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Study of Retanning Behaviour of Sulfonated Succinic Dihydrazide Formaldehyde Condensates Under Different Reactant Conditions

RASHID SALEEM[1,*], AHMAD ADNAN[1], MUHAMMAD RIAZ[2], MUHAMMAD HANIF[3] and FAHIM ASHRAF QURESHI[4,*]

[1]Department of Chemistry, GC University, Katchery Road, Lahore 54000, Pakistan
[2]Department of Chemistry, Government College University, Faisalabad-38000, Pakistan
[3]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan
[4]Office of Research, Innovation and Commercialization, COMSATS Institute of Information Technology, Chak Shahzad Campus, Park Road, Islamabad 45600, Pakistan

*Corresponding author: Tel: +92 51 90495258; E-mail: qureshifa@comsats.edu.pk; rashid_chemist@yahoo.com

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Sulfonated succinic dihydrazide resins were prepared by controlled reaction of succinic dihydrazide, formaldehyde and sodium metabisulfite, through a three steps reaction. Sodium metabisulfite/succinic dihydrazide (S/SDH) mole ratio were varied from 0.1 to 0.4 mol and formaldehyde/succinic dihydrazide (F/SDH) molar ratio ranges from 2 to 5 mol. The effects on the fluidity and viscosity of resin solutions were observed with varying degree of sulfonation and formaldehyde/succinic dihydrazide mole ratio. Viscosity of resin solutions increase with increasing formaldehyde/succinic dihydrazide ratio and decreased with increasing sodium metabisulfite/succinic dihydrazide ratio. The viscosity of the resin solutions increase with increasing molecular weight of polymer, until a critical molecular weight, at which point, gelation of resins occur. The resins were applied on chrome tanned leather and their influences were studied as retanning agent against commercial sulfonated melamine formaldehyde powder resin (Resin N. 2). Tear strength, tensile strength and elongation at break of retanned leathers were measured. Optical images and TGA were used to evaluate the fiber surface texture of leather and thermal stability of resins, respectively. FT-IR and proton NMR techniques were used to characterize the functionalities of the resin.

Key Words: Gelation of resin, Chrome tanned leather, Retanning agents, Thermo gravimetric analysis.

INTRODUCTION

In tanning, raw skins and hides are transformed into leather. Chrome tan is the most known tanning agent used over representing 80 % of world leather production[1]. Chrome tanned leather have high tensile strength and light weight[2]. Chrome has crosslinking ability with the acidic amino groups of collagen through coordination bonds. Physical and mechanical properties of leather is improved due to crosslinking[3]. In suede leathers, course nap and lack of fullness are some disadvantages of chrome tanned leather. Additionally, hexavalent chromium has been determined in mixture of Cr(VI) and Cr(III) in few Egyptians tanning industries in wet finishing baths[4]. Different types of retanning agents have been developed to improve properties of chrome tanned leather.

In vegetable retanning, mimosa and chestnut extracts are used. Synthetic organic tanning agents include aldehydes, their derivatives and polymers of different types like urethane, melamine and acrylate resins[5] Leather tanned with glutaraldehyde based resins turns into yellowish orange colour, which is usually not desirable. To prevent colour development, several attempts have been done to modify the chemistry for prevention of colour development, but none was found to be totally successful[6]. Novel succinic dihydrazide formaldehyde resins have been developed with good stability in liquid form and retanning property. The crosslinking mechanism of retanning with leather can be investigated by optical microscope and mechanical strengths of the fiber after treating with retanning agents.

Amino resins based tanning agents began to develop since the 1960. There are many appropriate commercial products available, including Relugan D and Resin N. 2. Melamine and formaldehyde first react together and later etherification is carried out by ethanolamine and other etherifying agents[7], stability of the product is more affected by the conditions of the process.

Fast reaction of melamine with formaldehyde changes characteristics of melamine resin as a tanning agent. To prevent its further polycondensation reaction, generally, lower alcohols are used but they affect the tanning performance of the resins. Hydrophilic groups like, hydroxyl, sulfamic acid, aromatic and aliphatic sulfonic acid and mostly sodium metabisulfite[8] are used to make melamine resins water soluble. Sulfonated urea formaldehyde and melamine formaldehyde resins have sensitivity to pH fluctuation during tanning operations and become deposited superficially[9] with loss of tanning effect. The major drawback of these resins is their unstability. The resin synthesized optimally in present study has good liquid stability for long time and shows less sensitivity to fluctuation in pH and further produces uniform tanning effect on leather.

