Thermal Sensitive Agents for Making Stimuli Responsive Leathers

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Abstract

Herein, we report the synthesis and application of a smart polymeric acrylic syntan (synthetic tanning material), which can respond to temperature and pH. Behavior of polymer at different pH (1-10) at room temperature (28°C) was studied. Also interactions with collagen were ascertained in order to understand the polymers' response towards secondary structures of collagen. Leather made using the experimental syntan demonstrated higher temperature resistance of 3±0.5°C compared to control syntan treated leathers (1±0.5°C) when exposed to heat under artificial simulation. Experimental leathers exhibited better strength and organoleptic properties. These smart leathers find its application in extreme climatic conditions of heat or cold.

Introduction

Skin is very sensitive towards stimuli and plays an important role in protection from extremes of environment, its sensitisation to multitude of senses such as light, temperature, pain and perspiration making it a smart material.[1-3] Skin from a flayed animal is susceptible to autolysis hence skin needs to be tanned to leather in order to prevent from putrefaction.[4] Skin is a thermoregulatory machine of own; when converted into leather, its thermal sensing capability is lost as it cannot maintain homeostasis. In order to regain some functionality of responsiveness, skin needs to be treated with certain smart chemicals during leather processing.

The conventional tanning method limits the physical properties of the final leather. This limited functionality is due to the type of processes employed and nature of chemicals used in leather making. Conventionally used acrylic syntans play a major role in modern leather processing. Skins or hides with loose grain structure were treated with acrylic syntans to achieve grain tightening and also have greater affinity towards other post tanning chemicals, which in turn increases the chemical uptake by leathers.[5,6] Acrylic syntans were formulated by combination of different acrylic monomers[7,8] to achieve better properties such as grain tightening,[9] filling, retanning,[10] light fastness, and waterproofing[11] on final leathers. The main limitation of conventional acrylic polymer is that they do not respond to thermal changes at specific temperature range. This necessitates for developing tailor made syntans, which can be functionalised to respond to thermal changes by co-polymerising with specific monomers, which in turn can sense heat or cold.

Poly N-isopropylacrylamide (NIPAM) is one of the thermoresponsive polymers being extensively studied since last few decades. The ability to undergo reversible phase separations at temperatures above its lower critical solution temperature (LCST) and its ability to respond to pH when copolymerized with other monomers, led to development of smart chemicals,[12-14] which are capable of responding to both temperature and pH.

In this study thermo responsive acrylic syntan was prepared by radical polymerization using three different acrylic monomers and treated at retanning stage of leather processing. The prepared syntan exhibit the properties of conventional acrylic syntan, alongside it possesses thermoresponsive properties. Post preparation, leathers were analysed for thermoresponsive character. Final leathers were evaluated for strength and organoleptic properties.

Experimental section

Materials

Methyl methacrylate (MMA, ≥99% pure), methacrylic acid (MA, ≥99% pure) was obtained from Loba Chemie Pvt. Ltd., potassium persulfate (PPS, ≥99% pure), sodium lauryl sulphate (SLS, ≥99% pure), sodium formate (≥99% pure), sodium bicarbonate (≥99% pure), sodium metabisulfite (≥99% pure) were purchased from MERCK Specialities Pvt. Ltd., sodium hydroxide (NaOH, ≥99% pure) from RANBAXY Laboratories and *N*-isopropyl acrylamide (NIPAM, ≥99% pure) from Sigma-Aldrich. All other leather chemicals were of commercial grade.

Preparation of thermoresponsive acrylic Syntan

Polymeric syntan was prepared by Radical polymerisation method. NIPAM 5g (0.044 mol) in 10 mL H_2O, MMA 1.5g (0.015 mol) in 20 mL H_2O with 0.7g SLS, MA 0.5g (0.006 mol), 0.02g sodium metabisulfite was added to a reactor and heated to 75°C, PPS (0.22g PPS in 10 mL H_2O) as initiator was added drop wise to the reactor vessel, reaction was continued in nitrogen atmosphere for 3h at 75°C, final pH of the experimental syntan was adjusted to 4.5 using NaOH and labelled

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as MTP02. Control syntan was prepared without using NIPAM. Demineralised water was used in syntan preparation. Small sample of the polymeric syntan was dried and used for analysis.

