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Mechanical and hydrodynamic swelling characteristics of bovine tanned leather post-treated by acrylic and glutaraldehyde tanning agents

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Abstract

Chromium tanned cow hides collected at two different stages (i.e. pre-neutralization and pre-finishing) have been treated separately with acrylic and glutaraldehyde based tanning agents. Both mechanical and hydrodynamic swelling properties of these treated samples were investigated. Observed results revealed that overall tensile properties and resistance against hydrodynamic swelling have been improved in all the treated samples as compared to those of untreated samples. Such improvement has been realized through measurement of crosslink densities via fitment of Mooney-Rivlin equation on the tensile plot. Leather post-treated with acrylic copolymer has envisaged superior results as compared to leather post-treated with glutaraldehyde based tanning agent. After one swelling / deswelling cycle, slight material loss has been incurred in all the samples, which is the highest for leather post-treated with glutaraldehyde. Such post-treatment of leather can be a useful measure to enhance the performance properties of leather samples already manufactured in the tannery.

Keywords: Crosslink density; Mooney-Rivlin equation; Swelling kinetics; Deswelling

Introduction

Leather is a durable and flexible material obtained by tanning of animal raw hide and skin (h/s), and leather processing involves a number of unit processes and operations (Thanikaivelan *et al.*, 2002). Basically, tanning is a unit process of converting putrescible outer covering of animals to non-putrescible leathers with definite physical, chemical, and biological properties (Dutta, 1985). In fact, tanning is a treatment of a natural fibre protein (i.e. collagen) from hides and skins, which leads to stabilization of the material. This stabilization is mainly an increase in resistance against hydrolysis which restricts swelling. This property change is mainly ascribed to the cross-linking of tanning material with collagen, filling effect of tanning material and is also promoted by hydrophobic coating of collagen fibre (e.g. fatliquoring) etc. In fact, an effective tanning agent potentially increases the number of new type of stable cross-linkages among the poly peptide chains. In addition, for transformation of collagen to leather, reactivity of collagen is also crucial, which is mainly decided by the content of acidic and basic amino acids, amino acids containing $-OH$ groups and peptide groups (Heidemann, 1993). Therefore, a potential tanning agent should possess the ability to generate crosslinks which should be stable at a temperature that is at least higher than the denaturation temperature of untanned collagen. Moreover, resistance to hydrodynamic swelling and tensile modulus are directly related to the crosslinking

density of leather which is generally dependent upon the performance of the tanning agents inside h/s matrix (Heidemann, 1993).

Acrylic type tanning agents or polyacrylates are synthesized mainly through addition polymerization. These tanning agents contain many carboxylic acid side groups that can give tanning property both reacting with multiple chrome centers on the leather and chemical binding to the collagen groups (Jankauskaitė *et al.*, 2012). Basically, polyacrylate type tanning agents are polyacrylic acids copolymerized with a portion of methacrylate or maleinate etc. Furthermore, a certain number of acrylic acid groups are esterified. Generally, the particular group of tanning agents should be of low molecular weight to ensure easy penetration inside h/s matrix (Heidemann, 1993).

Glutaraldehyde is a 5-carbon dialdehyde with a linear structure and is mainly available in acidic aqueous solutions (pH 3.0-4.0), in concentration ranging from less than 2% to 70% (w/v) (Migneault, 2004). Glutaraldehyde can react with various functional groups of protein, amine, thiol, phenol, and imidazole. Moreover, glutaraldehyde exists in multiple forms in aqueous solution. All of these forms might be reactive towards lysine residues of collagen bearing ϵ -amino group. All reported forms of glutaraldehyde have the ability to react and crosslink proteins (Tyagi *et al.*, 2014).

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The suitability of polyacrylic or poly methacrylic acid for use as a tanning agent, particularly in chrome tanning, is already established (Christner *et al.*, 1990). Variation of glass transition temperatures in the leathers being tanned with different tanning agents were compared by Jeyapalina *et al.* (Jeyapalina *et al.*, 2007). Recently a new synthetic tanning agent has been developed which is able to replace commercial urea formaldehyde resin in leather retanning process due to better retanning performance (Saleem *et al.*, 2013). Tyagi *et al.* reported the considerable improvement in thermal, mechanical and swelling resistance properties for bovine samples treated with 3 % GT-50 (w/w) (Tyagi *et al.*, 2014). Crosslinking and tensile strength in collagen based biomaterials (obtained by purifying dermal sheep collagen) was reported to be enhanced by treating with glutaraldehyde (Damink *et al.*, 1995).

In this work, the main objective is to improve the mechanical properties and resistance towards hydrodynamic swelling of the crusts already manufactured in tannery. These properties of the crusts may be improved by post-treatment with suitable tanning agent (i.e. aqueous solutions of glutaraldehyde and acrylic tanning agents). Contribution of different factors like region of hides (e.g. butt, neck), tanning agents (e.g. aldehyde, acrylic), and processing stages would be investigated regarding improvement in mechanical and hydrodynamic swelling properties.

Materials and methods

Materials

Raw materials like cow wet blues (shaved thickness = 1.1-1.3 mm, weight = 6 Kg) were supplied by Viswaat Chemicals Ltd., India. Leather auxiliaries like detergents, dyes, lubricating agents, tanning/ retanning agents, fixing agents etc. were provided by Viswaat Chemicals Ltd., India. Acrylic synthetic tanning agent like Relugan RE and glutaraldehyde tanning agent like Relugan GT-50 were provided by BASF India Limited.

Sample preparation

Both rechromed and crust leather samples were prepared following the generalized unit operations for leather manufacturing based on the recipes (Table I and Table II). Thereafter, prepared samples were further treated separately with Relugan RE and Relugan GT-50, and the solid contents of the end baths produced during RE & GT-50 treatment were evaluated (Table III).

