An Experimental Comparative Study on Silicone Oil and Polyethylene Glycol as Dry Leather Treatments

by

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Abstract

The application of leather dressing and lubricants is one of the important challenges in conservation of historic dry leathers, due to their effects on structural and visual properties and stability of leathers. This study aimed to investigate influence and stability of silicone oil and polyethylene glycol (PEG) on treated dry leathers, and application assessment of ascorbic acid (AA) as an antioxidant additive for PEG. The polymers, untreated and treated leather samples were submitted to heat accelerated ageing process. FTIR spectroscopy, colorimetry, pH measurements, investigation of mechanical properties and shrinkage temperature (Ts) were used to explain effect of treatments. Also, the oxidation of polymers during ageing process was monitored by FTIR spectroscopy. Results showed that silicone oil has better stability against thermal oxidation with compared to PEG. Ascorbic acid inhibited the PEG oxidation. Moreover, results revealed that the silicone oil has a better performance in treatment of dry leather than PEG or PEG+AA, due to its high stability and minimum changes in visual, structural and mechanical properties in treated leathers.

Introduction

The leather products have been useful materials since the dawn of human history.[1,2] Collagenous materials, such as leather, have been used for thousands of years due to the availability of such a natural resource and its resilience and flexibility.[3] As leather is widely used for historic clothing, upholstery, bookbinding and etc., historical and archaeological leathers constitute an important part of museum and archival objects.

These objects and artifacts are valuable treasures of historical information and cultural interest due to the history they represent.[2] However, leather is still considered as one of the most sensitive materials towards environmental hazards, hard use, etc.,[4] and their preservation is one of the biggest challenges in conservation. Wide variety application of leather, imposes a particular set of conditions, which can bring about deterioration in the leather.[5] In general, deterioration of leather is a chemical process in which there are a great number of contributing factors. These factors, in combination with the leather and tanning chemistry, leads to very diverse and complex degradation mechanisms.[6]

One of the major problems facing the historical leathers is excessive desiccating and drying. A common way to dealing with this phenomenon and its complications, such as brittleness, is application of leather dressing and lubricant treatments. For a long time, dressings used to be the standard treatment used in conservation of leathers. The dressings are usually applied in an attempt to slow deterioration, improve the appearance of leather, and perhaps restore some of its former strength and flexibility.[6-8]

There are, to date, several different methods of conserving leathers. In the course of different conservation studies, a variety of lubricants and dressings have been introduced and investigated. Some of these have included neat's-foot oil, lanolin, glycerin, British museum leather dressing (BML), Bavon, Marney's leather dressing, pliantine, and SC6000,[6,8-10] and or leather cream recommended by Larsen in 2007, the Dutch emulsion recommended by the Koninklijke Bibliotheek, The Hague, a modified leather dressing suggested by Fuchs in 2005 and Cire in 2013 recommended by the National Library of France.[11]

The effect of dressings on leather permanence has been studied, and almost invariably the researchers conclude that the dressings, as mentioned above, have no preservative effect[7,11,12]. Their main compounds are usually oils, fats and waxes.[11] Overuse of these materials, since the base components are fatty substances containing varying concentrations of unsaturated fatty acids, can cause oxidization and stiffening, discoloration and staining, a tacky surface that attracts dust and dirt, encouraging of microorganism-growth, depositing of spew on the surface, and hampering of future conservation efforts.[6,11]

Also, these materials do not contribute to the preservation of the constituent moisture and, on the other hand, destabilize collagen filaments, which dispose to overdrying.[13] The growing

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Manuscript received January 11, 2016, accepted for publication May 10, 2016.

production of the leather lubricants, accompanied by the arrival of new synthetic materials that both moisturize and resistant.[14] Hence, the application of synthesis polymer material has developed by leather conservators.

