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THE INFLUENCE OF OLIGOMERIC MELAMINE RESIN ON BOOKBINDING RESISTANCE TO ENVIRONMENTAL FACTORS

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Abstract

This paper aims to study the influence of the environmental factors upon the ageing resistance characteristics of bookbinding leather treated with an oligomeric melamine-formaldehyde resin modified by benzenesulfonation (BSMF). Leather treated with 0.25 g BSMF as dry matter (DM)/g leather acquired significant hydrothermal and dimensional stability to environmental factors, compared with the untreated leather, when subjected to identical accelerated ageing parameters (T = 50ºC, RH = 90% for 24h, SO_2 concentration in air = 0.04 mg/L). FTIR-ATR spectra and SEM images of treated leather indicated a minimal damage of the collagen structure: crosslinking bridges between resin and collagen functional groups proved to be stable to the accelerated ageing conditions, which must be assigned to the BSMF product ability to slow down the acid hydrolysis processes. This is related both to the crosslinking ability of BSMF between the collagen macromolecule chains and to its acid buffer behaviour.

Keywords: melamine-formaldehyde resin, bookbinding leather, collagen matrix reinforcement, accelerated ageing resistance

1. Introduction

Each material, the art objects are made of, has a particular response to environmental factors such as air relative humidity and temperature, light, dust, polluting gases etc. Numerous studies have investigated the influence of exogeneous and endogenous factors upon leather degrading in different museum artefacts [1, 2].

Conservation – restoration of bookbinding leather essentially makes use of chemical reagents, able to interact with the free functional groups of collagen in such a way that leather gains dimensional stability and hydrothermal

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resistance. At the same time, they must exhibit time delay effects upon leather deterioration under climatic factors.

Collagen, the main constituent of leather, is an organic substance, which changes its structure, appearance, physico-chemical and mechanical properties under the action of environmental factors in time. Thus, the conservation state is affected by physico-chemical and photochemical degradation.

The air relative humidity (RH) at values exceeding the maximum admissible limits of 50-65 % is considered to be one of the most aggressive deteriorating agents of organic materials, especially when air temperature isn't constant. High values of RH speed up the hydrolytic degradation of collagen by splitting of the polypeptide chain in tanned leather. This process is favoured by sulphur dioxide and nitrogen dioxide, present in polluted atmosphere. These gases contribute to the acid hydrolysis of leather and finally to advanced degradation of museum leather artefacts, in time [3-5].

The oligomeric benzenesulfonated melamine-formaldehyde resin (BSMF) is an effective reinforcement agent for old bookbinding leather. Treating leather with 0,25 g BSMF product (DM)/g leather results in higher values of the physico-mechanical characteristics, higher dimensional stability, superior antistatic behaviour, without affecting the leather grain appearance [6, 7].

This paper is dealing with the study of the BSMF influence upon the ageing resistance of the bookbinding leather subjected to accelerated ageing in condition atmosphere, under simultaneous action of temperature, RH and sulphur dioxide. The use of BSMF resin as conservation agent for leather museum objects is also assessed.

2. Experimental

2.1. Materials and methods

The following materials and methods were used:

- vegetable-tanned goat leather, used for the binding of religious book from the XIXth century, with no heritage value;
- benzenesulfonate melamine-formaldehyde resin (BSMF), in a 10% resin solution at pH 8.4; three oligomeric fractions were identified in the synthesized product;
- treatment with BSMF resin: volumes of 10 % resin solution at pH 8.4 were applied with a cotton pad both on grain and flesh side of each sample such that a BSMF/ leather mass ratio of 0.25 g (DM) /g was respected; samples were then air-dried for 24 hr;
- accelerated ageing test of leather samples, conducted in a KPW-1/4 conditioning chamber, at 50°C, 90% RH and 0.04 mg/L for 24 hr, according with SR EN ISO 17228/2006.