Characterization

Mechanical properties

The mechanical behavior including the crosslinking density of the samples was investigated by the tensile test. Initially, both the samples were conditioned at 25°C and 65 ± 2% R.H for 48 hours. The usual dog bone shaped specimens were punched out from the crusts with ASTM Die-C. The measurement as per ASTM D-2209-00 standard was carried out in a Hicks-Hounsfield UTM-H10 KS (Test Equipment, Surrey, England) maintaining a cross head speed of 254 ± 50 mm.min⁻¹ at 25°C. The averages of five tests were reported for each sample. The stress-strain curve was plotted with Lab Tensile software, from which the tensile modulus, tensile strength and elongation-at-break (EB) were calculated. In each case, the error corresponding to tensile modulus, tensile strength, EB measurement was limited to ± 1 %, ± 2 %, ± 2 %, respectively.

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

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

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

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

where, N_c is the crosslink density, R is the gas constant (8.314 J. deg⁻¹. mol⁻¹) and T is the absolute temperature.

Swelling

Circular test specimens of diameter 22 mm (approx.) were cut out from all the leather samples. Thicknesses of the circular samples were measured using a thickness measuring gauge (Type JO2), manufactured by S. C. Dey & Co., having range of 0.01-10 mm. At least 5 sets of the circular specimens of all the samples, i.e. untreated, Relugan RE treated, Relugan GT-50 treated samples, were weighed accurately by an electronic balance. Subsequently, they were allowed to

Table I. Recipes for the preparation of all the rechromed samples^a

Process	Ingredients	Samples (ingredients in %)			Running time
		BRA ₀ G ₀ / NRA ₀ G ₀	BRA ₁₀ G ₀ / NRA ₁₀ G ₀	BRA ₀ G ₁₀ / NRA ₀ G ₁₀	
Soak back	Water	200	200	200	
	Non-ionic detergent	0.5	0.5	0.5	
	Oxalic acid	1	1	1	30'
Rechroming	Water	100	100	100	
	Acid Black dye	1	1	1	10'
	Formic acid	1	1	1	20'
	Glutaraldehyde	3	3	3	20'
	Basic chromium sulfate	4	4	4	
	Chrome syntan	3	3	3	
	Non-ionic detergent	0.1	0.1	0.1	30'
	Sulphited fish oil	1	1	1	15'
	Phenolic syntan	1	1	1	
	Melamine syntan	1	1	1	20'
	Sodium formate	1	1	1	10'
	Polymeric syntan	3	3	3	2 × 10'+30'
Syntan treatment	Water	-	200	200	
	Relugan RE	-	10	-	60'
	Relugan GT-50	-	-	10	60'

^a = Following designations have been followed:

B = Butt portion of leather; N = Neck portion of leather; R = Rechromed leather; A = Acrylic syntan (Relugan RE); G = Glutaraldehyde syntan (Relugan GT-50); Subscript of A = % of Acrylic syntan (Relugan RE); Subscript of G = % of Glutaraldehyde syntan (Relugan GT-50).

swell in distilled water at 25°C for 72 h to ensure attainment of equilibrium swelling state. Thereafter, as the swelled samples reached the equilibrium state, were allowed to deswell for further 72 h in open air.

In each case, during swelling and deswelling, weights of samples were measured at specified time (i.e. at 30 min, 60 min, 120 min, 240 min, 360 min, 1440 min, 2880 min, and 4320 min or 72 h). The weight measurements of the samples undergoing swelling at specified point of time were executed after careful removal of the fluid adhered at the surface of the specimens with the help of blotting paper. Thereafter, at the end of swelling, solid contents of the baths have been determined for each sample (Table III). Finally, all the swelling data were analyzed based on the following parameters:

Calculation of the mol % uptake of the distilled water

Mol % uptake of water during swelling for the leather samples can be measured by the following equation (Mathew *et al.*, 2006):

$$Q_t = \frac{W_f - W_0}{M_s \cdot W_0} \times 100 \quad (3)$$

where, Q_t is the mol % uptake of water. W_f and W_0 are weights of the leather samples before and after the swelling and M_s is the molar mass of water.

Swelling coefficient

The swelling coefficient (α) helps to analyze the swelling behavior of leather samples. The wetting ability of the samples is determined by the swelling coefficient equation (Mathew *et al.*, 2006):

$$\alpha = \{A_s/W_0\} \times [1/d] \quad (4)$$

where, A_s is the weight of solvent absorbed at equilibrium swelling, and d is the density of the solvent used.