Collagen- polymer interaction studies

Collagen was extracted from teased tail fibers of *Wistar albino* rat (six months old) and washed with 0.9% NaCl at 4°C. Acid extraction method[15] was followed and 5% NaCl solution was used for purification. The precipitate was collected by centrifugation followed by dialysis against phosphate buffer. The concentration of collagen was determined from hydroxyproline content according to Woessner method.[16] The molar concentration of collagen was determined considering the average molecular weight of collagen as 300 kDa.[17] Structural conformations were studied using circular dichroism[18] and the extracted collagen was used for studying polymer interactions. Different concentrations of polymer containing solid content from 0.1 to 1% on weight basis was mixed with 1ml of collagen (8 μM) solution under continuous stirring for 3h at 4˚C. Then the reacted collagen- polymer (CP) solutions were analysed for stability.

Characterization of thermoresponsive Syntan

Solid content for syntans were measured according to standard procedure.[19] Particle size analysis was done using particle analyser (Zetasizer Nano series- ZS, Malvern) at 25˚C, scattering angle of 173°C and wavelength of 633 nm. The functional groups present in the syntan were analysed using FTIR spectrum (Jasco spectrometer, FT/IR-4000 Series). Polymeric syntan was made into pellet using Potassium Bromide (KBr) and analysis was carried out.

Clouding behaviour was observed by exposing the MTP02 sample to room temperature and photographs were taken using digital camera (Sony, Cyber-shot, 16.1 Megapixels with 8X optical zoom)

Leather processing and syntan application

Entire leather processing was done in a rotary drum, rotating at 4-6 revolutions per minute (rpm). All percentages were based on wet blue (chrome tanned leather) weight. Re-chromed wet-blue leathers of 1-1.1mm thickness were neutralized using 0.5% sodium formate and 0.5% sodium bicarbonate, pH of the leather was adjusted to 5.5-6, with drum running time of 45 min. After that leathers were rinsed in 100% H_2O. The pH adjusted leathers were further processed with 100% H_2O, 5% acrylic syntan (control and experimental syntan) with drum running time of 40 min. Then 2% synthetic fatliquor was offered with drum running time of 30 min and 2% dye was added and drum was rotated for 30 min. Fatliquoring was done in the same bath with 7% synthetic, 4% natural, 3% lecithin and 2% fish oil based fatliquors and were emulsified in 10% H_2O (weight basis). Three percentage of Phenolic syntan was offered with drum running time of 30 min. Leathers were fixed using 3% formic acid in 10% dilute H_2O and was offered in three feeds at 10 min interval each. Leathers were rotated in drum for another 30 min and liquor was drained. Finally, leathers were rinsed in 100% H_2O and piled on horse (Stand for drying leather).

Scanning Electron Microscopy (SEM) study of polymer treated leathers

SEM micrographs of the syntans and the leathers were studied using Hitachi S-3400 SEM microscope operating at 10-30 kV at room temperature of 25°C and relative humidity of 50%. The fracture ends of the specimens were sputter coated (Hitachi E-1010, Ion sputter) with a thin layer of gold prior to examination.

Thermal analysis

Thermoresponsive function analysis for leather was done according to the procedure mentioned,[20] leather surface images were taken by thermal imaging camera (E60, from FLIR), which has IR and visible systems with thermal sensitivity of less than 0.05°C temperature, measurement range of -20°C to +650°C. The samples were analyzed at room temperature of 25°C and relative humidity of 50%. Samples were strapped to the heating/cooling unit. It was ensured that the heating/cooling unit achieves equilibrium after setting the required temperature and then the images were taken focusing the leather samples. Samples were dismounted only after finishing the range of measurement.

