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Influence of the micro-structural factors upon thermal and mechanical properties of various bag leathers

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Abstract

Four different bag leathers, such as, Sheep Bag Leather (SBL), Buffalo Vegetable Tanned Leather (BVTL), Cow Drum Dyed Dry Milled Leather (CDDDML), and Cow Crocodile Print Leather (CCPL), were processed by different methods from respective wet-blues of Indian origin. Thermal degradation profile and mechanical properties of the samples were evaluated, and crosslink densities of each sample were measured by fitment of Mooney-Rivlin equation on stress-strain plots. Morphological characteristics (e.g. fibre structure, fibre thickness, splitting etc.) of all the specimens were investigated by image analyses of SEM photomicrographs. The highest crosslinking density for BVTL was attributed to its higher fibre and fibril thicknesses coupled with rigorous retanning by vegetable tannins and syntans. Embossing at higher temperature and pressure reduced CCPL's elongation-at-break value and hence stretchiness possibly due to the development of set properties within the CCPL matrix. SBL was noted to contain huge void spaces that increased its stretchiness, and melamine formaldehyde syntans showed pronounced influence in increasing the thermal resistance of both CCPL and CDDDML.

Keywords : Crosslink density; SEM; TGA; Fibre thickness

Introduction

Leather processing from animal hides and skins is basically the modification of fibrous protein, which requires a series of unit operations and processes. Different types of ingredients (i.e. natural/ mineral/ synthetic tanning/ retanning agents, fatliquoring agents, binders etc.) are incorporated during different stages of leather processing to achieve certain characteristics of leather. Mechanical behavior of any tanned leather, a key attribute from the end user point of view, depends on the leather structure, layer type (i.e. grain or corium), topographical zone, nature and size of defects, sort and age of cattle, tanning and finishing process, etc. (Milašiené and Bubnyté, 2007; O'leary and Attenburrow, 1996). In fact, mechanical properties of leather are dependent upon a large number of structural and molecular factors (e.g. molecular weight, cross-linking and branching of collagen fibre, crystal morphology, fillers, molecular orientation, phase separation, plasticity etc.). The collagen fibril diameter and tear strength were noted to be correlated in bovine leather, with stronger leather having thicker fibrils (Wells *et al*., 2013). In addition, numerous environmental or external factors, like temperature, pressure, type of deformation, moisture content, stress and strain amplitude and rate, thermal history etc., can influence mechanical properties (Nielsen and Landel, 1994; Arumugam *et al*., 1992; Bajza and Vrcek, 2001). In fact, mechanical behavior of a material is adjudged by the response of the material against the applied external forces (Hosford, 2005). Among the mechanical properties, stress-strain behavior can demonstrate the modulus, strength and toughness of the material. In this regard, tensile strength is an important physical criterion that is closely related to the durability of a leather article. Moreover, resistance against thermal degradation is directly linked with the durability and stability of a material. Both modulus and heat resistance of collagenous materials are directly proportional to the degree of cross linking (Charulatha and Rajaram, 2003). Indeed, the thermal degradation of a densely crosslinked sample should be slower, and should take place at higher temperature in comparison to samples having fewer cross-links.

Many researchers already established effects of poly-acrylates/ polyacrylic acids in improving thermo-mechanical behavior of chrome tanned leather (Nashy *et al*., 2010; Christner *et al*., 1990). Beneficial effects of titanium, melamine-formaldehyde resin, resorcinol tanning agent on chrome free leather have been reported (Zengin *et al*., 2012). In the past, various workers reported thermal denaturation characteristics of collagen and modified collagen (Zhang *et al*., 2006). Researchers concentrated on understanding the effects of pretanning processes on collagen structure and reactivity (Brown *et al*., 2013). Moreover, effects of retanning agents on dry heat resistance of leathers were studied extensively by Wu *et. al*., and they reported that

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*Corresponding author e-mail: pkantichattopadhyay@gmail.com the retanning agent possessing lower hydrophilic character provided the higher dry heat resistance in leather (Wu *et al*., 2013). Recently, visco-elastic behavior of leather was pursued by several workers (Langroudia *et al.,* 2012; Liu *et al*., 2007). Few workers reported the effect of biaxial stretching upon the fibre orientation and associated tensile modulus, and they noted that the fibre reorientation factor is a major cause behind change in the tensile modulus (Sturrock *et al*., 2004). Such biaxial stretching altered area retention of dried leather in addition to the alteration of mechanical properties (Liu *et al*., 2010). Most recently, significant findings were derived based on morphological studies of both fibre and fibre bundles of leather in two different modes (e.g. light transmission mode and light reflective mode) by metallographic sample preparation (Zhang *et al*., 2014). Therefore, dependencies of thermal and mechanical properties on the micro-structural attributes are important factors from the perspective of leather article end users.