2.2. Analyses

The following analyses were performed:

- *Shrinkage temperature* (T_s) of leather samples was determined on a Giuliani IG/TG Digital Shrinkage Temperature Tester, according with the SR EN ISO 5397: 1996 method;
- *Linear shrinkage coefficient* (I_s) was calculated from the length of the initial and shrinked leather sample;
- *The aqueous extract pH* was determined following a British standard method (British Standard Institution; BS1309, 1974). A leather sample, 0.25±0.002g was placed in 5 ml deionised water and mechanically agitated in a shaker for 24 hr, at 20±2°C and 65±2% relative humidity. The next day, the pH of the aqueous extract was measured using a standard pH meter.
- *FTIR-ATR* analysis; *FTIR-ATR* spectra were recorded on a Digilab/Excalibur FTS 2000 with ZnSe crystal, in attenuated total reflectance, scans number = 32, maximum resolution of 4 cm^{-1}, over the 700–4000 cm^{-1} range;
- *Morphology of collagen fibres* of the untreated and treated leather was determined by scanning electron microscopy, on a Vega 2 Tescan SEM microscope;

3. Results and discussion

3.1. Physico-chemical properties

The samples of untreated and BSMF-treated leather were analyzed before and after the accelerated ageing test, in terms of shrinkage temperature (T_c), percentage shrinkage (I_c) and pH of the aqueous extracts. The results of the above-mentioned analyses are presented in Table 1.

Table 1. Physico-chemical parameters of BSMF-treated leather, before and after the accelerated ageing test.

Leather sample	**Values of the physico-chemical parameters**					
	Before accelerated ageing			After accelerated ageing		
	T_c (ºC)	**I_c** (%)	Aqueous extract **pH**	**T_c** (ºC)	**I_c** (%)	Aqueous extract **pH**
Untreated	61	6.25	3.77	59	6.89	3.28
BSMF-treated	69	5.5	5.17	67	5.64	4.85

The untreated leather exhibited values of the physico-chemical parameters that are common to leathers with a high degree of acid damage. The acid damage is confirmed by the aqueous extract pH, which further decreased from 3.77 before ageing to 3.28 after ageing. During the artificial ageing, the percentage shrinkage increased by 78.57 %, which can be assigned to the progress of the acid hydrolysis of the peptide bonds of collagen macromolecule in the vegetable-tanned leather. By comparison, leather treated with the BSMF resin exhibited higher dimensional and hydrothermal stability and the pH of the aqueous extract did not decrease below 4 units

3.2. ATR-FTIR spectroscopy

It is well-known that, during conventional tanning process, the tanning agents establish cross-linking bridges between the active sites of neighbouring collagen macromolecules. Crosslinks reckon for the tanning effect, as the hydrothermal and dimensional stability is mainly determined by the collagen macromolecules crosslinking degree. FTIR-ATR is an analytic technique that has been used for several years for the study of the structural changes induced in the collagen macromolecule by the specific chemical processing operations in tanneries [8, 9].

Table 2 . Comparative assessment of the structural changes in leather, before and after the artificial ageing process.

Structural changes		**Before artificial ageing**		**After artificial ageing**	
		Untreated	**BSMF-treated**	**Untreated**	**BSMF-treated**
Amide I	ν_1 cm^{-1}	1635	1651	1681	1651
	A	0.001	0.001	0.001	0.002
Amide II	ν_2 cm^{-1}	1543	1543	1512	1543
Amide A	ν_1 cm^{-1}	3317	3317	3379	3317
	A	0.001	0.001	0.003	0.003
A_I/A_A ratio		1	1	0.33	0.66
$\Delta\upsilon = (\upsilon_1-\upsilon_2)$ cm^{-1}		92	108	169	108

Structural changes of collagen from the untreated and BSMF-treated bookbinding leather, before and after artificial ageing were assessed by means of semi-quantitative relationships, computed based on data given by the FTIR-ATR spectra. The computed data are given in Table 2.