EXPERIMENTAL

Succinic dihydrazide (powder, 99.7 % purity) was obtained from the Nice-Synth chemical industry limited and processed as received. Formaldehyde (36 % w/w) was obtained from Chemsol Pakistan and was used without further purification. Resin N. 2 (powder, condensation derivative of melamine, 96-98 % active substance) was obtained from Irisultati Sicuri Della Qualita (ICAI) and technical grade sodium metabisulfite (powder, 98 %) was also used as such.

The raw skins used for the present research were commercial Pakistani goat skins. Basic chromium sulphate (Chromosal B with 26% Cr_2O_3 and 33% basicity from LANXESS) was used in chrome tanning. Sodium formate, sodium bicarbonate, formic acid and sodium chloride of analytical grade quality were utilized. Resin N. 2 was comparatively used as a standard. The viscosity of resin solutions were determined by Brookfield viscometer (LV DVE 230) at 25 ºC. FT-IR (Bruker IFS 48) and NMR (Bruker Spectrometer 300 MHz) were used to obtain FT-IR and ^{1}H NMR spectra, respectively. Metallurgical microscope (Leica Q 550 IW) coupled with CCD camera was used to take optical images of the retanned skins. SDT Q600 machine (Universal V4.5A TA instruments) was used for thermal analysis. Tensile testing machine (STM 566F) and tear testing machine (STM 566ST) were used for mechanical testing of leather.

Preparation of sulfonated succinic dihydrazide formaldehyde resin: Sulfonated succinic dihydrazide formaldehyde resins were prepared by the following procedure. The succinic dihydrazide formaldehyde condensate was prepared by three step procedure.

Step 1: 0.2 mol of aqueous solution of formaldehyde **2** (36 %) was taken in a three neck round bottom flask, assembled with stirrer, thermometer and condenser, 90 g of water was added and heated to 55 ºC. The pH of formaldehyde solution was adjusted to 7.5 with 0.5 N sodium hydroxide solution. 0.1 mol of succinic dihydrazide **1** was added to reaction vessel and reaction temperature was increased to 60 ºC and stirred for 15 min to yield dimethylol succinic dihydrazide **3**.

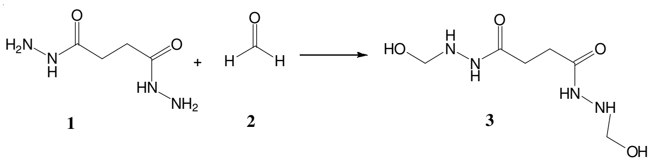
Step 2: Sodium metabisulfite (**4**) (0.01 mol) was added to reaction mixture and heated up to 80 ºC for 1 h.

Step 3: The pH of reaction mixture was adjusted to 5-6 by addition of few drops of 30 % (w/w) of formic acid. Reaction mixture was maintained in these conditions for 0.5 h. The pH of reaction mixture was raised to 7.5-8.0 with 0.1 N sodium hydroxide to quench the reaction. The reaction mixture was heated to 80 ºC for 1 h with constant stirring. The resulting resin solution was cooled to 25 ºC and filtered. The dry content of the resin was determined by drying a known quantity of resin in oven for 1 h at 103-105 ºC and adjusting dry contents up to 35 ± 1 % by water. The following experiments were performed under standard conditions with varying sodium metabisulfite/succinic dihydrazide and formaldehyde/succinic dihydrazide molar ratios.

RESULTS AND DISCUSSION

The route of the reaction for the synthesis of succinic dihydrazide formaldehyde condensate was devided into four steps.

