Obtaining and Characterization of a Benzenesulfonate Melamine-Formaldehyde Resin, with Applications in Leather and Fur Industry

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This paper presents a novel procedure for the chemical synthesis of a melamine-formaldehyde resin, modified by sulfonation with sulfanilic acid. The product was characterized by chemical analysis, FTIR spectroscopy, UV-VIS spectroscopy and GPC chromatography. Experimental data confirmed the obtaining of three linerar oligomeric fractions of the melamine-formaldehyde polycondensate class, having the average molecular weights of 1143 Da, 768 Da, and 607 Da, respectively. The obtained product has potential uses in leather and fur industry, as pre-tanning or antistatic agent.

Keywords: melamine-formaldehyde resin, sulfonation, oligomer, polycondensation

Melamine-formaldehyde resins (MFs) have found various applications in many fields, due to their specific properties: they act as thermosetting polymers [1], have high thermal stability [2,3], melting [4], chemical and abrasion resistance. These properties made them first choice materials as electroinsulating enamels, adhesives, rheological additives for concrete, controlled-release carriers for agrochemical fertilizers [5-8] etc.

Sulfonated melamine-formaldehyde resins (SMFs) are of interest as potential tanning materials [9-12], due to their particular structure comprising linear chains bearing enough hydroxyl groups, adjustable solubility and controlled molecular weights.

From a practical point of view, the obtaining of such macromolecular fractions is particularly difficult when polycondensation has to be limited to oligomers with 6 – 8 repeat units.

The short side chains are more flexible and more susceptible to steric positioning towards the chemical partners; thus, the interactions with complex substrates, such as the corium collagenous matrix and the wool keratins are favored, making the SMFs a more versatile auxilairy agents for leather and fur processing.

The aim of this paper is to draw up a chemical synthesis procedure for obtaining a novel melamine-formaldehyde oligomer resin, modified by benzenesulfonation with sulfanilic acid, with potential applications in leather and fur processing, as pre-tanning or antistatic agent.

Experimental part

Materials and methods

Chemical reagents*:* melamine and sulfanilic acid (Merck), 37 % formaldehyde, sodium hydroxide and sulfuric acid (Chimopar, Bucharest). All reagents were of synthesis grade.

Chemical analyses were performed according to the standards in force. The synthesized resin was also analyzed by FTIR spectroscopy, UV-VIS spectroscopy and size-exclusion chromatography (SEC).

FTIR spectra of the SMF product were recorded on a Digilab/Excalibur FTS 2000 spectrophotometer with resolution of 4 cm^{-1} and 24 scans, over the 400-4000 cm^{-1} range; the samples were pelleted in anhydrous KBr.

The UV-VIS absorption spectra were recorded on a Jasco 550 spectrophotometer, with 1mm quartz cuvette, scan speed: 200 nm/min and resolution: 1 nm, over the 190-600 nm range.

SEC was performed on a system equipped with two series of columns (2 x 300 mm each), filled with Sephadex G50 and Sephadex LH20, respectively, a programable ternary pump, injector and a Varian 9020 UV-VIS detector. Working conditions: solvent flow rate = 1 mL/min water, λ=254 nm.

Synthesis of the benzenesulfonate melamine-formaldehyde polycondensate

A four-stage procedure was designed for the synthesis of the benzenesulfonate melamine formaldehyde polycondensate [13], as follows: (1) controlled methylolation of melamine; (2) controlled benzene-sulfonation of the methylolated melamine; (3) controlled polycondensation of the benzenesulfonated melamine, in the presence of formaldehyde; (4) break off of the polycondensation process.

Synthesis was conducted in a reaction vessel, equipped with a thermostatic mantle, variable-speed stirrer, temperature and pH measuring devices.

The reagents were added in the following molar ratios: melamine: formaldehyde = 1: 2.5 and melamine: sodium sulfanilate = 1: 0.8. A quantity of melamine powder, corresponding to 0.96 mol of pure reagent was poured in the reaction vessel; about 120 mL deionized water at 80°C was added until a homogeneous paste was obtained; the paste was thermostated at 80°C for more 15 min. The alkaline formaldehyde solution was prepared from a 37 % solution corresponding to 2.4 moles of formaldehyde and a 10 % NaOH solution, until the *p*H 10.5 was reached. The sulfanilic acid sodium salt was prepared from 0.82 mol of sulfanilic acid and 300 mL of 6 % NaOH solution.

Melamine tri-methylolation was done by rapid injection of the alkaline formaldehyde into the melamine suspension; the reaction mass was vigorously mixed for 30 min at 80°C for complete melamine solubilization and *p*H was corrected to 10.5, if required.