Table II. Recipes for the preparation of all the crust samples^b

Process	Ingredients	Samples (ingredients in %)			Running time
		BCA ₀ G ₀ / NCA ₀ G ₀	BCA ₁₀ G ₀ / NCA ₁₀ G ₀	BCA ₀ G ₁₀ / NCA ₀ G ₁₀	
Soak back	Water	200	200	200	
	Non-ionic detergent	0.5	0.5	0.5	
	Oxalic acid	1	1	1	30'
Rechroming	Water	100	100	100	
	Acid Black dye	1	1	1	10'
	Formic acid	1	1	1	20'
	Glutaraldehyde	3	3	3	20'
	Basic chromium sulfate	4	4	4	
	Chrome syntan	3	3	3	
	Non-ionic detergent	0.1	0.1	0.1	30'
	Sulphited fish oil	1	1	1	15'
	Phenolic syntan	1	1	1	
	Melamine syntan	1	1	1	20'
	Sodium formate	1	1	1	10'
	Polymeric syntan	3	3	3	2 × 10'+30'
	Neutralization	Water	200	200	200
Sodium formate		1	1	1	
Neutralizing syntan		3	3	3	60'
Retanning/ Dyeing/ fatliquoring	Water	60	60	60	
	Acrylic syntan	4	4	4	20'
	Sulfonated aliphatic oil	2	2	2	20'
	Dicyna diamide syntan	3	3	3	
	Melamine syntan	3	3	3	
	GS powder	6	6	6	
	Acid Black dye	3	3	3	60'
	Styrene maleic anhydride co-polymer	2	2	2	20'
	Water	100	100	100	
	Anionic water repellent	1.5	1.5	1.5	
	Synthetic sperm substitute	3	3	3	
	Sulfonated aliphatic oil	1	1	1	
	Phospholipid based Semi-synthetic oil	0.5	0.5	0.5	
	Polymeric syntan	1	1	1	
	Preservative	0.3	0.3	0.3	
	Non-ionic detergent	0.2	0.2	0.2	40'
	Acrylic syntan	2	2	2	30'
	Formic acid	3	3	3	3 × 10'+30'
	Top dyeing	Water	100	100	100
Cationic Black dye		0.5	0.5	0.5	15'
Formic acid		1	1	1	20'
Chrome syntan		2	2	2	45'
Syntan treatment	Water	-	200	200	
	Relugan RE	-	10	-	60'
	Relugan GT-50	-	-	10	60'

^b C = Crust leather

Swelling index

Equilibrium swelling or swelling index of leather samples is measured by the following equation (Mathew *et al.*, 2006):

$$\text{Swelling index (\%)} = \frac{W_f - W_0}{W_0} \times 100 \quad (5)$$

Swelling-Deswelling kinetics

During both swelling and deswelling, weight of the sample was measured as a function of time for determining the degree of swelling, DoS and degree of deswelling, DoD . DoS can be expressed by the following equation (Sivanantham and Tata, 2012):

$$DoS = \frac{W_{ts} - W_0}{W_0} \quad (6)$$

where, W_{ts} is the weight of sample at time t in solvent. Similarly, expression of DoD can be the following (Sivanantham and Tata, 2012):

$$DoD = \frac{W_a - W_i}{W_i} \quad (7)$$

where, W_{ia} is the weight of sample at time t in air.

Fig. 1 depicts the variation of DoS with time which shows the power law behavior. Therefore, the experimental plot is fitted with Voigt-based equation:

$$S_t = S_e \left(1 - e^{-t/\tau}\right) \quad (8)$$

where, S_t (g/g) is swelling at time t , S_e is equilibrium swelling, t is time (min) for swelling S_t , and τ (min) stands for the "rate parameter".

In addition, the swelling time constant (τ_s) is estimated by fitting the swelling plot (Fig. 2) to the following expression based on Li-Tanaka theory (Sivanantham and Tata, 2012):

$$DoS = DoS_{max} - A_s \exp\left(-t/\tau_s\right) \quad (9)$$

where, DoS_{max} is the maximum degree of swelling, A_s is the amplitude of swelling.

Similarly, using the expression based on Li-Tanaka theory, the deswelling time constant (τ_d) is estimated by fitting the deswelling plots (Fig. 3) of individual samples to the following equation:

$$DoD = DoD_{max} - A_d \exp\left(-t/\tau_d\right) \quad (10)$$

where, DoD_{max} is the maximum degree of deswelling, A_d is the amplitude of deswelling.

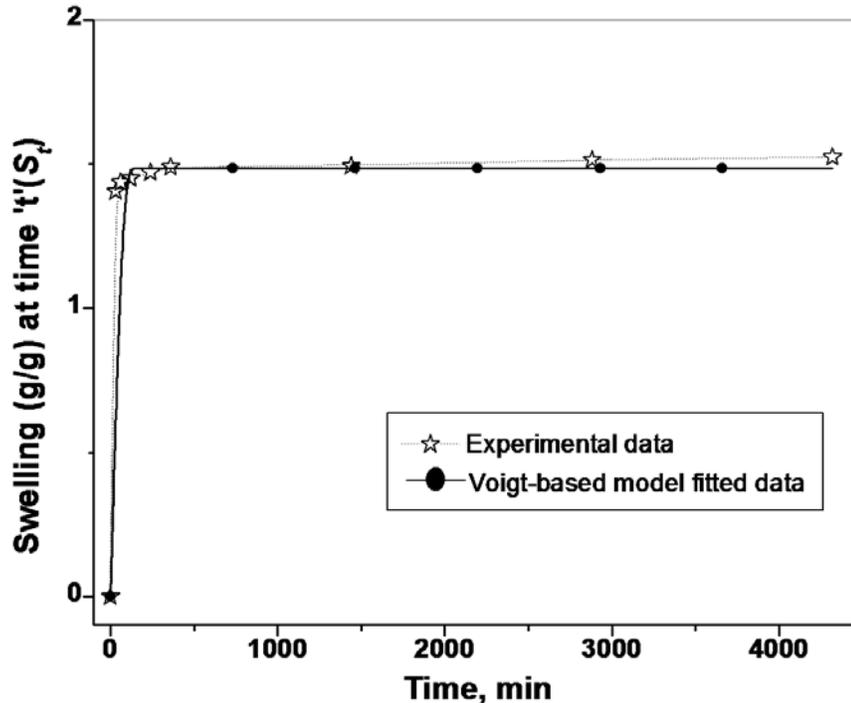


Fig. 1. Representative illustration regarding fitment of Voigt based equation to an experimental plot of swelling kinetics

