EFFECT OF ACID RAIN ON VEGETABLE TANNED LEATHER

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Abstract: In order to study the influence of gaseous pollutants on leather, the artificial acid rain was used to soak the vegetable tanned leather, and then the leather was aged for 25 days in 50°C and 100% relative humidity to accelerate the aging speed. The mechanical properties, micro hot table (MHT), FT-IR, optical microscope, DSC and TG were used to analyze the change of leather during the aging process every 5 days. The results showed that the mechanical properties and shrinkage temperature of aged leather were decreasing, and the collagen fibers were damaged and leaded the amide I and amide II band moving to low wave number. Furthermore, the thermal denaturing temperature and the temperature of decomposition at max rate of aged leather were both dropped too. The longer aging time was, the more obvious impacts existed. In conclusion, the artificial acid rain has a significant aging effect on vegetable tanned leather.

Keywords: artificial acid rain; vegetable tanned leather; accelerated aging

INTRODUCTION

Vegetable tanning is one of the oldest tanning methods, therefore many collagen-based cultural relics are vegetable tanned leather. In addition, vegetable tanned leather is also used in modern society because of unique properties (Popescu *et al.*, 2008). However, vegetable tanned leather is often exposed in atmospheric air so that air pollution will lead to the aging and damage of vegetable tanned leather (Barbara *et al.*, 2012; Miu *et al.*, 2009; Deselnicu, 2010). Vegetable tanned leather is affected slowly by gaseous pollutants, which makes the study of leather aging difficult. Studying of the influence of the air pollution on vegetable tanned leather could provide theoretical support and advice for preservation of leather cultural relics and degradation of vegetable tanned leather.

In order to accelerate aging and simulate the effect of gaseous pollutants, the artificial acid rain was used to soak the vegetable tanned leather, and then the leather was aged for 25 days in 50°C and 100% relative humidity. With the persistent temperature and humidity, the leather aging was accelerated, and the samples were taken out every 5 days to characterize the change in the aging process.

EXPERIMENTAL

Materials

Quebracho extract tanned calf leather was obtained from Leather and Footwear Research Institute, Bucharest, Romania. Other chemical reagents used in this study were research grade.

Sampling

In order to reduce experimental error and increase the comparability of samples, six large leathers (10cm×7cm) were sampled along the back bone line adjacently and used for mechanical property tests. Another six small leathers (3cm×2cm) were sampled under the corresponding large leather and used for morphology, structure and thermal analysis. Among the twelve samples, five large and five small pieces were used for aging test, and the left two pieces were used as control.

Preparation of Artificial Acid Rain

The artificial acid rain (Lesu *et al.*, 2005) was prepared as follows: 0.04ml concentrated sulphuric acid, 0.06ml concentrated hydrochloric acid and 0.02ml ammonium hydroxide were dissolved in 80ml distilled water, then 0.0296g $Ca(OH)_2$ was added and diluted to 2L volumetric flask. The pH of artificial acid rain was 3.25.

Leather Aging

Ten pieces of leather samples were soaked in the artificial acid rain (liquor's weight was 20 times based on leathers) for 48 hours. Then the samples were sealed and aged in 50°C and 100% relative humidity (RH) for 25 days. A large and a corresponding small leather pieces were taken out every 5 days and dried in nature for 48 hours, then the samples were placed in a 65% RH desiccators for a week to equilibrium.

Analytical Method

Mechanical Properties

After conditioning, tensile strength, tear strength and elongation at break of leather were tested by tensile machine (AI-7000S, China) following a standard method.

Optical Microscope Analysis

The samples were sliced into 12 µm pieces by freezing microtome (Leica Company in German). After hematoxylin and eosin staining, the cross sections were observed by SZX12 optical microscope (Olympus Optical Co., Ltd) at 40 times magnification.

Shrinkage Temperature

Shrinkage temperature (Ts) was determined by the micro hot table (A WT2000, China). A few fibers were separated and wetted with distilled on microscope slide, and more than two fibers should be observed in the sight. Then the fibers were covered with a cover glass and heated at 2°C/min on the hot table and Ts was recorded when more than two fibers were shrinked simultaneously and continuously. The final results were the average of three tests (Larsen, R., 2002).

FT-IR Test

Samples were ground with KBr and made into pellets, then a Nicolet10 FT-IR (American Thermo Scientific Corporation) was used to scan in the wavelength range of 400-4000cm^{-1} for 32 times.

DSC Test

Samples were placed in 20°C and 65% RH for 24 hours. The samples were put into sealed stainless steel crucibles and heated at 10°C/min in N_2 atmosphere (flow N_2:100mL/min) with a Netzsch DSC PC200 calorimeter (Germany).

TG Test

Samples were placed in 20°C and 65% RH for 24 hours. The samples were put into Al_2O_3 crucibles and heated at 10°C/min in N_2 atmosphere (flow N_2:100mL/min); the range of temperature was from 40 to 800°C with a NETZSCH TG 209 F1 thermogravimetric analyzer (Germany).

