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Full Length Research Article

ROLE OF ACRYLIC AND MELAMINE-FORMALDEHYDE BASED SYNTHETIC TANNING AGENT IN THERMO-MECHANICAL AND HYDRODYNAMIC BEHAVIOR TANNED COLLAGEN

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ABSTRACT

Three different samples of cow softy leather (i.e. CSM_0A_0, CSM_3A_0 and CSM_0A_3) have been prepared from a chrome tanned cow wet blue of Indian origin. CSM_0A_0 is the control sample wherein neither melamine formaldehyde based nor polyacrylate based syntan has been added. CSM_3A_0 and CSM_0A_3 contain 3% melamine formaldehyde based and 3% polyacrylate based syntan, respectively in addition to the other common auxiliaries used in all three samples. Other physical and chemical operations are maintained same in all the three samples. Thermal, mechanical and hydrodynamic swelling behavior of these three samples have been studied, and tried to be correlated with the crosslinking densities of the samples. The hydrodynamic swelling behavior has been studied in three different solvents (e.g. water, toluene and xylene) assuming definite solvent-cow collagen interaction parameters, and crosslink densities have been evaluated by applying the Flory-Rehner equation. While studying the mechanical behavior, some distinguished theoretical models (e.g. Mooney-Rivlin, Flory, and Martin, Roth & Stiehler (MRS)) have been tried to be fit with the experimental results obtained in stress- stain analyses. In this process, few constants for cow Cr tanned leather have been derived, which has not been reported in the literature till date.

INTRODUCTION

It is well known that leather is a material manufactured from collagen fibre network of hide and skin provided with certain characteristics which are intended for the end use and produced by some physical and chemical processes. Some of these characteristics are inherent, and some of them can be induced/ modified/ improved with the incorporation of certain leather auxiliaries (i.e. natural/ synthetic tanning agents, fatliquors, etc.). From the perspective of ultimate consumers, the mechanical behaviors of the materials are of prime importance in comparison to the chemical properties. The mechanical behavior of materials is dependent upon a large no of structural and molecular factors (like; molecular weight, crosslinking and branching, crystal morphology, fillers, molecular orientation, phase separation, plasticization etc.). Apart from these structural and molecular factors, there are many environmental or external factors (like; temperature [1], time, rate of stressing, pressure, type of deformation, moisture content, stress and strain amplitude, thermal history etc.) which affects mechanical behavior[2]. 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 [3, 4]. In this regard, the breaking stress should also be directly proportional to cross link density. Moreover, various kinds of imperfections in the crosslinked network structure can change the stress-strain behavior of crosslinked material [5-8]. The modulus may not be lowered by these imperfections, but the tensile strength and ultimate elongation may be greatly reduced. Case and Mark [9-12], have made theoretical calculations which show that a regular spaced crosslinked network should have a higher elongation-at-break (EB) than a network in which the spacing in between crosslinks varies in a random manner. Researchers [11-14] have also predicted that network containing tri-functional points should have greater EB than the network containing tetra-functional crosslinks. Tri-functional crosslinks impose less drastic action on chain motion than tetra-functional crosslinks. Crosslinks have less effect on the rigid high molecular materials because entanglements and interpenetration of molecules are as effective as crosslinks in producing strength, although their modulus is determined largely by the strength of Van-der-Waals intermolecular bonds, through-going covalent chains are needed to tie the structure for strength. Thermal resistance is also a significant characteristic of leather as the increased crosslink formation leads to improved heat resistance [15].

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Hence, the degradation of a sample will be slower and will take place at higher temperature in comparison to samples having lesser crosslinks. The ability of swelling in water/ solvents gradually deteriorates with increasing cross-link density [16]. During swelling, as the system attains equilibrium, the chemical forces tending to dissolve the crosslinked collagen network in a liquid are balanced by restraining forces exerted by the crosslinked collagen network. Melamine formaldehyde condensates [17, 18] and acrylic based resins [19] 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 [20]. Both the melamine based and polyacrylate based syntan try to crosslinks with collagen to give it more thermal, mechanical and hydrodynamic stability. In this paper, a comparative study has been executed based on the crosslinking ability of two different categories of syntans (i.e. melamine-formaldehyde condensate and polyacrylate based) within bovine hides. Thermomechanical and hydrodynamic behavior of the treated hides, as obtained experimentally, has been attempted to fit with the different theoretical models available in the literature.