Polyethylene glycol (PEG) and silicone oil are common synthetic polymers in conservation, as treatments of both dry and waterlogged leathers. Several studies have been dedicated to the introduction and investigation of PEG or silicone oil in conservation of leather during the last years.[8,15] Ershad-Langroudi and Mirmontahai[13,16] investigated the influence of PEG–nano-hydroxyapatite nanocomposite on treatment of historical leather bookbinding, and their results indicated that nanocomposite improve the thermal stability and mechanical properties of leather. White[17] compared silicone impregnation and sucrose bulking as methods of leather consolidation. In another study, Ludwick[6] evaluated silicone oil as a surface treatment for dry leather, in comparison to two other treatments, Klucel G and BML. Their obtained results indicated that silicone oil is more suitable for the treatment of leather. Also, there are many papers about lubrication of new leather with these material[18-20]

It is very important that used treatments have a long-term stability and do not have the capacity to break down or formation of harmful products over a long period of time.[21] However, PEG can be oxidized easily at environment conditions,[22] and its decomposition can cause changes in leather properties.[23,24] Hence, accurate assessment of material, before of treatment, is essential for appropriate conservation purposes.

Therefore, the aim of this study is to investigate the application of silicone oil and polyethylene glycol in treatment and lubrication of historic dried leather with the interaction of these polymers in the leather behavior. Also, application of ascorbic acid as an antioxidant of PEG was evaluated.

Materials and Methods

Accelerated Aging of Lubricants

PEG with average molecular weight of 400 (Merck Co.), PEG with ascorbic acid as an antioxidant additive (0.5% w/v; Acros Co.) and dimethyl silicone as silicone oil (KCC Co.) were studied as leather lubricants. Heat accelerated aging was used for thermal degradation evaluation. Samples were heated in an oven at 100°C for 72h, 130°C for 48h and 150°C for 48h. Thermal degradation was analyzed by ATR-FTIR spectroscopy during the aging process.[25]

Leather Treatment and Accelerated Aging

Samples were prepared from goat leather which was vegetable tanned traditionally and was lubricated with animal tallow three years ago in a village of southern Khorasan province of Iran. They were aged to simulate the historic leathers. The aging process was accomplished according to ISO 17228:2005.[26] Samples were placed in oven at a 100°C for 72 hours, before and after treatment. Aged samples (3 repeat) were treated with silicone oil, polyethylene glycol (30% v/v in ethanol) and polyethylene glycol with ascorbic acid as an antioxidant additive (0.5% w/w in 30% v/v PEG in ethanol) in a vacuum tank at 170 mm Hg pressure for 21 hours. Then, excessive treatment materials were removed by dryer paper and samples were dried in a desiccator. After treatment, samples artificially were aged again.[25]

Colorimetry

The colorimetric properties of aged and treated leather samples were analyzed with Salutron® Colortector Alpha apparatus as a portable colorimeter in terms of CIE Lab color coordinates [L* (brightness), a* (red - green) and b* (yellow - blue)]. The total color difference (ΔE), the chroma coordinate (C*) and the hue angle (h*) were calculated according equations 1, 2 and 3.[27] Color values were measured ten times for each leather sample, and their average was considered as CIE Lab color coordinates.

Equation 1. $$\Delta E = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]}$$

Equation 2. $$C = \sqrt{a^2 + b^2}$$

Equation 3. $$h = \arctan(b/a)$$

pH Measurement

The pH was measured according to ASTM D2810-01.[28] 2gr of leather samples were cut to small pieces and soaked in 40 mL of distilled water (20 times more than weight of the samples) for 12 hours. pH of the leather-water mixtures was assessed by using a Metrohm 744 pH meter calibrated between buffers pH 4 and 7.

ATR-FTIR Spectroscopy

ATR-FTIR analysis was carried out using a Nicolet 470 FTIR spectrometer and OMNIC 6.1a software (Nicolet instrument corporation, USA) equipped with PIKE MIRacle attenuated total reflectance (ATR) accessory with zinc selenide (ZnSe) crystal plate. All Spectra were collected in the range of 4000-650 cm^{-1} at 4 cm^{-1} resolution with 32 numbers of scan.

Shrinkage Temperature

Shrinkage temperatures of the leather samples were determined according to ASTM D6076-03.[29] The sample specimens, in the form of 12.5×76 mm strips, were soaked in water tank equipped with a vacuum pump. The wet specimens were inserted into the bath of water at room temperature. The water was heated at 3-4°C/min rate and the temperature at the first definite sign of shrinking was recorded.

Mechanical Properties

Mechanical Properties of dumbbell shape samples were assessed according to ASTM D2209-00[30] and D2211-00.[31] A ZWICK tensile tester machine, model 1446-60 was used for evaluation.