The performance of the BSMF-resin reinforcing/consolidation treatment is assessed by means of: A_I/A_A ratio, which is a measure of the crosslinking degree: the higher the A_I/A_A ratio, the higher the crosslinking degree [10]; The difference between the amide I frequency and the amide II frequency, $\Delta\nu = (\nu_1-\nu_2)$ cm^{-1} accounts for the presence of the denaturing processes; $\Delta\nu > 100$ cm^{-1} indicates the presence of chemically denatured collagen.

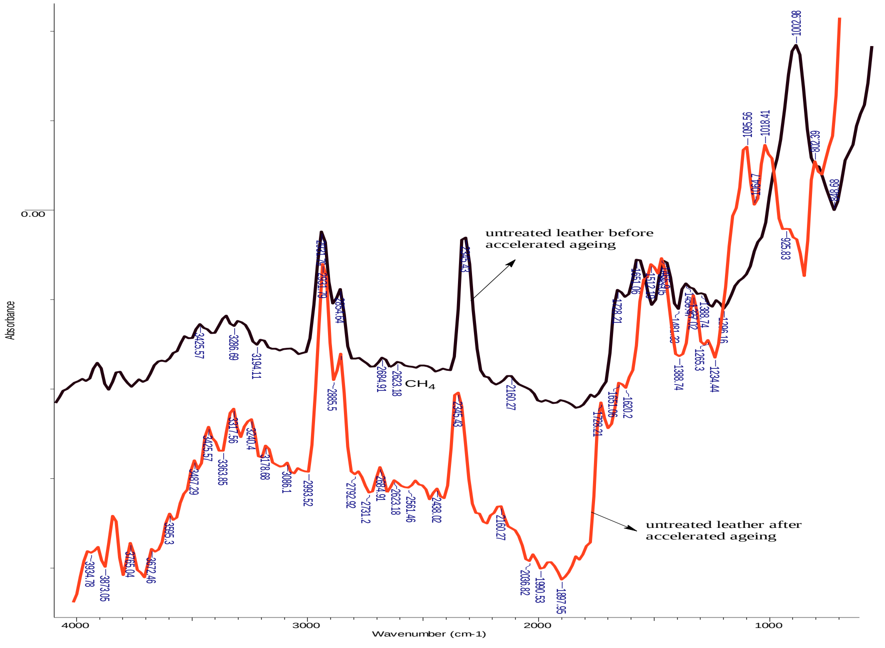

Figure 1. FTIR ATR spectra of untreated leather before and after accelerated ageing.

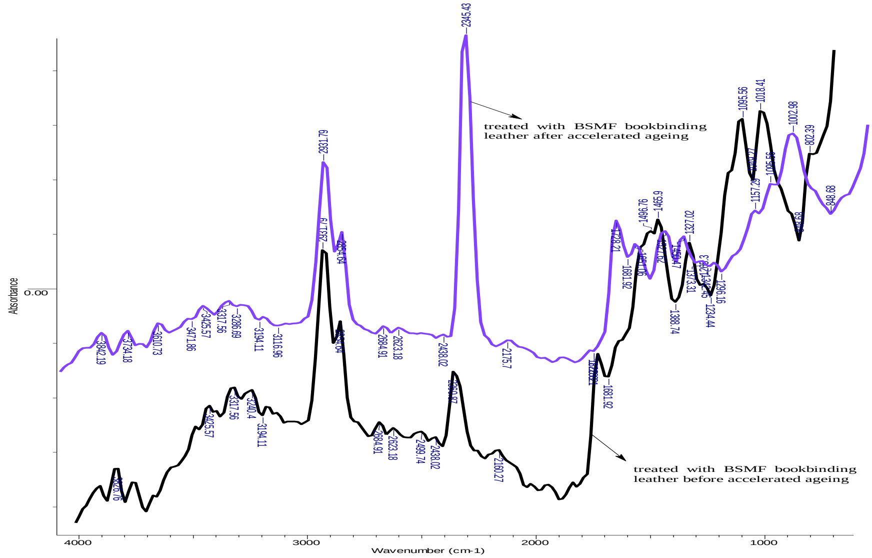

Figure 2. FTIR ATR spectra of treated leather with BSMF resin before and after accelerated ageing.