Experimental

MATERIALS AND METHODS

Cow wet blues of Indian origin (weight = 800-1100 g) and all the auxiliaries [e.g. fatliquors, syntans (Basyntan AN, Basyntan FB6 and Relugon RF), wetting agent, dye, preservative etc.] required for leather processing were provided by BASF India Ltd. Toluene [Grade - LR, density (at 20 ^oC) = 0.87, purity ≈ 99.5%) and Xylene [density (at 20 ^oC) = 0.85-0.87, purity ≈ 99.5%], used as swelling solvents, were purchased from Merck Specialties Private Limited, Mumbai, India.

Preparation of samples

Three samples (i.e. CSM_0A_0, CSM_3A_0 and CSM_0A_3) have been prepared based on the recipes shown in Table 1. CSM_0A_0 (control sample) is devoid of relugan RF (a polyacrylate based syntan) and Basyntan FB6 (a melamine formaldehyde based syntan). In the preparation of CSM_3A_0 and CSM_0A_3 3% Basyntan FB6 and 3% Relugan RF have been added, respectively, in addition to the other auxiliaries used in all the samples.

Characterization

Mechanical properties

The mechanical behavior including the crosslinking density of the samples was investigated by the tensile test. Initially, all the samples are 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 standard was carried out in a Hioks-Hounsfield UTM (Test Equipment, Surrey, England) maintaining a crosshead speed of 100 $mm.min^{-1}$ at 25 ^oC. For each sample, the averages of five tests are 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, EB measurement was limited to ± 1 %, ± 2 %, ± 2 %, respectively.

Thermogravimetric analyses (TGA)

TGA were carried out using thermogravimetric analyzer (model: Pyris 6 TGA) manufactured by Perkin-Elmer instruments, the Netherlands. The samples of about 5–10 mg were heated from ambient temperature to 850 ^oC in the nitrogen atmosphere maintaining a constant heating rate of 20 $^oC.min^{-1}$. The data of the weight loss versus temperature were recorded in the software.

Swelling

Previously weighed circular leather samples were allowed to swell in three different solvents (i.e. distilled water, toluene, and xylene) at ambient temperature (25 ^oC) for 72 h (the equilibrium swelling time). The swollen test pieces were taken out, and the weight was measured. Finally, these were allowed to dry in a vacuum oven to a constant weight.

Boil test

Boil test of all the three samples was carried out in water at atmospheric pressure and 65 ± 2% R.H for three different periods of time (i.e. 3 min, 5 min and 6.5 min). Initially, circular specimens of all the samples were cut out and immersed in the boiling water (at 100 ^oC). These were kept in the boiling water for those stipulated periods of time, and the respective shrinkages in area were measured by image analyses software (i.e. image J, NIH, USA) of the respective photographs.

RESULTS AND DISCUSSION

Mechanical properties

The stress-strain results obtained were tried to fit on different theoretical models (e.g. Mooney-Rivlin, Flory, MRS) predicted by different researchers [3, 21-25]. It is well established that Mooney-Rivlin [21,22] equation (eqn. 1) is suitable for incompressible or slightly compressible materials wherein $V/V_o \approx 1$ (i.e. the material is quite insensitive to small volume change).

$$\sigma = 2(\lambda - 1/\lambda^2)(C_1 + C_2/\lambda) \quad (1)$$

where, λ= extension ratio (extended length/original length), σ = applied stress, C_1 = enthalpy related constant accounting for cross-linking density, C_2 = constant related to the contribution of the entropy of the cross links. Mooney-Rivlin's [21, 22] equation (eqn. 1), Flory's [23, 24] equation (eqn. 2) and MRS[25] equation (eqn. 3) has been fitted with the experimental results within 25% to 60 % strain and obtained the representative plot as per Fig. 1a, 1b, 1c. Almost straight lines have been obtained for all the samples. Here, C_1 value has been calculated from the intercept and constant C_2 value from the slope of the straight line curve. Although literature [26, 27] had shown that C_2 value is not a constant, Mooney Rivlin equation fits reasonably well to experimental findings, Flory's equation is given by-

