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A Combined Effect of Melamine-Formaldehyde Resin and Regenerative Fat on Mechanical Properties of Skin

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ABSTRACT:
Two different samples of cow softy leather (i.e. CSM_0RF_8 and CSM_3RF_8) were prepared from a chrome tanned cow wet blue of Indian origin. Sample CSM_3RF_8 contains 3% Basyntan FB-6 (a melamine-formaldehyde based resin) and 8 % Lipoderm Eco AS (a fatliquor based on regenerative raw materials) wherein CSM_0RF_8 is devoid of any melamine-formaldehyde resin but had 8 % Lipoderm Eco AS, in addition to the other common auxiliaries used in both the samples. Other unit operations (physical and chemical) for manufacturing leather were maintained same in both the samples. Mechanical behavior of these samples was studied, and tried to be correlated with the crosslinking densities of the samples.

KEY WORDS: collagen, skin, crosslink density, modulus,

1. INTRODUCTION

Retanning agents influences the leather structure and properties (Virginija et al., 2012). Melamine formaldehyde condensates (Grim, 1942; Melinda et al., 2011) are well established as synthetic tanning agents in the field of leather manufacture. Basically, Melamine is a nitrogen-rich heterocyclic triazine used primarily in the synthesis of melamine–formaldehyde resins (MFR) for the manufacture of laminates, plastics, coatings, commercial filters, glues or adhesives, and moulding compounds (Tolleson et al., 2008). Melamine based syntan try to crosslinks with collagen to give it more mechanical stability (Tyagi et al., 2014).

Fatliquoring is an oil-addition process and is one of the key steps in leather manufacturing. Its function is to lubricate the leather's fibrous structure, and consequently it provides softness to the leather (Liu et al.,2002, Leticia et al., 2007). Fatliquoring prevent the leather fibres from sticking together, thereby providing sufficient pliability to the leather (Cheng-Kung et al., 2002, Janarthanan, 2013). The fatliquor becomes a part of the composition of leather (Janarthanan, 2013). Type of fatliquor applied in a fatliquoring process can affect the Mechanical properties of skin immensely (Liu et al.,2002).

The mechanical behavior of materials is also dependent upon a large no of structural and molecular factors (Nielsen et al., 1994). Among the mechanical tests, stress-strain tests are traditionally the most popular and are most widely used as these tests indicate the modulus, strength and toughness of the material. As per the prediction of kinetic theory, the modulus of the material increases as the degree of crosslinking increases (Treloar 1956; Flory, 1953). In this regard, the breaking stress should also be directly proportional to crosslink density.

In this work, a comparative assessment has been made based on the mechanical behavior of the skin treated with a melamine-formaldehyde resin and a regenerative fat.

2. EXPERIMENTAL

2.1 MATERIALS

Sample butt portion of cow wet blues of Indian origin (weight = 800-1100 g) and all the chemicals and auxiliaries [e.g. syntans like Basyntan FB-6, fatliquors like Lipoderm Eco AS and others wetting agent, dye, preservative etc.] required for leather processing were provided by BASF India Ltd.

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2.2 PREPARATION OF SAMPLES

Samples (CSM_0RF_8 and CSM_3RF_8) were prepared following the generalized unit operations for leather manufacturing from wet blue to crust following the researchers (Tyagi et al., 2014; Mondal et al., 2016) based on the recipes shown in Table 1.

Table 1: Receipes of cow softy samples

Unit Operation	Ingredients	Samples* (ingredients in %)		Time (min)	Remarks
		CSM_0RF_8	**CSM_3RF_8**		
Soak back	Eusapon(w)	0.2	0.2	30	1:3 dilution
	Water	200	200		
Drain/Wash				10	
Rechroming	Water	100	100	30	
	Formic acid	0.5	0.5		1:10 dilution
	BCS	4	4	60	
	Basyntan AN	2	2		
	Sodium formate	0.5	0.5	60	
Bacification	Sodium bi carbonate	0.5	0.5		
Drain/Wash				10	
Neutralization	Water	150	150	10	
	Sodium formate	2	2		
Drain/Wash				10	Check pH = 4.8
Dyeing & Retanning	Water	100	100	60	
	Luganil Brown FB3GN	1	1		
	Basyntan FO	6	6		
	Basyntan FB-6	**-**	**3**		
Fatliquoring	**Lipoderm Eco AS**	**8**	**8**	45	1:3 dilution
	Preservative	0.2	0.2		
Fixing	Water	100	100	50	
	Formic acid	1	1	(3 × 10 + 20)	1:10 dilution