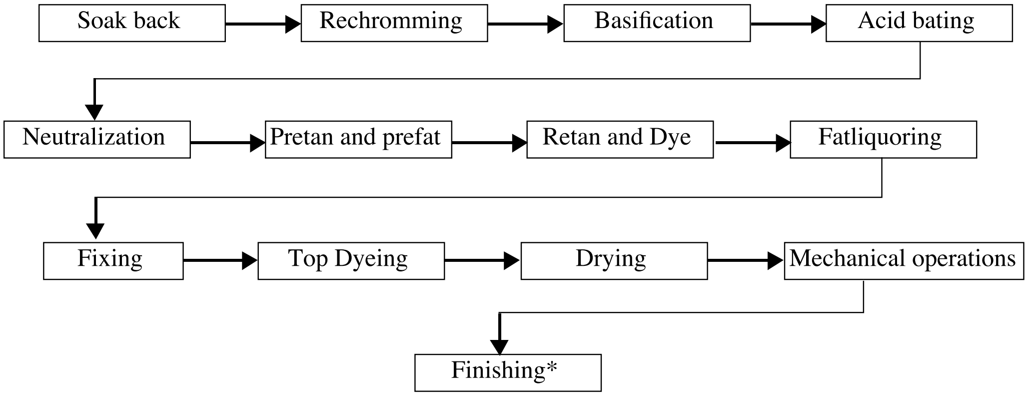
In the present work, mechanical and thermal characteristics of four different bag leathers, prepared from different wet-blues of Indian origin based on different standard recipes, have been attempted to be correlate with the morphological attributes, such as, structure, thicknesses of both fibre and fibre bundle and the role of the different structural and cross-linking components present inside the leather matrices.

Materials and methods

Different wet blues [i.e. cow wet blue (area = 13 sq. ft., thickness = 1.1-1.2 mm, weight = 1400 g), buffalo wet blue (area = 12 sq. ft., thickness = 1.2-1.3 mm, weight = 1500 g), and sheep wet blue (area = 5 sq. ft., thickness = 0.8-0.9 mm, weight = 400 g)], required for leather processing, were supplied by M/S Sheong Shi Tannery, Kolkata. All the auxiliaries (e.g. fatliquors, syntans, wetting agent, dye, preservative etc.) utilized during leather processing were provided by Viswaat Chemicals Ltd. and Schill & Seilacher GmbH & Co. (Table I). Other common chemicals were purchased from local suppliers.

Preparation of samples

Different leather samples [i.e. Sheep Bag Leather (SBL), Buffalo Vegetable Tanned Leather (BVTL), Cow Drum Died Dry Milled Leather (CDDDML), and Cow Crocodile Print Leather (CCPL)] were manufactured following the generalized unit operations for leather manufacturing from wet blue to crust (Fig. 1), based on the standard recipes (Table II). Following are the basic purposes for different unit operations: (a) soak back (to rehydrate the wet blue), (b) rechroming (to increase chromium content), (c) basification (to fix the added chromium compound), (d) acid bating (to open up the fibre bundles) (e) neutralization (to remove free acids and to reach desired pH level for subsequent operations), (f) dyeing (to impart color), (g) re-tanning (to reinforce and fill the substrate), (h) fatliquoring (to impart lubricating effect within fibrous networks) (i) fixing (to improve adhesive forces among the dye molecules and the collagen substrate), (j) top dyeing (to get desired color), (k) mechanical operations (to get required physical properties and appearance), (l) finishing (conducted only in case of CCPL to provide the desired embossing effect). In this regard, rechroming and acid bating operations were omitted in case of CCPL. In addition, CCPL was treated by dye solution, binder and silicone emulsion followed by embossing with crocodile print at 150°C and 250 atmospheric pressure.



