced that can be detected by an acoustic transducer and converted into electronic signals. This basic phenomenon may be defined as an acoustic emission event, which is translated by an AE analyzer as a "hit".[27] AE measurements and tensile stress-strain tests were performed simultaneously for the samples previously described. A small piezoelectric transducer was clipped against the leather sample. This transducer resonates at 150 kHz (Model R15, Physical Acoustics Corp., Princeton, NJ). AE signals emanating from this transducer when the Instron stretched the leather samples were processed with a Model 1220A preamplifier and an upgraded LOCAN-AT acoustic emission analyzer (Physical Acoustics Corp.). The analyzer records the energy of each hit, its amplitude, and its duration. Only hits giving maximum amplitudes greater than 35 dB (threshold) from the transducer were counted. The upgraded LOCAN AT, which exceeds the 20 MByte limit of the old LOCAN's, is connected to a PC base with enhanced graphing and data acquisition software (Microsoft WINDOWS compatible) with all the features and options of the SPARTAN 2000. This AE system has been used in our research center (ERRC) for studying the deformation and fracture mechanisms of fabrics, leather and bio-composites. Our typical test samples are dumbbell (dog bone) or rectangular shape with a thickness less than 3 mm.

Differential Scanning Calorimetry (DSC)

DSC analysis was performed for leather samples using a Multi-Cell Differential Scanning Calorimeter (MC-DSC) from Calorimetry Science Corporation (Lindon, UT). This instrument was equipped with four removable cells; the cell design of the MC-DSC easily accommodates solid as well as liquid samples. It is designed specifically for the study of biopolymers (such as collagen) thermal stability in dilute solution. The MC-DSC can collect melting temperature (T_m), enthalpy (H), and heat capacity (C_p) data on three samples in a single experiment. With an operating temperature range of -40 to 200 °C, scan rates of 0.1 to 2.0 °C/min in both the heating and cooling directions, and sensitivity at the 5 μcal/°C level, the MC-DSC can be used to study the thermal denaturation of most proteins at concentrations in the vicinity of 1 mg/mL. The lower and upper temperature was 30 °C and 130 °C respectively, the heating rate was 1.5 °C/min and equilibrium period was 10 min. There are four stainless steel cells, so three samples could be tested (the 4th cell is for reference) at each run. Samples were prepared by grinding the leather into powder using the Wiley Mill. The powdered leather samples were soaked overnight in distilled water and then filtered. The moist samples (100-250 mg) were weighed into ampoules that were sealed and placed in the calorimeter. In this study, the temperature at the peak of the calorimetry trace was considered to be the denaturation temperature.

RESULTS AND DISCUSSION

The samples that were coated and subjected to 225.6 kJ/m^2 of radiation are graphed in Figure 2. It shows a negative correlation between the color change (ΔE) and the amount of coating, in which the more coating applied the less the color will change. These are actually positive results on using the mixture of tocopherol and glycerol for improving fading resistance or color fastness of leather. This is largely ascribable to the effect of tocopherol, the antioxidant, which is a free radical scavenger that stops the chain reaction induced by the release of free radicals caused by either UV and or heat.

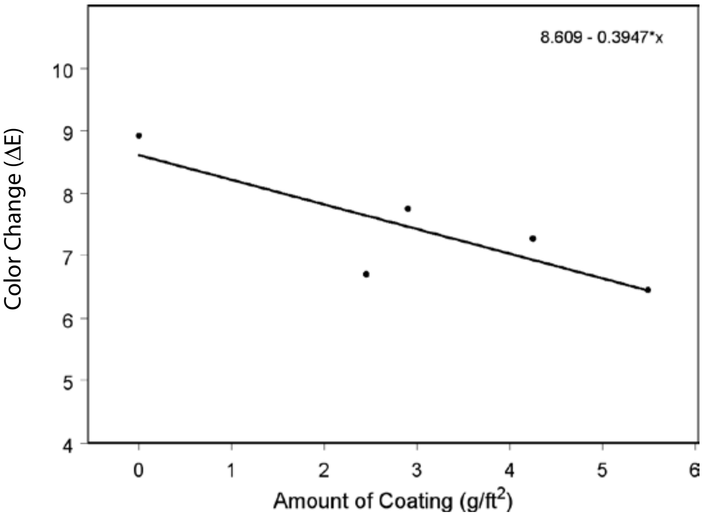

Figure 2 - Color change (ΔE) versus amount of coating.