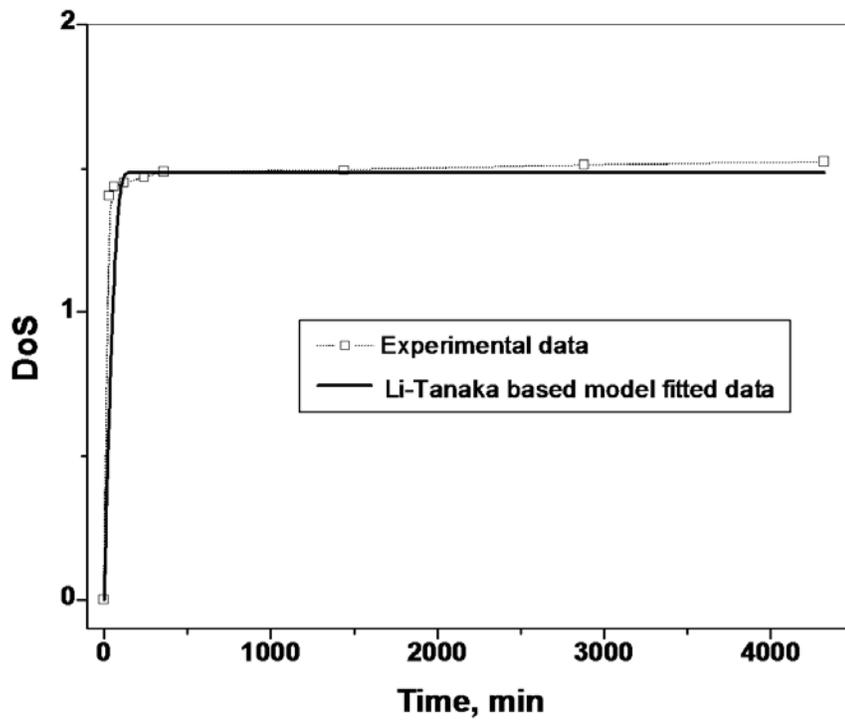


Fig. 2. Representative illustration regarding fitment of Li-Tanaka based equation to an experimental plot of swelling kinetics

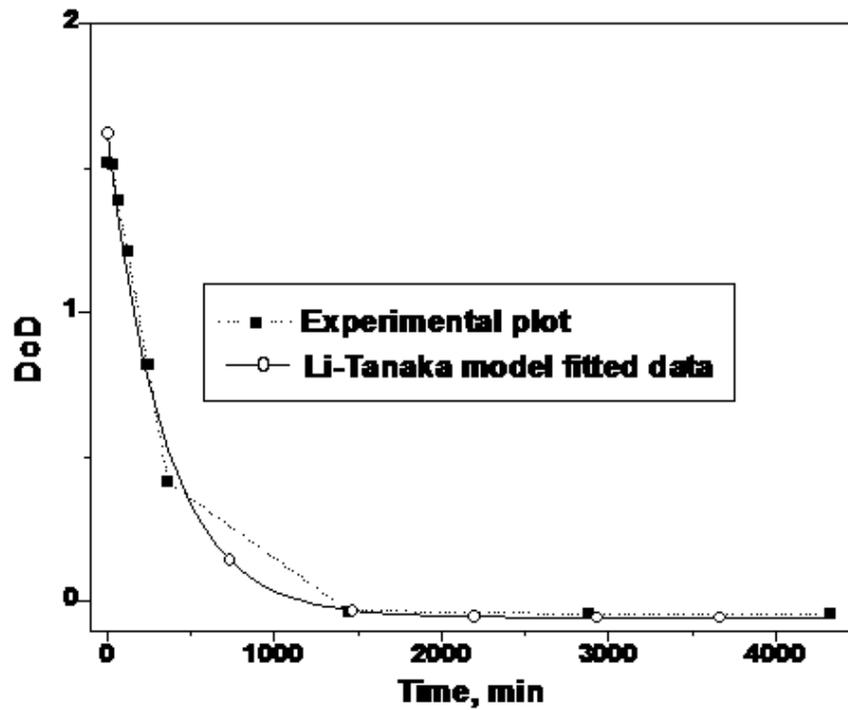


Fig. 3. Representative illustration regarding fitment of Li-Tanaka based equation to an experimental plot of deswelling kinetics

Table III. Solid contents of the end bath for various samples

Sample Name	Solid content of end bath (%)	
	after RE / GT-50 treatment	after 72 h swelling
BCA ₀ G ₀	-	0.2005
NCA ₀ G ₀	-	0.1783
NRA ₀ G ₀	-	0.1884
BRA ₀ G ₀	-	0.1485
BCA ₁₀ G ₀	3.8335	0.2173
NCA ₁₀ G ₀	3.8799	0.2096
NRA ₁₀ G ₀	2.9029	0.1895
BRA ₁₀ G ₀	2.8853	0.1679
BCA ₀ G ₁₀	4.4089	0.2174
NCA ₀ G ₁₀	2.6949	0.2179
NRA ₀ G ₁₀	2.81	0.1988
BRA ₀ G ₁₀	3.2187	0.2089

Results and discussion

Mechanical properties

In general, it can be observed that the tensile properties (e.g. tensile modulus, tensile strength) of untreated samples (Fig. 4a) are improved by treatment with either Relugan RE (Fig. 4b) or Relugan GT-50 (Fig. 4c). Stress-strain plots clearly show that the Relugan RE treated samples tolerate higher level of stresses than both the GT-50 treated and untreated leathers at all the strain levels. Table IV shows that tensile strength, modulus, and crosslink densities of Relugan RE treated and GT-50 treated leathers are superior as compared to the respective untreated samples (i.e. NCA₀G₀, NRA₀G₀, BCA₀G₀, BRA₀G₀). On the contrary, elongation-at-break values of the treated samples are reduced as compared to those of the untreated samples (Table IV). This can be possible as both acrylic and glutaraldehyde molecules may form