Results and Discussion

ATR-FTIR technique has been applied to investigate structural changes of PEG, PEG with ascorbic acid (PEG+AA) and Silicone oil (Figure 1). Spectra of PEG and PEG+AA showed peaks at 3700-3200 cm^{-1} (O-H), 2866 cm^{-1} (CH_2 stretching), 1456 cm^{-1} (CH_2), 1350 cm^{-1} (CH_2), 1249 cm^{-1} (C-O-C), 1200-1000 cm^{-1} (C-O-C stretching)[32-34] and silicone oil showed adsorptions at 1258 cm^{-1} (Si-CH_3), 1082 cm^{-1} (Si-C), 1011 cm^{-1} (Si-O), 900-730 cm^{-1} (Si-C), 701 cm^{-1} (Si-O), 686 cm^{-1} (H_3C-Si-CH_3) and 662 cm^{-1} (Si-C-H).[35-37] Accelerated aging resulted to characteristic changes in 1780-1680cm^{-1} for PEG. This new band is assigned to the carbonyl stretching vibration and indicates that new carbonyl groups were produced due to thermal degradation.[22, 38]

Thermo-oxidation mechanism of polyethylene glycol is shown in Scheme 1, regarding to Lai and Liau (2003). In the beginning, PEG is oxidized to α-hydroperoxide form. Due to thermally labile of this peroxide, it can be decomposed by a radically mechanism. The degradation products are ultimately transformed to formic esters, a product with carbonyl groups, which can result to formation of formic acid.[38]

Formation of carbonyl groups as a scale of PEG thermal degradation has been assessed, according to both height and area of peak intensities (Figure 2). It indicates an increase in PEG degradation during accelerated aging. But the ascorbic acid prevented oxidation of PEG, because the spectra of PEG+AA do not show any visible change in the absorptions compared with the PEG. Moreover, the spectra of silicone oil do not show any change during the accelerated aging. It indicates the high thermal stability of silicone oil.

Figure 3 shows diagrams of ΔL, Δa, Δb, ΔC and the total color difference (ΔE) of leather samples. It signifies a low change in colorimetric parameters of treated leather with silicone oil. Results indicate a great color stability and better efficiency of silicone oil for preserving of visual and aesthetic values of leather relics after accelerated aging process with compared to PEG (with or without ascorbic acid). In addition, ascorbic acid was not effective as an antioxidant for color stability of PEG treated leathers. Moreover, it has caused to decrease in color stability.

The average of pH contents and shrinkage temperatures (Ts) are shown in Figure 4. It signifies a little decrease of pH for untreated leathers from 4.82 to 4.76. Silicone oil resulted a very low pH change in leathers from 4.78 to 4.81. It is decreased to 4.79 after accelerated aging. It indicates the stability of the treated leathers with silicone oil. However, the PEG treatment particularly with ascorbic acid has reduced the pH of leathers to 4.65 and 4.53, which has more pH reduction compared to untreated and treated leathers with silicone oil. The decrease causes to protein hydrolysis, and diminution of hydrothermal stability of leather.

The untreated samples exhibited a wide range of Ts between 64-65°C, before and after aging. The use of PEG, pure or with ascorbic acid, has decreased the Ts to 60-62°C. As following the aging, it was observed that the average shrinkage temperature of

