The Use of Mixed Tocopherols to Improve UV and Heat Resistance of Leather

by

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Abstract

Most leather products are constantly exposed to outdoor environments, therefore UV and heat resistance are very important qualities, particularly for non-chrome-tanned (chrome-free) leather. In recent years, we have addressed this problem and focused on an environmentally friendly finishing process that will improve the UV and heat resistance of leather. Tocopherols are well-known antioxidants commonly used in the cosmetic and food industries. Moreover, tocopherols have been reported as potent free radical scavengers and highly protective agents for collagen fibers against UV and heat damage. Our previous research on alpha-tocopherol showed that it significantly improved UV and heat resistance of leather. Mixed tocopherols are more abundant and are produced from a renewable source such as soybeans. We have investigated its potential to be applied to leather for improving UV and heat resistance. Experiments were conducted by adding 5 to 12% mixed tocopherols to the grain layer finishes of chrome-free leather. The treated samples were tested in a weatherometer, where they were exposed to artificial sunlight at a high temperature. Colorfastness and mechanical properties tests showed that mixed tocopherols significantly improved UV and heat resistance of leather.

Resumen

La mayoría de los productos de cuero son constantemente expuestos al medioambiente exterior, haciendo que la resistencia al calor y la radiación UV sean importantes cualidades, particularmente en cueros curtidos sin cromo (exentos de cromo). En años recientes hemos enfrentado este problema y enfocamos hacia un sistema eco-amigable de acabado que mejora las resistencias del cuero a UV y al calor. Tocoferoles son bien reconocidos antioxidantes comúnmente utilizados en las industrias de cosméticos y alimentos. Más aun, tocoferoles han sido reportados como potentes agentes atrapadores de radicales libres y altamente protectores de las fibras del colágeno contra UV y los daños por calor. Nuestras previas investigaciones sobre alfa tocoferol demostraron que mejora significativamente las resistencias del cuero hacia UV y calor. Mezclas de Tocoferoles aún más abundantes y originados de una fuente renovable, tal como los fríjoles de soya. Nosotros hemos investigado tales por su potencial para ser aplicados en cueros para mejorar la resistencia hacia la radiación UV y al calor. Experimentos fueron ejecutados con la adición de 5 a 12% de mezclas de tocoferoles a los acabados de la flor para cueros exentos de cromo. Las muestras así tratadas fueron probadas en un simulador climático, donde fueron expuestas a luz solar artificial a una alta temperatura. Solidez del color así como pruebas de las propiedades físicas demostraron que mezclas de tocoferoles significantemente mejoraron las resistencias del cuero a UV y calor.

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Introduction

Leather products are constantly exposed to outdoor environments, therefore UV and heat resistance are very important qualities. Consumers expect leather to be able to withstand exposure to extreme and varying temperatures and sunlight over time. Many studies have demonstrated physical/chemical changes of collagen induced by ultraviolet (UV) radiation.[1-2] Sionkowska reported that solar radiation induces photodegradation of collagen.[3] Fujimori revealed that a solution of collagen, after UV irradiation, loses the ability to form natural fibrils.[4] For synthetic polymers, UV absorbents such as hydroxybenzophenones have been widely used to improve the light stability of both plastics and their colorants.[5] UV absorbents such as cinnamates and salicylates are also commonly used in skin care products such as sunscreens.[6-7] On the other hand, tocopherols (TCP) are natural antioxidants that are often used as additives to protect food and cosmetic products from oxidation. It has been reported that tocopherols, light yellow colored fat-soluble vitamins, are potent free radical scavengers and highly protective agents against UV skin damage.[8] The principal role of tocopherols as antioxidants is to neutralize free radicals and prevent a chain reaction resulting in the formation of peroxides or other products due to their subsequent degradation.[9] The 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.

