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### EFFECT OF ACRYLIC AND MELAMINE-FORMALDEHYDE BASED SYNTANS IN THERMO-MECHANICAL AND HYDRODYNAMIC BEHAVIOR OF CHROME TANNED BOVINE LEATHER- A COMPARATIVE ASSESSMENT

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#### ABSTRACT

Three different samples of cow softy leather (i.e. CSM0A0, CSM3A0 and CSM0A3) were prepared from a chrome tanned cow wet blue of Indian origin. CSM0A0 was the control sample wherein neither melamine formaldehyde based nor polyacrylate based syntan was added. CSM3A0 and CSM0A3 had 3% melamine formaldehyde based and 3% polyacrylate based syntan, respectively in addition to the other common auxiliaries used in all three samples. Other unit operations (physical and chemical) for manufacturing leather were maintained same in all the three samples. Thermal, mechanical and hydrodynamic swelling behavior of these three samples was studied, and tried to be correlated with the crosslinking densities of the samples. The hydrodynamic swelling behavior was studied in three different solvents (e.g. water, toluene and xylene) assuming definite solvent-bovine collagen interaction parameters, and crosslink densities were 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)) were tried to be fit with the experimental results obtained in stress-stain analyses. In this process, few constants for cow Cr tanned leather were derived as value of constant A in MRS equation remained in the range of 0.9-1.0 and value of constant B in Flory's equation remained in the range of 0.001-0.003, which were earlier not reported in the literature. From all the performed experimentations, it was found that polyacrylate based syntans formed better crosslinks (calculated crosslinking density  $6.02 \times 10^{-3} \text{ Mol.m}^{-3}$ ) with chrome tanned bovine leather in comparison to melamine formaldehyde based syntans (calculated crosslinking density  $2.61 \times 10^{-3} \text{ Mol.m}^{-3}$ ) and subsequently provided better thermal and solvent resistance as well the tensile strength to leather.

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#### 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 (Milašienė et al., 2007), time, rate of stressing, pressure, type of deformation, moisture content, stress and strain amplitude, thermal history etc.) which affect mechanical behavior (Nielsen et al., 1994). Among the mechanical tests, stress-strain tests are traditionally the most popular and are most widely used as these tests indicate the modulus, strength and toughness of the material. As per the prediction of kinetic theory, the modulus of the material increases as the degree of crosslinking increases (Treloar 1956; Flory, 1953). In this regard, the breaking stress should also be directly proportional to cross link density. Moreover, various kinds of imperfections in the crosslinked network structure can change the stress-strain behavior of crosslinked material (Ferry, 1980; Soper et al., 1972; Tonelli, 1974; Andrady, 1981). The modulus may not be lowered by these imperfections, but the tensile strength and ultimate elongation may be greatly reduced. Literature (Case, 1960; Case et al., 1964; Mark, 1982, 1985), have reported 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 (Mark,



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1982, 1985; French, 1972; Mark et al., 1984) 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. Crosslinking has 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 (Charulatha, 2003). 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 (Langmaier et al., 2005). 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 (Grim, 1942; Melinda et al., 2011) and acrylic based resins (George, 1940) are well established as synthetic tanning agents in the field of leather manufacture. Basically, Melamine is a nitrogen-rich heterocyclic triazine used primarily in the synthesis of melamine-formaldehyde resins (MFR) for the manufacture of laminates, plastics, coatings, commercial filters, glues or adhesives, and moulding compounds (Tolleson et al., 2008). 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 was 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, was attempted to fit with the different theoretical models available in the literature

## EXPERIMENTAL

### 2.1 Materials

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  $\approx$  99.5%] and Xylene [density (at 20 oC) = 0.85-0.87, purity  $\approx$  99.5%], used as swelling solvents, were purchased from Merck Specialties Private Limited, Mumbai, India.