$$\sigma = (N_c RT/2)(\lambda - 1/\lambda^2)(1 + B/\lambda) \quad (2)$$

Table 1. Receipes of different cow softy samples

Unit Operation	Ingredients	Samples* (ingredients in %)			Time (min)	Remarks
		CSM_0A_0	CSM_3A_0	CSM_0A_3		
Soak back	Eusapon(w)	0.2	0.2	0.2	30	1:3 dilution
	Water	200	200	200		
Drain/Wash					10	
Rechroming	Water	100	100	100	30	
	Formic acid	0.5	0.5	0.5		1:10 dilution
	BCS	4	4	4	60	
	Basyntan AN	2	2	2		
	Relugan RF	-	-	3	45	
	Sodium formate	0.5	0.5	0.5	60	
	Sodium bi carbonate	0.5	0.5	0.5		
Drain/Wash					10	
	Water	150	150	150	10	
	Sodium formate	2	2	2		
Drain/Wash					10	Check pH = 4.8
Dyeing	Water	100	100	100	60	
	Luganil Brown FB3GN	1	1	1		
	Basyntan FO	6	6	6		
	Basyntan FB-6	-	**3**	-		
Fatliquoring	Lipoderm Liquor EA-1	8	8	8	45	1:3 dilution
	Preservative	0.2	0.2	0.2		
Fixing	Water	100	100	100	50	
	Formic acid	1	1	1	(3 × 10 + 20)	1:10 dilution

Sample designation: CS = Cow softy, M = Melamine formaldehyde syntan, A = Acrylic resin syntan (numerical suffixes indicate the % of the respective ingredients added in the sample)

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

Samples	Stress at different strain levels (MPa)			Tensile strength (MPa)	Elongation at break (%)	C_1*	Crosslinking Density ($\times 10^{-3}$) Mol. m^{-3}	C_2	Calculated values of constant *B* from Flory Equation	Calculated values of constant *A* from MRS Equation
	10 %	20 %	30 %							
CSM_0A_0	1.24	3.11	5.21	26.68	88.60	3.209	2.59	0.007	0.0022	0.962
CSM_3A_0	1.28	3.16	5.33	31.93	95.40	3.239	2.61	0.009	0.0027	0.966
CSM_0A_3	1.80	7.16	11.90	36.37	69.28	7.457	6.02	0.013	0.0020	0.970

* Crosslinking density has been analyzed within a strain range (25 ~ 60 %)

where R = 8.314 $J.deg^{-1}.mole^{-1}$, T =298 K, N_c is cross-linking density ($moles.m^{-3}$) and B = constant up to a significant strain(fits well with in our experimental range of strain 25 to 60%). MRS equation is given by-

$$\sigma = (E\,\varepsilon/\,\lambda^2)exp(A(\lambda-1/\,\lambda)) \quad (3)$$

where A=constant

Eqn. 2 and eqn. 3 also fits well to the experimental findings within our experimental range of strain. The calculated values for constant *B* from Flory' equation and constant *A* from MRS equation has been reported in table 2. This can be safely concluded that value of *B* for Cr tanned cow leather remains in the range of 0.001-0.003 and value of *A* remains in the range of 0.9-1.0. Table 2 shows the C_1 and cross-linking density values of all the samples, which have been evaluated based on the following equation:

$$C_1=1/2(RTN_c) \quad (4)$$

It has been found that the crosslink densities of the samples are in the following order: $CSM_0A_3 > CSM_3A_0 > CSM_0A_0$ [Table 2]. In case of CSM_0A_3, the added polyacrylate based syntan may interact with the central Cr^{3+} ion of the Cr complexes by virtue of available COO^- groups of polyacrylate side chains [Fig. 4]. On the other hand, in CSM_3A_0, the added melamine based syntan bears basic amino groups ($-NH_2$) which can form chelated rings involving the Cr^{3+} [Fig. 3], and in this process weaker crosslinks might be generated. It can be possible since in comparison to $-COO^-$, $-NH_2$ acts as weaker ligand to the central Cr^{3+} ion, and hence, the Cr^{3+}- NH_2 coordination linkage should be less stable as compared to Cr^{3+}- COO^- linkage. From the structural point of view, melamine can also interact with the collagen polypeptide chains by means of H bonding and London- Van-der-Waals forces, but such interactions are much weaker in nature. It is also a well established fact that % EB decreases with increase in cross-linking density. It can be noted that in comparison to CSM_0A_0, the cross-linking density has been slightly increased in CSM_3A_0, but % EB has not been decreased in CSM_3A_0. Therefore, it can be presumed that the melamine based crosslinks are actually physical crosslinks which are weaker in nature. Weaker crosslinks allow the chain slippage in CSM_3A_0, which is evident in the respective high EB values. On the contrary, in CSM_0A_3, the substantially increased crosslink density value is reflected in its higher modulus values [Table 2].

