Effects of Alpha-Tocopherol Addition to Polymeric Coatings on the UV and Heat Resistance of a Fibrous Collagen Material—Chrome-Free Leather

Cheng-Kung Liu, Nicholas P. Latona, Mila Ramos

United States Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, Pennsylvania 19038-8598

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ABSTRACT: The US is the world's 3rd largest hide producing country and currently produces approximately 35 million cattle hides annually. The majority of hides are tanned into leather, which is composed of collagen fibers interwoven into fibrous networks. Most leather products are constantly exposed to outdoor environments, therefore UV and heat resistance are very important qualities, particularly for nonchrome-tanned (chrome-free) leather. In recent years, we have focused on using environmentally friendly antioxidants that will improve the UV and heat resistance of chrome-free leather. Tocopherols are well-known antioxidants commonly used in the cosmetic and food industries. They are known as potent free radical scavengers and highly protective agents for collagen fibers against UV damage. We have investigated their potential to improve the UV and heat resistance of chrome-free leather. Experiments were conducted by adding 5–12% α-tocopherol to the polymeric topcoat on the grain of chrome-free leather. The treated samples were tested in a weatherometer, where they were exposed to artificial sunlight. Colorfastness and mechanical property tests showed that α-tocopherol significantly improved UV and heat resistance of leather. Dynamic mechanical tests showed that α-tocopherol reduced the hardening effects on leather caused by UV irradiation. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3086–3091, 2011

Key words: collagen fibers; leather; antioxidants; fibrous materials; mechanical properties

INTRODUCTION

The US beef industry produces approximately 35 million cattle hides annually, which are the highest value coproduct of the meat industry. Conversion of hides into leather is a multi-billion dollar industry and involves many sophisticated chemistry and mechanical operations. The resultant leather is composed of type I collagen fibrils with an average diameter of 150 nm, which are bundled together into collagen fibers that give leather its strength and mechanical properties.[1] Although the majority of leather is tanned using Cr-III salts, environmental concerns over the use and disposal of chrome-tanned leather encourage the use of chrome-free leather, which is tanned with organic tannages such as glutaraldehyde, particularly in the European automotive leather markets.[2] Our observation showed that there is no significant difference in tensile strength and elongation at break between these two types of leathers; however, the resiliency of chrome-tanned leather is superior to chrome-free leather.[3] UV- and heat resistance of leather are very important qualities, particularly for chrome-free leather used in outdoor and automobile applications.[4] Considerable chemical/structural information has been shared between leather chemists and medical and cosmetic chemists, through their common interests in the chemistry of skin. Many studies demonstrated physicochemical changes of collagen induced by UV radiation.[5–9] Sionkowska reported that solar UV radiation induces collagen photodegradation.[7] Fujimori revealed that a collagen solution, after UV irradiation, loses the ability to form natural fibrils.[8] We carried out a study using a fadometer to gain a better understanding of how environmental factors (such as temperature, humidity, and radiation dosage) affect the colorfastness and mechanical properties of chrome-free leather.[10] Data showed that increases in radiation dosage and temperature have a detrimental effect on the colorfastness and mechanical properties of leather. An intriguing interaction between the levels of humidity and radiation dosage was also observed. Measurements revealed

Correspondence to: C.-K. Liu (chengkung.liu@ars.usda.gov).

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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 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.[10] 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.

Tocopherols 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.[11] 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.[12] The thermal stability of leather may also 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 2nd position. α-tocopherol is a type of tocopherol with formula $C_{29}H_{50}O_2$, which is a water-insoluble alcohol that occurs in plant oils (especially wheat germ oil), egg yolks, and liver, and is also produced synthetically. In the early phase of this project, we applied α-tocopherol directly to the grain layer of leather and also studied the addition of α-tocopherol to the fatliquoring process.[9,13,14] Following exposure in a fadeometer, the treated samples were evaluated by colorimetry and mechanical testing to determine UV resistance. Data showed that coating leather with α-tocopherol significantly improved the color fading resistance and strength retention when exposed to UV radiation.