Tocopherols occur naturally in mixtures of four different forms: alpha (α)-, beta (β)-, gamma (γ)- and delta (δ)-tocopherol. All of these forms consist of a chromanol ring with a long aliphatic side chain, bound to the chromanol ring at the 2 position. The proportion of the individual tocopherols is typically: alpha-tocopherol <20%, beta-tocopherol <10%, gamma-tocopherol 50 – 70% and delta-tocopherol 10 - 30%. In the early phase of this project, we applied alpha-tocopherol to the grain layer of leather and also studied the addition of alpha-tocopherol to the fatliquoring process.[10-12] Following exposure in a fadeometer, the treated samples were evaluated by colorimetry and mechanical testing to determine UV- and heat resistance. Data showed that coating leather with alpha-tocopherol significantly improved the color fading resistance and strength retention when exposed to UV radiation and high temperature. A polarizing microscope equipped with a Berek compensator was employed to determine the birefringence of the untreated and treated leather collagen fibers to determine the treatment effects on the degree of orientation.[12] Data showed that leather coated with alpha-tocopherol exhibited significant improvement in tensile strength retention and color fading resistance against UV radiation and heat. We also studied the addition of alpha-tocopherol to the fatliquoring drums, but this treated leather did not show a similar improvement.

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.[13] Data showed that an increase in radiation dosage and temperature have a detrimental effect on the colorfastness and mechanical properties of leather. Observation, however, showed an intriguing interaction between the levels of humidity and radiation dosage. Measurements revealed that an increase in humidity during irradiation resulted in a greater color change, an indication of decreased colorfastness, and a decrease in tensile strength. However, after the UV radiation dosage reached a certain level, an increase in humidity may actually have helped maintain both properties. 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.[14] 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 our previous studies, tocopherols were either coated on leather or added in the fatliquoring bath; the samples were not finished with polymeric coatings.[10-14] In this study, however, tocopherols were mixed with finish coatings. Finishing is a process to apply film-forming materials, so-called “coatings” on the grain surface to provide abrasion and stain resistance and perhaps more importantly, to color and beautify the leather. It is also the last step to cover any minor surface defects such as small scratches and cracks. The specific steps in the finishing process are dependent on the requirements of the final product. Full grain leathers typically have a polymeric finish applied to the grain surface by a roller coater or a spray gun. Corrected grain leathers have one or more basecoats applied, which improves the adhesion of the final topcoat; the topcoat is then applied and dried. In this report, we will describe experiments that were conducted by adding 5% to 12% (w/w) mixed tocopherols (hereafter referred as mTCP) to the grain layer finishes of chrome-free leather. The treated samples were placed inside a weatherometer, where they were exposed to artificial sunlight at high temperature and then evaluated for the efficacy of UV and heat resistance.

Experimental

Materials and Procedures

Leather Preparation

Bovine hides were tanned with glutaraldehyde using the retanning and fatliquoring process previously reported for the preparation of the chrome-free samples.[12] The leather was colored with 6% Sandoderm Brown G Powder (Clariant Corp., Fairlawn, NJ). The wet samples were set-out and vacuum-dried. Square pieces approximately 30.5- x 30.5-cm were cut out near the ASTM standard butt test area.[15]

All pieces were sprayed manually with a water-based acrylic basecoat (Quaker Color, Quakertown, PA) in a spray booth (the amount of basecoat is listed in the second column of Table 1). Pieces were allowed to cure completely for 30 minutes before the topcoat was applied. In this investigation, we used mTCP (Cargill Health & Nutrition, Excelsior, MN) that were composed of about 20% alpha-tocopherol, 5% beta-tocopherol, 60% gamma-tocopherol and 15% (w/w) delta-tocopherol. The topcoat finish solutions were mixed with mTCP to give final mTCP concentrations of 5, 7, 9, and 12% (w/w) as shown in the first column of Table 1. The topcoat was also a water-based acrylic polymer. Topcoat lacking mTCP served as control. The experimental topcoats were manually applied to leather as constant as possible (the amount of topcoat is listed in the third column of Table 1). The pieces were then allowed to air dry overnight before being placed into a constant temperature/humidity room.