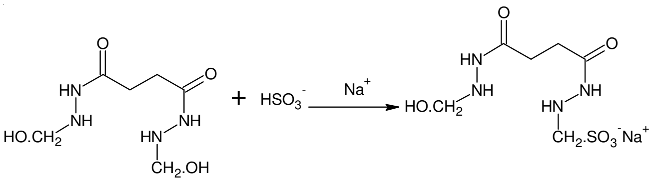
Methylolation of succinic dihydrazide (1): Succinic dihydrazide (**1**) reacts with formaldehyde (**2**) through addition reaction by nucleophilic attack of succinic dihydrazide on carbonyl functionality of formaldehyde in alkaline media, which produces methylol succinic dihydrazide (**3**). Different parameters like pH, reaction time, reaction temperature and molar concentration of reactants affect this methylolation step.



Sulfonation of dimethylol succinic dihydrazide (3): Methylolated succinic dihdyrazide (**3**) was sulfonated by sodium metabisulfite (**4**). Sulfonating agent first hydrolyzed in water to form hydroxide and bisulfite ions as shown below.

$$\underset{\mathbf{4}}{Na_2S_2O_5} + H_2O \longrightarrow 2Na^+ + 2OH^- + 2HSO_3^-$$

Hydroxide ion raises the pH of solution to 9-10 and the bisulfite ion take part in sulfonation of methylolated succinic dihydrazide (**3**) in basic media.

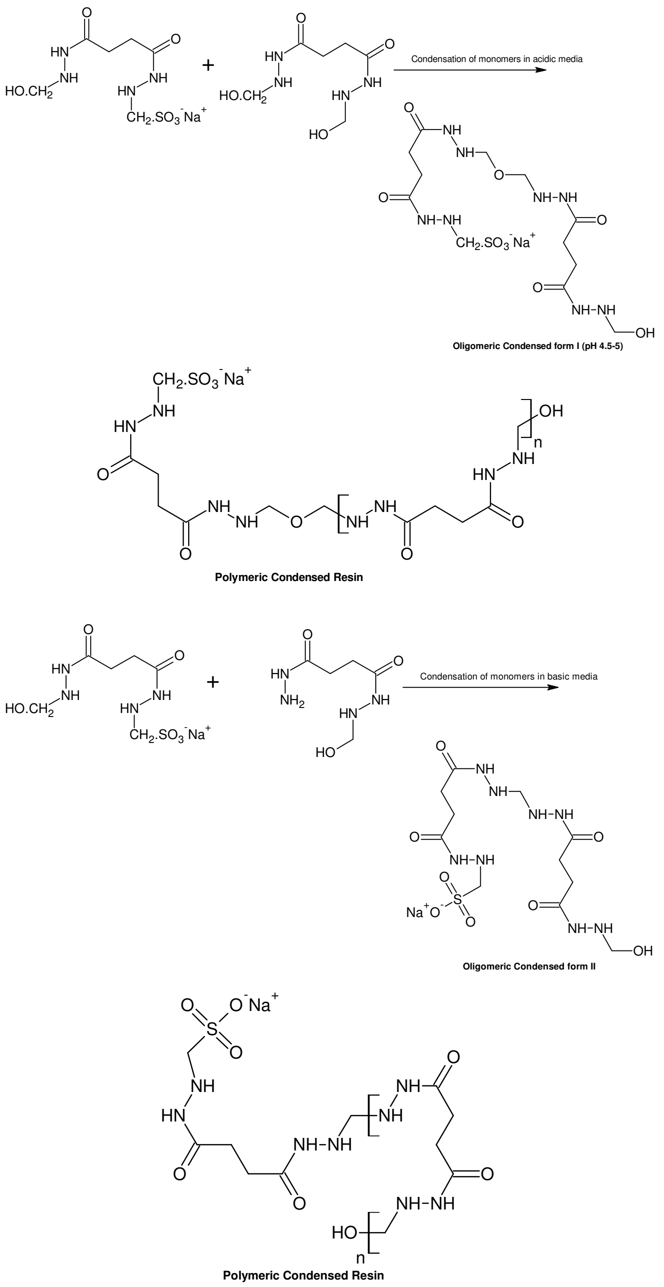


3 5

Sodium metabisulfite (**4**) is sulfonating agent and its molar ratio *vs.* succinic dihydrazide varies from 0.1 to 0.4. Sulfonation step is affected by pH, reaction temperature and time.