Physical strength and organoleptic properties of Leather

Physical Testing of sampling was done according to standard procedure.[21] Tensile strength[22], tear strength[23] and grain crack index[24] were measured as per the standard procedures and compared with UNIDO norms.[25] Prior to testing, specimens were conditioned at 20±2 °C and RH 65±2% for 48 h. Values reported were average of four samples. Strength properties of the crust leathers were measured using an INSTRON universal testing machine. Organoleptic properties were assessed for softness, fullness and grain smoothness by standard hand evaluation technique. Four experienced leather technologists evaluated the samples and ratings were given to each sample. Experts rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better properties exhibited. Organoleptic properties were evaluated based on individual perception and is not a precise measurement of the particular property. Water-vapour permeability tests were performed to determine the ability of leather to permeate the amount of water vapours in terms of mg/unit area and for a specified period of time using Croydon England test method (SATRA 06121). Test samples are subjected to expose from grain surface to silica gel beads, which were placed in a container. This container was subjected to cyclic rotations for 12 h duration and differential weight of the container was noted and water vapour permeability was calculated. Softness analysis[26] of leather was done using ST-300 Leather softness tester. Porosity and air permeability testing of leathers was done using advance

automated humid air porometer (HCFP-1100AE, Porous materials Inc).

Effluent parameters

Wastewater obtained after leather processing using control and experimental syntan were collected and analysed for COD, BOD and TS according to the standard procedures.[19]

Results and Discussion

Characterization of thermoresponsive syntan

Total solid content of control and experimental (MTP02) syntan were analysed and it was observed around 31 and 30±2%, as leather processing was carried out by offering chemicals on the weight basis hence it was necessary to estimate the weight content of polymer present in the syntan. Number average molecular weight was estimated using dynamic light scattering (DLS) method and it was found to be 542±6.4 and 322±3.8 kDa for the control and MTP02 syntan. The low molecular weight of the MTP02 syntan may be due to higher solubility of NIPAM. Particle size of control and experimental syntan were observed to be 950±20 and 350±20 nm (Fig. 1), which was also analysed by DLS method, particle size of the experimental syntan was much lower compared to the control syntan. A lower particle size material penetrates the leather matrix in lesser time and with minimal effort, penetration throughout cross section of leather can be achieved easily. As the acrylic type of polymers were well known for their ability to absorb other post tanning chemicals, MTP02 syntan treated leathers showed higher affinities towards leather. This was well indicated by physical strength and organoleptic property values.

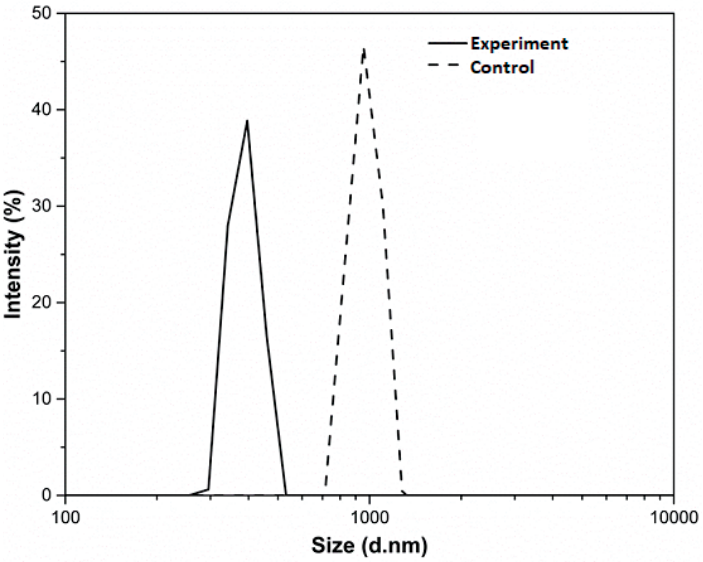

Figure 1. Particle size distribution of control and experiment (MTP02)

