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OLIGOMERIC MELAMINE RESIN AS CONSOLIDATION AND ANTISTATIC AGENT FOR OLD BOOKBINDING LEATHER

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Abstract

This paper presents a study on the use of an oligomeric melamine-formaldehyde resin modified by benzenesulfonation (BSMF), as consolidation-antistatic agent for old bookbinding leather. Leather treated with 0.25 g BSMF/g leather acquires good dimensional stability to the action of climatic factors and higher physico-mechanical parameters, due to BSMF ability to evenly penetrate the leather section and to establish physical bonds with the functional groups of the dermal collagen. The antistatic effect was assessed by direct measurement of stored electrostatic charge, Q and of superficial resistivity, ρ_s. Treating leather with the BSMF product results in significant decrease of both electrostatic charge and superficial resistivity, which confirms the superior antistatic properties of the tested resin.

Keywords: melamine-formaldehyde resin, oligomer, bookbinding leather, consolidation, antistatic treatment

1. Introduction

One important step in the conservation-restoration of leather artefacts is the consolidation of the collagen matrix, which imparts mechanical strength and dimensional stability to the collagenous fibrous structure; these effects slow down the leather object deterioration under the action of weathering factors [1, 2].

Numerous studies were dedicated to the use of polyacrylic and ureo-formaldehyde resins for the consolidation of old bookbinding leather. Synthetic resins impart good mechanical strength to leather, but due to high molecular weights and viscosity, they present low diffusion capacity, leading to uneven distribution in leather section and structure [3].

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In leather and fur industry, sulfonated melamine-formaldehyde resins are successfully used as synthetic tanning agents or synthans and as antistatic agents [4-7].

Surface antistatic treatment is less studied in the conservation-restoration of heritage objects, even if most of old leather book covers present dust and other impurities deposits. It is known that electrostatic charging of heritage objects is a major issue both during storage and manipulation during conservation-restoration activities.

Dust particles are strongly attracted by electric charged surfaces and affects objects appearance; inorganic components such as silicates exert an erosion effect, while fungal components can determine the microbiological deterioration of collagen-based materials [8].

Excessive electrostatic charging of heritage leather objects can be counteracted only by changing the intrinsic characteristics of collagen fibres; this can be done by covering them with highly polar macromolecular polymers, bearing a certain hydrophilic-hydrophobic balance, able to increase hydrophilicity and decrease superficial conductibility of the treated material [9-11].

This paper is dealing with the potential use of a benzenesulfonate melamine-formaldehyde oligomeric resin as consolidation and antistatic agent for old bookbinding leather. The relationship between the improvement of the physico-mechanical behaviour and of antistatic properties of the treated leather and the interactions between the collagen fibres and the oligomer resin was studied.

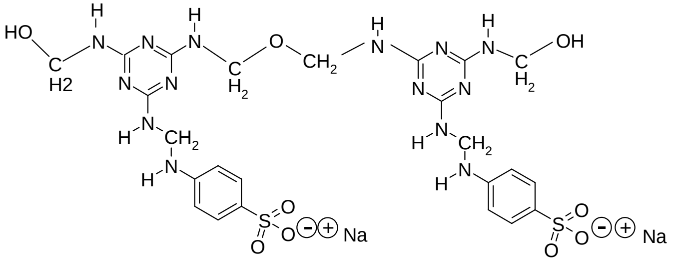
2. Experimental

2.1. Materials

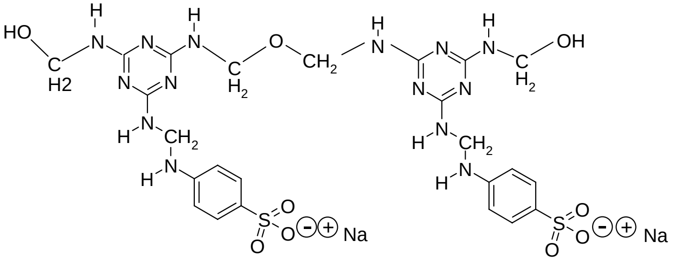
- Vegetable-tanned goat leather, used for the binding of a religious book from the XIXth century, with no heritage value;
- Benzenesulfonate melamine-formadehyde resin (BSMF), synthesized in accordance to literature [12] and having the following characteristics: clear, yellowish liquid with pH = 8.4 at 10 % resin solution and 0.31 mg/l residual formaldehyde. The dry matter content (DM) was 24÷27 %, with 4÷6 % minerals and 25-30 % total nitrogen. Three oligomeric fractions of the melamine-formaldehyde polycondensate class, having the chemical structures given in Figure 1, were identified in the synthesyzed product; Elemental formulas, medium molecular weights, nitrogen content and mass percentage of each fraction are given in Table 1.