Acidic pH condensation: Under acidic condition, resin condensation takes place. During this condensation, ether linkage is developed. Reaction mixture undergoes at higher rate, further condensation under reduced pH of the solution, leads to viscous solution due to high molecular weight up to such extent that gelation of the product usually occurs.

Basic pH condensation: The resin solution is stabilized in this step. The reaction is quenched by raising pH to 7.5-8.0 with 0.2 N sodium hydroxide. Otherwise the product may go to gelation with high molecular weight. During this stage, condensations of resin take place and methylene bridges are formed between methylol moiety of methylolated succinic dihydrazide with amino functionality of other monomethylolated succinic dihydrazide, which results in stabilization of the resin.



Viscosity behaviour of resins: Fig. 1 shows the effects of formaldehyde/succinic dihydrazide (F/SDH) mole ratios on the viscosity of resin solutions (35 % solid contents) at 25 ºC at constant sodium metabisulfite/succinic dihydrazide (S/SDH) mole ratio (Table-1). It was found that viscosity of resin solutions increase with increasing F/SDH ratio for all the reactions carried out at similar conditions[10,11]. This is due to high rate of condensation in these resins having more N-methylol functionalities[12]. Therefore degree of branching and polymerization increases in all cases due to presence of N-methylol functional groups.

Resin application as tanning agent

Sample preparation: Pakistani goat skins were processed in the beam house by conventional method. The skins were resoaked after pickling in 10 % NaCl for 20 min. Depickled skins were processed by conventional methods with chrome tan (chromosal B).

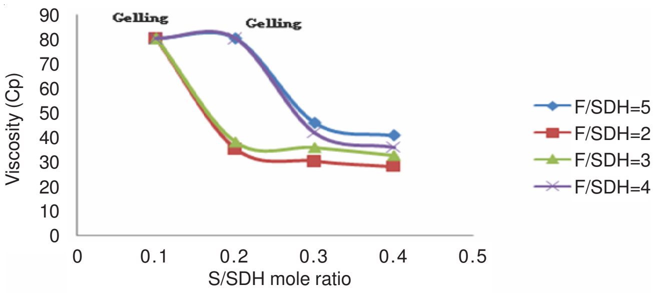


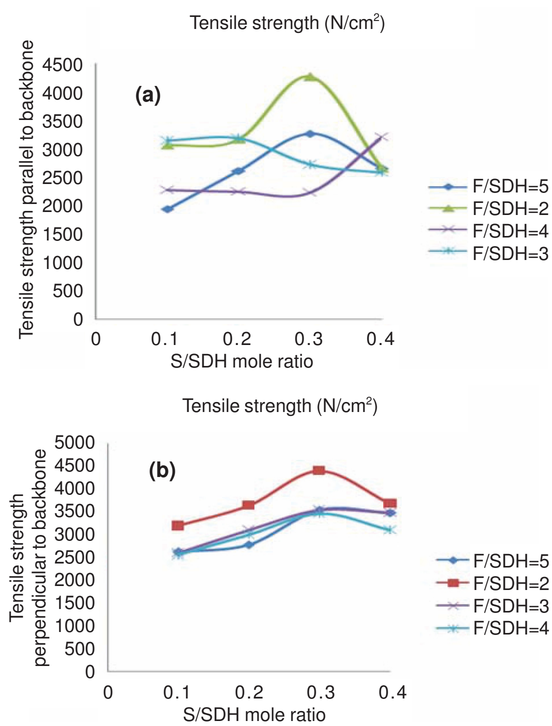
Fig. 1. Viscosity variation with various S/SDH and F/SDH mole ratio

The skins were processed in the lab with processing conditions in Table-2 while comparing retanning behaviour of synthesized resins with standard resin (Resin N.2). Percentages of the chemicals were calculated on the weight basis of shaved skin.

Mechanical properties: Specimens in dumb bell shape were cut with 110 mm length and 25 mm neck widths and used for measurement of tensile strength and % elongation at break. The mechanical properties were measured by the average of three longitudinal and traverse readings. These tests were performed on tensile testing machine (STM 566F) and tear testing machine (STM 566ST) was used for determination of tear strength as per standard method[13]. The results are tabulated in Table-3.