Benzenesulfonation was carried out by slowly adding the sodium sulfanilate to the tri-methylolated melamine,

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at pH_{max} = 11; the reaction mass was mixed for another 30 min, at 80 °C.

Polycondensation was initiated soon after the sulfonation, by rapid cooling down the reaction mass to 55°C and lowering the *p*H to 6 with 10% H_2SO_4 solution. The resulting precipitate-free mixture was agitated for 60 min at 55°C. Polycondensation was interrupted by rapid alkalinization with 6 % NaOH solution, when *p*H was raised from 6 to 10. After *p*H stabilization, the reaction mass was heated to 80 °C and vigorously mixed for 30 min further on, with permanent *p*H correction.

Purification of the reaction product

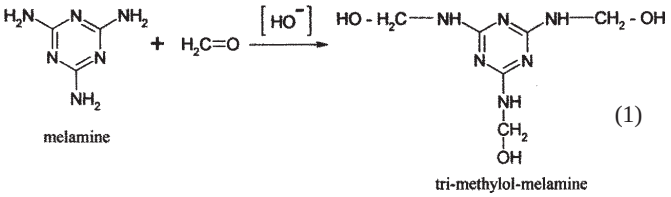
The reaction mass was separated on a SAVANT Speedvac Concentrator centrifuge, by centrifugation for 30 min, at RCF = 7.000 G and 80°C. The superior half of the supernatant was collected with a syringe needle from the centrifuge tubes, put in 100 mL vials and freeze-dried. The lyophilized powder was preserved in sealed plastic vials.

Results and discutions

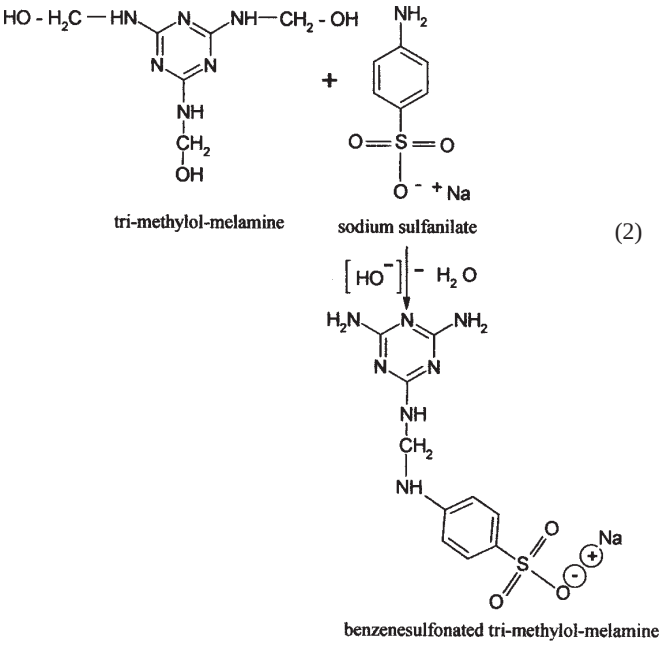
Synthesis of the benzenesulfonate melamine-formaldehyde resin

The SMF products are obtained by a two-stage synthesis: (1) synthesis of a sulfonated tri-methylol melamine (SMMM); (2) polycondensation of SMMM with formaldehyde under strict control of the process parameters.

When the sodium sulfanilate is chosen as sulfonation agent, the first synthesis stage comprises the following reactions (1 and 2):

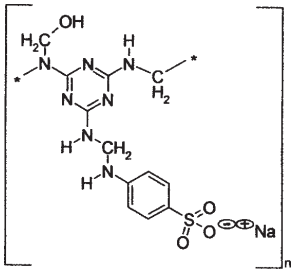


(1)



(2)

When conducted in acid media, the second polycondensation stage (3) results in products with the hypothetical structures given below:



(3)

The first and the last stages of the synthesis process mainly affect the building up of the postulated resin structure (structure (3)). Thus, methylolation dictates the branching degree of the polycondensate, while break off of the polycondensation process dictates the value of the average molecular weight. Benzenesulfonation of the methylolated resin provides the product solubility but affects the subsequent polycondensation kinetics. The evolution of the control parameters during the SMF synthesis (*p*H and temperature) is given in figure 1.