TGA

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 all the samples are depicted in Fig.2 (a), (b), (c), (d). It can be observed that within 150-320 ^oC, the degradation profiles of all the samples are almost similar in nature. The gentle and flat nature of the TGA curve within this particular range indicates

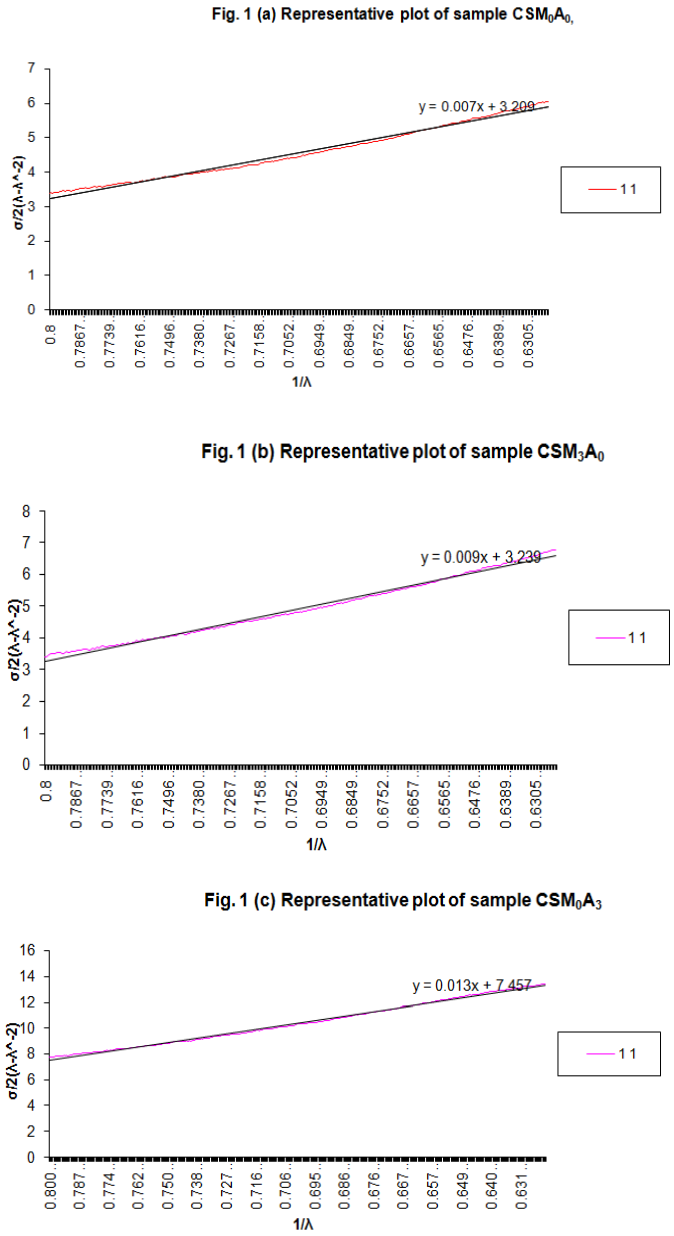

Fig. 1. Representative fitting plot of Samples (a) CSM_0A_0 (b) CSM_3A_0 (c) CSM_0A_3

considerable thermal resistance of the samples. Within the temperature range ~315-480 ^oC, all the samples starts degrading steeply. Table 3 and Fig. 2 clearly shows the fact that as the temperature is increased from ~315 ^oC to 480 ^oC, the undegraded polymer proportion is drastically dropped from 80 % to a mere 35.8 %.

