TESTING OF ARTIFICIALLY AGED LEATHER IN ACID RAIN

GONG YING[1], MADALINA IGNAT[2], WUYONG CHEN[3], YANPING GAO[3], LUCRETIA MIU[2], PETRU BUDRUGEAC[4]

[1] *College of Chemistry and Chemical Engineering, Yunnan Normal University, Yunnan China*

[2] *INCDTP - Division Leather and Footwear Research Institute, Bucharest, Romania*

[3] *National Engineering Laboratory for Clean Technology of Leather Manufacture (NELCTLM), Sichuan University (SCU), Sichuan, China*

[4] *National Institute for Research and Development in Electrical Engineering ICPE-CA, Bucharest, Romania*

To assess the resistance of calf leather tanned with quebracho to acid rain, the changes in shrinkage temperature, melting temperature and enthalpy of crystalline zone, and contact angle of a liquid drop as artificially aging in acid rain were determined. Acid air aging of leather was revealed to bring about the weak decrease of shrinkage temperature, melting temperature and absolute value for enthalpy of leather crystalline zone. On the other hand, there is not a significant difference between values of contact angle of initial and aged samples. All these results show that the investigated leather exhibits a good resistance to acid rain.

Keywords: leather, artificial aging, acid rain.

INTRODUCTION

The chemical pollutants play an important role in the deterioration of leathers at all levels of structural hierarchy, from molecular to microscopic levels (Florian, 2006). Gaseous pollutants from wet air, especially CO_2, SO_2, NO_x, combined with water, oxygen and ozone could form acid rain, which has an important aging effect on collagen based materials. Sulphurous acid results by reaction of sulphur dioxide with water. Sulphur dioxide can also react with oxygen and ozone and forms sulphur trioxide, which reacts with water, resulting in sulphuric acid. So obtained mixture of sulphurous acid, sulphuric acid, sulphur dioxide and air could cause hydrolysis of collagen and tannins that determines the deterioration of leather. This deterioration leads to changes of physical-chemical properties of leather. Therefore, it is important to investigate artificial aging of leathers in acid rain. The objective of this work was the determination of the resistance of leather manufactured from calf skin tanned with quebracho to acid rain.

EXPERIMENTAL

Material

The leather was produced at National Research & Development Institute for Textile and Leather, Division Leather and Footwear Research Institute (INCDTP-ICPI) by an original procedure, using calf skin as raw material and quebracho as tannin.

Aging Conditions

The preparation of artificial acid rain: 0.04 mL H_2S0_4 (98%), 0.06 mL HCI (36-38%), 0.02 mL NH_4OH (25-28%) were dissolved in 80 mL distilled water and then

0.0296 g Ca $(OH)_2$ was added in the solution. The solution had a constant volume of 2L. The pH of float was determined to 3.25.

Artificial acid rain aging: each quebracho tanned leather sample was soaked in a float of artificial acid rain solution in a sealed beaker at room temperature (about 25°C) for 48 hours. Then the soaked samples were covered by sealed bags and put in a sealed box for 0, 5, 10, 15, 20 and 25 days at 100% relative humidity and 50°C respectively. The treated samples were dried 48 hours in the air. And then the samples were placed in desiccators to adjust to a constant weight over a week for further tests.

Determination of Shrinkage Temperature

The shrinkage temperature was determined by the following methods:

- the standardized method for determination the shrinkage temperature described in SR EN ISO 3380 – 2003 and TEST IUP 16 of the International Union of Leather Technologists and Chemists Societies (Williams, 2000), using Leather Shrinkage Temperature Tester GIULIANI, IG/TG, 2001;

- Micro Hot Table (MHT) method by the procedure described by Larsen *et al.* (1993) using a MHT apparatus produced by Caloris – Romania.

DSC Analysis

The DSC curves were recorded using DSC 204 F1 Phoenix apparatus produced by Netzsch – Germany in the following conditions: sample mass 2-3 mg; nitrogen flow (purity of nitrogen is higher than 99.999%; 20 $mL\cdot min^{-1}$); heating rate of 10 $K\cdot min^{-1}$, and the temperature range 25^0C … 280^0C.

Contact Angle Measurements

Contact angle measurements were made using an equipment which allows analyzing static or dynamic phenomena which take place when a liquid drop interacts with a solid surface (VCA OPTIMA). For each sample a 5 μL water drop was used and maintained in contact with the leather surface for 180 seconds. Five pictures per second were made and the results were processed by using a special soft called VCA Optima XE.

RESULTS AND DISCUSSION

Determination of Shrinkage Temperature

The values of shrinkage temperatures (T_s) determined by standardized and MHT methods are listed in Table 1. The inspection of this Table shows:

- For a given t there is a difference between the values of T_s determined by different methods. These differences are due to different shapes of samples used in the two methods of shrinkage temperature determination, namely a rectangular shape for standardized method, and few fibers for MHT method.
- The increase of aging duration determines a weak decrease of T_s value. However, for a given method and $t \geq 10$ days, the differences between T_s values are smaller than 3^0C, which could be due to non-homogeneity of samples and/or to inherent experimental errors.

Table 1. The values of shrinkage temperature (T_s) determined by standardized and MHT methods

Method → t/day*	Standardized method T_s/^{0}C	MHT T_s/^{0}C
0	80	70
5	75	71
10	74	67
15	73	68
20	73	69
25	71	69

* t = duration of aging in acid rain

DSC Analysis

DSC curves associated to thermal transitions which typically occur in leather samples measured in open crucibles and nitrogen flow display a broad endothermic peak followed by smaller endotherms (see Figures 1 and 2). The broad peak in the temperature range (50 – 120) °C is associated with thermal dehydration of the sample. The one or two endotherms that occur at T > 220°C were ascribed to thermal melting (denaturation) of the crystalline collagen embedded in the amorphous matrix (Popescu *et al.*, 2008). It was shown that temperatures corresponding to these peaks are well correlated with the thermal stability of the crystalline (rigid) fraction of collagen in collagen based materials.