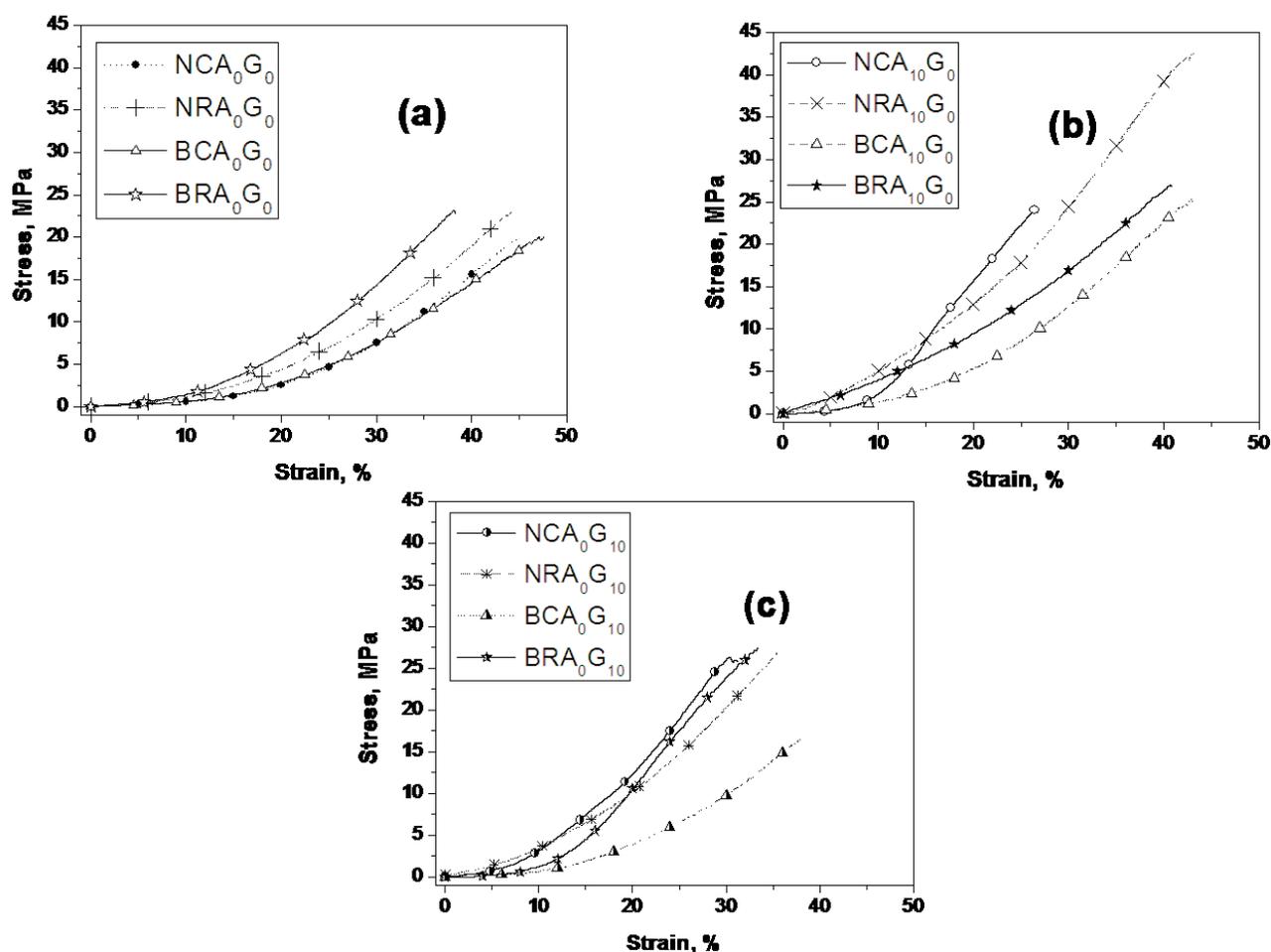


Fig. 4. Stress-strain plots of the (a) Untreated (b) RE treated, (c) GT-50 treated samples

crosslinking points of higher functionality inside collagen matrix. Theoretically, networks containing tetra-functional crosslinking points should have a lower elongation-at-break than networks containing tri-functional crosslinks (Nielsen and Landel, 1994). It is to be noted that among the untreated samples, rechromed samples (i.e. NRA_0G_0 and BRA_0G_0) produce better tensile properties in comparison to the corresponding crust samples (i.e. NCA_0G_0 and BCA_0G_0). This can be possible as average thicknesses and hence the cross-sectional areas of the crust samples are greater as compared to the respective rechromed samples. It may give rise to lesser compactness of the crust samples in comparison to rechromed samples (Table IV). Such enhancement in thickness for crust samples might be due to excessive swelling during the post-neutralization stages. Reduction in compactness for crusts is also reflected in the lowering of crosslink densities for untreated crust samples as compared to the untreated rechromed samples (Table IV). In this regard, remarkably better elongation-at-break for BCA_0G_0 as compared to BRA_0G_0 indicates presence of higher extent of void spaces in BCA_0G_0 . Such higher extent of void spaces in BCA_0G_0 ensure easier orientation of macromolecules in the direction of applied tensile force as inter-chain distances are widened owing to excess swelling during post-neutralization stage. Indeed, $\text{NRA}_{10}\text{G}_0$ shows the highest crosslink density as well as tensile strength among all the samples. It can be possible since the $-\text{COO}^-$ of Relugan RE can be co-ordinated with the Cr^{3+} of the Cr-complex during the rechroming stage. On the contrary, crust samples are comparatively crowded with different types of molecules unlike the

rechromed sample. Moreover, in case of rechromed samples, the change of elongation-at-break owing to RE treatment is less pronounced than that happened owing to GT-50 treatment (Table IV). In this regard, Madhan *et al.* (2002) reported that the treatment of collagen fibre with acrylic polymer like polymethacrylic acid is likely to open up the collagen molecule through electrostatic forces as they contain active sites for charge interactions. As acrylic syntans possess the ability to open up the collagen molecule through electrostatic forces, these can minimize the interchain interactions preferably in the direction perpendicular to the backbone. This in turn can increase the mobility of collagen macromolecules towards the applied force giving rise to higher elongation-at-break as compared to GT-50 treated samples.