In this study, however, α-tocopherol was mixed with finish coatings. Finishing is a process to apply film-forming polymeric 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.[15] 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 5–12% (w/w) α-tocopherol (hereafter referred as TCP) to the topcoat 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.[9] The leather was colored with 6% Sandoderm Brown G Powder (Clariant, Fairlawn, NJ). The wet samples were set-out and vacuum-dried. Square pieces approximately 30.5 cm × 30.5 cm were cut out near the ASTM standard butt test area.[16]

All pieces were sprayed manually with a water-based acrylic basecoat (Quaker Color, Quakertown, PA) in a spray booth. Pieces coated with basecoat (~ 31.5 g/m^2) were allowed to cure completely for 30 min before the topcoat (~ 74 g/m^2) was applied. In this investigation, we used TCP obtained from Sigma (St. Louis, MO). The topcoat finish solutions were mixed with TCP to give final TCP concentrations of 5, 7, 9, and 12% (w/w). The topcoat was also a water-based acrylic polymer. Topcoat lacking TCP served as control. The pieces were then allowed to air dry overnight before being placed into a constant temperature/humidity room.

For UV testing (wavelength range: 276–400 nm), 14 cm × 6.5 cm 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 225.6 kJ/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.[17]" 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 Delmhorst moisture meter (Towaco, NJ) was

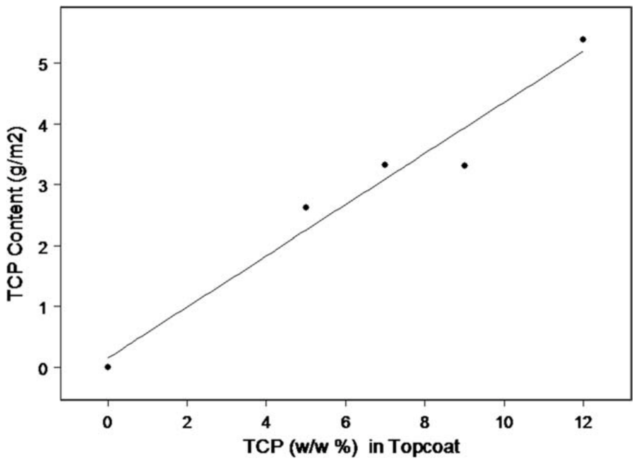

Figure 1 The relationship between TCP concentration in topcoat and the TCP content on the leather grain.

(14 ± 2)%. The colorfastness to light of the specimen was evaluated by measuring the color difference (ΔE) between the exposed samples and the unexposed original samples, using the color-insights® QC Manager System (BYK-Gardner, Silver Spring, MD), which is an absorptiometric colorimeter often used for fabrics. ΔE was calculated using the colorimetric method established by The International Commission on Illumination.[18] The smaller the value of ΔE indicates a better colorfastness of the tested samples. A ΔE of 1.0 is the smallest color difference the human eye can see.

Leather properties testing

The dynamic mechanical analysis was performed for 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 were collected and analyzed using Rheometric Scientific (Piscataway, NJ) Orchestrator software, version 6.5.7.

Tensile property measurements included tensile strength (MPa), elongation at break (%), and fracture energy (J/cm^3). Rectangular shaped leather samples (1 cm × 10 cm) were cut near the ASTM standard test area.[16] An upgraded Instron mechanical property tester, model 1122 (Instron, Norwood, MA), and Testworks-4 data acquisition software (MTS Systems, 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 5 cm/min.

RESULTS AND DISCUSSION

As demonstrated in Figure 1, the TCP content (g/m^2) on the leather appears to have a linear relationship with the TCP concentration (w/w %) in the topcoat; the correlation coefficient is as high as 0.98. In fact, the value of TCP content (g/m^2) on the leather was not only dependent on the TCP concentration (w/w %) in the topcoat but also dependent on the amount of topcoat applied to the leather. Although, we made a great effort to keep the amount of topcoat constant for all samples; inevitably, there were some very small variations. The deviation from this linear relationship as shown in this figure is probably attributable to the small experimental error in the amount of topcoat applied to the leather.

Color lightfastness

The ΔE (color difference) was measured for each of the samples. As can be seen in Figure 2, the ΔE value decreased significantly as the TCP concentration increased. In particular, the sample with 12% TCP in the topcoat yielded a ΔE of 0.926, which indicated after the weatherometer test that the color difference was not detectable by the human eye. Good resistance to color fading in sunlight or artificial light is important for all upholstery leather, but is particularly critical in automotive leather, where the seats can be exposed to intense sunlight at high temperatures for very long periods of time.