Table 3. Thermal degradation characteristics of all the samples

Sample	Temperature, ^oC			
	95%	75%	50%	25%
CSM_0A_0	95.62	336.19	393.18	578.30
CSM_3A_0	100.29	337.19	392.28	637.38
CSM_0A_3	96.89	342.44	401.84	638.13

Moreover, it can be clearly noted that CSM_3A_0 has initially (up to ~ 320 ^oC) [20] shown higher heat resistance owing to the presence of melamine which on heating deaminates first to 'melam' and then to 'melon'. As the temperature of the sample is increased beyond 320^oC, the degradation of 'melam' / 'melon' takes place [28, 29]. It is well established that 'melam' / 'melon' posses a remarkable thermal resistance, which eventually degrades further in three stages [28]. Fig. 2 enumerates the crossing over of the plots corresponding to CSM_3A_0 and CSM_0A_3 at around 615-620 ^oC. In this context, it was reported by earlier workers that above ~ 620 ^oC, the melamine condensate undergoes thermal degradation with quantitative formation of volatile products [28]. Therefore, the drop in heat resistance for CSM_3A_0 with respect to CSM_0A_3 can be attributed to aforementioned effect. It can also be observed that as compared to other samples, the control sample (CSM_0A_0) suddenly starts deteriorating at around ~ 490-500 ^oC, with a faster rate, which can be attributed to the absence of any syntan. The enhanced thermal stability of CSM_3A_0 and CSM_0A_3 as compared to the control sample is quite evident from the greater quantity of residue formed for CSM_3A_0 and CSM_0A_3 at 840 ^oC [Table 4]. In this regard, slightly higher residue formation for CSM_0A_3 in comparison to CSM_3A_0 reiterates the better thermal resistance for CSM_0A_3. From table 4, it is clearly indicated that CSM_0A_3 showed higher % remained up to 440 ^oC because it contains transitional metal based poly acrylates which generally melts at around 425-485 ^oC [30]. Moreover, the temperatures corresponding to DTG (differential thermogram) peaks have been reported in table 4, which is also in the order $CSM_0A_3 > CSM_3A_0 > CSM_0A_0$, this further establish the clear advantage for CSM_0A_3 regarding thermal stability and crosslink formation over the other two samples.

Swelling

The swelling behavior of the three samples CSM_0A_0, CSM_3A_0 and CSM_0A_3 is reported in table 5. Table 5, shows the increased resistance against swelling or the reduced swelling index for the samples, CSM_3A_0 & CSM_0A_3, as compared to that of CSM_0A_0 when water is used as solvent. On the contrary, the situation is completely the reverse when toluene or xylene is used as solvent in the swelling test. In this case, CSM_3A_0 & CSM_0A_3 show inferior resistance against swelling in contrast to that of CSM_0A_0. It appears that the presence of Basyntan FB6 (a synthetic tanning agent based on melamine-formaldehyde condensate) in CSM_3A_0 reduces the hydrophilicity of the sample in contrast to that of CSM_0A_0 which is devoid of Basyntan FB6 (Table 1). Since, the solubility of melamine in water at 20 ^oC is about 0.3 g per 100 ml (just 0.3%), the solubility of Basyntan FB6 in water is very low. Therefore, the incorporated melamine-formaldehyde (m-f) molecules can reduce the intimate interaction possibilities between water and collagen in CSM_3A_0. However, such interaction between water and collagen would not be affected in CSM_0A_0 in the absence of m-f macromolecules. In fact, bulky macromolecules of m-f are unable to penetrate deep inside the collagen matrix, and hence remain mainly at or near proximity of the crust surface. In this way, these macromolecules can function as a potential barrier against the movement of water molecules from the surroundings to the interior part of the system. Besides, m-f macromolecules can have the capacity to get attached with the polypeptide chains of the collagen in the following manner:

1. 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 [Fig. 3].