Figure 3 demonstrates an inverse correlation between Tensile Strength and coating amount. Presumably, glycerol has a negative effect on the tensile strength after being exposed to UV and heat. Leather containing glycerol may absorb more thermal energy than the samples without glycerol. Glycerol has three hydroxyl functional groups that make glycerol a strong polar molecule. Due to the interaction of the three polar hydroxyl groups of glycerol, the hydrogen bonds within the collagen fibers could be weakened thus reducing the tensile strength of the leather product at high heat as in a Fade-Ometer.

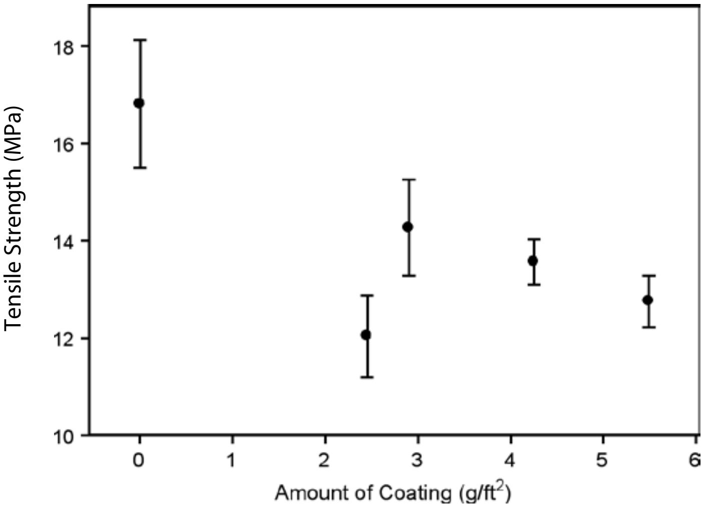

Figure 3. - Tensile strength versus amount of coating.

The fracture energy measurement (Figure 4) shows that there is no correlation with an increasing amount of coating. This is because fracture energy is measuring the area under the stress-strain curve. This value is dictated by both tensile strength and elongation. Since glycerol is also a lubricant that may help with the elongation, the lubricating effect may counter balance the negative effect of glycerol on the tensile strength. Therefore, the fracture energy was not significantly affected by the amount of coating.

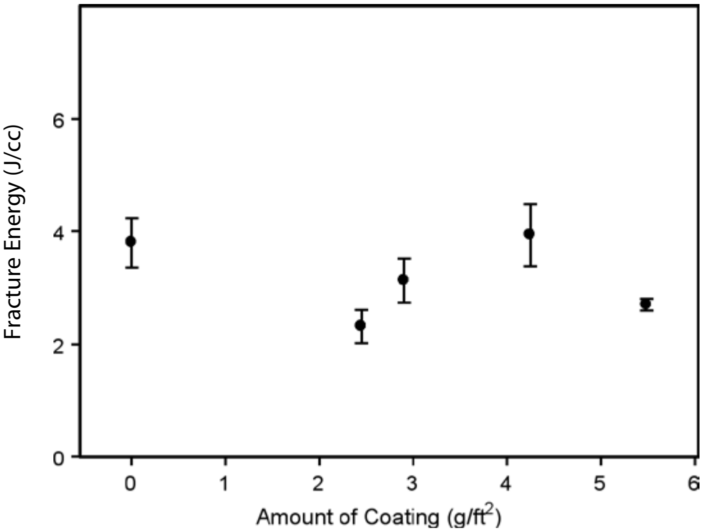

Figure 4. Fracture energy versus amount of coating.