### 2.2 Preparation of samples

Three samples (i.e. CSM0A0, CSM3A0 and CSM0A3) were prepared following the generalized unit operations for leather manufacturing from wet blue to crust (Figure 1), based on the recipes shown in Table 1. The following unit operations were followed in series one after the another: (a) soak back (for rehydration of wet blue), (b) rechroming (for increasing chrome content), (c) basicification (for fixation of added chromium compound), (d) neutralization (for removing free acids and acquiring desired pH level for subsequent operations), (e) dyeing (for imparting color), (f) retanning (for reinforcing and filling), (g) fatliquoring (for desired lubrication of polypeptide chains) and (h) fixing (for improving bondage of the added ingredients with the collagen substrate) as the last wet end operation. CSM0A0 (control sample) was devoid of both relugan RF (a polyacrylate based syntan) and Basyntan FB6 (a melamine formaldehyde based syntan). In the preparation of CSM3A0 and CSM0A3, 3% Basyntan FB6 and 3% Relugan RF was added, respectively, in addition to the other auxiliaries used in all the samples in different unit operations. After sammying (for removal of physically adhered water from the substrate), setting (for leveling the grain side of the substrate) and drying (for reducing water content of the substrate to  $\sim$  10 %) operations, crust leather of all three samples were prepared.

## 2.2 Characterization

### 2.2.1 Mechanical properties

The mechanical behavior including the crosslinking density of the samples was investigated by the tensile test. Initially, all the samples were conditioned at 25 oC and  $65 \pm 2\%$  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



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Equipment, Surrey, England) maintaining a crosshead speed of 10 inch.min<sup>-1</sup> on 100 kg load at 25 oC. For each sample, the averages of five tests were reported. The force-elongation curve was plotted with Lab Tensile software, from which the tensile strength and elongation percentage were calculated. In each case, the error corresponding to tensile modulus, tensile strength, EB measurement was limited to ± 1 %, ± 2 %, ± 2 %, respectively.

### 2.2.2 Thermogravimetric analyses (TGA)

The thermal stability of samples were studied through thermogravimetric analyzer (model: Pyris 6 TGA manufactured by Perkin-Elmer instruments, the Netherlands) [Cañdenasa et al., 2000; Santhosh et al., 2006]. 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<sup>-1</sup>. The data of the weight loss versus temperature were recorded in the software.

### 2.2.3 Swelling test

Test specimens of circular diameter of 32 mm (approx.) were cut from the molded slab. These samples were weighed accurately before 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 in glass-stoppered bottle after removing surface fluid by blotting with filter paper (Biswas et al., 2010). Finally, these were allowed to dry in a vacuum oven to a constant weight.

### 2.2.4 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 32 mm (approx.) diameter of all the samples were cut out and immersed in the boiling water (at 100 oC). These were kept in the boiling water for above 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

### 3.1 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 (Treloar, 1956; Mooney, 1940; Rivlin et al., 1951; Flory, 1976; Flory et al., 1982; Martin et al., 1956). It is well established that Mooney-Rivlin (Mooney, 1940; Rivlin et al., 1951) equation (eqn. 1) is suitable for incompressible or slightly compressible materials wherein the material is quite insensitive to small volume change).

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

where,  $\lambda$  = extension ratio (extended length/original length),  $\sigma$  = 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 (Mooney, 1940; Rivlin et al., 1951) equation (eqn. 1), Flory's (Flory, 1976; Flory et al., 1982) equation (eqn. 2) and MRS (Martin et al., 1956) equation (eqn. 3) was fitted with the experimental results of three samples within a limit of 25% to 60 % strain and resulted in the representative plot as per Figure 2a, 2b, 2c. Almost straight line was obtained for all the samples. Here,  $C_1$  value was calculated from the intercept and constant  $C_2$  value from the slope of the straight line curve. Although literature (Rivlin et al., 1952; Treloar, 1944) 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-

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

where  $R = 8.314 \text{ J.deg}^{-1}.\text{mole}^{-1}$ ,  $T = 298 \text{ K}$ ,  $N_c$  is cross-linking density (moles.m<sup>-3</sup>) 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-



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

where  $A = \text{constant}$

Eqn. 2 and eqn. 3 also fit well to the experimental findings within our experimental range of strain. The calculated values for constant  $B$  from Flory's equation and constant  $A$  from MRS equation was reported in Table 2. This was safely concluded that value of constant  $B$  for Cr tanned cow leather remains in the range of 0.001-0.003 and value of constant  $A$  remains in the range of 0.9-1.0.