Swelling

As leather is basically a fibrous collagen material, swelling characteristics of leather depends on various factors such as, a) hydrophobicity/ hydrophilicity of the sample, b) crosslink density, c) nature and stability of crosslinks, d) pH, e) temperature, f) extent of void spaces within the network, g) fibre-filler interactions etc. Swelling of collagen and other fibrous proteins, basic components of leather, in a solvent or solution is governed by the Donnan membrane effect, and by the cohesion of the protein (Bowes and Kenten, 1950). Moreover, hydrodynamic swelling of leather in a solvent is closely related to the wettability of leather towards that particular solvent. In fact, the process of leather wetting in water constitutes of four general steps: a) water spreads

Table IV. Tensile properties of various samples

Sample name	Avg. Thickness, mm	C_l	$N_C = 2C_l/RT$, mol.m ⁻³	Tensile strength, MPa	Elongation-at-break (%)	Stress at different strain %		
						10 %	20 %	30 %
NCA_0G_0	1.482	0.90	725.86	19.76	44.70	0.55	2.58	7.51
NRA_0G_0	1.262	1.85	1491.51	23.56	45.00	1.16	4.38	10.30
BCA_0G_0	1.956	0.96	773.24	19.98	47.60	0.57	2.81	7.51
BRA_0G_0	1.350	2.28	1842.19	23.14	38.12	1.42	6.29	14.31
$\text{NCA}_{10}\text{G}_0$	1.642	3.71	2993.04	24.07	26.48	2.36	15.67	-
$\text{NRA}_{10}\text{G}_0$	1.292	8.30	6703.22	42.50	43.10	5.11	12.89	24.39
$\text{BCA}_{10}\text{G}_0$	1.810	2.25	1813.46	25.30	42.90	1.39	5.26	12.63
$\text{BRA}_{10}\text{G}_0$	1.618	6.50	5243.56	27.00	40.70	4.00	9.49	16.87
$\text{NCA}_0\text{G}_{10}$	1.626	5.02	4048.08	26.00	31.08	3.20	12.25	26.00
$\text{NRA}_0\text{G}_{10}$	1.320	5.65	4563.83	27.27	35.92	3.48	10.16	20.24
$\text{BCA}_0\text{G}_{10}$	1.934	1.36	1097.16	20.47	43.50	0.69	3.89	9.77
$\text{BRA}_0\text{G}_{10}$	1.630	5.21	4206.64	27.50	33.40	1.20	10.60	24.04

over and wets the leather surface; b) water penetrates into the leather; c) water wets the fibre network; d) the leather rehydrated by water due to the attractive interaction between water and leather (Herrmann, 2006).

Among the untreated samples, butt samples (i.e. BRA₀G₀ and BCA₀G₀) show higher S_e values as compared to those of the neck samples (Table V). The comparatively higher quantity of water retention at equilibrium in the butt area can be ascribed to less compact fibre structures in the butt area owing to higher angle of weave. In fact, fibres weaving, fibre bundles splitting, separation and coalescence can influence the wetting and swelling characteristics of leather (Jankauskaitė *et al.*, 2012). The lower S_e values for neck area based sample indicate intense cohesive forces among fibre and fibre bundles owing to lower angle of weave in the neck region. Moreover, it has been observed that rechromed samples envisages higher S_e values than the corresponding crust samples (i.e. BRA₀G₀ > BCA₀G₀ and NRA₀G₀ > NCA₀G₀). Higher swelling in the equilibrium for rechromed samples can be attributed to better hydrophilicity of the samples as compared to crust samples as crust samples are loaded with varieties of hydrophobic ingredients (e.g. anionic water repelling agent, sulfonated aliphatic oil, synthetic sperm substitute, phospholipid based semi-synthetic oil) which are completely absent in the rechromed samples (Table I and Table II). Moreover, greater water holding capacity of rechromed samples may indicate availability of higher extent of void spaces as the filling materials (reinforcing / non-reinforcing) and retanning agents such as, vegetable tannins, styrene-maleic anhydride copolymer, dicyandiamide syntans are absent in these samples (Table I).

Moreover, hydrophobic ingredients like melamines are present at lesser quantity inside the rechromed samples (Table I). Hence, availability of greater void spaces and higher hydrophilicity may ensure higher retention of water molecules inside the rechromed samples as compared to the crust samples.

The swelling time constants (τ_s) of treated and untreated samples have been evaluated via fitment of both Voigt-based equation (equation 8) and Li-Tanaka equation (equation 9) on the experimental swelling plot (Fig. 1 and 2). It is to be noted that the order of τ_s values for the untreated samples (i.e. NRA₀G₀ > BRA₀G₀ > NCA₀G₀ > BCA₀G₀) is slightly different than the order for S_e values of the samples (Table V). Samples from neck area shows higher S_e values (Table V and Table VI) and accordingly lower swelling rate (equation 8 and 9) owing to greater compactness as a result of lower angle of weave. Interestingly, lower swelling rate is observed in case of rechromed samples despite better hydrophilic character and availability of greater void spaces in rechromed samples. Here, the higher crosslink densities in the rechromed samples (Table IV) can be responsible behind such lower swelling rate for the rechromed samples (Table V and Table VI).