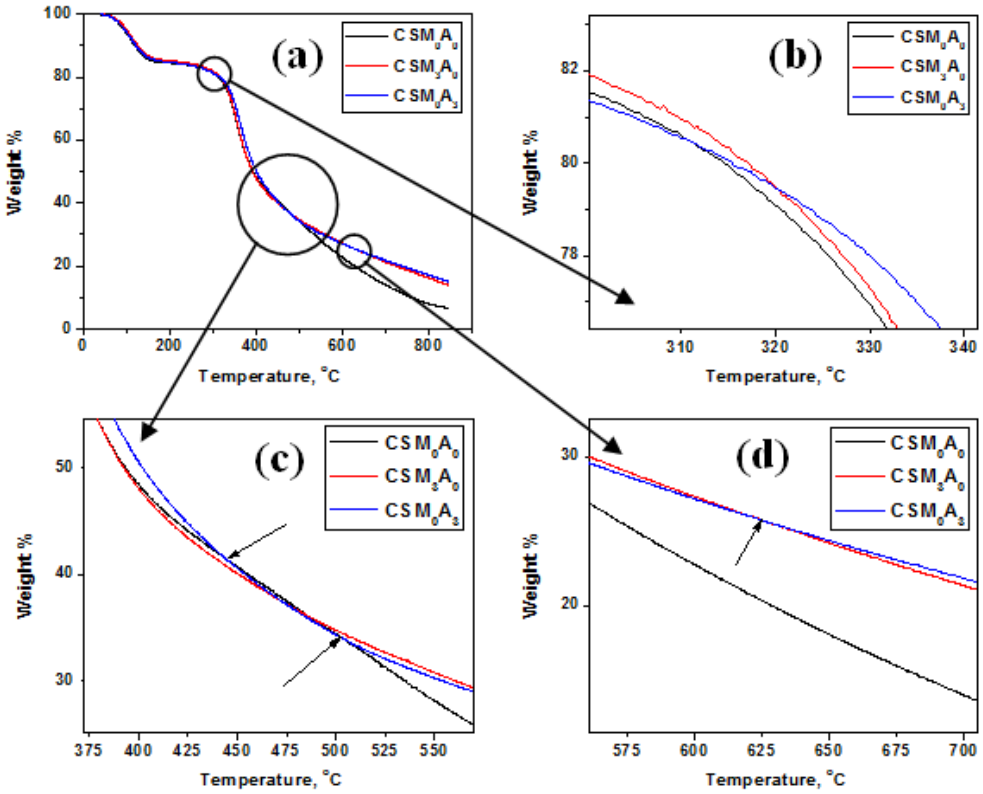

Fig. 2. TGA results of the samples CSM_0A_0, CSM_3A_0, and CSM_0A_3

2. H-bonding interactions between terminal methylol groups of m-f macromolecules and suitable sites of polypeptide chains (e.g. > C=O group of amide linkage) [18] [Fig. 3].
3. London- Van-der-Waals forces involving π orbitals of the both heterocyclic part of m-f macromolecule and of amide linkages of collagen polypeptide chains.

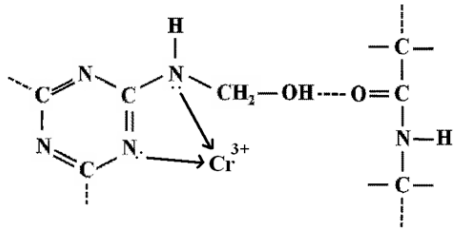

Fig. 3. The possible interaction of melamine with collagen chains through chelation involving Cr^{3+} of chrome complex and H-bonding

Thus, the added m-f macromolecules may interact strongly with polypeptide chains thereby resisting the incoming water molecules to get attached with collagen as the hydrophilicity of collagen has been dropped substantially owing to partial blockade of the hydrophilic moiety of polypeptide chains by m-f macromolecules. In case of CSM_0A_3, the swelling index becomes further less than that of CSM_3A_0 (Table 5). This can be possible as the added Relugan RF (a synthetic tanning agent base on polyacrylate) bears the $–COO^-$ groups that can be involved in the co-ordinate bonding with Cr^{3+} central metal ion of the olated Cr-complex. The possibility of extra crosslink formation is highly feasible as more than one $–COO^-$ groups of polyacrylate macromolecule possibly involve themselves as ligands of two or more different Cr^{3+} central metal ions of olated Cr-complexes as depicted in Fig. 4.