Clouding behaviour of thermoresponsive polymer

Clouding behaviour exhibited by thermoresponsive polymer (MTP02) was analysed from pH 1-10 at room temperature, photographs were taken (Fig. 2). This observation was made at room temperature in order to check the feasibility for leather application. Polymer responded differently at different pH under constant temperature condition. Immediate coagulation of polymer was observed at pH 1 and 2, phase change occurred at much less than room temperature and also settling of polymer was observed indicating complete phase separation. From pH 3 to 5, clouding was observed indicating the phase changing in the range of normal room temperature and it exhibited colloidal nature without any phase separations. From pH 6-10 clouding was observed at temperatures more than 37°C, this observation also implies the polymers is tuneable towards temperature and pH. Clouding temperature of the polymer was studied visually by raising the temperature of the polymer. From table I, it can be observed that the thermal sensitivity of the polymer can be varied based on change in pH. Also, starting point of the clouding was mentioned with an error of 2°C for clarifying the range at which the actual clouding started.

Table I
Clouding behaviour of the polymer at different pH

pH	Clouding Temperature (°C)
1	6±2
2	14±2
3	22±2
4	30±2
5	37±2
6	42±2
7	48±2
8	56±2
9	65±2
10	72±2

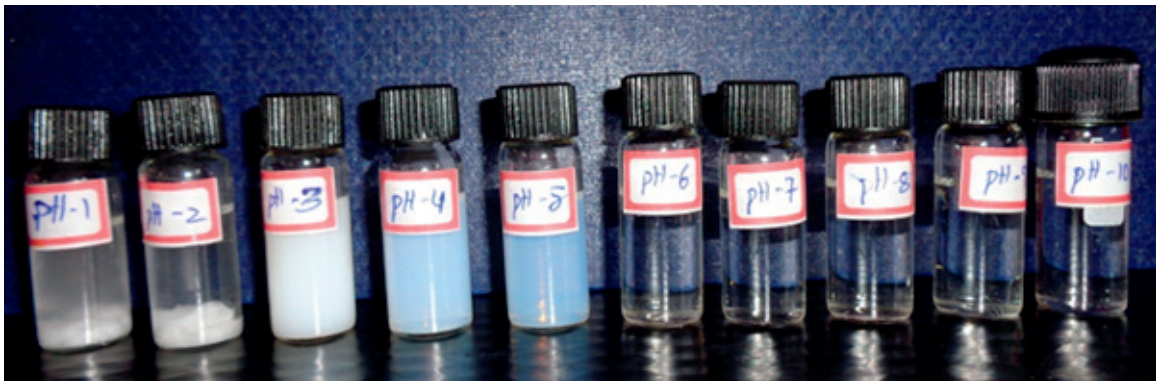

Figure 2. Clouding behaviour of polymer at room temperature

Polymer interaction with collagen

Polymer and its interactions with collagen were studied by identifying the functional groups using FTIR technique. (Fig. 3) Spectral conformation of collagen by vibration and stretching occurring at amide I (C=O stretch vibrations), amide II (N-H bending with C-N stretch vibration) and amide III (C-N stretching with N-H bending of amide linkages) occurring at 1659, 1550, and 1240 cm^{-1} provide information about secondary structure of collagen. The peaks at 1730 and 1250 cm^{-1} show associated non-ionized carboxyl groups and N–H stretching of amide II.[27]

FTIR spectra of collagen (untreated) in our study showed peaks at 1640, 1552 and 1244 cm^{-1} concurring with above reported values. Peaks representing amide I give information about the secondary structure hence the peaks arising at the intervals between 1600-1700 cm^{-1} are more important to confirm the structure. Collagen-polymer (CP) showed amide I, amide II and amide III occurring at 1634, 1537, and 1237 cm^{-1}. Occurrence of this blue shift might be due to the interaction of polymer with collagen molecule.