Leather strength has great importance in the physical assessment (Fig. 2). It gives indication of conditions of fiber bundles. Physical measurements like tensile strength, tear strength and elongation at break were performed to show the effects of prepared polymers as synthetic tanning agent and to illustrate the effects of different resins synthesized at different conditions.

The optimum results help to choose the most suitable conditions for the synthesis of succinic dihydrazide formaldehyde condensate.



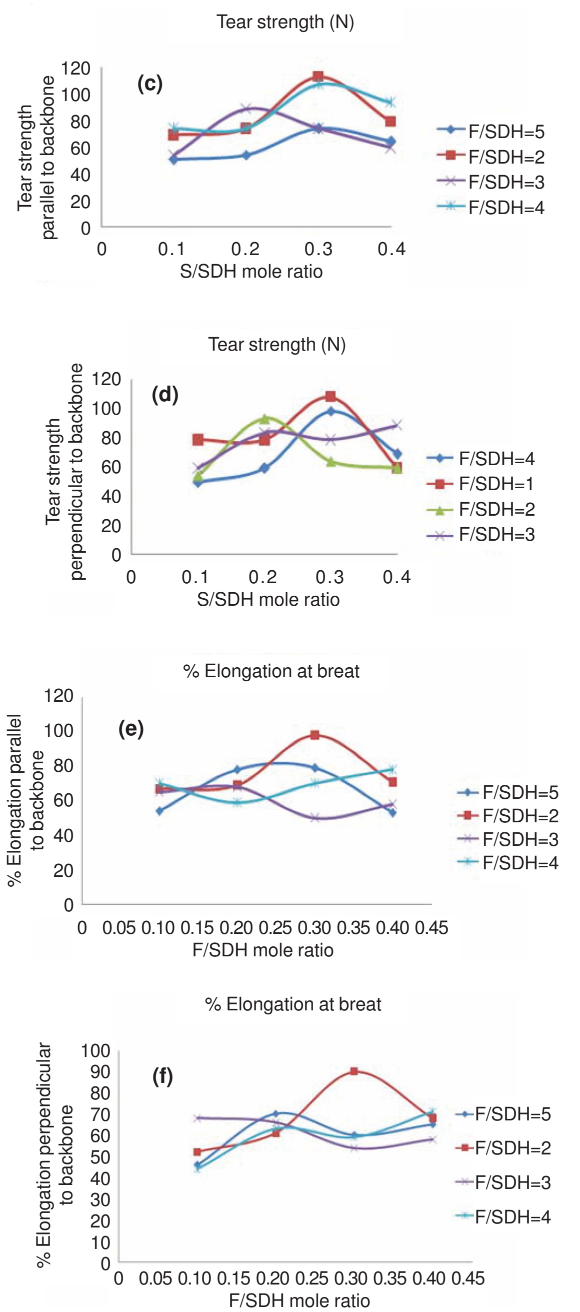


Fig. 2. Physical assessment of leather; (a) Effect of polymer on tensile strength parallel to backbone; (b) Effect of polymer on tensile strength perpendicular to backbone; (c) Effect of polymer on tear strength parallel to backbone; (d) Effect of polymer on tear strength perpendicular to backbone; (e) Effect of polymer on % elongation parallel to backbone; (f) Effect of polymer on % elongation perpendicular to backbone

Table-3 and Fig. 2 shows that resin synthesized at F/SDH mole ratio equal to 2 and S/SDH mole ratio equal to 0.3 shows optimum tear and tensile strength with maximum per cent elongation at break as compared to Resin N. 2. Resin synthesized under these conditions reacts properly with active sites of leather fibers to form new stable composite material. As the mole ratio and degree of sulfonation is increased, molecular size and solubilizing factor change which limit the reactivity of the resin with collagen fiber.

Optical images: Optical microscopy was used to look into the skin fiber structure and physical effects of polymer treatments on the skin. Optical microscopy of cross section (X50) of the goat skin, before and after the retanning process, showed clearly the significant effect of the synthesized polymers on the fibers compared with chrome tanned and chrome/Resin N.2 retanned.

In Fig. 3 optical images of only chrome tanned sample shows the appearance of collagen compact banding patterns, whereas skins treated with synthesized polymer shows absence of banding pattern.