Table 1. Main characteristics and mass percentage of the BSMF fractions.

Fraction	Fraction mass content %	Elemental formula	Medium molecular weight Da	Nitrogen content (%)
1	29.67	$C_{36}H_{24}N_{21}O_{13}S_3Na_3$	1143	25.72
2	28.28	$C_{24}H_{30}N_{14}O_9S_2Na_2$	768	25.52
3	42.05	$C_{18}H_{26}N_{13}O_8SNa$	607	29.98



Fraction No.1



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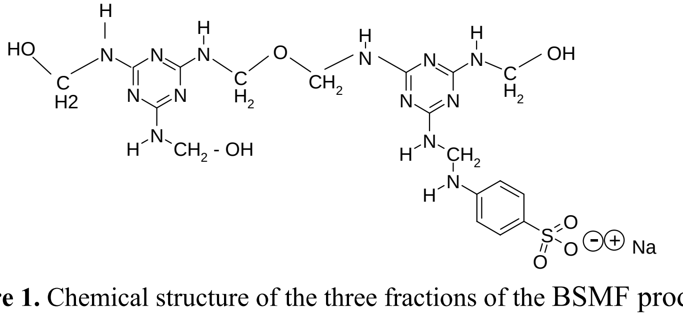

Fraction No.3

Figure 1. Chemical structure of the three fractions of the BSMF product

2.2. Methods

Leather samples of 80x150 mm were cut from the book cover, conditioned at 20°C and 60 % RH and subjected to consolidation-antistatization treatment, as follows:

- *leather preparation,* by dry wiping for dust removal, wet wiping with ethanol and air drying at room temperature;

- *treatment* with the BSMF resin; volumes of 4 ml aqueous solution of BSMF were applied both on grain and flesh side of each sample, with a cotton pad; samples were then air-dried for 24 hours. Working variants, differing by BSMF concentration in the treating mixture and by BSMF resin: leather mass ratio, are given in Table 2.
- *Softening treatment* with a glycerine and ricin oil mixture

Tabel 2. Working variants for the consolidation-antistatic treatment

Variant	Leather sample	Treatment variant	
		Content of BSMF product in the treating solution % v/v	BSMF resin/ leather g (DM)/g leather
1	P0*	0	0
2	P1	100	0.30
3	P2	80	0.25
4	P3	60	0.20

untreated leather

2.3. Analyses

Initial and treated leather samples were characterized by:

- *FTIR-ATR* analysis; *FTIR-ATR* spectra were recorded on a Digilab/Excalibur FTS 2000 with ZnSe crystal, in attenuated total reflectance, scans number = 24, maximum resolution of 4 cm^{-1}, over the 700 – 4000 cm^{-1} range;
- *Shrinkage temperature* (T_s) of leather samples was determined on a Giuliani IG/TG Digital Shrinkage Temperature Tester, according to SR EN ISO 5397: 1996 method. *Shrinkage coefficient* (I_s) was calculated from the length of the initial and shrinked leather sample;
- Tensile strength and elongation at break were determined according to international standards SR EN ISO 2419:2003 and SR EN ISO 3376:2003, on a Zwick/Roell Z05 dynamometer with a starting height of test area of 50 mm and crosshead speed of 100 mm/min. Experimental data were processed with the testXpert V 12.1 associated software.
- Morphology of collagen fibers from the untreated and treated leather was determined by Scanning electron microscopy, on a Vega 2 Tescan SEM microscope;
- The antistatic effect of the BSMF oligomer was assessed by direct determination of superficial electrostatic charge on a FM 300 fieldmeter and superficial resistivity on a Keithley 6517 A electrometer, according to the ASTMD-257 method. Experiments were conducted in air at 20 ± 2 ºC and 60% RH.

All experimental data are reported as the mean of three determinations.