TABLE I

Coating Experiments

*mTCP Concentration in Topcoat (w/w%)	Basecoat (g/ft^2)	Topcoat (g/ft^2)	**Coating Amount (g/ft^2)	mTCP Content (g/ft^2)
0.00	4.59	6.13	10.72	0.00
5.00	5.09	5.69	10.78	0.17
7.00	6.44	4.59	11.03	0.20
9.00	5.21	3.44	8.65	0.19
12.00	4.80	4.27	9.07	0.32

*Contain 38.5% water in solution.
**Coating Amount (g/ft^2) = Basecoat (g/ft^2) + Topcoat (g/ft^2)

For UV testing (wavelength range: 276 - 400nm), 14-x 6.5m pieces were cut out parallel to the backbone of the finished square pieces and were irradiated at Quaker Color, Quakertown, PA, in a Ci4000 Xenon Weather-Ometer® (a weatherometer manufactured by Atlas Material Testing Technology, Chicago, IL) for total radiation dosage of 225.6kJ/m^2 according to the automotive test specification SAE J-1885: "Accelerated Exposure of Automotive Interior Trim Components using a Controlled Irradiance Water Cooled Xenon-Arc Apparatus."[16] The settings for the weatherometer were as follows during the light cycle: black panel temperature 89 °C, dry bulb temperature of 62°C, and RH 50%. After irradiation, the samples were conditioned in a constant temperature and conditioning room at 20 ± 2°C and 55 ± 5% RH. The moisture content of the leather according to the Delmhurst moisture meter was 14 ± 2%. The colorfastness to light of the specimen was 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;[17] ΔE was calculated using the equation: $\Delta E = (\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$. L* represents the difference between light and dark. a* represents the difference between green (-a*) and red (+a*), and b* represents the difference between yellow (+b*) and blue (-b*).[17]

Scanning Electron Microscopy

We used the field-emission environmental scanning electron microscope (ESEM) to examine the cross section of the coated leather samples. ESEM is advantageous over conventional scanning electron microscopy because a relatively high vacuum in the specimen chamber is not needed to prevent atmospheric interference with primary or secondary electrons. Our ESEM was operated at low vacuum (40 Pa) with the voltage set at 15 kV, spot size 5.0 and working distance of approximately 10 mm. The samples were not sputtered with either gold or carbon coatings, thus preserving the original characteristics of the leather samples.

Leather Properties Testing

Mechanical property measurements included tensile strength (MPa), elongation (elongation at break, %), Young's modulus (MPa) and fracture energy (J/cm^3). Tensile strength is the stress in tension that is required to fracture the leather. Young's Modulus is defined as the ratio of stress over strain from 0 to 10% of the leather sample and is an indication of the stiffness. Fracture energy is defined as the energy needed to fracture leather samples. This physical quantity is sometimes mentioned as "toughness". Rectangular shaped leather samples (1- × 10-cm) were cut near the ASTM standard test area.[15] An upgraded Instron mechanical property tester, model 1122 (Instron, Norwood, MA), and Testworks-4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. These properties were measured with a sample length of 5 cm between the two grips. The strain rate (crosshead speed) was set at 5cm/min. We used a data analysis/graphics software, Axum version 6 (MathSoft Inc., Cambridge, MA.) to derive regression models and construct 2-D or 3-D regression plots. The regression equations and corresponding correlation coefficients were listed in the plots.

The dynamic mechanical analysis was performed on a Rheometrics RSA II analyzer (Piscataway, NJ). Storage modulus (E') and loss modulus (E") were measured as the function of temperature. The gap between the two jaws holding the sample at the beginning of each test was 23 mm; a nominal strain of 0.1% was used with a frequency of 10 Hz. Each leather sample was equilibrated in the sample chamber under dry nitrogen prior to running the test. Temperature was increased at a heating rate of 10 °C/min. Data was collected and analyzed using Rheometric Scientific (Piscataway, NJ) Orchestrator software, version 6.5.7.