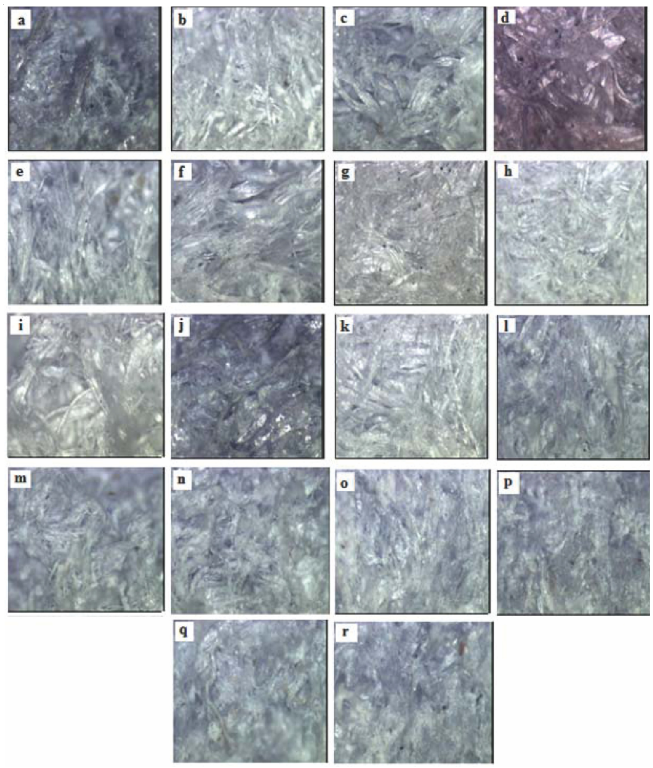


Fig. 3. Optical micrographs for cross section of fiber structure (x50); (a) Chrome tanned leather; (b) Retanned with resin N. 2; (c) Retanned with SDH resin # 01; (d)Retanned with SDH resin # 02; (e) Retanned with SDH resin # 03; (f) Retanned with SDH resin # 04; (g) Retanned with SDH resin # 05; (h) Retanned with SDH resin # 06; (i) Retanned with SDH resin # 07; (j) Retanned with SDH resin # 08; (k) Retanned with SDH resin # 09; (l) Retanned with SDH resin # 10; (m) Retanned with SDH resin # 11; (n) Retanned with SDH resin # 12; (o) Retanned with SDH resin # 13; (p) Retanned with SDH resin # 14; (q) Retanned with SDH resin # 15; (r) Retanned with SDH resin # 16; SDH - Succinic dihydrazide

As the degree of sulfonation is increased, more solubilizing groups decrease reactivity of the polymer with collagen. Tanning property of resin decreases with increase of formaldehyde to succinic dihydrazide ratio. It has been observed that as formaldehyde to succinic dihydrazide ratio is increased, more methylol groups are produced which crosslink to form high molecular weight resin which has little substantivity with leather collagen structure. The compositing effect of the polymer SDH # 03 is better in tannin performance as compared to Resin N. 2 and other resins of the series due to synthesis at optimum conditions for sulfonation and formaldehyde to succinic dihydrazide ratio.

Thermogravimetric analysis: Thermogravimetric analysis follows the mass change of a substrate as a function of temperature or time at a specific temperature field[14]. As the crosslinking

TABLE-1
EXPERIMENTAL DATA AND CHARACTERISTICS OF SYNTHETIC RESINS

Trials	Sodium metabisulfite/succinic dihydrazide (S/SDH)	Formaldehyde/succinic dihydrazide (F/SDH)	Viscosity (Centipoise)	Solid contents
1	0.1	2	Gelling	35 ± 1
2	0.2	2	35	35 ± 1
3	0.3	2	30	35 ± 1
4	0.4	2	28	35 ± 1
5	0.1	3	Gelling	35 ± 1
6	0.2	3	38	35 ± 1
7	0.3	3	35.8	35 ± 1
8	0.4	3	32.6	35 ± 1
9	0.1	4	Gelling	35 ± 1
10	0.2	4	Gelling	35 ± 1
11	0.3	4	41.5	35 ± 1
12	0.4	4	35.6	35 ± 1
13	0.1	5	Gelling	35 ± 1
14	0.2	5	Gelling	35 ± 1
15	0.3	5	45.6	35 ± 1
16	0.4	5	40.5	35 ± 1