RESULTS AND DISCUSSIONS

Mechanical Properties

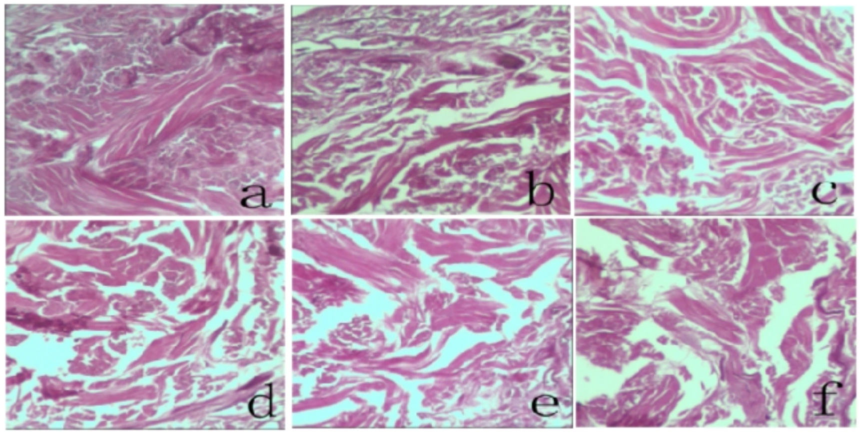
Table 1. Mechanical properties and Ts of leathers

Sample	Tensile strength N/mm^2	Tear strength N/mm	Elongation at break %	Ts ℃
VL-0	7.6	31.4	26.674	83.7
VL-5	7.5	30.9	26.582	85.1
VL-10	7.2	28.7	25.899	80.7
VL-15	7.0	27.3	25.340	73.2
VL-20	5.9	24.8	25.095	71.0
VL-25	5.7	24.2	23.934	70.4

VL-0: control, VL-5: aging 5 days, VL-10: aging 10 days, VL-15: aging 15 days, VL-20: aging 20 days, VL-25: aging 25 days

As shown in Table 1, the tensile strength, tear strength and elongation at break of vegetable tanned leather were reduced with the increase of aging time, and the Ts was dropped too. Because of the damage of the artificial acid rain, the fibers and cross-linking between collagen were broken down, which decreased the stability and mechanical properties of leather.

Optical Microscope Photograph



a: VL-0 b:VL-5 c:VL-10 d:VL-15 e:VL-20 f:VL-25

Figure 1. Optical micrographs of aged leather (at a magnification of 40×)

As shown in figure 1, the collagen fibers of control were tight, but the gaps of collagen fibers were enlarged with the increase of aging time. These phenomena indicated that the collagen fibers were damaged by acid rain, which proved the conclusions of mechanical properties and Ts.

FT-IR Analysis

Table 2. The shift of Amide I and Amide II band of aged leather

Sample	Amide I cm^{-1}	ΔAmide I cm^{-1}	Amide II cm^{-1}	ΔAmide II cm^{-1}
VL-0	1648.66	0	1544.86	0
VL-5	1645.38	3.28	1532.60	12.26
VL-10	1639.81	8.85	1528.66	16.20
VL-15	1636.28	12.38	1525.49	19.37
VL-20	1631.85	16.81	1458.12	86.74
VL-25	1632.82	15.84	1457.90	86.96

The wave number of 1700 ~ 1500 cm^{-1} was a characteristic absorption peak of amide I and amide II band in leather, so they were selected to analyze the changing of leather during the aging process (Cyril *et al.*, 2006). As shown in table 2, with the increase of aging time, the amide I and amide II band were moved to lower wave number, and the amide II band was dropped significantly. During the process of aging test, main changes have been taken place on the group of C=O and NH, indicating that the collagen structure was changed because of acid rain.

Thermal Stability

Table 3. DSC and TG properties of aged leather

Sample	T_d/°C	ΔT_d	$\Delta_d H$/J/kg	T_{max}/°C	ΔT_{max}
VL-0	92.3	0	283.1	322.4	0
VL-5	88.3	4.0	260.7	313.8	8.6
VL-10	87.5	4.8	248.5	311.7	10.3
VL-15	86.5	5.8	235.3	310.7	11.3
VL-20	86.4	5.9	233.2	308.5	13.9
VL-25	83.7	8.6	230.8	300.4	22.0

For DSC, T_d was the thermal denaturing temperature of leather; $\Delta_d H$ was peak area of the DSC curves and represented enthalpy during heating process (Budrugeac *et al.*, 2010). In TG/DTG curve, T_{max} was the temperature of decomposition at maximum rate (Marcilla *et al.*, 2011). These values were listed in table 3. The results showed that T_d, $\Delta_d H$ and T_{max} were dropped with the increase of aging time. During the aging, multi-point hydrogen bonds between vegetable tanning agent and collagen peptide chains were destroyed and leaded to the cross-linking degree between collagen and tanning agent reduced, therefore thermal stability of leather was decreasing. After the destruction of the collagen fibers and cross-linking effect of tanning agent, it was easy to break down the structure of leather; therefore T_d, $\Delta_d H$ and T_{max} were also dropped.

CONCLUSION

The vegetable tanned leather was aged by artificial acid rain, with the increase of aging time, the mechanical properties were decreasing; the collagen fibers were broken down and the gap of fibers were enlarged; the Amide I and Amide band were moved to lower wave number; the thermal-stability was dropped obviously. In conclusion, the acid rain has a significant aging effect on vegetable tanned leather which leaded structure changed and performance reduced. Furthermore, with the increase of aging time, the impact on leather is more evident.

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