Results and Discussion

As demonstrated in Figure 1, the mTCP content (g/ft^2) on the leather appears to have a close relationship with the mTCP concentration in topcoat. The value of mTCP content (g/ft^2) was calculated by multiplying the amount of topcoat (g/ft^2) to the mTCP concentration (w/w %) in the topcoat and 61.5 % solid fraction.

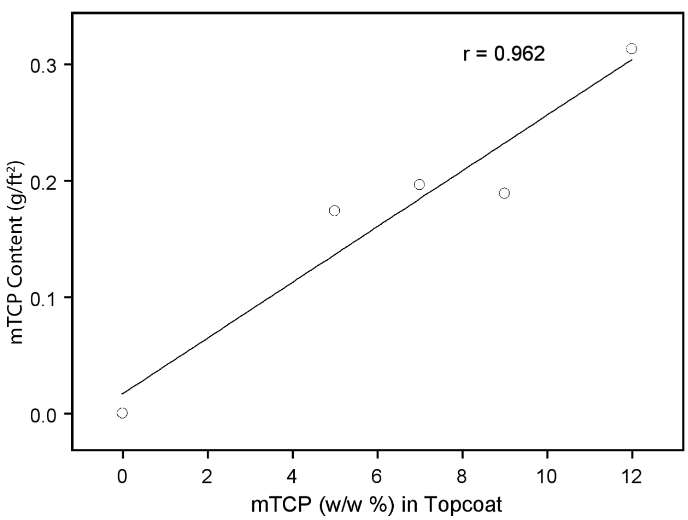

Figure 1. – The relationship between mTCP concentration in topcoat and the mTCP content on the leather grain.

Figure 2a shows a cross-sectional view of the uncoated grain layer of fibrous structure, and Figure 2b shows that a layer of coating is formed on top of the grain, with sponge-like texture. This coating can lead to an increase in the thickness of leather. Figure 3 displays a 3D regression plot of thickness as a function of the amount of topcoat and basecoat applied to the leather. It shows that the thickness of leather after coating increases significantly as more basecoat and topcoat are applied to leather.

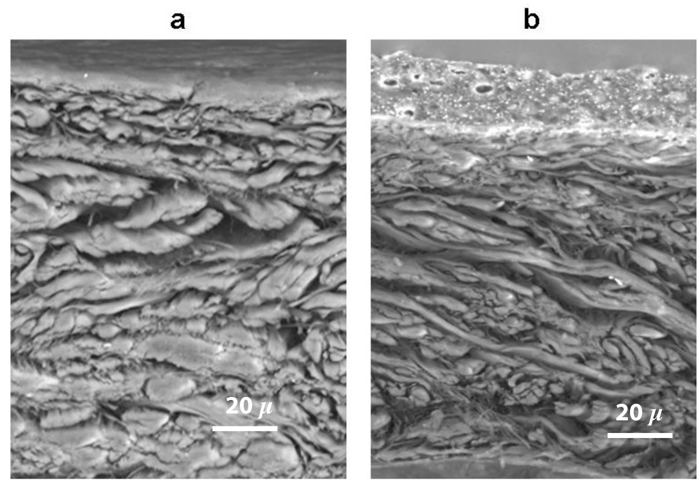

Figure 2. – Scanning electron micrographs of cross-section of (a) uncoated and (b) coated leather.

