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A Comparative study of thermal behaviour of chrome tanned buff leather treated with aromatic sulfonic acids syntan and sulfones combined sulfonic acids syntans

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Abstract:

Three different samples of buff softy leather (i.e. BSS_6, BSS^1S_6 and BSS^2S_6) were prepared from a chrome tanned buffalo wet blue of Indian origin of substance 1.1-1.2 mm. BSS_6 was the sample wherein 6% phenol sulfonic acid based syntan was added. BSS^1S_6 and BSS^2S_6 had 6% two different syntans based on condensation product of sulfones and aromatic sulfonic acids, in addition to the other common auxiliaries used in all the three samples. Other unit operations (physical and chemical) for manufacturing leather were maintained same in all the three samples. Thermal behavior of these samples were studied, and tried to be correlated with the crosslinking densities of the samples and theoretical predictions.

Key words: *sulfones, aromatic sulfonic acid, crosslink density, TGA, retanning*

1. Introduction

Retanning agents influences the leather structure and properties(Jankauskaite et al., 2012). It is an established fact that water-soluble inorganic or organic salts of sulfonic acids containing as substituents higher molecular aliphatic, cycloaliphatic or alkylaryl radicals are very useful tanning agents. An organic sulfonic acid may be represented by a general formula R- SO_3H, where R- may be derived from many different sources as Alkane, alkene, alkyne and arene etc. The R group may also contain some secondary functionalities as ether, ester, amine, carboxylic acids, phenol etc. The nature of R group largely determines the physical properties of sulfonic acids. Aromatic sulfonic acids have very good tanning properties(Xianglong et al., 2019).These are prone to thermal decomposition ie. desulfonation at elevated temperatures, however alkane derived sulfonic acids shows excellent thermal stability while arene based sulfonic acids are generally thermally unstable(Considine D M, 2007).

A sulfone is a O=S=O group connected to two R groups. Poly(sulfone) has the characterstics properties such as chemical inertness, excellent strength, stiffness, high resistance to radiation & temperature, dimension stability and biocompatibility with collagen(Subramaniam & Sethuraman, 2014). It is also reported in the literature(Masri & Friedman, 1988) that alkyl vinyl sulfones have a strong chemical affinity for protein functional groups.

Literature (tyagi et al., 2020), reported that phenol sulfonic acid syntan treated chrome tanned buff leather showed slight thermal resistance in the temperature range ~350 ºC to 450 ºC which was attributed to the resistance provided by cyclic sulfones that got formed during the thermal degradation of sulfonic acids. Based on that, we have prepared three sample from the chrome tanned buff wet blue, one is treated with phenolic sulfonic syntan and other 2 were treated with condensation product of sulfones and aromatic sulfonic acids and comparative study of their thermal behaviour was executed to find out whether the already present sulfones in the syntan have some effect on the thermal stability of treated leather.

2. Experimental

2.1 Materials

Sample butt portion of buff wet blues of Indian origin (weight = 800-1100 g) and all the auxiliaries [e.g. fatliquors, syntans (phenolic sulfonic acid based, sulfones & aromatic sulfonic acids based and others), wetting agent, dye, preservative etc.] required for leather processing were provided by Smit & Zoon company, one syntan based on Condensation product based on sulphone and aromatic sulfonic acids was provided by BASF India Ltd and the other was provided by BASF Indian Ltd.

2.2 Preparation of samples

Following the researcher(Tyagi et al., 2014, 2018), all the Samples (BSS_6, BSS^1S_6 and BSS^2S_6) were prepared adopting the generalized unit operations for leather manufacturing from wet blue to crust, based on the recipes shown in Table 1.

The phenol sulfonic acid syntan we have used (6%) in our sample BSS_6, is a white powder of phenol sulfonic acid condensate with active matter more than 93 % and pH ~ 6.0–7.0 (10% solution). While BSS^1S_6 contains syntan (6%) based on condensation of sulphone & aromatic sulfonic acids with active matter than 93 % and pH ~ 3.0–3.5 (10% solution). On the other hand sample BSS^2S_6 was treated with a synatn (6%) that is a condensation product based on sulphone and aromatic sulfonic acids from BASF Indian Ltd. Sulphirol HF 377 is a fatliquor used to give good softness to leather. It is a sulphited marine oil with active matter approx 65 %. Synthol GS 606, is a natural and synthetic phosphated fatty polymer with active content approx 38% and pH ~ 6.5–7.6 (10% solution).

All the other auxiliaries (except test syntans) were common for all the samples in different unit operations. After sammying, setting and drying operations, crust leather of all three samples were prepared.

2.3 Characterization

Thermogravimetric analyses (TGA)

The thermal stability of the samples were studied through thermogravimetric analyzer (model: Pyris 6 TGA manufactured by Perkin-Elmer instruments, the Netherlands)(Cárdenas et al., 2000; Santhosh et al., 2006). The samples of about 5–10 mg were heated from ambient temperature to 800 °C in the nitrogen atmosphere maintaining a constant heating rate of 20 °C.min^{-1}. The data of the weight loss versus temperature were recorded in the software.