The cross-linking density values of all the samples, were evaluated from the calculated  $C_I$  values based on the following equation as reported in Table 2:

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

It was 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 as depicted in Figure 3 (Virginija et al., 2012). On the other hand, in  $CSM_3A_0$ , the added melamine based syntan bears basic amino groups ( $-NH_2$ ) which may form 4 membered chelated rings involving the  $Cr^{3+}$  [Figure 4 (a)], and in this process, weaker crosslinks might be generated in comparison to  $CSM_0A_3$  [Figure 3]. 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 (Xiu-Lian et al., 2005), but such interactions are weaker in nature in comparison to polyacrylate interactions with collagen.

It is also a well established fact that % EB decreases with increase in cross-linking density. It was noted that in comparison to  $CSM_0A_0$ , the cross-linking density slightly increased in  $CSM_3A_0$ , but % EB decreased. Therefore, it can be presumed that the melamine based crosslinks are physical crosslinks which allow the chain slippage in  $CSM_3A_0$ , which was evident in the respective high EB values. On the contrary, in  $CSM_0A_3$ , the substantially increased crosslink density value was reflected in its higher modulus values [Table 2].

### 3.2 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 Figure 5 (a), (b), (c), (d).

It was observed that within 150-320 °C, the degradation profiles of all the samples were almost similar in nature. The gentle and flat nature of the TGA curve within this particular range indicates considerable thermal resistance of the samples. Within the temperature range ~315-480 °C, all the samples started degrading steeply. Table 3, Table 4 and Figure 5 (b), 5(c) clearly shows the fact that as the temperature was increased from ~315 °C to 480 °C, the undegraded polymer proportion was drastically dropped from 80 % to a mere 35.8 %. Moreover, it was clearly noted that  $CSM_3A_0$  initially (up to ~ 320 °C) [Tolleson, 2008] showed 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 was increased beyond 320°C, the degradation of 'melam' / 'melon' took place (Costa et al., 1988; Shin Ono et al., 1998). It is well established that 'melam' / 'melon' possesses a remarkable thermal resistance, which eventually degrades further in three stages (Costa et al., 1988). Figure 5 (d) enumerates the crossing over of the plots corresponding to  $CSM_3A_0$  and  $CSM_0A_3$  at around 615-620 °C. In this context, it is reported by earlier workers that above ~ 620 °C, the melamine condensate undergoes thermal degradation with quantitative formation of volatile products (Costa et al., 1988). Therefore, the drop in heat resistance for  $CSM_3A_0$  with respect to  $CSM_0A_3$  can be attributed to aforementioned effect. It was also observed that as compared to other samples, the control sample ( $CSM_0A_0$ ) suddenly started deteriorating at around ~ 490-500 °C, 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 °C [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 °C because it contains transitional metal based poly acrylates which generally melts at around 425-485 °C (Sadeghi, 2005). 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.

### 3.3 Swelling

The swelling behavior of the three samples  $CSM_0A_0$ ,  $CSM_3A_0$  and  $CSM_0A_3$  is reported in Table 5.  $CSM_3A_0$  &  $CSM_0A_3$  show the increased resistance against swelling or the reduced swelling indices as compared to that of  $CSM_0A_0$  when water is used as solvent [Table 5]. 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 °C is about 0.3 g /100 ml (just 0.3%) [OECD, SIDS, 2007], 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 [Figure 4 (a), (b)].
2. H-bonding between terminal methylol groups of m-f macromolecules and suitable sites of polypeptide chains (e.g.  $>C=O$  group of amide linkage) [Melinda et al., 2011] (Figure 4).
3. London- Van-der-Waals forces involving  $\pi$  orbitals of the both heterocyclic part of m-f macromolecule and of amide linkages of collagen polypeptide chains (Xiu-Lian et al., 2005).