* Operation conducted only for CCPL

Fig. 1. Schematic representation of generalized crusting process for various samples

Table I. List of leather auxiliaries showing manufacturers and technical characteristics

Sl. No.	Name of the auxiliary	Technical characteristics	Manufacturer
1	Vicalan NT953	Fatty alcohol polyglycol ether	VCL[1]
2	Vinsul VM70	Sulphited fish oil	VCL
3	Vicatan CRS	Technically pure chromium combined with aromatic sulfonic acid condensates	VCL
4	Vicatan VKM	Naphthalene sulfonic acid condensate	VCL
5	Vicatan HUM	Aqueous dispersion of an acrylic copolymer	VCL
6	Vegrassol CS14	Aliphatic hydrocarbons and alcohols sulfonated by special methods	VCL
7	Vicatan VOS	Phenol condensation products	VCL
8	Vicatan FV6	Based on melamine resin	VCL
9	Vicatan FS3	Based on Dicynadiamide.	VCL
10	Wattle GSP200	Mimosa GS powder(double bleach)	
11	Quebracho	Quebracho extract	
12	Chestnut Veg CN 200	Chestnut extract	
13	Vicatan DL	Aromatic sulfonic acid condensation product	VCL
14	Vicastol SP	Based on functional substitute of sperm oil and hydrocarbon emulsified	VCL
15	Vicastol 94V	Aliphatic hydrocarbons and alcohols sulfonated by special methods	VCL
16	Vicatan NP	Base on synthetic neatsfoot oil combined with special softener	VCL
17	Veprovol VA	Combination of natural phospholipids with synthetic softener	VCL
18	Vicastol SL	Blend of specially treated lanolin with saturated hydrocarbon	VCL
19	Perfectol HQ	Aqueous emulsion of high molecular weight paraffines in combination with highly effective waterproofing additives	Schill&Scillecher
20	TolcideC-30	Based on ThiocyanomethylthioBenzothiazole (TC MTB)	
21	Nitotan Red RSNI	C.I. Acid Red 114 (azo dye)	Nitin Dye Chem Pvt. Ltd.
22	Vicosin 2255	Aqueous polyacrylate dispersion	VCL
23	Texzyme HS	Anti wrinkle and high softening enzyme based on protease	Tex-Biosciences Pvt. Ltd.
24	Suprinil HK Dark Brown 01 liquid	Highly concentrated solutions of metal complex dye in water and water miscible solvent	BASF India Ltd.

[1] Viswaat Chemicals Limited

Characterization

Scanning Electron Microscopy (SEM)

The morphological structures of gold coated fractured surfaces for each leather samples were observed under SEM (ZEISS EVO-MA 10) at 20KX magnification. Thereafter, thicknesses of collagen fibres and fibrils were measured by analyzing photomicrographs by image analyses software, Image J, NIH, USA.

Mechanical properties

The mechanical behavior was investigated by the tensile test. Initially, all the samples were conditioned at 25°C 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 500 mm.min^{-1} at

25°C. For each sample, the averages of four test specimens were reported. The force-elongation curve was plotted with Lab Tensile software, from which the tensile strength (TS) and elongation-at-break (EB) were calculated. In each case, the error corresponding to tensile modulus, TS, EB measurement was limited to ± 1 %, ± 2 %, and ± 2 %, respectively

Crosslink density of samples were measured based on the Mooney-Rivlin equation (equation 1) which is suitable to measure the degree of crosslinking via fitment of the data obtained from stress-strain results (Tyagi *et al.,* 2014).

$$\frac{\sigma_{av}}{2(\lambda-\lambda^{-2}} = C_1 + \frac{C_2}{\lambda} \quad ....(1)$$

Here, C_1 and C_2 are constants. The values of C_1 and C_2 were determined by fitting the plot of $\frac{\sigma_{av}}{2(\lambda-\lambda^{-2}}$ against $\frac{1}{\lambda}$ to the Mooney-Rivlin equation. The value of C_1 was used to determine crosslink density by equation 2:

$$N_C = \frac{2C_1}{RT} \quad ....(2)$$

Here, N_C is the crosslink density, R is the gas constant (8.314 J.deg^{-1}.mol^{-1}) and T is the absolute temperature.

Thermo Gravimetric analyses (TGA)

The thermal stabilities of samples were studied by thermogravimetric analyzer (model: Pyris 6 TGA manufactured by Perkin-Elmer instruments, the Netherlands). About 5–10 mg of samples were heated from ambient temperature to 600°C in the nitrogen atmosphere at the heating rate of 20°C.min^{-1}, and the weight loss vs. temperature plot along with the derivative thermograms (DTG) were recorded in the software. The error in measurement was limited to ± 2 %.