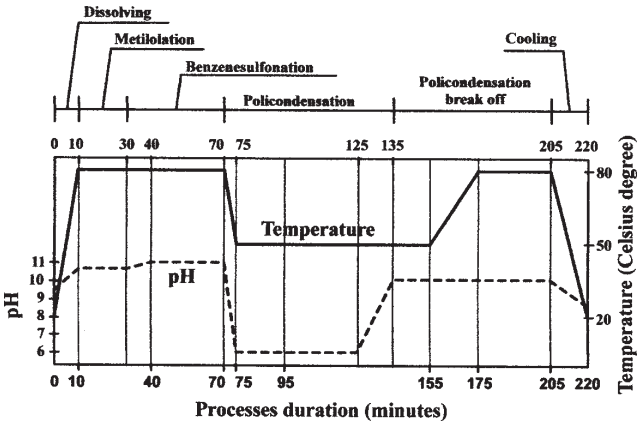


Fig. 1. Evolution of the control parameters during the SMF synthesis

Characterization of the SMF product

Chemical analysis

The chemical and physicochemical parameters of the synthesized SMF product and the corresponding determination methods are given in table 1.

The measured equivalent nitrogen mass fraction was 0.268 : 1 (reported to the dry SMF matter), which is in excellent agreement with the 0.2613:1 theoretical value (relative error is (26.80 – 26.13)/26,13 = 0.0256 %) and confirms the chemical structure postulated in the synthesis design step. The theoretical molecular weight of the oligomer repeat unit (structure 3), having the elemental formula $[C_{12}H_{14}N_7O_4Sna]_n$ is about 375 Da, and the corresponding nitrogen mass fraction is approx 0.2613 (98 / 375 = 0.2613).

FT-IR Spectroscopy

The FTIR spectra of the isolated and purified product, as given in figure 2, is in good agreement with the designed structure (3) of the SMF product.

The convolute peak at 1348 cm^{-1} is assigned to the triazine cycle, the peak at 603 cm^{-1} corresponds to the – S – CH2 – bond, while the 1031 cm^{-1} and the 684 cm^{-1} peaks confirm the presence of the sulfite ion. The secondary amine main chain is confirmed by the 1172 cm^{-1} peak. The absorption bands in the 1150 – 1050 cm^{-1}range and the 1122 cm^{-1} peak confirm the presence of the C-O-C bonds from the linear chain-substituted ether groups. The peak in the 3000 ÷ 3800 cm^{-1} range can not be assigned to water presence in sample (the sample was lyophilized

Table 1
CHEMICAL AND PHYSICOCHEMICAL PARAMETERS OF THE SMF PRODUCT

Crt. No.	Parameter / Property	UM	Value	Method/Apparatus
1.	Dry matter content	%	22,80	STAS 8574 / 1992
2.	Vacuum dry residue	%	22,93	STAS 1883 – 84
3.	Ash (at 800 °C)	%	5,31	SR EN ISO 4047 : 2002
4.	Total nitrogen content	%	26,80	SR EN ISO 5397 : 1996
5.	Total soluble matter	%	22,12	SR-EN ISO 4098: 2006
6.	Insoluble matter	%	0,68	SR-EN ISO 4098: 2006
7.	pH of 10 % solution	units	8,4	SR ISO 10523:1997
8.	Residual aldehyde content	g / l	0,31	Air stripping / Redox titration

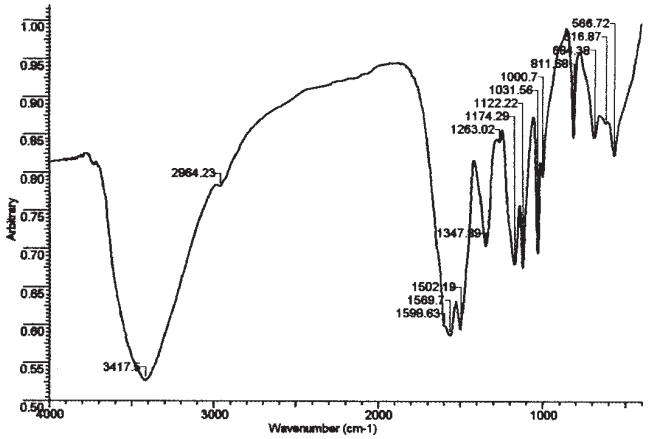


Fig. 2. The FT-IR spectra of the synthesized SMF resin

and the KBr pellet was obtained in anhydrous conditions) but to a significant number of free methylol groups.

UV-Vis Spectroscopy

The experimental UV-Vis spectra of the SMF resin were processed with a dedicated software from the *SpectraManager* series. The UV-Vis spectrum of the synthesized resin was recorded in water and is given in figure 3.