In all the RE treated samples, higher τ_s values are obtained in comparison to respective untreated samples (Table V and Table VI), which implies lesser degree of swelling (equation 9) as a result of increased crosslinking densities for all RE treated samples with respect to untreated ones (Table IV). In general, RE treatment reduces S_e values except NCA₁₀G₀ where the water retention at equilibrium is noted to be

Table V. Data corresponding to Fitment by Voigt-based equation on swelling plot [11]

Sample	Chi ² /DoF	R ²	S _e	Error (%)	τ _s , min	Error (%)
BCA ₀ G ₀	0.0003	0.99701	1.48372	0.745424	10.44496	12.88907
BRA ₀ G ₀	0.0011	0.99652	1.58479	0.804523	10.64963	13.40788
NCA ₀ G ₀	0.0015	0.9939	1.2741	1.06585	10.5363	18.12243
NRA ₀ G ₀	0.0033	0.98571	1.29292	1.64434	11.8022	22.87265
BCA ₁₀ G ₀	0.00305	0.98057	1.11191	1.929113	12.83368	23.57546
BRA ₁₀ G ₀	0.00353	0.98279	1.26996	1.804781	11.40251	26.60205
NCA ₁₀ G ₀	0.00091	0.99631	1.40166	0.828304	10.84011	13.35501
NRA ₁₀ G ₀	0.00342	0.98257	1.2437	1.823591	12.48751	23.2018
BCA ₀ G ₁₀	0.00106	0.99577	1.41106	0.884441	9.725734	17.69111
BRA ₀ G ₁₀	0.00385	0.98535	1.4405	1.669559	12.60557	20.95046
NCA ₀ G ₁₀	0.00067	0.99743	1.43365	0.687058	8.716116	17.69372
NRA ₀ G ₁₀	0.00186	0.99159	1.3266	1.266395	13.74948	14.06572

enhanced. It is also observed that the solid content of the end bath, generated during processing of $NCA_{10}G_0$, is the highest (Table III). Such solid content (3.8799%) can be owing to the following: a) considerable extent of RE molecules may be unable to penetrate into the hide matrix from the bath, b) ingredients already present prior to swelling may transfer from matrix to the bath. During RE treatment, the penetration of RE molecule inside NCA_0G_0 might be hampered as the bigger RE molecules may experience higher restrictions owing to compact nature of the neck region of the crust.

Among the GT-50 treated samples, the τ_s values for rechromed samples are in the higher side in comparison to crust samples (Table V). It indicates the possibility of higher number of stable crosslink formation as a result of easier availability of free $-NH_2$ groups (both ϵ -amino and α -amino) of collagen in rechromed samples. These free $-NH_2$ groups can interact with $-CHO$ groups of GT-50 through nucleophilic substitution via formation of carbon-nitrogen double bond (Morrison and Boyd, 1987). Moreover, GT-50 may also interact with other less reactive unoccupied functional groups, like, guanidiny, secondary amino and hydroxyl groups (Migneault *et al.*, 2004). On the contrary, for the GT-50 treated crust samples, τ_s are reduced as compared to untreated samples despite increase in cross-linking densities (Table IV). This may be possible owing to formation of physical crosslinks in larger proportion in comparison to generation of chemical crosslinks. Moreover, crosslink density may have improved in the direction along the backbone, whereas in the perpendicular direction of backbone the crosslink density may not be increased that much.

Deswelling

Deswelling is the reverse process of swelling, which is related to change of a macromolecule from a relaxed rubbery state to a glassy or more preferably to a partially rubbery state as leathery state lies in between glassy and rubbery state (Ganji *et al.*, 2010). The deswelling time constants (τ_d) of treated and untreated samples have been evaluated via fitment of Li-Tanaka equation on the experimental deswelling plot (Fig. 3). Deswelling time constants (τ_d) are found in the following order: $BCA_0G_0 > NCA_0G_0 > BRA_0G_0 > NRA_0G_0$ (Table VII). This order is completely reverse to the order obtained for τ_s (Table VI). During deswelling, the transition from relaxed rubbery state to partially rubbery state would be faster if the relaxed flexible chains become rigid and strained easily. The τ_d values for almost all the RE treated samples have been increased in comparison to the untreated samples except the butt crust sample (Table VII). This can be possible as the treatment by acrylic syntans can already increase the rigidity of the macromolecular chains irreversibly through formation of stable crosslinks via coordinate linkage between Cr^{3+} and $-COO^-$ group of RE chains (Jankauskaitė *et al.*, 2012). Such improvement of crosslink density in RE treated samples as compared to untreated samples has already been recorded earlier (Table IV). For the butt crust samples, RE treatment has resulted in degradation of τ_d values as the crosslink density for $BCA_{10}G_0$ is not substantially higher with respect to the untreated sample (Table IV). Hence, swelled $BCA_{10}G_0$ might be more relaxed, and hence deswelling would be faster (Table VI). On the contrary, for GT-50 treated samples, τ_d values for almost all samples have been slightly elevated as the swelled GT-50

Table VI. Data corresponding to Fitment by Li-Tanaka based equation on the swelling plot