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 became 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 (Virginija et al., 2012). 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 (Figure 3).

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. 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 strong ligand (i.e.  $-COO^-$ ). Moreover, in addition to six membered chelated rings [Figure 4 (b)], possible formation of a few four membered chelated rings [Figure 4 (a)] in  $CSM_3A_0$  may further reduce 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

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

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

Here,  $\phi_r$  was calculated using the following expression:

$$\frac{1}{\phi_r} = 1 + \frac{W_s \times \rho_r}{W_i \times \rho_s} \quad (6)$$

where  $W_i$  and  $W_s$  are the weights of the leather sample in air and in swollen state, respectively.  $\rho_s$  and  $\rho_r$  are the densities of the solvent and the cow leather ( $\sim 0.9 \text{ g.cm}^{-3}$ ), respectively. The reported value of collagen-water Flory-Huggins interaction parameter  $(\chi)_{CW}$  is  $0.49 \pm 0.05$  (Troy, 2009), Collagen-toluene Flory-Huggins interaction parameter  $(\chi)_{CT}$  and collagen-xylene Flory-Huggins interaction parameter  $(\chi)_{CX}$  was assumed based on the theoretical calculations as below-

Hoy's solubility parameters ( $\square$ ) for type I dentin collagen (containing 70% collagen and 30% water), i.e.  $\square_c$  is  $34.6 \text{ (J.cm}^{-3}\text{)}^{1/2}$ , and for type I dentin collagen (containing 90% collagen and 10% water),  $\square_c$  is  $30.8 \text{ (J.cm}^{-3}\text{)}^{1/2}$  [Code et al., 2003, Pashley et al., 2007]. Since leather hide contain 30% collagen (Buljan et al., 1998), so  $\square_c$  may be safely assumed as  $\sim 40.0 \text{ (J.cm}^{-3}\text{)}^{1/2}$ . Hoy's solubility parameters for water ( $\square_w$ ), toluene ( $\square_t$ ) and Xylene ( $\square_x$ ) are known to be at  $48 \text{ (J.cm}^{-3}\text{)}^{1/2}$ ,  $18.2 \text{ (J.cm}^{-3}\text{)}^{1/2}$  and  $18.0 \text{ (J.cm}^{-3}\text{)}^{1/2}$ , respectively. The Flory-Huggins solution theory uses  $\square$  to determine whether two polymers (A and B) will be miscible or not, and can be expressed by eqn. (7) [Beth et al., 2003]:

$$(\chi)_{AB} = [V_{ref}(\square_A - \square_B)^2]/RT \quad (7)$$

In this equation,  $V_{ref}$  is an appropriate chosen reference volume ( $\text{cm}^3.\text{mol}^{-1}$ ), and  $R$  is the universal gas constant ( $\text{J. mol}^{-1}.\text{K}^{-1}$ ). So for a particular polymer, at particular reference volume and fixed temperature,  $(\chi)_{AB}$  will be proportional to  $(\square_A - \square_B)^2$ . Thus, for collagen water system,  $(\chi)_{CW} = k(\square_C - \square_W)^2$ , where  $k$  is constant. Since,  $(\chi)_{CW} = 0.49$  (Troy, 2009),  $\square_w = 48 \text{ (J.cm}^{-3}\text{)}^{1/2}$ ,  $\square_c = 40 \text{ (J.cm}^{-3}\text{)}^{1/2}$ , the constant  $k$  for would be simply evaluated as  $0.00765625$ . This  $k$  value can be utilized to find out Collagen-toluene Flory-Huggins interaction parameter,  $(\chi)_{CT}$ , from the relation  $(\chi)_{CT} = k(\square_C - \square_T)^2$ , where  $\square_C = 40 \text{ (J.cm}^{-3}\text{)}^{1/2}$  and  $\square_T = 18.2 \text{ (J.cm}^{-3}\text{)}^{1/2}$ . In this way, the value obtained for  $(\chi)_{CT}$  is  $3.638$ . In the similar fashion, the value obtained for collagen-xylene Flory-Huggins interaction parameter  $(\chi)_{CX}$  is  $3.705$ .