Acoustic Emission Studies

For many years, acoustic emission (AE) has been recognized as a powerful method for characterizing leather properties.[28, 29] In one of the earlier AE investigations from ERRC, the sounds emitted by leather were studied when it was stretched (in a tensile test) and the relationship between tensile strength and AE quantities examined.[27] A correlation was observed between the initial acoustic cumulative energy and the tensile strength of leather. We also designed an AE method to gain insight into the reason for tear failure.[29] Measurements showed that the samples stronger in tear strength gave a significantly lower acoustic count. In contrast, the samples with poor tear strength generated more sound pulses, i.e., more acoustic counts.[29] More recently, we applied AE technology to measure the degree of opening-up of the leather structure.[30] This research project was in response to the urgent need for an effective means to identify the proper liming conditions that produced a sufficient degree of opening-up. We demonstrated that a history plot of acoustic emission counts could detect a change in the degree of opening up of the fiber structure associated with an increase in liming time. The results of this work have provided a route to monitor the degree of opening up of leather. Moreover, our previous studies also demonstrated that the AE technique is very instrumental in characterizing the degree of lubrication of fibrous materials treated with lubricants.[26] We observed that the stiffer the leather, the greater the amount of acoustic hits emitted in a tensile test. We also exploited the AE technique to measure the flexing endurance of leather coatings. An acoustic sensor was clipped to the grain layer of finished leather in a tensile test to collect various acoustic quantities.[31] Observations showed that a change in the flexibility of the coatings can be analyzed by examining the plot of the AE count rate as a function of time. We observed that a quantitative association exists between the flexibility of coatings and the acoustic counts produced at an initial tensile stretch. The results of this AE research have provided a route to examine the flexing endurance of leather coatings.

In this study, we performed the AE tests in conjunction with the tensile tests. We believe the AE results may reveal some structural information that the other methods cannot offer. Figure 5 shows the AE energy as a function of coating amount. It demonstrates that the AE energy increases with coating amount. This is attributed to its more robust fiber structure as a result of an application of the mixture of glycerol and tocopherol.

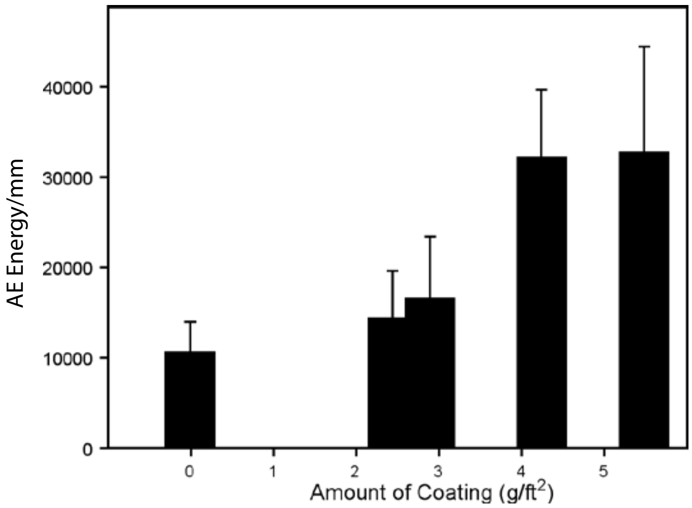

Figure 5. - AE energy/mm.

Plotting the rate of hits as a function of time is a basic way to graph AE activities. Figure 6 displays the chronological course of the test, demonstrating the hits rate vs. time profiles during the tensile testing of leather after UV exposure. Figure 6a shows that the non-tocopherol treated sample produces multiple peaks in the hits rate vs. time curve. The multiple peaks (from 0 to 30 sec on Figure 6a) indicate a partially fractured leather sample; with some unbroken fiber bundles still holding the leather together. The final peak shown on the figure is probably due to the subsequent breakage of those remaining fiber bundles. In contrast, the tocopherol treated sample after UV exposure as shown in Figure 6b yields only one major peak. This sample emits very little sound for the first twenty-seconds stretched, followed by a steep increase in the hits rate to a peak point at around 40 seconds, and then a sudden decrease as the leather is totally fractured. Multiple-peaks as shown in Figure 6a implies the existence of non-uniform stress sharing and a premature fracture in the leather structure. In contrast, a single peak as shown in Figure 6b indicates that the leather structure uniformly shares the tensile stress without premature breakage or fracture. This may be attributed to a better lubricated fiber structure by the mixture of glycerol/tocopherol, in that the fibers are more free to move and to slip over each other, thereby lining up in the direction of stretching and consequently sustaining a higher tensile stress. A fibrous structure is a necessity for the energetic acoustic activities demonstrated in Figure 6. In other words, the profiles of the acoustic hits demonstrated previously are a unique phenomenon for a fibrous structure. Leather consists of collagen fibers with a very complex structure, a network of interwoven fiber bundles with large spaces unevenly distributed among them. It has been reported that fiber bundles (20-200 µm) of leather are comprised of very fine element fibers (10 µm), which can further be divided into even finer fibrils (0.01-0.5 µm).[32]