Sample	Chi ² /DoF	R ²	DoS _{max}	Error	A _d	Error	τ_s , min	Error
BCA ₀ G ₀	0.00097	0.99701	1.48372	0.01194	-1.48358	0.0333	10.44562	1.44571
BRA ₀ G ₀	0.00128	0.99652	1.58479	0.01377	-1.5846	0.03837	10.65013	1.53398
NCA ₀ G ₀	0.00146	0.9939	1.2741	0.01467	-1.27391	0.04088	10.53646	2.05104
NRA ₀ G ₀	0.00353	0.98571	1.29293	0.02297	-1.29255	0.06369	11.80425	2.90626
BCA ₁₀ G ₀	0.00356	0.98057	1.11191	0.02317	-1.11127	0.06395	12.83799	3.26304
BRA ₁₀ G ₀	0.00412	0.98279	1.26996	0.02476	-1.26965	0.06878	11.40337	3.2627
NCA ₁₀ G ₀	0.00106	0.99631	1.40166	0.01254	-1.40149	0.03491	10.84052	1.55566
NRA ₁₀ G ₀	0.00399	0.98257	1.24364	0.0245	-1.24304	0.06772	12.4941	3.12304
BCA ₀ G ₁₀	0.00262	0.99107	1.42095	0.01809	-1.37364	0.05427	9.725734	1.8762
BRA ₀ G ₁₀	0.0067	0.97815	1.42237	0.03093	-1.42237	0.08748	12.60557	2.2489
NCA ₀ G ₁₀	0.00078	0.99743	1.43365	0.01064	-1.43362	0.02986	8.71601	1.65201
NRA ₀ G ₁₀	0.00217	0.99159	1.3266	0.01815	-1.32603	0.0499	13.75248	2.08909

Table VII. Data corresponding to Fitment by Li-Tanaka based equation on the deswelling plot

Sample	Chi ² /DoF	R ²	DoD _{ma}	Error	A _d	Error	τ _d , min	Error
BCA ₀ G ₀	0.00586	0.99073	-0.05561	0.04596	1.67821	0.06699	286.84744	38.04581
BRA ₀ G ₀	0.00635	0.98994	-0.03605	0.04573	1.71894	0.07152	221.06234	23.50394
NCA ₀ G ₀	0.00506	0.98914	-0.06006	0.04132	1.46242	0.06327	257.14262	28.788
NRA ₀ G ₀	0.00601	0.98732	-0.04903	0.04405	1.49823	0.07012	195.68858	23.37947
BCA ₀ G ₁₀	0.0069	0.98342	-0.07802	0.04846	1.37529	0.07374	268.31856	37.4637
BRA ₁₀ G ₀	0.0104	0.98075	-0.06638	0.05926	1.56797	0.0907	257.94179	38.6281
NCA ₁₀ G ₀	0.00831	0.98588	-0.08453	0.0535	1.63188	0.08064	285.6041	37.18158
NRA ₁₀ G ₀	0.00974	0.98016	-0.05833	0.05713	1.49838	0.08802	246.24461	37.2393
BCA ₀ G ₁₀	0.00984	0.98383	-0.08657	0.05742	1.67217	0.08851	245.56154	33.45288
BRA ₀ G ₁₀	0.01741	0.97462	-0.09059	0.07586	1.77483	0.11822	226.93128	38.67164
NCA ₀ G ₁₀	0.00923	0.98517	-0.08588	0.056	1.68497	0.08535	265.69354	34.99125
NRA ₀ G ₁₀	0.01189	0.97776	-0.09155	0.06119	1.59522	0.09949	192.49189	27.56937

treated samples would be relaxed since glutaraldehyde reacts reversibly with amino groups of proteins over a wide pH range (\geq pH 3.0), except between pH 7.0 to 9.0 where only a little reversibility is observed (Migneault *et al.*, 2004).

Table VII shows that the untreated samples possess the lowest DoD_{max} values, and the GT-50 treated samples show the highest DoD_{max} values. The DoD_{max} values for the RE treated samples lay in between the untreated and GT-50 treated samples. Moreover, crust samples depict the higher DoD_{max} values than those of rechromed samples. In this regard, DoD_{max} values can be directly related to the solid contents (%) of the end baths after swelling (Table III). Higher solid content of end bath after swelling indicates higher material loss, and such material loss should be higher for crust samples as crust samples are populated with different types of molecules reversibly attached within the leather matrix. Higher solid content (%) of the end baths after swelling for both RE and GT-50 treated samples may be ascribed to the following:

a) $-COO^-$ group of RE can be involved competitively in the salt link formation with $-NH_3^+$ group of protein which is already interacted with $-SO_3^-$ group of acid dye as well as of aliphatic oil used as lubricating agent. Thus, $-COO^-$ group can make free a portion of the bound acid dye or sulphonated aliphatic oil which can move to water from the leather matrix during swelling.

b) $-CHO$ group of GT-50 can strongly interact with the available $-NH_2$ group of collagen, and thereby can displace some molecules which are already attached to the $-NH_2$ group of collagen by weaker bonding forces.

Conclusion

(a) Substantial improvement in crosslink densities is achieved for all the leather samples which are reflected in the enhancement both in the mechanical properties as well as in the resistance towards hydrodynamic swelling.

(b) The improvement in these properties is more pronounced in case of leathers treated with crosslinking agents based on acrylic copolymers as compared to glutaraldehyde based tanning agents as glutaraldehyde, if present $\leq 10\%$, interacts reversibly with the collagen chains at acidic pH.

(c) As a result of one complete cycle of swelling / deswelling, a little quantity of material loss has been incurred in all the samples, and this material loss is the highest in case of glutaraldehyde treated leather followed by RE treated leather.

(d) Such post-treatment of leather can be a useful measure to overcome shortcomings in the mechanical properties of leather samples already manufactured in the industry.

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