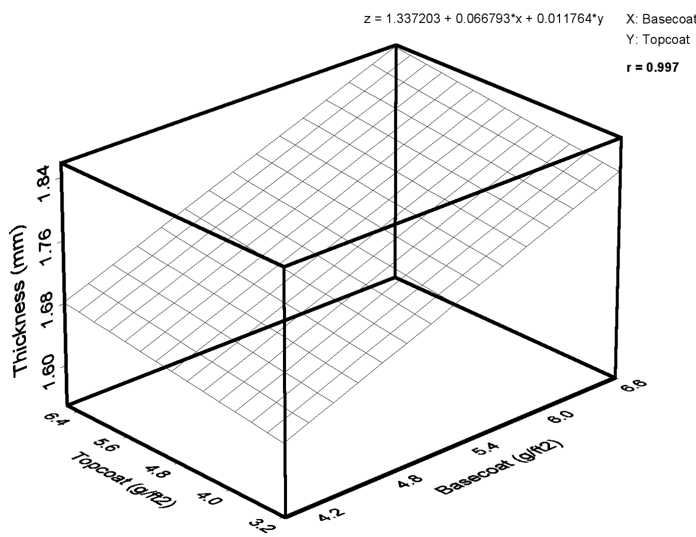

Figure 3. – Thickness of coated leather as a function of topcoat and basecoat added to leather.

Color Lightfastness The ΔE (color change) was measured for each of the samples. As can be seen in Figure 4, the ΔE value decreased as the mTCP content increased. Observation showed that ΔE not only decreased with the mTCP content on the leather but also decreased with the total amount of coatings (i.e. topcoat plus basecoat) applied to the leather. It, however, showed that the mTCP content has greater influence on the ΔE (delta E), than the total amount of coatings.

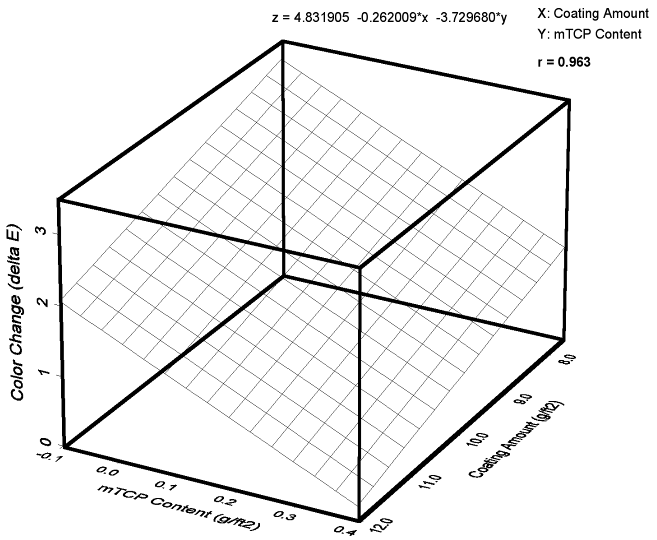

Figure 4. – Color Change (ΔE) as a function of coating amount and mTCP content.

Tensile Properties

After weatherometer tests, the leather was evaluated for tensile properties to assess the effects of mTCP and amount of coating on UV and heat resistance (Figure 5a). As seen in this figure, demonstrates that the mTCP has a substantial beneficial effect on tensile strength, whereas, the amount of coating (basecoat plus topcoat) appears to have very little effect on the tensile strength. On the other hand, the elongation (Figure 5b) data shows a small decrease with mTCP, but a substantial decrease as the amount of coating increases. One possibility is that during artificial weathering testing, the coating polymers were annealed by the high heat and resulted in stiffer leather, which exhibited lower extensiabily and decreased the elongation.

Stiffness

For most leather products, particularly for garments, upholstery and footwear, adequate pliability is a very important quality requirement. The quantitative assessment of pliability or its reverse term, stiffness, can be based on measurements of the resistance to a small deformation by tensile stress. The resistance may be quantitatively represented best by the initial slope of the load-displacement curves or the stress-strain curves in the elastic deformation region, i.e., the Young's modulus. It is commonly known that the higher the Young's modulus, the stiffer the leather is. This physical quantity has been associated with leather softness, temper, and handle. Figure 6 shows a 3D regression plot of the resultant stiffness (as represented by Young's modulus) as a function of tocopherol content and coating amount. It demonstrates that the stiffness of leather, in general, is affected very little by the mTCP content, whereas stiffness increases with the coating amount. It appears that the coating amount has more pronounced effects on stiffness than the mTCP content. The addition of a thicker coating would act as an additonal force to be overcome in order to deform the sample, and thus stiffness increases.