Tensile properties

After weatherometer tests, the tensile properties of the leather were evaluated to assess the effects of TCP concentration in topcoat on UV and heat resistance (Fig. 3). The results demonstrated that the TCP concentration in topcoat has a substantial beneficial

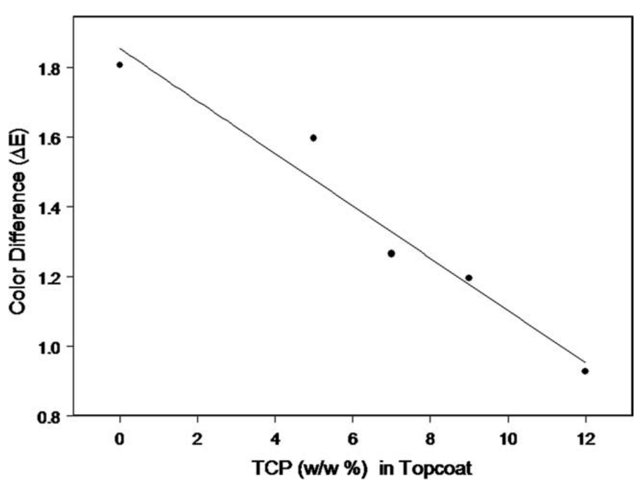

Figure 2 Color difference (ΔE) as a function of TCP concentration in topcoat.

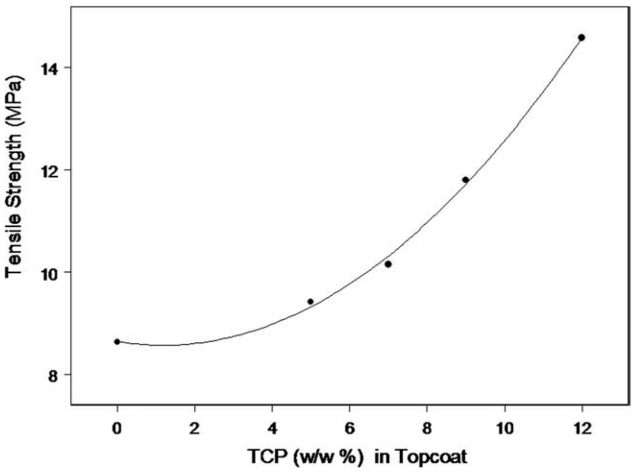

Figure 3 Tensile strength following exposure to 225.6 kJ/m^2 in a weatherometer as per test specification SAEJ-1885.[17]

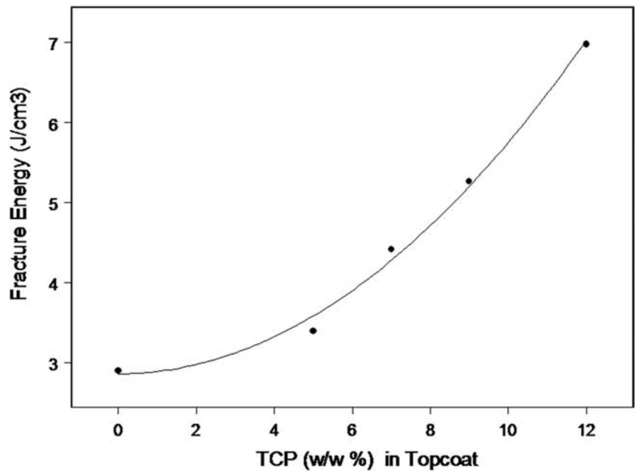

Figure 5 Fracture energy following exposure to 225.6 kJ/m^2 in a weatherometer as per test specification SAEJ-1885.[17]

effect on tensile strength. The control samples (no TCP added to topcoat) yielded 8.63 MPa tensile strength, whereas after adding 12% TCP to topcoat, the resultant tensile strength increased to 14.58 MPa. On the other hand, the elongation at break (Fig. 4) data also show a significant increase with TCP concentration in topcoat.

Fracture energy has been described in a previous report as a physical quantity associated with the energy required to fracture leather.[19] We have characterized the toughness of leather by measuring the fracture energy, which is obtained by integrating the area under the force–elongation curve. There is not always a linear relationship between fracture energy and tensile strength, because fracture energy is governed by both tensile strength and elongation at break. Previously we reported that contrary to tensile strength, the sampling angle shows little effect on the toughness. Our investigation also demonstrated a strong correlation between tear strength and toughness. Good toughness reflects a superior balance of strength and flexibility with good deformability, thereby minimizing the stress concentration and yielding a better tearing strength.[20] Figure 5 demonstrates that, similar to the tensile strength, the toughness of leather steadily increases as TCP concentration in the topcoat also increases.