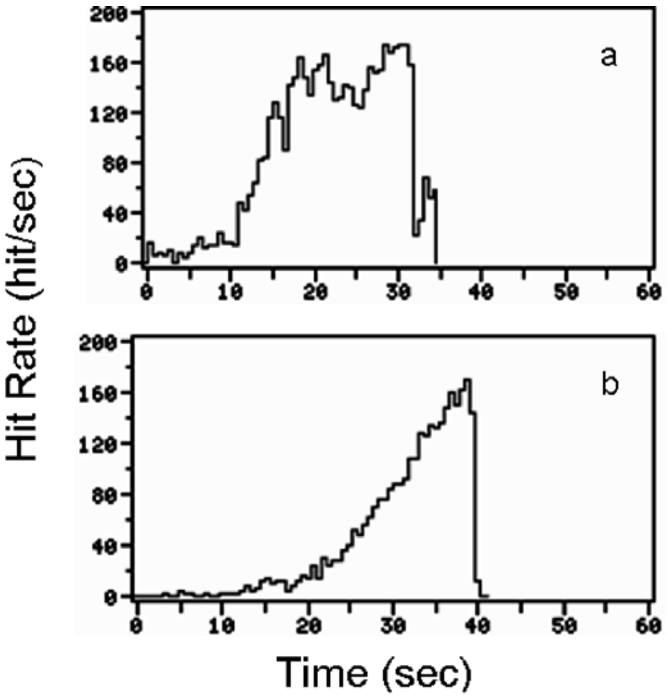

Figure 6. - Hit rate versus time.

DSC Studies for Denaturation Temperature

Bovine leather consists of type I collagen that has a unique triple helix molecular structure. By heating collagen in water at a certain temperature the water molecules can gain sufficient energy to compete for the hydrogen bonds maintaining the triple helix configuration and thus cause protein denaturation, unwinding of the collagen triple helix, and localized gel formation. This temperature is commonly known as the "denaturation temperature," which is governed by the strength of bonding between collagen molecules.[33, 34] It is reasonable to assume that the higher the denaturation temperature, the greater this bonding strength, i.e., the more stable the molecular structure. DSC thermograms from 30 °C to 130 °C were obtained for leather samples from various treatments. The melting (denaturation) of collagen is indicated by a sudden increase in thermal energy (heat flow) required for maintaining a temperature (endothermic), as illustrated in Figure 7, where curve **a** is for un-irradiated samples, and curves b and c are samples that were UV-irradiated to 225.6 kJ/m^2. The glycerol containing sample (Figure 7, curve c) demonstrates a melt peak location that is almost the same as that of the un-irradiated sample (Figure 7, curve a), thus indicating that glycerol is providing some protection against the UV and heat in this study. The corresponding denaturation temperature may be reported as either the onset or the peak temperature.