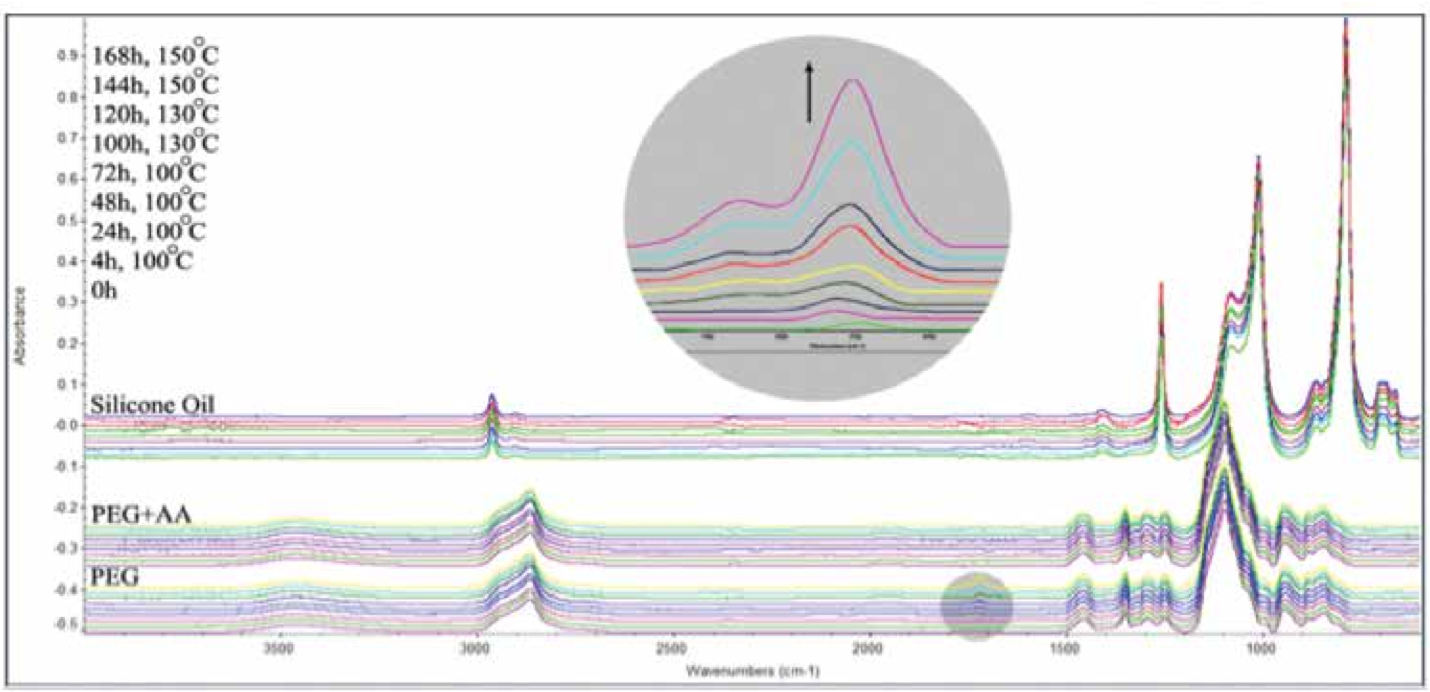
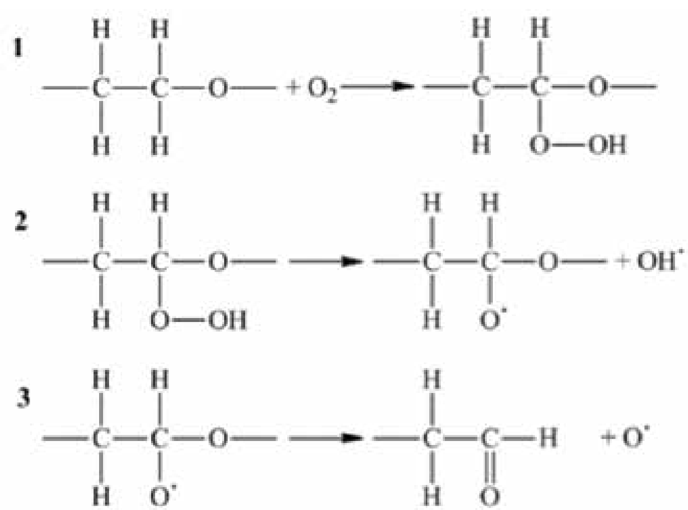


Figure 1. ATR-FTIR spectra of PEG, PEG+AA and silicone oil during heat accelerated aging process; Highlighted: a detailed carbonyl region in the ATR-FTIR spectra of PEG.

the PEG treated samples decreased from 62 to 50°C. Similarly, the average Ts of the PEG+AA treated samples reduced from 60 to 52°C. Accordingly, the use of PEG does not improve performance on hydrothermal stability of leather and accelerate the destruction rate, while silicone oil improved the hydrothermal properties of leathers and Ts has increased to about 69°C. Also, due to the high stability of the silicone oil, only a little change in Ts is observed after aging process.