Since, at equilibrium,  $V_0$  for water is  $\sim 18$ ,  $\rho_s = 1.0 \text{ (g.cm}^{-3}\text{)}$ , for toluene  $V_0$  is  $\sim 106.2$ ,  $\rho_s = 0.867 \text{ (g.cm}^{-3}\text{)}$  and for xylene  $V_0$  is  $\sim 122.03$ ,  $\rho_s = 0.87 \text{ (g.cm}^{-3}\text{)}$ .

With the calculated values  $(\chi)_{CW}$ ,  $(\chi)_{CT}$  and  $(\chi)_{CX}$ , Crosslinking density in all the three systems (collagen-water, collagen-toluene, collagen-xylene) for all the samples were calculated using Flory-Rhener equation (eqn. 5 and eqn. 6). In water, the crosslink densities calculated can be found in the following order:  $\text{CSM}_0\text{A}_3 > \text{CSM}_3\text{A}_0 > \text{CSM}_0\text{A}_0$  [Table 5], which exactly identical to the order found in the model fitment results of tensile properties [Table 2]. The highest resistance against solvent (toluene and xylene) swelling can be noted in the control sample. Such observation reestablishes the increased lyophilicity for sytan treated samples as hydrophilic groups (i.e.  $-\text{COO}^-$  and  $-\text{NH}_2$ ) are already involved in the crosslink formation. Therefore, the leftover hydrophobic groups in sytan 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  $\text{CSM}_0\text{A}_3$ . This can be possible as the  $\pi$  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.

### 3.4 Boiling test

All the samples were undergone the boil test and the extent of deformations in the samples after boiling were 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 was observed that shrinkage has not occurred in any sample after boiling for 3 min.  $\text{CSM}_0\text{A}_0$  was shrunked to 95.7 % of its initial area after 5 boiling, and further shrunked to 80 % after 6.5 min boiling [Table 6]. Interestingly,  $\text{CSM}_3\text{A}_0$  did not shrunked but swelled to 110 % after 5 min, and thereafter shrunked to 95% after 6.5 min boiling. On the other hand,  $\text{CSM}_0\text{A}_3$  did not shrunked at all within any time period. In fact,  $\text{CSM}_0\text{A}_3$  got swelled to 105% after 5 min boiling, and the extent of swelling was increased to 115% after 6.5 min boiling [Table 6]. For  $\text{CSM}_3\text{A}_0$  and  $\text{CSM}_0\text{A}_3$ , the resultant swelling rather than shrinkage after 5 min boiling indicates that crosslinks, initially present in the samples, remain intact up to that particular time period of boiling. As the boiling time was further increased to 6.5 min, crosslinks present in  $\text{CSM}_3\text{A}_0$  may have partially ruptured as the crosslinks in  $\text{CSM}_3\text{A}_0$  are altogether weaker in nature in comparison



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to those of CSM<sub>0</sub>A<sub>3</sub>. Thus, the continuity in swelling in CSM<sub>0</sub>A<sub>3</sub> irrespective of elapsed time period reaffirms the superiority of CSM<sub>0</sub>A<sub>3</sub> over CSM<sub>3</sub>A<sub>0</sub> in terms of strength of crosslinks, crosslink density and associated thermal resistance as well as mechanical strengths.