3. Results and discussion

3.1. Assessment of the consolidation capacity of the BSMF product

3.1.1. FTIR ATR Spectroscopy

FTIR ATR spectra of both untreated and treated leather samples are given in Figure 2.

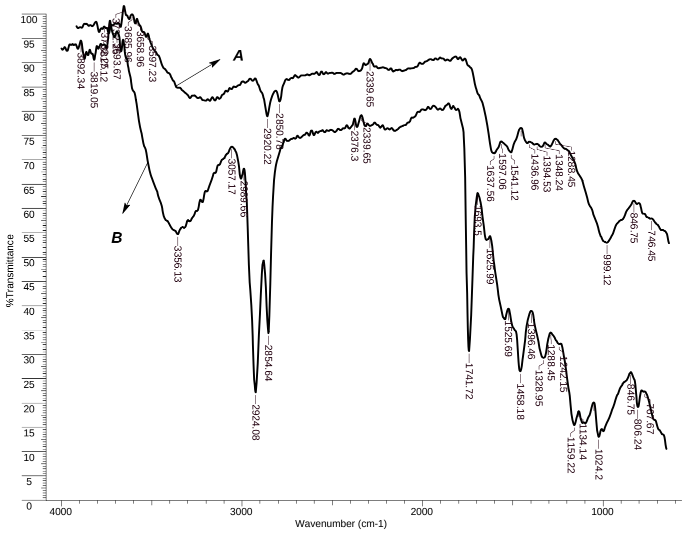

Figure 2. FTIR ATR spectra of untreated leather (A) and leather treated with 0.25 g BSMF/g (B).

- Both A and B spectra presents absorption bands which are characteristic to the polypeptide chain of collagen, namely in the 1680-1630 cm^{-1} range: deformation vibrations of the carbonyl C=O group (amide I), and in the 1570-1515 cm^{-1}, which mark the carbonyl bond (amide II) [13]. The absorption peaks at 2920-2924 cm^{-1} can be assigned to the aromatic C-H vibrations, specific for elagotannins found in oak and chestnut extracts [14].
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- The spectrum of treated old leather (Spectrum B) indicates the presence of the BSMF resin; absorption bands at 1350-1280 cm^{-1} (1288 cm^{-1}) are specific to the -C-N- bond from the aromatic secondary amine group, while the convolute peak at 1328 cm^{-1} indicates the presence of the triazine cycle.

- The presence of the softening agent is confirmed by the 1750-1735 cm^{-1} (1741 cm^{-1}) band, which is assigned to the CO-O- group of the saturated esters from the softening compositions.
- The 3570-3200 cm^{-1} (3356 cm^{-1}) band can be associated with the presence of both water and a great number of methylol groups. The methylol groups, both in free form and associated with collagen by hydrogen bonds, are responsible for the consolidation effect induced by the BSMF in the old bookbinding leather [15, 16].

3.1.2. Physico-mechanical properties of the tested old bookbinding leather

Breaking strength (T_n) and elongation at break (E_b) of untreated and cured leather were calculated from the experimental load-strain curves (Figure 3). Experimental and calculated values of the physico-mechanical properties of the tested old leather are given in Table 3.

Table 3. Experimental and calculated values of the physico-mechanical properties of the tested old leather.

Values of physico-mechanical properties	Working variant/Sample			
	1 / P0	**2 / P1**	**3 / P2**	**4 / P3**
g BSMF (DM) / g leather	0	0.30	0.25	0.20
Shrinkage temperature (T_s), ºC	61	62	63	61
Shrinkage coefficient (I_s), %	6.25	5.8	5.5	6.0
Medium thickness of sample, mm	0.50	0.50	0.50	0.50
Medium width of sample, mm	1.0	1.0	1.0	1.0
Maximum tensile load (F_{max}), N	48.86	53.43	59.17	50.18
Breaking strength (T_n), N/mm^2	97.72	106.86	118.34	100.36
Elongation at break (E_b), %	4.92	2.89	5.04	2.12