Results and discussion

SEM

Among the SEM photomicrographs, prominent and thick fibre bundles can be observed in case of BVTL (Fig. 2a), which can be reflected in the measured thickness of the fibre

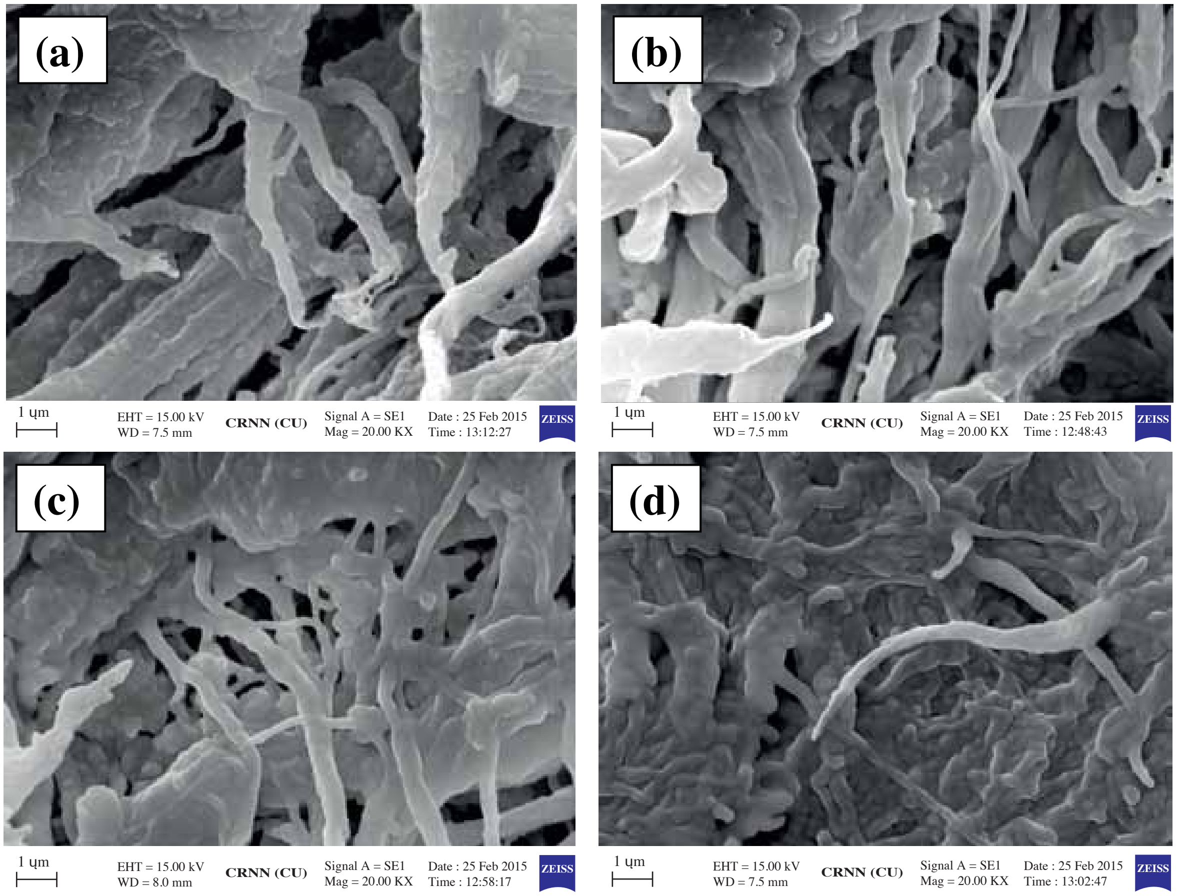


Fig. 2. SEM photomicrographs of (a) BVTL, (b) SBL, (c) CDDDML and (d) CCPL at 20 KX magnification