### CONCLUSION

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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*Table 1: Recipes of different cow softy samples*

Unit Operation	Ingredients	Samples* (ingredients in %)			Time (min)	Remarks
		CSM <sub>0</sub> A <sub>0</sub>	CSM <sub>3</sub> A <sub>0</sub>	CSM <sub>0</sub> A <sub>3</sub>		
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		
Bacification	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	
Neutralization	Water	150	150	150	10	
	Sodium formate	2	2	2		
Drain/Wash					10	Check pH = 4.8
Dyeing & Retanning	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 °C)**

Samples	Stress at different strain levels (MPa)			Tensile strength (MPa)	Elongation at break (%)	$C_1^*$	Crosslinking density ( $\times 10^{-3}$ ) Mol. m <sup>-3</sup>	$C_2$	Calculated values of constant $B$ from Flory Equation	Calculated values of constant $A$ from MRS Equation
	10 %	20 %	30 %							
CSM <sub>0</sub> A <sub>0</sub>	1.24	3.11	5.21	26.68	88.60	3.209	2.59	0.007	0.0022	0.962
CSM <sub>3</sub> A <sub>0</sub>	1.28	3.16	5.33	31.93	95.40	3.239	2.61	0.009	0.0027	0.966
CSM <sub>0</sub> A <sub>3</sub>	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 %)

**Table 3: Thermal degradation characteristics of all the samples**

Sample	Temperature, °C			
	95%	75%	50%	25%
CSM <sub>0</sub> A <sub>0</sub>	95.62	336.19	393.18	578.30
CSM <sub>3</sub> A <sub>0</sub>	100.29	337.19	392.28	637.38
CSM <sub>0</sub> A <sub>3</sub>	96.89	342.44	401.84	638.13

**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 <sub>0</sub> A <sub>0</sub>	94.15	83.65	79.07	76.92	54.13	41.48	37.93	36.12	6.80	338.4
CSM <sub>3</sub> A <sub>0</sub>	94.40	84.27	79.45	77.28	54.13	40.84	37.57	36.12	14.3	341.7
CSM <sub>0</sub> A <sub>3</sub>	95.05	83.65	79.45	77.98	57.46	41.48	37.57	35.89	15.26	346.6

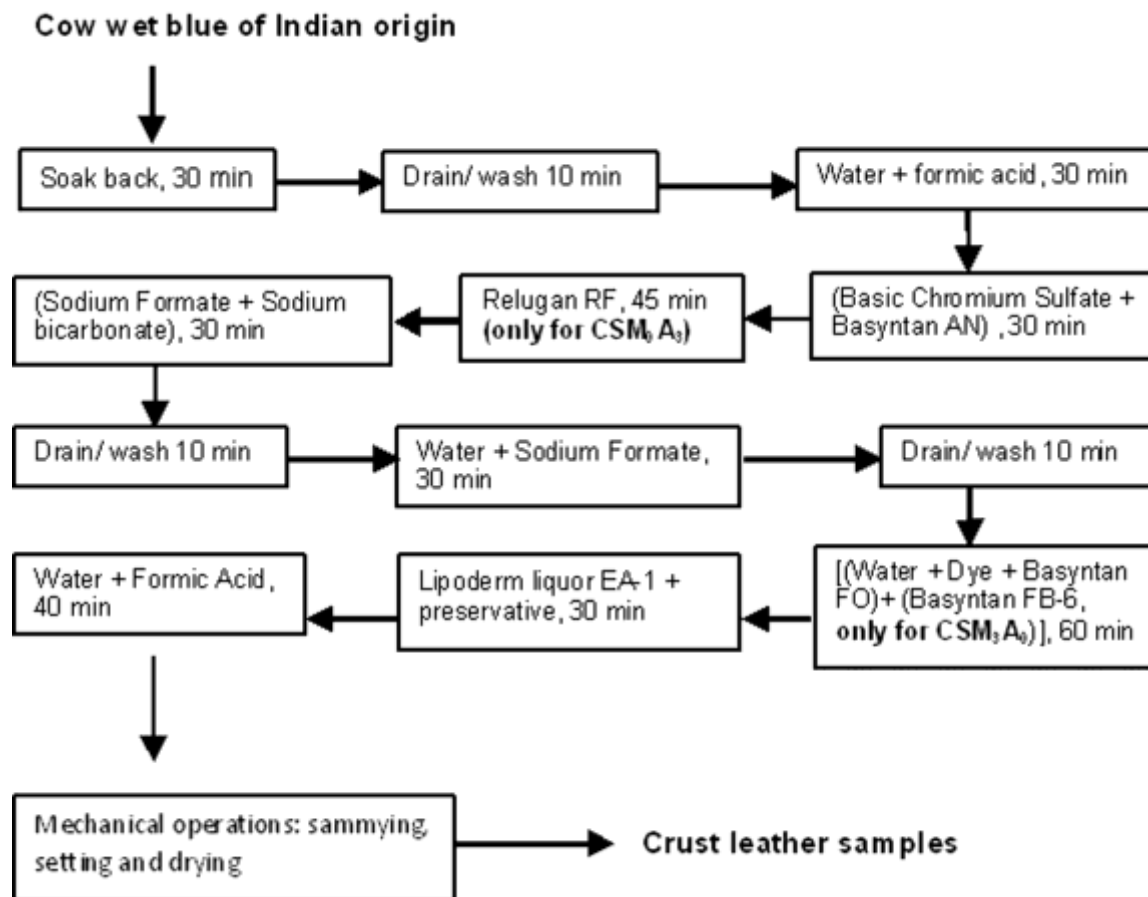
**Table 5: Swelling-deswelling results of the samples in three different solvents (at 25 °C) after 72 h**