*Sample designation: CS = Cow softy, M = Melamine-formaldehyde based, Basyntan FB-6 syntan, RF= Regenerated fatliquor Lipoderm Eco AS (numerical suffixes indicate the % of the respective ingredients added in the sample).

The following unit operations were followed in series one after the another (Thanikaivelan *et al.*, 2002, Tyagi et al., 2014): (a) soak back (for rehydration of wet blue), (b) rechroming (for increasing chrome content), (c) basicification (for fixation of added chromium compound), (d) neutralization (for removing free acids and acquiring desired pH level for subsequent operations), (e) dyeing (for imparting color), (f) retanning (for reinforcing and filling), (g) fatliquoring (for desired lubrication of polypeptide chains) and (h) fixing (for improving bondage of the added ingredients with the collagen substrate) as the last wet end operation.

CSM_3RF_8 contains 3% Basyntan FB-6 (a melamine-formaldehyde based resin) and 8 % Lipoderm Eco AS (a fatliquor based on regenerative raw materials) wherein CSM_0RF_8 is devoid of any melamine-formaldehyde resin but had 8 % Lipoderm Eco AS, in addition to the other auxiliaries used in both the samples in different unit operations. After sammying (for removal of physically adhered water from the substrate), setting (for leveling the grain side of the substrate) and drying (for reducing water content of the substrate to ~ 10 %) operations, crust leather of both the samples were prepared.

2.2 CHARACTERIZATION

MECHANICAL PROPERTIES

The mechanical behavior of the samples was investigated by the tensile test. Initially, both the samples were conditioned at 25 ^oC and 65 ± 2% R.H for 48 h. The usual dog-bone shaped specimens for the measurement of the mechanical properties were punched out from the crusts with ASTM Die-C. The measurement as per ASTM D-2209 standard was carried out in a Hioks-Hounsfield UTM-H10 KS (Test Equipment, Surrey, England) maintaining a crosshead speed of 100 $mm.min^{-1}$ on 100 kg load at 25 ^oC. For each sample, the averages of five tests were reported. The force-elongation curve was plotted with Lab Tensile software, from which the tensile strength and elongation percentage were calculated. In each case, the error corresponding to tensile modulus, tensile strength, elongation at break (EB) measurement was limited to ± 1 %, ± 2 %, ± 2 %, respectively.

3. RESULTS AND DISCUSSION

The stress-strain results obtained for both the samples are reported in Table 2.

Table 2: Tensile properties of samples (at 25 ^oC)

Samples	Stress at different strain levels (MPa)			Tensile strength (MPa)	Elongation at break (%)
	10 %	20 %	30 %		
CSM_0RF_8	1.25	3.09	5.20	26.68	88.6
CSM_3RF_8	1.73	3.91	6.27	31.73	74.2

The significant higher level of stress at 10%, 20% and 30% stain for sample CSM_3RF_8 in comparison of CSM_0RF_8 indicates the formation of more crosslinks in CSM_3RF_8 than CSM_0RF_8.

The higher crosslinks formation in CSM_3RF_8 may be because of the reason that added Basyntan FB-6 (a melamine-formaldehyde based syntan) can have the capacity to get attached with the polypeptide chains of the collagen in the following manners:

- The added melamine based syntan bears basic amino groups ($-NH_2$) which can form chelated rings involving the Cr^{3+} as the central metal ion [Figure 1 (a), (b)].
- H-bonding between terminal methylol groups of melamine-formaldehyde macromolecules and suitable sites of polypeptide chains (e.g. > C=O group of amide linkage) [Melinda et al., 2011] (Figure 1).
- London- Van-der-Waals forces involving π orbitals of the both heterocyclic part of melamine-formaldehyde macromolecule and of amide linkages of collagen polypeptide chains (Xiu-Lian et al., 2005).