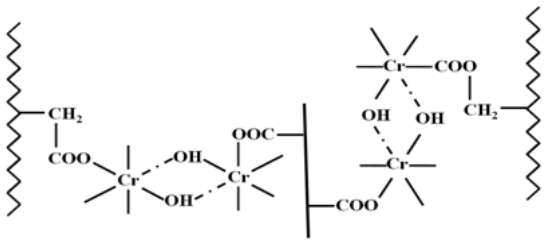

Fig. 4. possibility of Crosslinks between polyacrylates and polypeptide chain of cow collagen

Thus, formation of extra crosslink involving coordinate bonds can be possible in both CSM_0A_3 and CSM_3A_0, which is unlikely in the control sample. These linkages are much stronger than that of interactions originating from H-bonding or London-Van-der-Waals forces. It can be noted that the resistance of CSM_0A_3 against aqueous swelling is superior to that of other samples which has already been reflected in their respective swelling indices (Table 5). As compared to CSM_3A_0, the greater resistance against swelling in CSM_0A_3 can be attributed to the stronger coordination linkage formation involving much strong ligand (i.e. $–COO^-$). Moreover, in addition to the stable 5-6 membered chelated ring, formation of a few four membered chelated ring (Fig. 3) in CSM_3A_0 may further reduces the overall stability of crosslinks.

Swelling measurements were also utilized to determine the crosslinking density of all the 3 samples as reported in table 5. The Flory–Rhener equation (eqn 5) can be used to estimate the crosslinking density as

$$\ln(1-v_2) + v_2 + \chi v_2^2 = -V_0 n_c \left(v_2^{1/3} - \frac{v_2}{2}\right) \quad (5)$$

Table 4. Percentage of sample remained at different temperatures

Sample name	Percentage of sample remained at different temperatures									DTG peak (°C)
	100°C	251°C	320°C	330°C	380°C	444°C	471°C	485°C	840°C	
CSM_0A_0	94.15	83.65	79.07	76.92	54.13	41.48	37.93	36.12	6.80	338.4
CSM_3A_0	94.40	84.27	79.45	77.28	54.13	40.84	37.57	36.12	14.3	341.7
CSM_0A_3	95.05	83.65	79.45	77.98	57.46	41.48	37.57	35.89	15.26	346.6

Table 5. Swelling-deswelling results of the samples in three different solvents (at 25 °C) after 72 h

Sample	Solvent	Weight (g)			Thickness (mm)*			Swelling index (S) #	Crosslink density
		Initial	Swelled	Deswelled	Initial	Swelled	Deswelled		
CSM_0A_0	Water	0.3890	0.8619	0.3865	1.65-1.67	1.85-1.86	1.67-1.69	1.215681	0.001877
	Toluene	0.4236	0.6960	0.3827	1.65-1.67	1.73-1.75	1.72-1.74	0.643059	0.000681
	Xylene	0.4235	0.7050	0.3434	1.65-1.67	1.67-1.68	1.67-1.68	0.664699	0.00079
CSM_3A_0	Water	0.3893	0.8134	0.3997	1.54-1.55	1.68-1.70	1.57-1.59	1.089391	0.002121
	Toluene	0.4017	0.6995	0.3990	1.55-1.56	1.55-1.57	1.55-1.57	0.741349	0.000615
	Xylene	0.3992	0.6921	0.3963	1.56-1.58	1.56-1.58	1.56-1.58	0.733717	0.000741
CSM_0A_3	Water	0.3697	0.7415	0.3765	1.33-1.35	1.46-1.48	1.35-1.37	1.00568	0.002308
	Toluene	0.3484	0.6062	0.3705	1.33-1.35	1.34-1.36	1.34-1.36	0.739954	0.000616
	Xylene	0.3730	0.6413	0.3738	1.36-1.38	1.38-1.40	1.38-1.40	0.719303	0.000751

#Swelling indices have been calculated based on the following formula:

$$\text{Swelling index } (S) = \frac{\text{Swelled weight of the sample - Initial weight of the sample}}{\text{Initial weight of the sample}}$$

where ϕ_f is the volume fraction of crosslinked collagen (cow leather) in the swollen mass, V_0 is the molar volume of the solvent, χ is the Flory–Huggins polymer–solvent interaction term, and n_c is the physical degree of crosslinking.