Table II. Comparative recipes of different bag leathers

Unit Operations	Ingredients	% of ingredients (w/w) SBL	BVTL	CDDDML	CCPL*	Time (min)	Remarks
Soak back	Water	150	150	150	150		
	Vicalan NT953	0.25	0.25	0.25	0.25		
	Oxalic acid	0.5	0.5	0.5	3	60	
Rechroming	Water	100	100	100			
	Formic acid	0.75	0.75	0.75		10+20	1:10 Dilution
	Basic chromium sulfate	4	4	4			
	Vicatan CRS	2	2	2			
	Vinsul VM90	1	1	1		60	
Basification	Sodium formate	0.5	0.5	0.5			
	Sodium bicarbonate	0.5	0.5	0.5		60	1:16 Dilution
Acid bating	Vicazyme FL	0.5	0.5	0.5		120	L/O/N (except CCPL)
Neutralization	Water	100	100	100	100		
	Sodium formate	1	1	1	1		Neutralization pH = 5.4-5.5
	Vicatan VKM	1	2	1	2		
	Ammonium bi carbonate	1.25	0.25	1.5			
Pretannning	Water	60	60	60	60		
	Vicatan HUM	2	4	3	3	30	1:3 Dilution
	Vicastol CS14	1	1	2			
	Veprovol VA	1	1	1		20	
Retanning & dyeing	Vicatan VOS	2		2			
	Vicatan FV6			4	4		
	Vicatan FS3	2	2				
	Wattle	2	5		8		
	Quebracho	2	4	4	8		
	Chestnut		4		8		
	Dye	3	3	3	3		
	Vicatan DL	1	1	1	1		
	Vinsul VM70				2	120	L/O/N (for CCPL)
Fatliquoring	Water	100	100	100	100		
	Perfectol HQ			7			
	Veprovol VA	2	2	3	2		
	Vicastol NP	2	2		2		
	Vicastol SL			3			
	Vicastol 94V	2	2	2	2		
	Vicastol SP	2	2	2	2		
	Vicalan NT953	0.2	0.2	0.2	0.2		
	Preservative	0.2	0.2	0.2	0.2	90	1:5 Dilution
Fixing	Formic acid	2	2	2	2	3*10+30	1:10 Dilution
Top dyeing							
	Water			150			
	Dye			1		20	
	Formic acid			1.5		3*10+20	

*CCPL has sprayed twice cross with a mixture of 100 parts Dye solution, 150 parts Vicosin 2255 and 750 parts Water followed by a cross spray with 10 parts HM 12521 and 1000 parts water before print (at 150^{0}C and 250 atm. pressure).

bundles (Table III). In fact, thicknesses both fibre and fibre bundles are the highest for BVTL (Table III). On the other hand, SBL shows lots of cavities among its fibre bundles, which may be created owing to removal of natural fats and oils from the leather during degreasing operations (Fig. 2b). Presence of ruptured fibres with very few void spaces is the

Table III. Fiber and fiber bundle thicknesses of various samples

Sample	Fiber bundle Thickness (μm)		Fiber Thickness (μm)	
	Range	Average	Range	Average
SBL	40.35 - 73.82	55.29	0.66 - 2.95	1.87
BVTL	79.69 - 126.00	105.27	2.67 - 4.85	3.67
CCPL	50.77 - 121.34	85.36	2.65 - 4.56	3.42
CDDDML	62.13 - 103.83	87.58	2.15 - 4.86	3.66

characteristics of CCPL, which can be expected as embossing is associated with application of huge compressive force that can reduce the distances among fibres and fibrils (Fig. 2d). The applied embossing force may be responsible behind the flat look of CCPL wherein fibres and fibre bundles may have stuck together. In this regard, considerable splitting of fibre bundles can be observed in CDDDML which can be due to separation of fibrils from the fibre bundles owing to considerable reduction in inter-fibril cohesive forces by the action of enzymes, added lubricants and applied mechanical forces during milling operation (Fig. 2c).

Mechanical properties

Comparative stress-strain plots of the samples showing moduli are noted to be in the following order: BVTL > CCPL > CDDDML > SBL (Fig. 3). Respective inherent strengths of the raw materials can be decisive factor behind the tensile moduli as the inherent strength of buffalo hide is the highest whereas sheep skin's inherent strength is the lowest, and the inherent strength of cow hide is in between those of buffalo hide and sheep skin. Moreover, larger quantity of acrylic copolymers based crosslinking agents and vegetable tanning agents used during manufacture of BVTL can enhance its tensile modulus. In fact, in the presence of acrylic polymer, the collagen supra-molecular structures can be opened up through electrostatic forces as these acrylic polymers contain active sites for charge interactions. Such an opening up is likely to facilitate vegetable tannin molecules to diffuse into the collagen matrix and bring about improved stability to BVTL (Madhan *et al.,* 2002). Interestingly, CCPL shows comparatively higher modulus than that of CDDDML despite the absence of rechroming step during manufacture of CCPL (Table II). Higher tensile modulus for CCPL can be due to the following reasons:

a) In contrast to CDDDML, acid bating is not executed in CCPL (Table II), and hence the degradation of collagen network by bating agents or enzymes in CCPL is not possible.