3. Results and discussion

For the analysis of thermal behavior of materials, TGA technique may be used, whereby weight of a substance is recorded as function of time or temperature, in an environment which is heated in a predetermined manner. The TGA results of the samples are depicted in Figure 1 (a), (b), (c), (d) and Figure 2 (a), (b), (c).

It was observed that within 150-250 °C, the degradation profiles of all the three samples were almost similar in nature. The gentle and flat nature of the TGA curve within 150-250 °C indicates considerable thermal resistance of the samples. Within the temperature range ~250-350 °C, all the three samples started degrading steeply. Table 2 (a), Table 2 (b) and Figure 2 (c), clearly shows the fact that as the temperature was increased from ~250 °C to 350 °C, the undegraded polymer proportion was drastically dropped from ~83 % to a mere ~55 %. It was also observed that all the three samples showed slight thermal resistance from ~350 - 400 °C. Further It was observed that as compared to other two sample, the sample BSS_6 started deteriorating at a faster rate from ~280 - 380 °C, and a much faster rate from ~380 - 480 °C and curve flattened at around ~ 480 °C as shown in Figure 1(d). The enhanced thermal stability of BSS^1S_6 and BSS^2S_6 as compared to the BSS_6 is quite evident from the greater quantity of undegraded polymer proportion at ~ 480 °C which is ~19 % for BSS^1S_6 and BSS^2S_6 in comparison to a mere ~8 % for BSS_6 [Table 2(b)] and also curve flattening for BSS^1S_6 and BSS^2S_6 at around ~ 550 °C in comparison to BSS_6 which flattened at around ~ 480 °C .

The above behavior may be correlated with available literature(Granados-Focil, 2006) as the degradation of sulfonic acids starts above 240 °C with an evolution of water and SO_2 as a function of temperature and this evolution of SO_2 is coupled with water at high temperatures. The literature(Patai, S., Rappoport, 1991) reported that desulfonation can occur as a multi-step process where the first step is migration of the aromatic carbon from the sulfur to the oxygen, followed by evolution of SO2 and generation of Ar-OH. This hydroxyl substituted ring could react rapidly with the adjacent sulfonic acid to form a cyclic sulfone and water. The sulfones offers high resistance to thermal degradation and their decomposition temperature range from 300 ^{0}C to 710 ^{0}C, where cyclic sulfones are thermally more stable(Lecouvet et al., 2013; Li et al., 2003; Subramaniam & Sethuraman, 2014; Takenaka et al., 2018; Weh & De Klerk, 2017). The literature(Crossland et al., 1986; L. H. Perng, 2000; Li Hsiang Perng, 2001) reported the formation of SO_2 and phenol, from the scission of sulfones, at a temperature around 450 ^{0}C or earlier. The experimental findings of slight thermal resistance of all the three sample in the temperature range ~350 °C to 450 °C may be attributed to the formation of cyclic sulfones and flattening of curve after 480 °C is related to the further degradation of the produced cyclic sulfones as reported in literature(Crossland et al., 1986; L. H. Perng, 2000; Li Hsiang Perng, 2001). The experimental findings of enhanced thermal stability of samples BSS^1S_6 and BSS^2S_6 in the range of ~280 °C to 550 °C may be attributed to the presence of already existing sulfones in the syntans along with sulfonic acids in comparison to BSS_6 which only contains sulfonic acid based syantan.

Moreover, the temperatures corresponding to DTG (differential thermogram) is shown in Figure 2 (a), (b), (c) and DTG peaks have been reported in Table 2(b), which is almost similar in all the three samples that reflect almost no change in crosslink formation(Charulatha & Rajaram, 2003) also the residue formation at ~800 ºC reconfirms it.

4. Conclusions

On the basis of above experimental findings, it is safe to conclude that at least at concentrations 6 %, sulfones containing sulfonic acids based syntans provide higher thermal stability to Cr tanned buff leather in comparison to syntans those contains only sulfonic acids, which is well reflected in the TGA finding.

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Table 1: Recipes of Buff softy samples

Unit Operation	Ingredients	Samples* (ingredients in %)			Time (min)	Remarks
		BSS_6	**BSS^1S_6**	**BSS^2S_6**		
Soak back	SYNTHOL EM 336	0.5	0.5	0.5	45	
	Formic Acid	0.5	0.5	0.5		
	Water	100	100	100		
Drain/Wash					10	
Rechroming	Water	100	100	100	60	