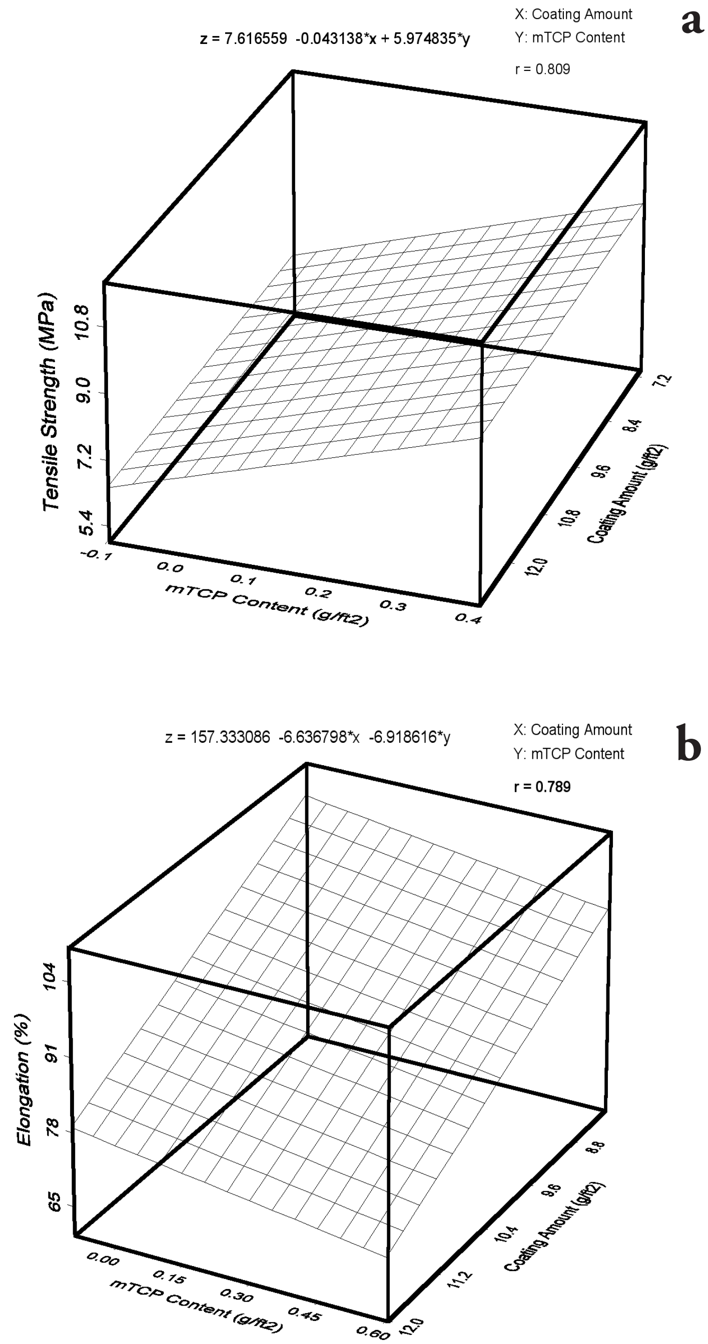

Figure 5. – (a) Tensile strength (b) elongation following exposure to 225.6 kJ/m^2 in a weatherometer as per test specification SAEJ-1885.[16] Note: 1 MPa = 10^6 N/m^2 = 145 psi = 1.02 x 10^5 kg/mm^2.