b) Incorporating higher proportion of neutralizing syntan in CCPL may ensure better dispersion of vegetable tannins, syntans etc. in the matrix.

c) Applying higher percentage of fatliquoring agents (e.g. synthetic, lanoline, lecithin based oils) in CDDDML can reduce its elasticity as compared to CCPL.

d) Usage of substantially huge quantity of vegetable tanning materials, like, wattle, chestnut, quebracho in CCPL effectively reinforce the hide matrix, which is not possible in case of CDDDML.

e) The embossing or printing operation at high temperature (150°C) and pressure (250 psi) conducted on CCPL can generate set properties in the matrix which in turn may enhance rigidity and immobilization of the collagen chains against the applied tensile force.

f) Milling operation executed on CDDDML can produce softness via breaking down weaker bonds within the matrix leading to easier relative movement or flow of the collagen chains or chain segments in the direction of the applied tensile force.

EB profiles for various samples are noted to be in the following order: SBL > CDDDML > BVTL > CCPL. In general, EB of a three dimentional polymeric composite system like leather mainly depends upon the following factors:

a) orientation of fibres and fibrils along the direction of the applied force,

b) availability of void spaces inside the leather matrix,

c) presence of lubricating or plasticizing agents (e.g. oil, wax etc.), reinforcing fillers, crosslinking or tanning agents (e.g. vegetable tannins, mineral tanning agents, synthetic tanning agents etc.)

In case of SBL, the highest EB value among all the samples might be due to presence of greater extent of void spaces owing to removal of inter-fibriliar materials during the pre-tanning stage. Moreover, in the sheep skin, the presence