Here, ϕ_f was calculated using the following expression:

$$\frac{1}{\phi_f} = 1 + \frac{W_S}{W_i}\frac{\rho_f}{\rho_s} \quad (6)$$

where W_i and W_S are the weights of the leather sample in air and in swollen state, respectively. ρ_s and ρ_f are the densities of the solvent and the cow leather (~0.9 $g.cm^{-3}$), respectively. Since, at equilibrium, For water V_0 is ~18, ρ_s =1.0 ($g.cm^{-3}$) and χ=0.49 (assumed), for toluene V_0 is ~106.2, ρ_s=0.867 ($g.cm^{-3}$) and χ=0.39 (assumed) and for xylene V_0 is ~122.03, ρ_s=0.87 ($g.cm^{-3}$) and χ=0.29 (assumed).

In water, the crosslink densities calculated using Flory–Rhener equation can be found in the following order: CSM_0A_3 > CSM_3A_0 > CSM_0A_0 [Table 5], which exactly identical to the order found in the model fitment results of tensile properties [Table 2]. On the contrary, in toluene and xylene, the calculated crosslink densities are observed to be much lesser in all the samples. In fact, the highest resistance against solvent (toluene and xylene) swelling can be noted in the control sample. Such observation reestablishes the increased lyophilicity for syntan treated samples as hydrophilic groups (i.e. $–COO^-$ and $-NH_2$) are already involved in the crosslink formation. Therefore, the leftover hydrophobic groups in syntan treated samples effectively contribute in the increased hydrophobicity of the samples. In this regard, the melamine formaldehyde treated sample shows reduced crosslink density as compared to CSM_0A_3. This can be possible as the π orbitals of toluene and xylene may interact with the orbitals of both melamine and collagen, and thus it can interfere and weaken the London-Van-der-Waals forces already existing between melamine formaldehyde and collagen.

Boiling test

All the samples are undergone the boil test and the extent of deformations in the samples after boiling have been measured with the help of image analyses of the respective photographs of the deformed samples. Results of the image analyses have been recorded in Table 6. It has been observed that shrinkage has not occurred in any sample after boiling for 3 min. CSM_0A_0 has been shrinked to 95.7 % of its initial area after 5 boiling, and has been further shrinked to 80 % after 6.5 min boiling [Table 6].

Table 6. Boiling characteristics of all the samples in boiling water

Sample	% Shrinkage/ Swelling			
	At t =0 min	After 3 min.	After 5 min.	After 6.5 min.
CSM_0A_0	0	0	4.3 (Shrinkage)	20 (Shrinkage)
CSM_3A_0	0	0	10 (Swelling)	5 (Shrinkage)
CSM_0A_3	0	0	5 (Swelling)	15 (Swelling)

Interestingly, CSM_3A_0 has not shrinked but swelled to 110 % after 5 min, and thereafter shrinked to 95% after 6.5 min boiling. On the other hand, CSM_0A_3 has not shrinked at all within any time period. In fact, CSM_0A_3 has swelled to 105% after 5 min boiling, and the extent of swelling has increased to 115% after 6.5 min boiling [Table 6]. For CSM_3A_0 and CSM_0A_3, the resultant swelling rather than shrinkage after 5 min boiling indicates that crosslinks, initially present in the samples, remain intact up to this particular time period of boiling. As the boiling time is further increased to 6.5 min, crosslinks present in CSM_3A_0 may have partially ruptured as the crosslinks in CSM_3A_0 are altogether weaker in nature in comparison to those of CSM_0A_3. Thus, the continuity in swelling in CSM_0A_3 irrespective of elapsed time period reaffirms the superiority of CSM_0A_3 over CSM_3A_0 in terms of

strength of crosslinks, crosslink density and associated thermal resistance as well as mechanical strengths.

Conclusions

On the basis of above observations, the resultant conclusions can be the following:

1. At lower concentration (3 %), polyacrylate based syntans form stronger and higher crosslinks than that of melamine formaldehyde based syntans with Cr tanned bovine leather.
2. Advantages for polyacrylate based syntans in terms of crosslinks are well reflected in all the experimental finding, such as, crosslinking density value (derived by Mooney-Rivlin eqn., Flory-Rehner eqn.), larger value of constant *A* (derived from MRS equation), DTG temperature, residue formation, higher resistances to ambient swelling and boil test.
3. The value of constant *A* for MRS theoretical model, in case of cow leather should lie in the range of 0.9-1.0.

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