Dynamic Mechanical Behavior

We also determined the storage modulus[18-19] for the leather samples using a dynamic mechanical analyzer (DMA). Fibrous materials such as leather generally demonstrate a mechanical behavior that may incorporate a blend of both elastic and viscous characteristics; this is referred to as viscoelasticity.[19-22] We previously reported that besides the elasticity, the viscous component or viscosity plays an important role in determining the stress-strain curves even at the very beginning of the leather deformation.[20] The viscoelasticity is commonly measured by either dynamic or static tests.[23] In the dynamic tests as conducted in the current study, a sinusoidal variation of strain is imposed on the material and a variation of the responding stress is observed. As to the static tests (as reported in our previous papers), a constant strain or a constant stress is imposed, and the variation of the stress (relaxation) or the strain (creep) as a function of time is observed.[14, 24] The storage modulus (E') and loss modulus (E") in viscoelastic solids such as leather measure the stored energy (E'), representing the elastic portion, and the energy dissipated as heat (E"), representing the viscous portion. Storage modulus is known to be associated with the stiffness of materials, whereas loss modulus is linked to the plasticity of leather. The relationship between the storage and loss moduli are as follows:

$$E = E' + iE'' \quad (1)$$

Where, E is a complex modulus (also named dynamic modulus) and i is the square root of -1.

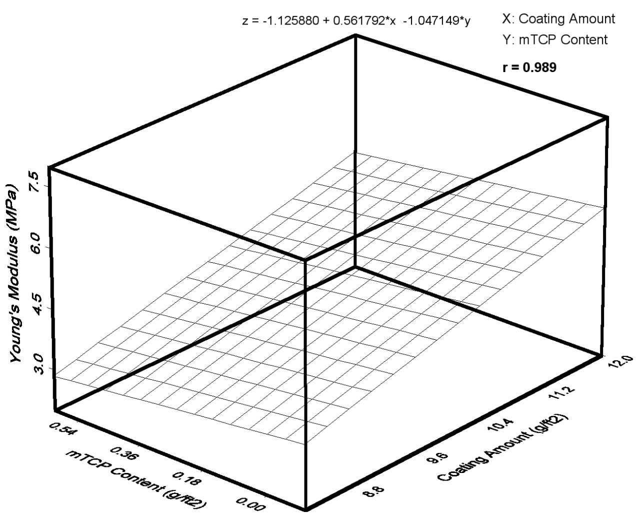

Figure 6. – Young's Modulus as a function of mTCP content and coating amount following exposure to 225.6 kJ/m^2 in a weatherometer as per test specification SAEJ-1885[16].

DMA tests showed that mTCP has a significant effect on E' (Figure 7a). Before UV irradiation in the weatherometer, the curves of E' vs. temperature look very similar for control and mTCP treated samples. However, E' increased significantly after UV irradiation for both control and mTCP treated samples as seen in Figure 7a. However, except at the lowest temperatures examined (less than approximately 8 ºC) the increase in E' was greatly reduced in samples containing mTCP. We believe this is because mTCP plays a protective role against UV and heat damage. A similar behavior was also observed for E", as demonstrated in Figure 7b. It is worthy to note, however, that E" is much smaller that E', indicating that the elastic component in the leather is the dominant factor in governing the mechanical properties. This is demonstrated in Figure 8, which shows the relationship of the complex modulus vs. temperature plot to have a very similar pattern to that of the E' vs. temperature profile in Figure 7a.