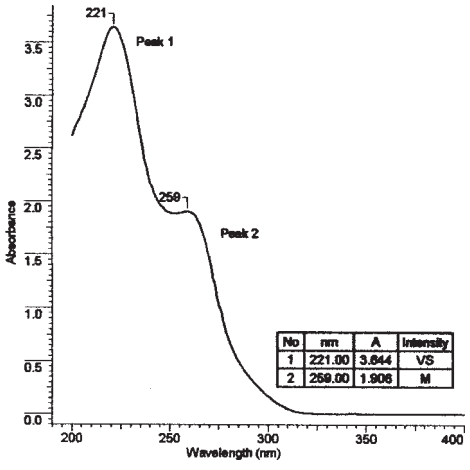


Fig. 3. The UV-Vis spectrum of the benzenesulfonate melamine-formaldehyde resin, in water

Two absorption bands can be pointed out: the absorption band assigned to the disubstituted benzene cycle (260 nm) and those assigned to the triazine cycle (220 nm) [14,15].

The GPC analysis

The experimental chromatogrames were processed with the PeakFit 4.12 and Derive 6.10 software applications, making use of the calibration curve and the deconvolution method. The calibration curve was recorded on a standard polystyrene sodium sulfonate (PSSNa) with known molecular weight (13000, 6800 and 1400) and on guaiacol. The equation of the SEC column calibration curve is given by equation (4):

$$y = e^{\frac{b}{x^2}+a} \quad (4)$$

where:

x –elution time

y–medium molecular weight of fraction

a = 5.56;

b = 2463.82

Peaks adjustment was based on the deconvolution parameters and on the distribution function, which is a four-parameter nonlinear function with a typical chromatographic tailing.

The distribution of the molecular populations is given in the SEC chromatogram deconvolution curve (fig. 4), which points out three molecular fractions. Mass percentage of each fraction in the SMF synthesis product, elemental formula, average molecular weight and nitrogen mass percentage of each fraction are given in table 2.

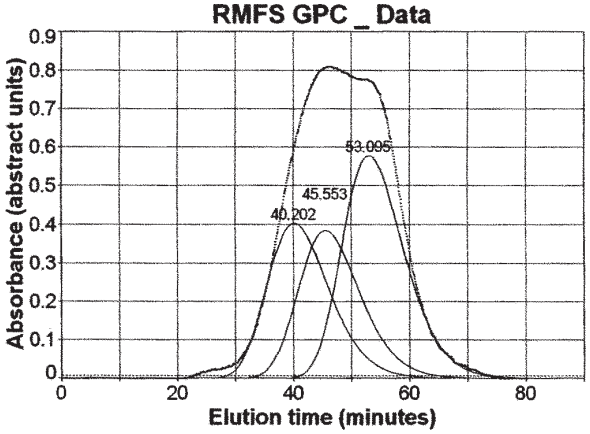


Fig. 4. The deconvoluted chromatogram of the synthesized SMF resin

Fraction	Mass percentage in the SMF product %	Elemental formula	Average molecular weight Da	Nitrogen content %
F1	29,67	$C_{36}H_{24}N_{21}O_{13}S_3Na_3$	1143	25,72
F2	28,28	$C_{24}H_{30}N_{14}O_9S_2Na_2$	768	25,52
F3	42,05	$C_{18}H_{26}N_{13}O_8SNa$	607	29.98