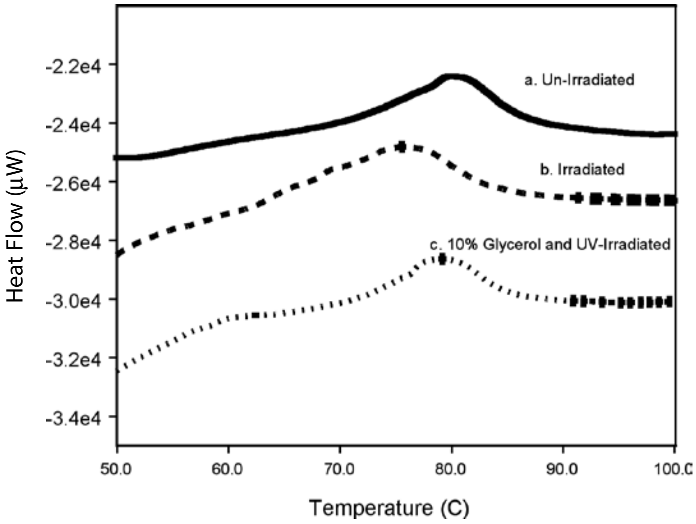

Figure 7. – DSC thermograms; a: un-irradiated control, b. UV-irradiated control, c. 10% glycerol and UV-irradiated.

The onset temperature did not show a close relationship with the color change data. Instead, a rather clear correlation was observed between denaturation temperature (indicated by the melting peak) and color change as demonstrated in Figure 8. Presumably for the same reasons that cause degradation of colorant molecules, this can also lead to the breakage of bonds between the collagen molecules. In our previous studies, we also observed that the UV-irradiated leather fibers lost a significant degree of orientation in their molecular chains. The UV radiation and heat caused disorientation in the collagen molecular chains, thereby resulting in a lower birefringence.[20]

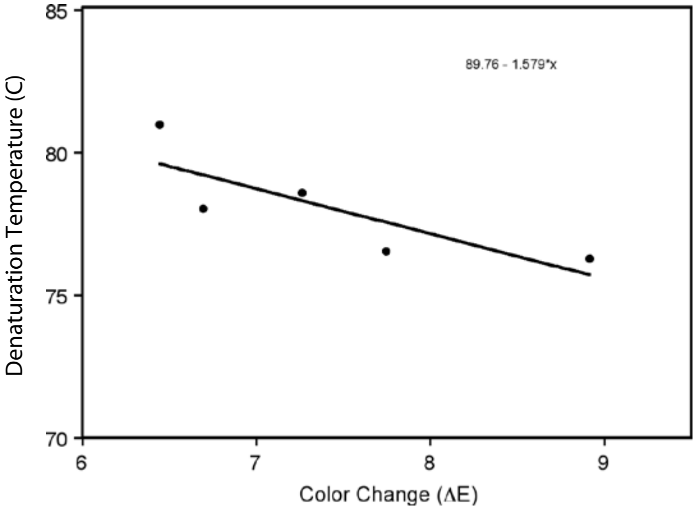

Figure 8. - Color changes versus denaturation temperature.

Conclusions

UV and heat resistance are very important qualities for leather products. This study showed that leather coated with glycerol/tocopherol exhibited significant improvement in color fading resistance against UV irradiation and heat. However, tensile tests showed that this mixture may cause some minor tensile strength loss. This was ascribed to the increased heat absorption of glycerol. Nevertheless, no correlation or general trend was found with the fracture energy because of the positive effect of glycerol on elongation (extensibility). Moreover, it is interesting to note that either the AE hit rate or the count rate increases with the increasing amount of coating. This may imply that there is a more robust fibrous structure produced by adding the glycerol/tocopherol mixture. Furthermore, it was observed that a more aggressive mixing method is needed than the stir bar, such as a shear mixer; however an ultrasonic horn or mixer could be tried as well. The emulsification of the oily antioxidant is very critical so that efficient application of the coating mixture on leather can be attained. A uniform emulsion of the very fine oils must be attained first and then maintained by preventing the oils from aggregating together by using an effective emulsifying agent other than SDS. Because SDS is a strong anionic detergent, the interaction of the collagen fibers/fibrils with its negatively charged sulfate groups may have caused some damage to the leather protein structure thus reducing the protective action of glycerol and antioxidant mixture. On the other hand, glycerol might be substituting randomly for some monomeric SDS molecules in a micellar structure of the detergent thus making the detergent micelles less uniform in size and decreasing their function in the emulsion. For further studies, other emulsifying agents such as powdered gum acacia, decoction of Irish Moss, yolk of egg, tincture of senega, saponin and milder detergents such as sophorolipids, a surfactant derived from agricultural feedstocks can be tried.[35]

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