Tensile strength is one of the most important mechanical properties of leather [39]. Lubrication or fat liquoring greatly affects the physical properties.[40] The mechanical properties of samples are shown in Figure 5. The results indicate a relative increase in mechanical strength of untreated samples after aging. Also, the physical properties of leather have improved by PEG treatment. But these properties have dropped sharply after aging due to the oxidation of PEG and its effects on the leather. However, the use of ascorbic acid, as antioxidants, prevents the reduction in PEG (+AA) treated samples. Whereas, silicone oil treatment does not lead to significant changes in mechanical strength of leather, before and after the aging.



Scheme 1. Mechanism of thermo-oxidation of polyethylene glycol, regarding to Lai and Liau 2003.[38]

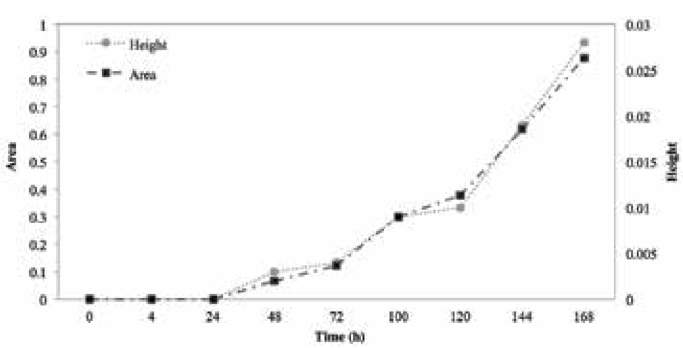


Figure 2. Increase the height and area of peak intensities between 1800 and 1650 cm^{-1} indicates the production of carbonyl groups, as a scale for oxidation of PEG, during the accelerated aging.

The FTIR spectra of all samples were baseline corrected on 900-1800 cm^{-1} wavenumber range. Figure 6 shows the FTIR spectrum of untreated and unaged sample (Or).

The peaks at 1650 cm^{-1} for the amide I and 1550 cm^{-1} for the amide II absorptions are interesting.[41] The Δv (v_{AI}-v_{AII}) value is corresponding to collagen denaturation.[42,43] The difference in wavenumbers between the AI and AII band positions in FTIR spectra of leather samples (corium layer) are shown in Figure 7. The PEG treatment, with or without ascorbic acid, has led to an increase in the Δv value. Whereas, FTIR spectrum of silicone oil treated leather shows small shift in peak positions of amide I and II. In other words, the denaturation of collagen has been increased after the use of PEG treatment, whereas silicone oil treated leather have a better structural stability.

Conclusion

In this study, silicone oil and polyethylene glycol, with and without ascorbic acid, were compared for their effectiveness in the treatment of dry leathers as well as their chemical stability. The FTIR results showed that aging process causes to severe oxidation in PEG, whereas ascorbic acid inhibits the change, while, silicone oil had great heat stability. The results confirmed that the treatment of leather samples with polyethylene glycol decreased

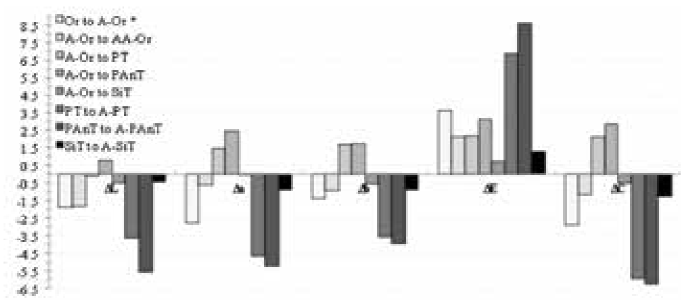


Figure 3. ΔL, Δa, Δb, ΔC and total color difference (ΔE) of leather samples. *Or: Untreated sample; PT: Treated sample with PEG; PAnT: Treated sample with PEG+AA; SiT: Treated sample with silicone oil; A-: Aged sample; AA-: Twice aged sample.