TABLE-2
APPLICATION PROCESS DETAIL OF RETANNING

Process	Chrome/SDH polymer		Chrome/Resin N. 2	
Depickling and tanning	50 % water 8 % sodium chloride 0.5 % sodium formate 35 % water 0.5 % formic acid pH 3-3.5 4 % chromosal B 8 % chromosal B	15 min 10 min 5 min 30 min 6-8 h	50 % water 8 % sodium chloride 0.5 % sodium formate 35 % water 0.5 % formic acid pH 3-3.5 4 % chromosal B 8 % chromosal B	15 min 10 min 5 min 30 min 6- 8 h
Drain neutralisation and retanning	50 % water 0.3 % formic acid 10 % SDH Polymer 70 %hot water @ 40 ºC 5 % sulfated fat liquor 1 % formic acid	15 min 45 min 45 min 15 min	50 % water 0.3 % formic acid 10 % Resin N.2 70 % hot water @ 40 ºC 5 % sulfated fat liquor 1 % formic acid 15 min	15 min 45 min 45 min

TABLE-3
EFFECT OF SYNTHESIZED RESINS ON MECHANICAL PROPERTIES OF LEATHER

Sample	Mechanical tests of leather					
	Tensile (N/cm^2)	Tear (Newton)	Elongation (%)	Tensile (N/cm^2)	Tear (Newton)	Elongation (%)
	Parallel to Backbone			Perpendicular to Backbone		
Resin N.2	2158.3	49	71	2508.3	68.8	57
SDH # 01	3062.4	68.6	67	3185	78.4	52
SDH # 02	3164.5	73.5	69	3634.1	78.4	61
SDH # 03	4264.8	112.7	98	4390.2	107.8	90
SDH # 04	2654.2	78.4	71	3675	58.8	68
SDH # 05	3142.3	53.9	65	2597.9	53.9	68
SDH # 06	3184.9	88.2	68	3096.5	93.1	66
SDH # 07	2722.2	73.5	50	3529.2	63.7	54
SDH # 08	2580.7	58.8	58	3470.8	58.8	58
SDH # 09	2280.5	73.5	70	2542.7	58.8	44
SDH # 10	2245.7	73.7	59	2994.4	83.3	63
SDH # 11	2232.2	107	70	3452.2	78.4	59
SDH # 12	3204.1	93.1	78	3096.5	88.2	71
SDH # 13	1939.5	49.98	54	2603.0	49	46
SDH # 14	2613.3	53.9	78	2776.6	58.8	70
SDH # 15	3266.6	73.5	79	3538.8	98	60
SDH # 16	2654.1	63.7	53	3470.7	68.6	65

ability of the polymer increases, it forms stable polymer cross-linked matrix, results in thermal stability and ultimately increased the thermal stability of the polymer collagen composite (Fig. 4).

As the resin crosslinking ability increases, the density of fiber decreases showing better fiber separation. Thermal degradation of sulfonated succinic dihydrazide formaldehyde resin