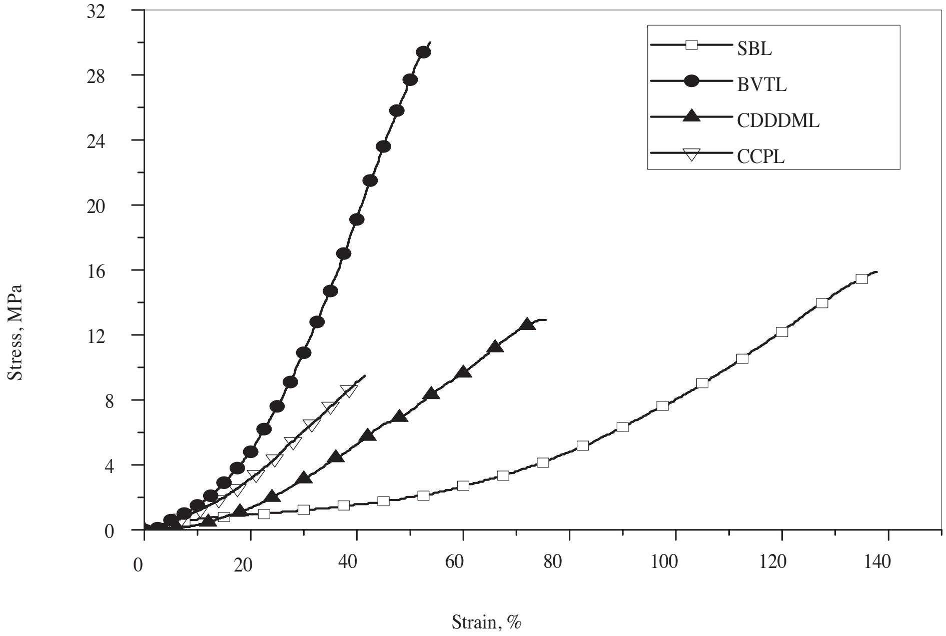


Fig. 3. Tensile properties of various samples

of strata of fat cells in the corium affects the interlayer cohesive forces between grain and corium and thus affects the mechanical properties of the SBL (Fig. 3). On the other hand, low EB values for both BVTL and CCPL can be ascribed to lack of void spaces in the matrix together with steric hindrances imposed by the bulky vegetable tannin molecules around the collagen chains (Table V). As a result, the conformational rotations of protein macromolecules may be hindered, which eventually can resist the elongation as well as orientation of macromolecular collagen chains in the direction of applied tensile force. The tensile strengths of four different types of leathers are in the following order: BVTL > SBL > CDDDML > CCPL. The lower tensile strengths for both CDDDML and CCPL may be ascribed to their reduced toughness as these materials are less capable to absorb and tolerate the applied strain energy. This may be possible because of deficiency in structural organization that can be responsible behind stress concentration which should facilitate faster crack initiation leading to ultimate rupture of the specimens. Owing to possible development of thermoset properties at higher temperature and pressure, mechanical properties have been affected in CCPL including the impairment of tensile strength. The highest tensile strength for BVTL is due to its favorable structural parameters like the lower angle of weave greater number of fibrils in a fibre, increased thickness of fibre bundle as well as fibre etc. (Table III). This is because, a thick fibre should be made of greater number of thick fibrils, and several studies show that collagen fibrils of larger diameter are normally present in the stronger tissue (Wells *et al*.,2013). Interestingly, better tensile strength has been recorded in case of SBL as compared to both the cow leather samples (i.e. CDDDML and CCPL), which may be due to easier orientation of fibrils and fibres in the direction of applied force as huge void space is available in SBL (Mondal and Chattopadhyay, 2016). In this regard, it is well known that strength of leather depends on orientation of fibres, and the comparatively stronger leather possesses the higher orientation index than that of the weaker leather (Basil-Jones *et al*., 2011; Basil-Jones *et al*., 2013).

Thermal properties

Initially, the thermal degradation of cow leathers (i.e. CDDDML and CCPL) occurs in a rapid fashion as compared to both SBL and BVTL (Fig. 4 and Table IV). In fact, upto 150°C, the highest degradation (~ 18%) has been registered for CDDDML among all the samples, which can be ascribed to the evaporation of moisture content as well as the vaporization and removal of fats and oils in a huge quantity that have been incorporated earlier during fatliquoring of CDDDML. Interestingly, within 150-350°C, thermal degradations of both CDDDML and CCPL have been arrested, which are realized from the absence of DTG peaks at ~280-285°C (Table IV), and thus both the samples demonstrated better resistance against thermal degradation in comparison to both SBL and BVTL. The possible reason can be the usage of melamine-formaldehyde resin (4%) during