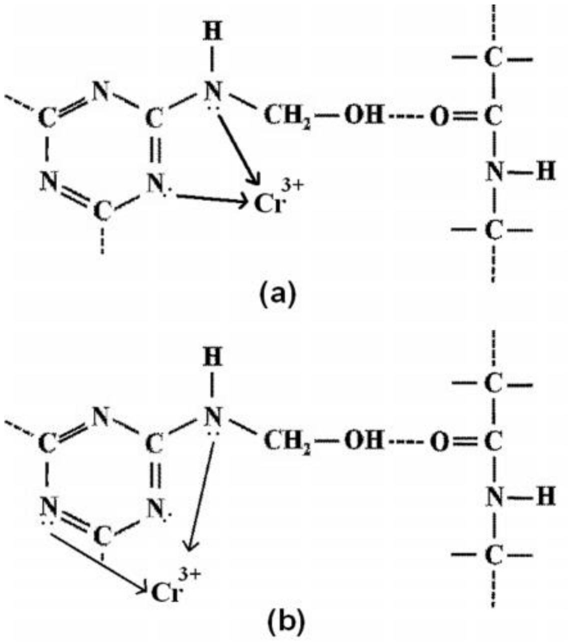

Figure 1: The possible interaction of melamine with collagen chains through H-bonding and chelation rings involving Cr^{3+} of chrome complex having (a) 4 membered ring (unstable), (b) 6 membered ring (stable).

Thus, the added melamine-formaldehyde macromolecules in CSM_3RF_8 may interact strongly with polypeptide chains and resulted in higher modulus and high value of tensile strength in comparison to CSM_0RF_8 which is devoid of such syntan (Figure 2). The %EB is quite less for CSM_3RF_8 in comparison of CSM_0RF_8. It is also a well established fact that % EB decreases with increase in cross-linking density which is depicted in Figure 2. Further it is resulted that % EB value is quiet high for both the samples of skin this may be because of the fact that Lipoderm Eco AS, the fat emulsion we have used in both the samples, have a very high affinity for leather fibres and it is reported in the literature (Janarthanan, 2013) that small, stable emulsion droplets give even and deep penetration of oil into the collagen fibre and in the case of the dispersion and uniformity of oil, the smaller the emulsion droplets are, the better are the effects.

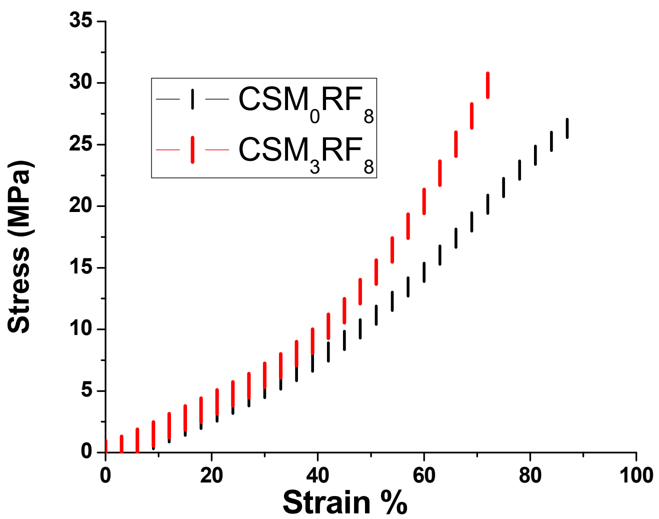

Figure 2: Plot of Mechanical Properties of the samples CSM_0RF_8 and CSM_3RF_8

4. CONCLUSIONS

On the basis of above observations, the resultant conclusions can be drawn that at least in lower concentration Basyntan FB-6 syntan (melamine-formaldehyde condensate) can form extra crosslinks with chrome tanned skin, which is reflected through high values of modulus and tensile strength and despite the higher crosslinks formation, Lipoderm Eco AS (a regenerative fat) can maintain the high % EB due to its high affinity to collagen and smaller particle size.

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