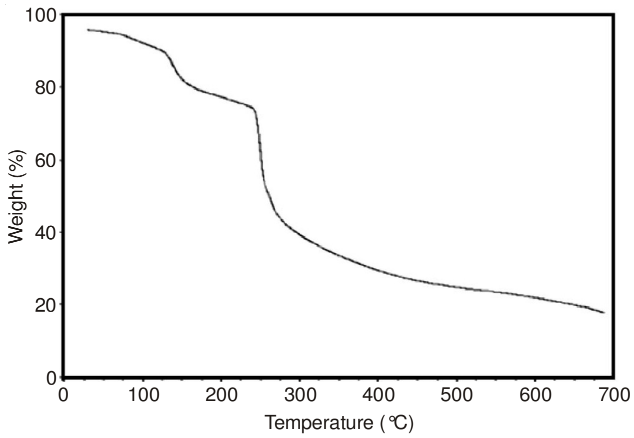


Fig. 4. TGA of optimized synthetic resin

(precipitated out in methanol) occurs in four stages. The per cent mass loss 19.45 % occurs at 160 °C which corresponds to loss of water entrained in the resin. The second loss of mass 6.31 % extends up to 240 °C due to release of formaldehyde upon further condensation of the resin. Radicals are formed above 240 °C by crosslinking which induce the cyclic structure formation in the polymer which further undergoes extensive fragments above 300 °C. Third degradation step starts at 240 °C and ends at 450 °C for the resin. The mass loss in this step is 47.6 %, which indicates degradation of polymer. Fourth degradation step starts at 450 °C and goes up to 680 °C. The mass loss per cent at this step is 8.33 %. The polymer having thermal stability up to 250 °C with per cent mass loss up to 7 % is good for leather heat fastness.

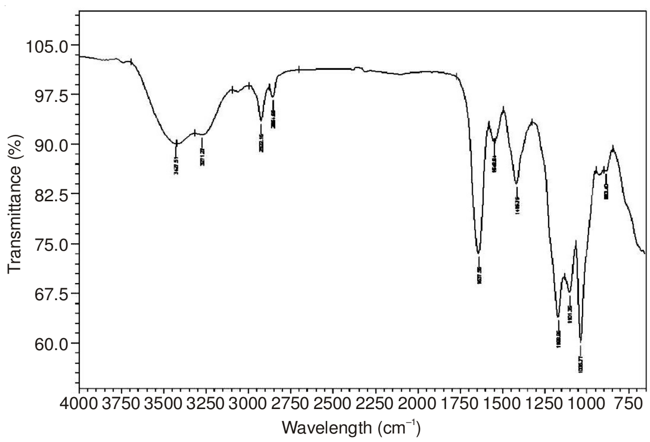


Fig. 5. FTIR of optimized synthetic resin

Structural elucidation: Infrared spectrum of resin (SDH # 03) was studied using KBr pellet in the range of 4000-700 cm^{-1} (Fig. 5). Two broad bands at 3427 and 3271 cm^{-1} attributed to OH group and NH groups. Signal at 2922cm^{-1} indicates C-H stretching vibrations. The peaks at 1035 and 1637 cm^{-1} indicates the ether linkage and carbonyl groups in the compound. The absorption at 1166 cm^{-1} indicates the stretching vibrations of C-S and S=O functionality of $R-SO_3$- group. The ^{1}H NMR spectrum was recorded in D_2O solvent, where sulfomethylene hydrogen corresponds to doublet peaks at 6.93 ppm, doublet peaks signal at 6.49 ppm are due to hydroxymethylene protons. The difference of position of signals of these methylene protons is due to difference in deshielding of the surrounding environment. Signal at 4.63 ppm are assigned to proton attached to nitrogen with neighboring to carbonyl group. Second hydrogen of hydrazide moiety shows multiplet peaks at 2.61 ppm. The protons attached to ethylene group in between the carbonyl groups shows a singlet peak at 3.17 ppm due to symmetrical environment.

Conclusion

Sulfonated succinic dihydrazide formaldehyde resins were prepared and characterized by ^{1}H NMR and FT-IR spectral analysis. The variation of viscosity at constant F/SDH ratio and varied S/SDH ratios were studied. The results showed that viscosity of the resin solutions increases as F/SDH ratio increases and decreased on increasing S/SDH ratio. Therefore, F/SDH molar ratio is directly proportional with the viscosity whereas S/SDH ratio shows inverse relation with the viscosity behaviour. All the resins were applied on the leather as retanning agents and mechanical properties of the leather were evaluated. The results showed that the resin synthesized at F/SDH ratio 2 and S/SDH ratio 0.3 shows optimum performance as a synthetic tanning agent. As F/SDH ratio increases, the molecular weight of the resin increases which in turn shows little reactivity of resin with collagen fiber. Further, as S/SDH ratio increases, it imparts resin more water soluble character and results in less substantively with the collagen fiber. The resin synthesized at optimum conditions show thermal stability up to 250 °C with mass loss of 7 % and is not sensitive to fluctuations in pH as compared to Resin N. 2 and results in better uniform tanning.

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