	BCS	5	5	5		
	SULPHIROL HF 377	4	4	4		
	Sodium formate	1	1	1	30	
Bacification	Sodium bi carbonate	1	1	1	60	
Drain/Wash					10	
Neutralization	Water	100	100	100	30	
	SYNTAN NS 321	2	2	2		
	Sodium formate	1	1	1		
	Sodium bi carbonate	2.5	2.5	2.5	90	
Drain/Wash					10	Check pH = 6.4
Dyeing, Retanning & Fatliquoring	Water	100	100	100	30	
	SYNTHOL GS 606	6	6	6		
	SYNTAN SF 156 (**Test Syntan**)	6	-	-	60	
	SYNTAN DM 262 (**Test Syntan**)	-	6	-		
	Basyntan UR (**Test Syntan**)	-	-	6		
	Dye	2	2	2		
	SYNTHOL GS 606	6	6	6	45	
Fixing	Formic acid	3	3	3	45 (3 × 15)	1:10 dilution

*Sample designation: BS = Buff softy, S = Phenolic sulfonic acid based syntan, SS = Sulphones and sulfonic acid based syntan (numerical suffixes indicate the % of the respective ingredients added in the sample, superscript 1 and 2 indicates, 2 different syntans as given in recipe)

Table 2 (a): Thermal degradation characteristics of the samples

Sample	Temperature, °C			
	95%	**75%**	**50%**	**25%**
BSS_6	82.66	306.66	359.00	430.50
BSS^1S_6	83.00	312.66	372.00	462.00
BSS^2S_6	83.33	315.50	373.50	461.66

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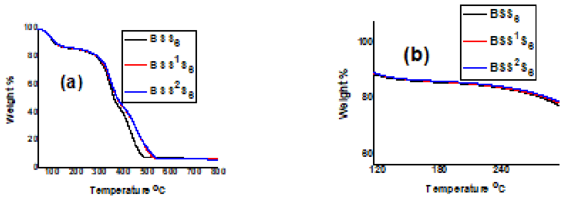
Table 2 (b): Percentage of sample remained at different temperatures

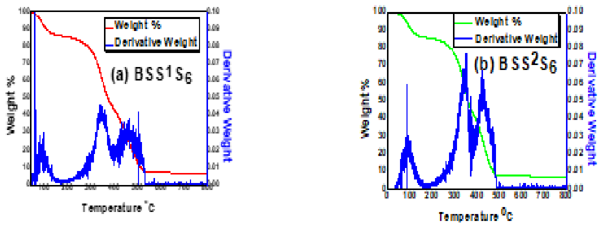
Sample name	Percentage of sample remained at different temperatures											DTG peak (ºC)
	100ºC	150ºC	250ºC	300ºC	320ºC	350ºC	***400ºC***	***450ºC***	***480ºC***	600ºC	700ºC	800ºC	
BSS_6	91.32	86.34	83.05	76.59	70.64	54.93	***38.33***	***16.89***	***8.62***	7.60	7.13	6.95	351.33
BSS^1S_6	91.56	86.70	83.29	77.73	72.91	59.30	***43.14***	***29.35***	***18.88***	7.04	6.80	6.81	347.33
BSS^2S_6	91.67	86.78	83.68	78.25	73.73	59.94	***43.66***	***29.29***	***19.44***	6.66	6.37	6.28	351.00

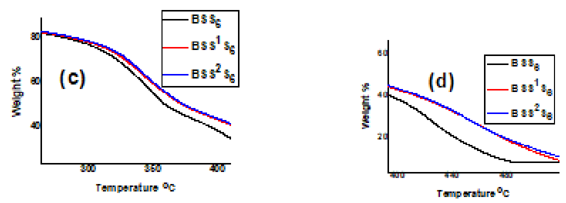
Figure legends

Figure 1: TGA plots of the samples BSS_6, BSS^1S_6 and BSS^2S_6, depicting (a) complete temperature range (40 to 800 ºC), (b) Thermal resistance from 150 ºC to ~ 250 ºC, (c) drastic weight change from ~ 250 ºC to ~ 350 ºC, (d) further drastic weight loss of BSS_6 after ~ 425 ºC.

Figure 2: TGA plots of the samples BSS_6, BSS^1S_6 and BSS^2S_6, depicting (a) BSS^1S_6 with differential thermogram, (b) BSS^2S_6 with differential thermogram, (c) BSS_6 with differential thermogram.







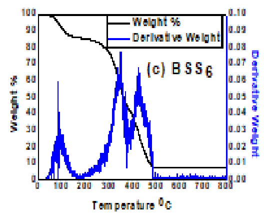


Figure 1: TGA plots of the samples BSS6, BSS1S6 and BSS2S6, depicting (a) complete temperature range (40 to 800 oC), (b) Thermal resistance from 150 oC to ~ 250 oC, (c) drastic weight change from ~250 oC to ~ 350 oC, (d) further drastic weight loss of BSS6 after ~ 425 oC.

Figure 2: TGA plots of the samples BSS6, BSS1S6 and BSS2S6, depicting (a) BSS1S6 with differential thermogram, (b) BSS2S6 with differential thermogram, (c) BSS6 with differential thermogram