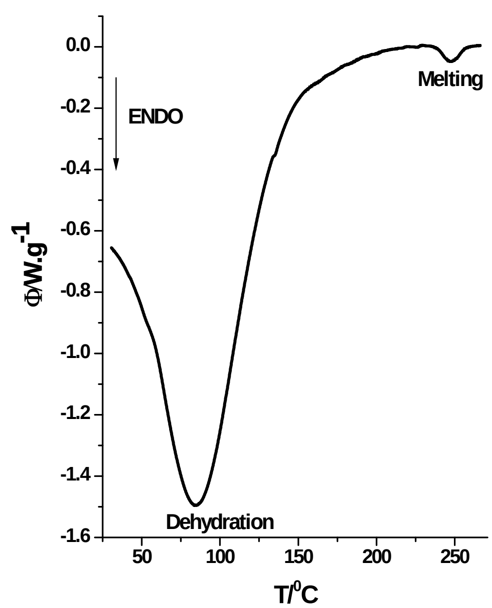

Figure 1. DSC curve obtained by analysis of initial (unaged) leather

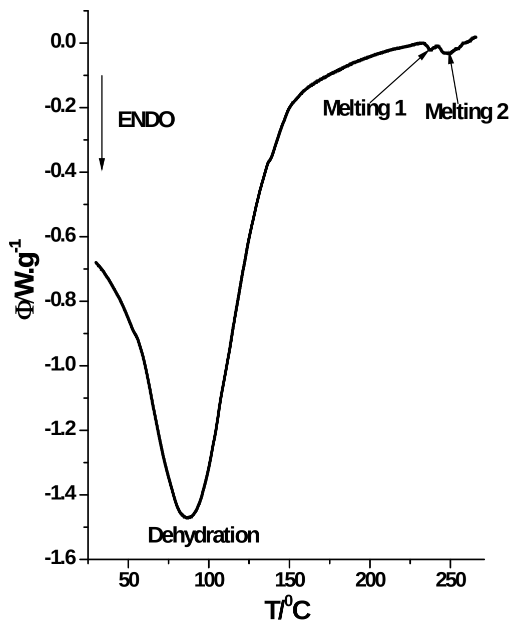

Figure 2. DSC curve obtained by analysis of leather aged in acid rain for 10 days

Dehydration process is characterized by temperature corresponding to the first minimum in DSC curve (T_{min}), while the melting process is characterized by melting temperature (T_m) and corresponding enthalpy (ΔH). The values of these parameters are listed in Table 2.

Table 2. The values of characteristic parameters of dehydration and melting processes for initial and aged samples

Process→	Dehydration	Melting of crystalline zone	
t/day	$T_{min}/^0C$	$T_m/^0C$	$-\Delta H/J.g^{-1}$
0	84.5	247.4	3.2
5	83.8	248.4	4.2
10	86.8	237.8	0.4
		249.0	1.7
15	83.8	251.8	2.7
20	82.6	252.0	2.2
25	79.1	252.5	2.1

According to data listed in this Table, the increase of aging duration determines a weak increase of melting temperature of crystalline zone of leather. This means that the aging in acid rain determines a weak increase of rigidity of crystalline zone.

The absolute value of ΔH can be correlated with the relative content of crystalline zone. According to data listed in Table 2, the relative content of this zone increases after 5 days of aging, and is lower and practically constant after 10 days of aging. The sample aged for 10 days exhibits two distinct melting processes. Such behavior shows that this leather exhibits two kinds of crystalline zone.

Contact Angle Measurements

The obtained results indicate that the samples are hydrophilic (the contact angle is <90°) (see Figure 3). The values of contact angle are listed in Table 3. The differences between the blank and the treated samples are insignificant, meaning that the treatment does not affect the surface properties.

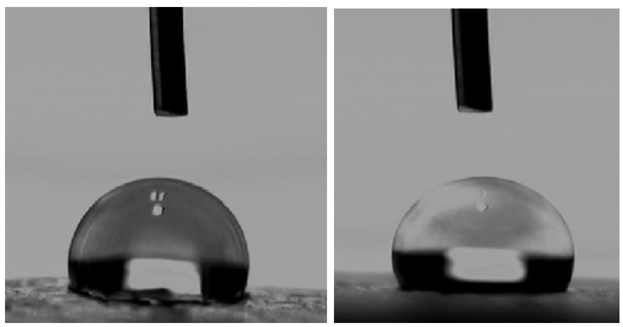

Figure 3. Water drop on leather surface

Table 3. The values of contact angle for initial and aged samples

t/day	contact angle
0d	23.07
5d	22.31
10d	22.58
15d	18.33
20d	18.75
25d	21.56

CONCLUSIONS

- The changes in shrinkage temperature, melting temperature and enthalpy of crystalline zone, and contact angle of a liquid drop corresponding to calf leather tanned with quebracho, as the result of artificially aging in acid rain were determined.
- The application of standardized (TEST IUP 16) and MHT methods have shown a weak decrease of shrinkage temperature when the aging duration increases.
- The use of DSC analysis in nitrogen flow has shown that both melting temperature and absolute value of enthalpy corresponding to crystalline zone of leather exhibit a weak decrease when aging duration increases.
- The results obtained at determination of contact angle of a liquid drop have shown that the values of contact angle are not practically changed as a result of artificially aging.

- All obtained results highlight that the investigated leather has a good resistance to acid rain.

Acknowledgments

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