Sample	Solvent	Weight (g)			Thickness (mm)*			Swelling index (S) #	Crosslink density
		Initial	Swelled	Deswelled	Initial	Swelled	Deswelled		
CSM <sub>0</sub> A <sub>0</sub>	Water	0.3890	0.8619	0.3865	1.65-1.67	1.85-1.86	1.67-1.69	1.215681	0.00187
	Toluene	0.4236	0.6960	0.3827	1.65-1.67	1.73-1.75	1.72-1.74	0.643059	0.00716
	Xylene	0.4235	0.7050	0.3434	1.65-1.67	1.67-1.68	1.67-1.68	0.664699	0.00630
CSM <sub>3</sub> A <sub>0</sub>	Water	0.3893	0.8134	0.3997	1.54-1.55	1.68-1.70	1.57-1.59	1.089391	0.00212
	Toluene	0.4017	0.6995	0.3990	1.55-1.56	1.55-1.57	1.55-1.57	0.741349	0.00669
	Xylene	0.3992	0.6921	0.3963	1.56-1.58	1.56-1.58	1.56-1.58	0.733717	0.00601
CSM <sub>0</sub> A <sub>3</sub>	Water	0.3697	0.7415	0.3765	1.33-1.35	1.46-1.48	1.35-1.37	1.00568	0.00230
	Toluene	0.3484	0.6062	0.3705	1.33-1.35	1.34-1.36	1.34-1.36	0.739954	0.00670
	Xylene	0.3730	0.6413	0.3738	1.36-1.38	1.38-1.40	1.38-1.40	0.719303	0.00607

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**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 <sub>0</sub> A <sub>0</sub>	0	0	4.3 (Shrinkage)	20 (Shrinkage)
CSM <sub>3</sub> A <sub>0</sub>	0	0	10 (Swelling)	5 (Shrinkage)
CSM <sub>0</sub> A <sub>3</sub>	0	0	5 (Swelling)	15 (Swelling)