Table 2
MASS PERCENTAGE, ELEMENTAL FORMULA, AVERAGE MOLECULAR WEIGHT AND NITROGEN CONTENT OF THE SMF RESIN FRACTIONS

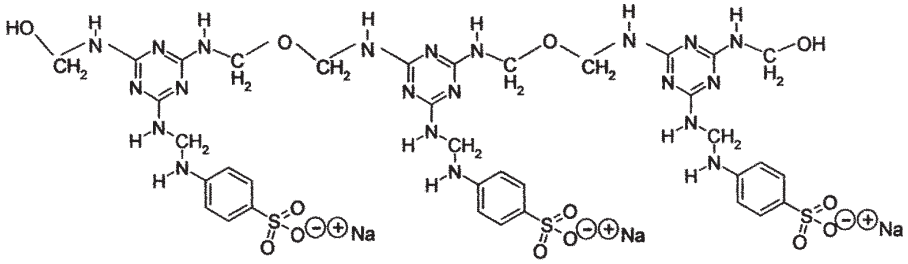


Fig. 5. Chemical structure of F1 fraction

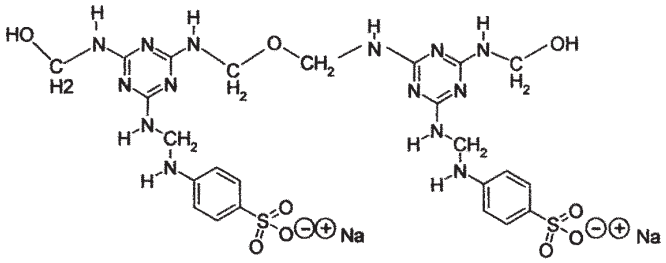


Fig. 6. Chemical structure of F2 fraction

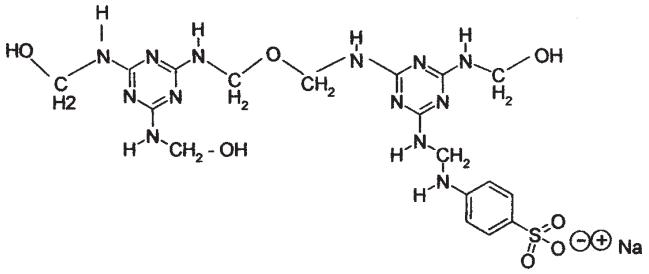


Fig. 7. Chemical structure of F3 fraction

The postulated chemical structures of the three SMF resin fractions are given in figure 5, 6 and 7, respectively.

Conclusions

The SMF product was obtained by polycondensation of methylolated melamine and formaldehyde, followed by the attachement of side benzenesulfonate chains. Any other tri-methylolated triazine can be used instead of melamine. Reagents were added in molar ratios that did not observe the stoechiometric ratios, as follows: melamine: formaldehyde = 1: 2.5 and melamine: sodium sulfanilate = 1: 0.8. The molecular weight of the SMF product was mainly controlled by temperature and pH of the reaction mass.

The synthesized benzenesulfonate melamine-formaldehyde product exhibits a polymodal molecular weight distribution. The SEC analysis proves the existence of three fractions, having the average molecular weights of 1143 Da, 768 Da, and 607 Da, respectively. The theoretical overall nitrogen content of the SMF product is 27,07 %, which is in good agreement with the experimental nitrogen content, of 26,80 % (relative error is (27,07 – 26,80) / 27,07 = 0,99 %, which is < 1 %). The postulated chemical structures of the oligomer fractions were confirmed by FT-IR, UV-Viz and SEC analyses.

The product synthesized in the present work is particular due to the linear structure of its oligomeric edifice, which allows the adoption of a particular conformation in aqueous solutions, able to penetrate the leather and wool fiber microstructure.

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References

1.SUBHASH, B., RASHMI ,S., BIRBAL, B., E-Journal of Chemistry, **6**(1), 2009, p.120
2.LUKEY C.A., HILL D.J., POMERY P.J., Polymer Degrad Stabil, ,**78** (3), 2002, p. 485
3.DEVALLENCOURT, C., SAITER, J. M., FAFET, A., UBRICH, E., Thermochimica Acta, **259** (1), 1995, p.143
4.GINDL, W., DESSIPRI E., WIMMER, R., Holzforschung, **56** (1), 2002, p.103
5.UCHIDA, J., SUGIYAMA, T., SUDOH, Z., NAHAYAMA, K, US Patent No. 6458870, 2002
6.WONNER, J., SCOLL, F, SCHOETTIG, F., WOELFERT, G., US Patent, No. 6579964, 2003
7. ALBRECHT, G., EIBL L., HUBER C., KERN A, US Patent, No. 5750634, 1998
8.LAHALIH, S., ABSI-HALABI M. US Patent, No. 4820766, 1989
9.DAWSON W.O, US Patent No. 2316741, 1943
10.COVINGTON, A.D., MA, SONG, IULTCS Congress Proceedings, London, 1997, p.565
11.WINDUS, W., HAPPICH, W.F., IULTCS Congress Proceedings, Haag Scheveningen, 1963, p.32
12.D'AQUINO, A., D'ELIA G., NAVIGLIO, B., SEGGIANI, M., TOMASELLI, M, VITOLO, S, J. Soc. Leath. Tech. Chem., **87** (5), 2003, p. 189
13. MAIER, S.S., DESELNICU, V., MAIER, V, PRUNEANU, M., Patent application OSIM-A/00680, 2007
14. BALABAN, A.T., BANCIU, M., POGANYI, I., Aplicaţii ale metodelor fizice în chimia organică, Editura Ştiinţifică şi Enciclopedică, Bucureşti, 1983, p.11
15. ANDERSON, R., BENDELL, D., GROUNDWATER, P., Organic Spectroscopic Analysis, Editura The Royal Society of Chemistry, 2004, p.1

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