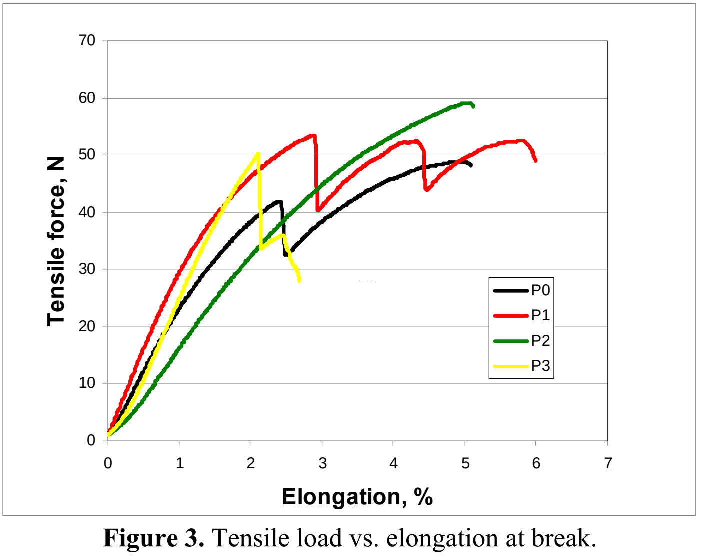

Figure 3. Tensile load vs. elongation at break.

Data from Table 3 indicate that, along with the increase of the BSMF: leather mass ratio, the shrinkage temperature increased; a maximum of the T_s was recorded at a BSMF: leather mass ratio = 0.25:1 (sample P2), which provided a maximum penetration of the resin into the leather structure. A higher offer of 0.3 g BSMF (sample P1) determined the increase of the stiffness of exterior layers only, which explains the stepwise shape of the load-elongation curve, starting from the inner layer to the superficial ones. The highest improvement of the physicomechanical properties was obtained for sample P2, which exhibited a maximum breaking strength of 118.34 N/mm^2 and the lowest elongation at break and shrinkage coefficient, equal to 2.12 % and 5.5 %, respectively (Figure 4). These values assure high mechanical strength and dimensional stability for the old bookbinding leather.

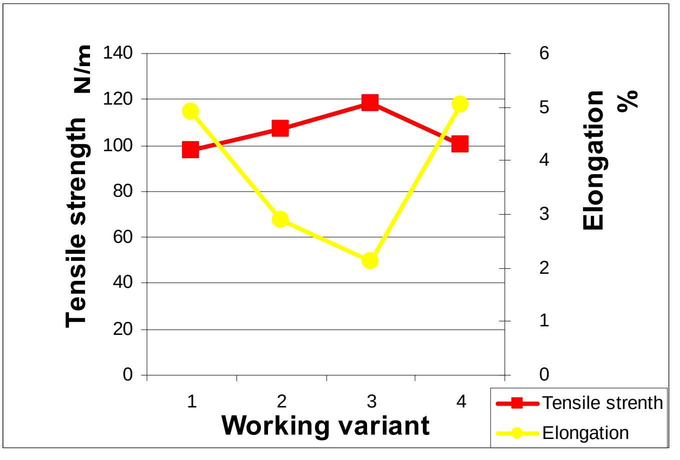

Figure 4. Comparative values of tensile strength and elongation at break vs. the working variant.