ATR-FTIR spectra, recorded for the untreated and BSMF-treated leathers before the accelerated ageing process, are typical for the polypeptidic structure of collagen macromolecule (see Figures1 and 2). The absorption bands at 1651cm^{-1} (1680-1630 cm^{-1}) are characteristic to the stretching vibrations of the CO bond from the carbonyl group (amide I), while the bands at 1544 cm^{-1} (1570-1515 cm^{-1}) are characteristic to the stretching vibrations of the C–NH group from the carbonyl group (amide II). The absorption bands from the 1300-1420 cm^{-1} range are specific to the COO^- group identified at 1404 cm^{-1} and are in accordance with similar data from the speciality literature [11, 12].

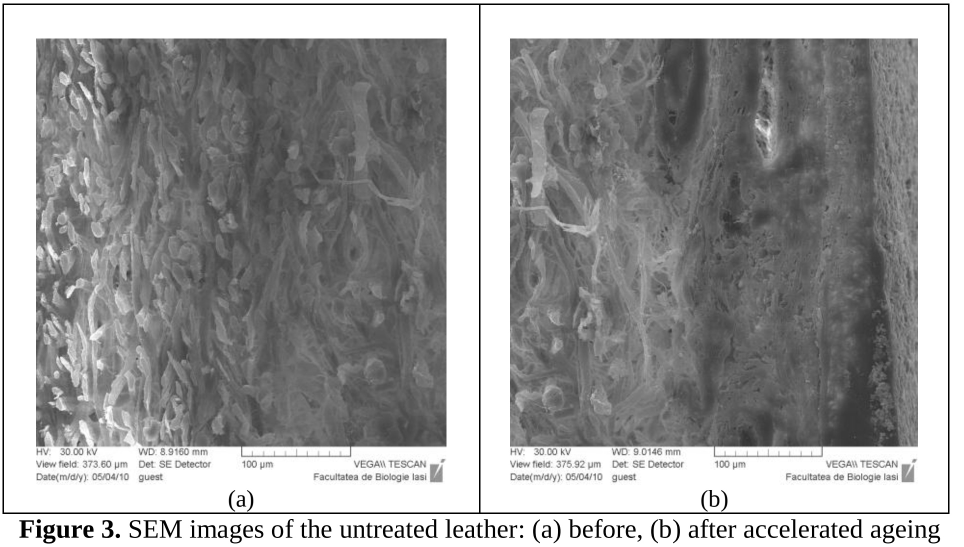

Figure 3. SEM images of the untreated leather: (a) before, (b) after accelerated ageing of old bookbinding leather.