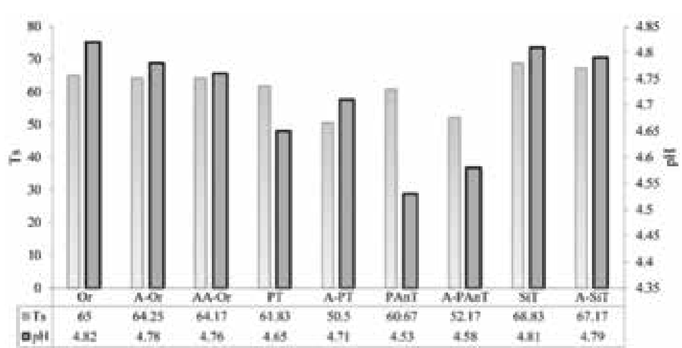


Figure 4. The average data of Ts and pH of leather samples.

the color stability, pH and shrinkage temperature of leather. The physical properties have improved by PEG, but dropped sharply after aging. However, the use of ascorbic acid prevents of reduction strength in PEG treated leather. Whereas, treated leather with silicone oil exhibit great improvements in hydrothermal stability without any significant changes in pH, color and physical properties. Also, the FTIR results indicate that the PEG treatment increased denaturation of collagen; whereas silicone oil treatment has a good structural stability. Therefore, silicone oil could be selected as a better treatment for historic or new dried leathers.

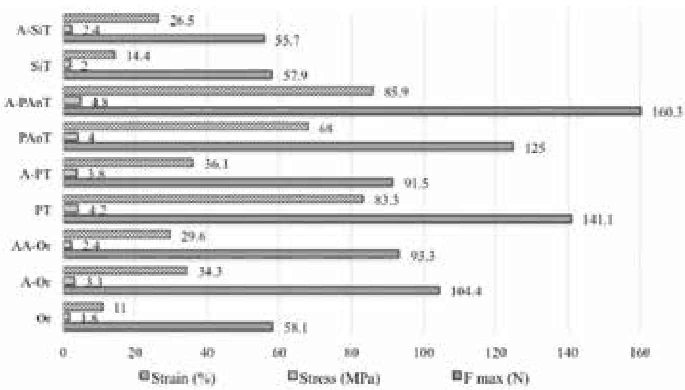


Figure 5. Average of mechanical properties of leather samples.

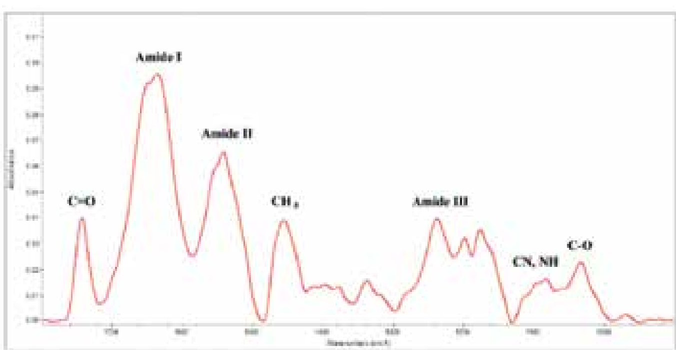


Figure 6. ATR-FTIR spectrum of untreated and unaged sample (Or) with functional groups according to Koochakzaei and Achachluei (2015).[41]

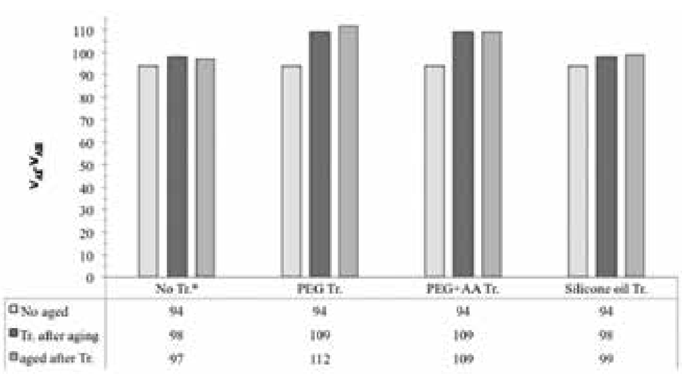


Figure 7. The difference between $\mathbf{v}_{AI}$ and $\mathbf{v}_{AII}$ ($\Delta\mathbf{v}$) as denaturation index in FTIR of corium layer; * Tr.: treatment.

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