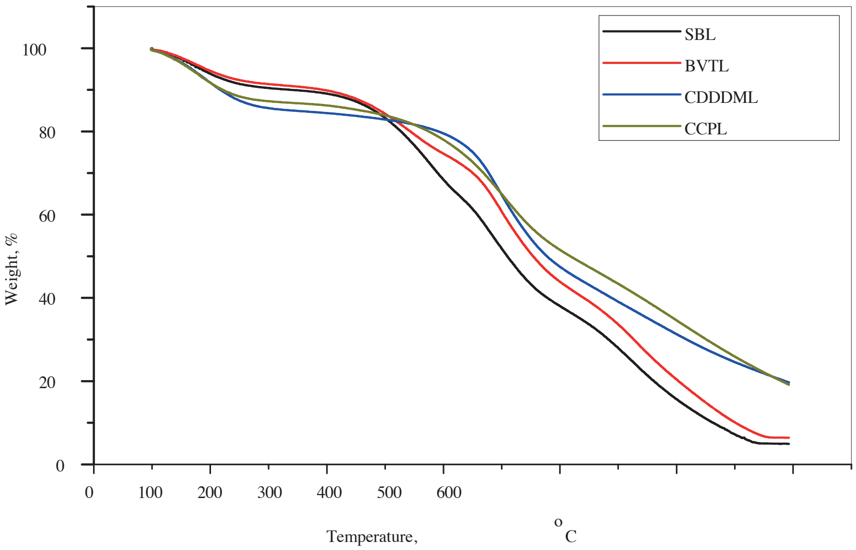


Fig. 4. Thermal properties of various samples

processing of both CDDDML and CCPL (Table II), and the melamine-formaldehyde resin decomposes within 345-347°C (Bann and Miller, 1958). In fact, the added melamine-formaldehyde resin may have delayed the decomposition process resulting in huge amount of residue formation (i.e. ~20%) upto 600°C for both the cow samples (i.e. CDDDML and CCPL), whereas residue contents for both SBL and BVTL are remarkably low (i.e. 6.4% and 5%, respectively). This can be possible via reaction between olated/ oxolated Cr^{3+} complex and amines of melamine formaldehyde. In this context, interaction between Cr^{3+} complex and ammonia, pyridine, amines were reported, wherein axial water molecule of Cr^{3+} complex was replaced by ammonia, amines etc (Heier *et al.,* 2014). In fact, this reaction was utilized to produce Cr^{3+} complexes that can act as sensors to detect the presence of amines (Heier *et al.,* 2014). Nashy *et al*. (2012) confirmed possible interactions between amines of collagen and Cr^{3+} complex in the chromium tanned leather. Thus, enhanced thermal stability imparted by melamine formaldehyde within cow samples can be expected. On the other hand, SBL showed the lowest overall thermal resistance among all the bag leathers, which can be ascribed to its lowest inherent fibrous strength, the higher angle of weave, lower fibril and fibre thickness (Table III) etc. Moreover, during processing of SBL, the lowest quantity of syntan has been used, with the complete absence

Table IV. DTG peaks and respective MRDs[1] of different samples

Sample	1st Peak (°C)	MRD (%/ min)	2nd Peak (°C)	MRD (%/ min)	3rd Peak (°C)	MRD (%/ min)	4th Peak (°C)	MRD (%/ min)
SBL	87.02	3.4	285.52	6.8	343.20	8.0	467.21	5.7
BVTL	90.0	2.5	280.1	4.1	348.8	8.9	467.65	5.6
CDDDML	92.1	4.1	Absent	Absent	349.06	9.6	Absent	Absent
CCPL	90.2	4.7	Absent	Absent	352.54	6.8	480.1	3.6

[1] MRD = Maximum Rate of Decomposition

of melamine type syntans in the recipe (Table II). Therefore, SBL shows the lowest crosslinking density (Table V), evaluated by Moony-Rivlin equation.

Beyond 250°C, thermal degradation profile for BVTL is noted to be slightly better than SBL (Fig. 4), which may be owing to its higher crosslinking density reflected in the superior tensile modulus (Table V), as comparatively higher extent of retanning agents including vegetable tannins (i.e. wattle, quebracho, chestnut) has been incorporated in BVTL (Table II). These vegetable tannins comprise of numerous phenolic –OH groups which can be invloved in H-bond formation within BVTL (Wu *et al*., 2013). Within 250-350°C, drastic thermal degradation has been noted for SBL followed by BVTL, which is reflected their multiple degradation peaks (2 nos.) within that particular temperature range (Table IV). Such degradation in a rapid fashion may be possibly due to deamination of collagen as deamination might be the dominant decomposition process within 250–350°C. Ammonia originates from deamination reactions of collagen involving free $-NH_2$ groups from arginine and lysine (51 and 25 residues/1,000 residues) and peptide –NH– groups (Cucos and Budrugeac, 2014). In this regard, SBL should contain the highest extent of free $-NH_2$ groups as SBL manufacture is associated with the usage of lowest quantity of vegetable tannins (Table II). In fact, application of higher amount of vegetable tannins reduces the availability of free $-NH_2$ groups. This is because, functional groups of tannins interact mainly with amine ($-NH_2$) or imine (–NH–) groups of collagen. At a higher temperature range, a further reduction in mass may be attributed to thermal decomposition/ volatilization of the peptide chains, backbones, glycosaminoglycans leading to ultimate conversion into elemental carbon.

Table V. Crosslink densities and tensile properties of various samples

Sample name	C_1	$N_C = 2C_1/RT$, mol.m^{-3}	Tensile strength, MP$_a$	Elongation-at-break (%)
BVTL	39.23	0.031668	30.0	53.75
SBL	7.33	0.005917	15.87	137.80
CCPL	16.83	0.013586	9.5	41.50
CDDDML	11.53	0.009307	12.92	75.50

Conclusion

It can be concluded that both mechanical and thermal properties of a bag leather depend largely on inherent strength of the raw material, extent, type and combination of tanning agents (e.g. vegetable tannins, acrylic syntans, melamine-formaldehyde syntans), influence of mechanical operations (e.g. milling, embossing), thickness and orientation of fibres and fibre bundles. Higher thickness of fibres/ fibre bundles with more number of fibrils in a fibre was the key factor behind enormous mechanical strength and crosslink density of bag leather produced from buffalo hide. Addition of melamine-formaldehyde syntans improved thermal resistance of bag leathers manufactured from cow hides whereas embossing at high pressure and temperature reduces elongation-at-break of bag leather via generating set properties.

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