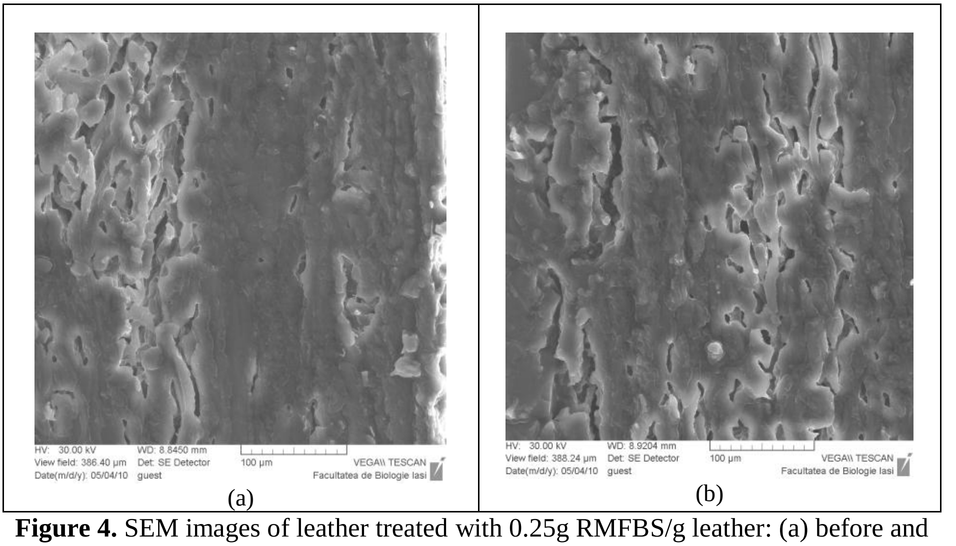

Figure 4. SEM images of leather treated with 0.25g RMFBS/g leather: (a) before and (b) after accelerated ageing of old bookbinding leather.

Spectra recorded after the accelerated ageing exhibit an intensification of the 2345 cm^{-1} (2700-2250 cm^{-1}) peaks, which must be related to the formation of tertiary amine bonds. The 1180–1000 cm^{-1} band indicates the presence of sulphate ions, generated during the acid degradation process.

After the accelerated ageing process, FTIR-ATR spectra recorded for the untreated leather (Figure 1) indicate a shift of the amide I characteristic band from 1635 la 1681 cm^{-1} and a shift of the amide A band from 3317 la 3379 cm^{-1}. The A_I/A_A ratio has the lowest value equal to 0.33, which indicates a low cross-linking degree and the denaturing of the collagen matrix. This state can be assigned to the breaking of the hydrogen bonds and of the peptide bonds in the main chain, which have a decisive contribution to the stabilization of the collagen macromolecule.

The BSMF-treated leather has a A_I/A_A ratio equal to 0.66, which indicates a minimal degradation of the collagen macromolecule; the crosslinking bonds between the resin and the collagen functional groups are strong and stable in the accelerated ageing conditions. Hence, the BSMF product has a noticeable ability to slow down the acid hydrolysis processes, due to its ability to establish crosslinks between the collagen chains and to its buffering effect.

3.3. Scanning electron microscopy of leather samples

The SEM images of collagen fibres in the untreated and BSMF-treated leather samples, before and after the accelerated ageing process, are given in Figures 3 and 4. The appearance of the collagen fibres surface explains the reinforcing ability of the BSMF oligomer resin. The sample treated with 0.25 g BSMF/g leather exhibited collagen fibbers enveloped by the resin product, the filling of the interfibrillar space and the setting up of a well-defined tridimensional network, unaffected by the process. By comparison, the accelerated ageing resulted in the degradation and the thinning of collagen fibres in the untreated leather.

4. Conclusions

An offer of 0.25 g BSMF (DM)/g leather provides bookbinding leather with high values of shrinking temperature Tc (an increase of $\Delta Tc = 8^{o}C$ compared with the untreated leather) and a decrease of the shrinkage coefficient by 78.57 %, which denotes strength and dimensional stability both to high temperature and high relative humidity of air, and to sulphur dioxide action, without affecting the treated leather grain.

The BSMF resin acts as an acid buffer: it preserves the pH of the aqueous extract at a value of 4.5 even at accelerated ageing, which avoids the acid damage of leather even at prolonged exposure to environmental factors.

ATR-FTIR spectra reveal minimal/minimum alteration of collagen macromolecular edifice of BSMF-treated leather, compared with the untreated leather. Crosslinking bridges between the resin and the functional groups of collagen prove to be strong and stable to the accelerated ageing factors, fact which allows the use of the oligomeric BSMF product as a leather conservation chemical agent, due to its crosslinking and acid buffering effects.

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