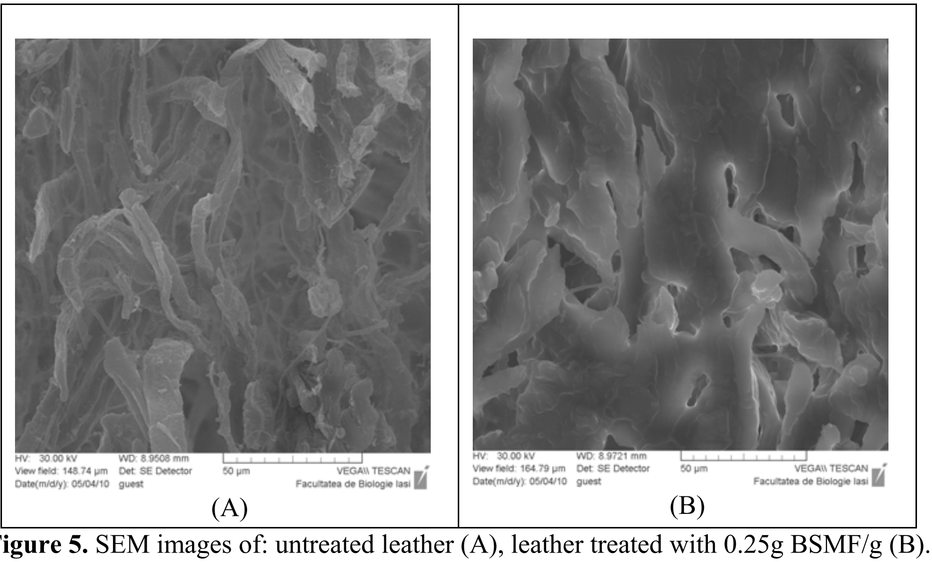

Figure 5. SEM images of: untreated leather (A), leather treated with 0.25g BSMF/g (B).

3.1.3. Scanning electron microscopy of leather samples

Comparative microscope images of original and treated leather (see Figure 5, A and B) can explain the consolidation and antistatic effect of the BSMF oligomer. The BSMF oligomer coats the fibrillar elements of collagen, fills the interfibrillar spaces and eventually forms a tridimensional network, due to: (a) precipitation that occurs at pH = 4, which is characteristic for the old leather section [17] and (b) the establishment of numerous hydrogen bonds between the collagen functional groups and the resin's free methylol groups.

3.2. Antistatic effect of the BSMF resin

Table 4. Values of electrostatic charge and superficial resistivity of untreated and treated leather.

Determination	Untreated leather		Old bookbinding leather treated with the BSMF resin					
	P0		P1		P2		P3	
	Q kV/m	ρ_s x10^{11} Ω/ cm^2	Q kV/m	ρ_s x10^9 Ω/ cm^2	Q kV/m	ρ_s x10^9 Ω/ cm^2	Q kV/m	ρ_s x10^9 Ω/ cm^2
1.	803	1.77	198	3.51	178	3.20	318	5.89
2.	799	1.76	203	3.54	180	3.22	321	5.91
3.	798	1.81	199	3.53	182	3.27	321	5.99
Mean value	800	1.78	200	3.53	180	3.23	320	5.93

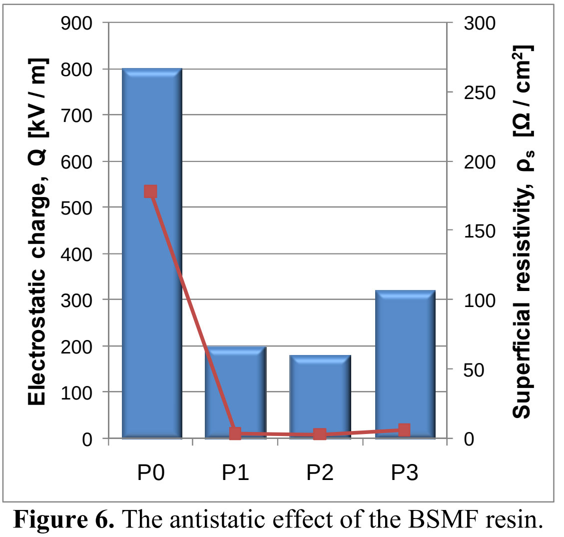

Figure 6. The antistatic effect of the BSMF resin.

Experimental values of superficial electrostatic charge (Q) and superficial resistivity (ρ_s) for the original and treated leather are given in Table 4 and Figure 6. One can easily see the strong antistatic effect of the BSMF: the superficial electrostatic charge decreased by four times compared with the original leather (samples P1 and P2), while the superficial resistivity decreased by fifty times, irrespective of the BSMF: leather mass ratio.

4. Conclusions

The BSMF resin is effective as consolidation–antistatic agent for old bookbinding leather. The antistatic effect can be explained by the BSMF ability to penetrate the leather section, to cover the collagen fibers and to fill the interfibrillar spaces, due to its linear, oligomeric structure and low-molecular weight; a BSMF: leather mass ratio of 0.25 g (DM)/g assures the highest dimensional stability to climatic factors and superior physico-mechanical properties.

The methylol groups of the BSMF molecule account for its antistatic effect: the numerous free and bound methylol groups increase the superficial hydrophilicity of collagen fibers, leading to a significant decrease of the electrostatic charge and superficial resistivity, irrespective of the BSMF:leather mass ratio. The treated leather gains long-lasting antistatic properties.

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