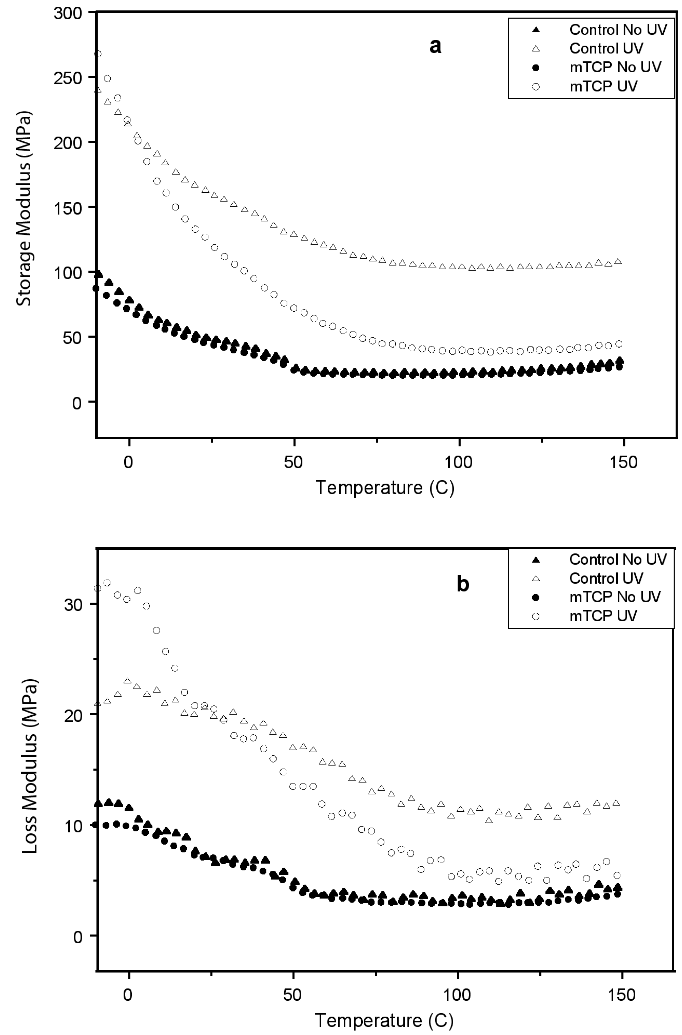

Figure 7. – (a) Storage modulus and (b) loss modulus vs. temperature in Dynamic Mechanical Testing.

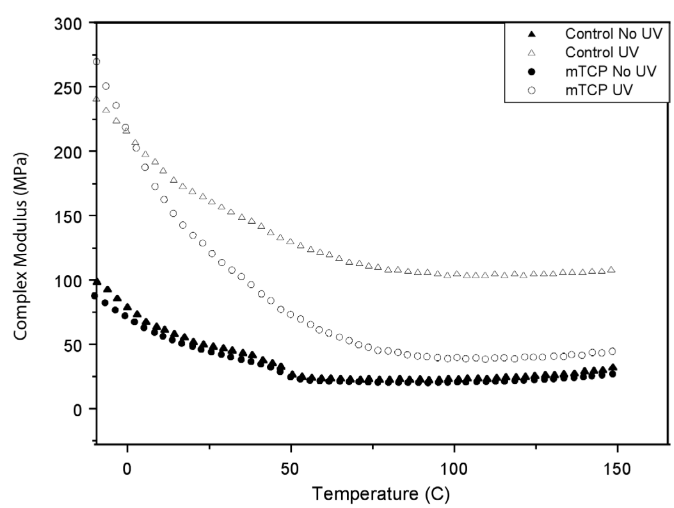

Figure 8. – Complex modulus as a function of UV treatment and the presence or absence of mTCP.

Conclusions

This research aims to develop a process treatment that is environmentally friendly and yet significantly increases the UV and heat resistance of chrome-free leather. Mixed tocopherols are abundantly available in nature and are produced from a renewable source such as soybeans. This preliminary study showed that mTCP worked well as a UV-resistant additive to topcoats for chrome-free leather. Moreover, dynamic mechanical tests showed that mTCP improved the stability and viscoelasticity of leather against UV and heat damage. The results of this research could lead to the production of high quality, durable leather, thereby contributing to the viability of the domestic tanning industry.

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