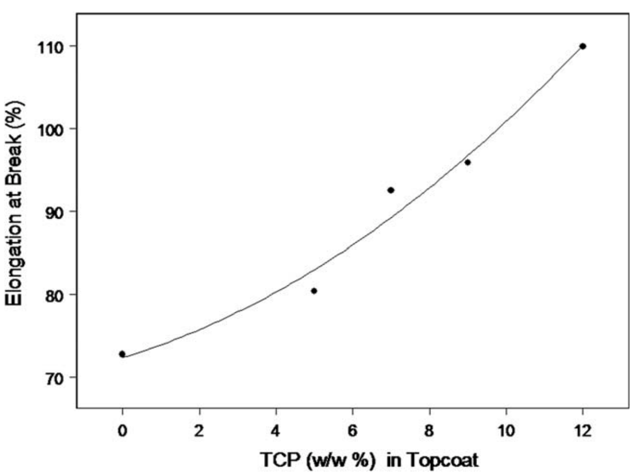

Figure 4 Elongation at break following exposure to 225.6 kJ/m^2 in a weatherometer as per test specification SAEJ-1885.[17]

Dynamic mechanical behavior

We also determined the storage modulus 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.[21,22] 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.[23] The viscoelasticity is commonly measured by either dynamic or static tests.[24] 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.[25] 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.

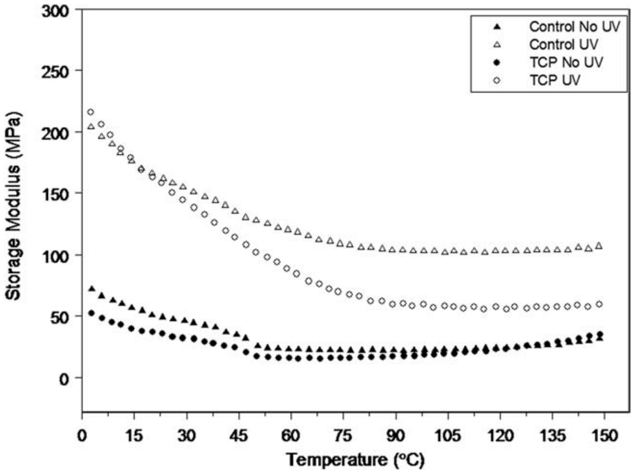

Figure 6 Storage modulus (E') versus temperature in dynamic mechanical testing.

DMA tests showed that TCP has a significant effect on E' (Fig. 6). Before UV irradiation in the weatherometer, the curves of E' versus temperature look very similar for both the control and TCP treated samples. After UV irradiation E' increased significantly for both the control and TCP treated samples as seen in Figure 6. The TCP treated sample begins to diverge from the control sample around 22°C and remains lower than the control at higher temperatures. We believe this is because TCP plays a protective role against UV and heat damage. The lower E' indicates that the leather treated with TCP will have better elasticity at higher temperatures, which will prove useful for automotive-type leathers, in which the interior cabin temperatures can reach a maximum of 90°C.[26] A similar behavior was also observed for E'' at temperatures above 75°C, as demonstrated in Figure 7. It is worthy to note, however, that E'' is much smaller than E', indicating that

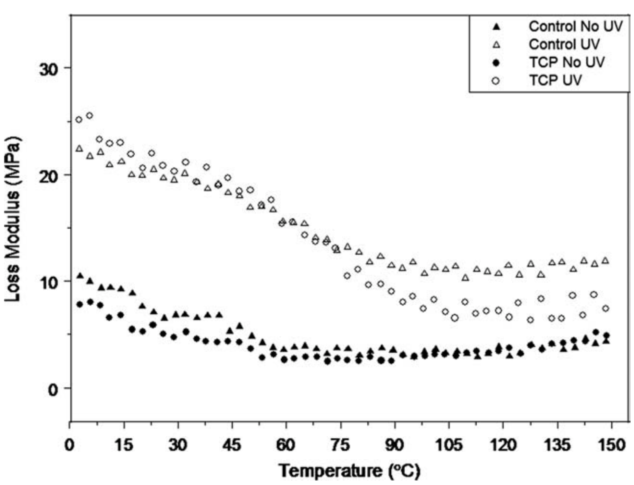

Figure 7 Loss modulus (E'') versus temperature in dynamic mechanical testing.

the elastic component of leather is the dominant factor in governing the mechanical properties.

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. Tocopherols are abundantly available in nature and are produced from a renewable source such as soybeans. This study showed that α-tocopherol worked well as a topcoat additive to improve the UV and heat resistance of chrome-free leather. Moreover, dynamic mechanical tests showed that α-tocopherol improved the stability and viscoelasticity of leather against UV damage. The results of this research could lead to the production of high quality, durable leather, thereby enhancing the competitiveness of the domestic tanning industry in both domestic and export markets, and consequently improving the economical well being of tanners and farmers.

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