*Figure 1: Flowchart showing the sample preparation process*

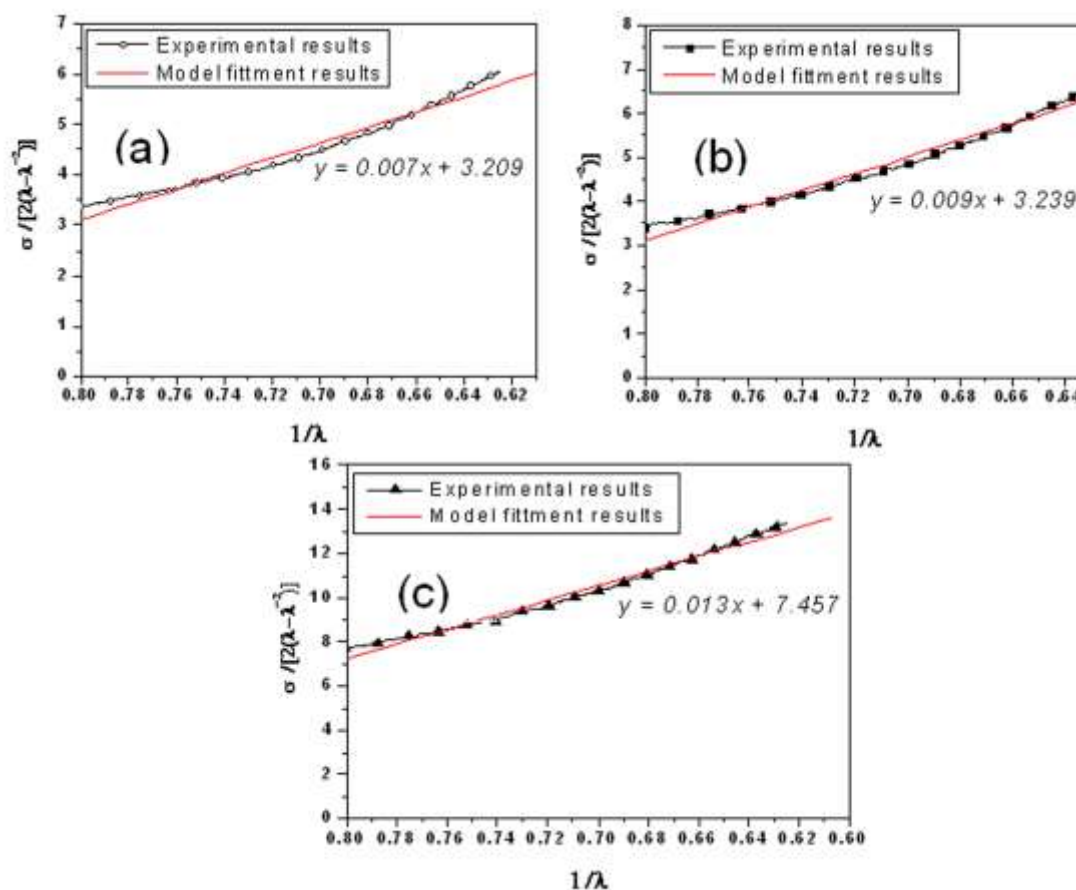


Figure 2: Representative fitting plot of Samples (a) CSM<sub>0</sub>A<sub>0</sub> (b) CSM<sub>3</sub>A<sub>0</sub> (c) CSM<sub>0</sub>A<sub>3</sub>.

Figure 3: Possible representation of a typical crosslink between polyacrylates and polypeptide chain of cow collagen.

Figure 4: The possible interaction of melamine with collagen chains through H-bonding and chelation rings involving Cr<sup>3+</sup> of chrome complex

having (a) 4 membered ring (unstable), (b) 6 membered ring (stable).

5. Figure 5: TGA plots of the samples CSM<sub>0</sub>A<sub>0</sub>, CSM<sub>3</sub>A<sub>0</sub>, and CSM<sub>0</sub>A<sub>3</sub>, depicting (a) complete temperature range (RT to 850 °C), (b) crossing over of plots ~ 320 °C, (c) crossing over ~ 425 – 480 °C, (d) crossing over ~ 625 °C