Circular dichroism spectroscopic studies have been employed to understand the stability of collagen when treated with polymer, as collagen is the main constituent of leather. Interaction with polymer were monitored by the change in molar ellipticity value of at 222 and 197 nm, from (Fig. 4) it can be observed that the collagen as standard showed negative and positive peaks at 197 and 222 nm. Collagen when treated with different concentrations of polymer there is a change in stability (Molar ellepticity plot shown in Fig. 4 inset). It can also be observed that the stability of collagen increased with addition of 0.1 (CP-10) and 0.5 % (CP-50) polymer (weight %). This conformation supports the FTIR analysis and gives the proof of collagen stabilization by treatment of polymer.

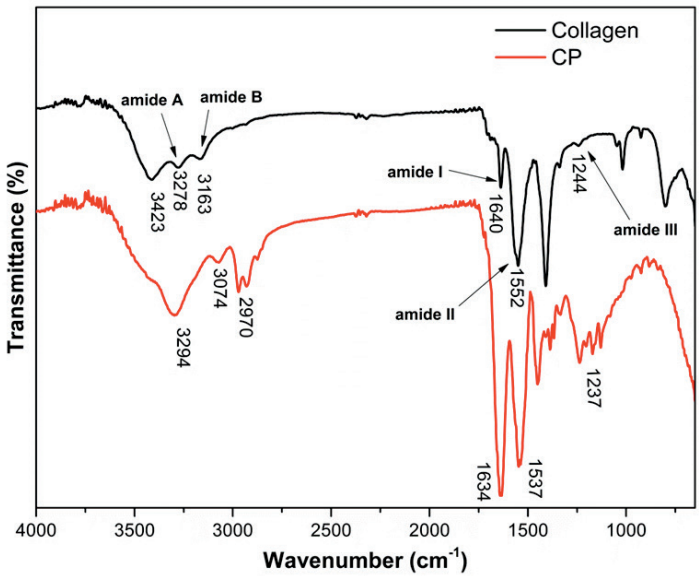

Figure 3. Fourier transform infrared spectroscopy analysis of collagen and collagen-polymer (CP) samples

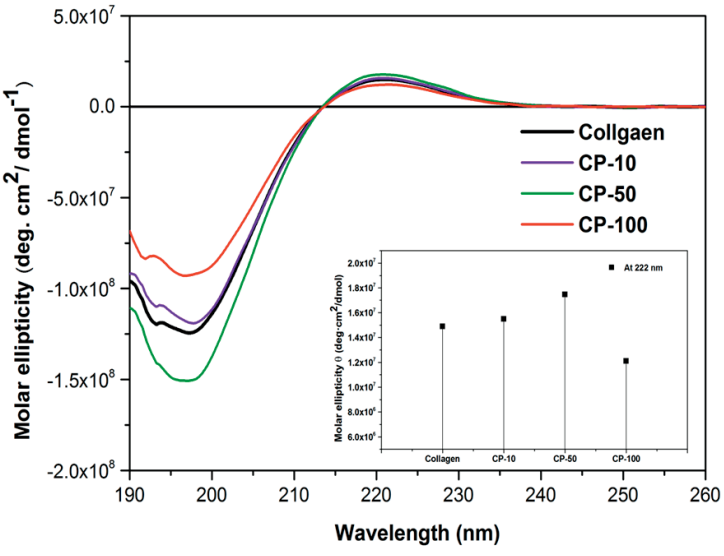

Figure 4. Circular dichroism spectra for understanding stability of collagen-polymer interactions

Application of syntan in leather making

Detailed study of the polymeric syntan was also carried out in order to understand its behaviour towards leather. Application of syntan at post tanning stage of leather processing and performance of leather was evaluated by various testing methods.

Infrared thermal imaging of syntan treated leathers

Thermal imaging of leather was intended to understand the comfort of the wearer. Human body responds to heat or cold by internal mechanism of thermo regulation. With change in temperature, physiological changes also occur in the body.[28] In order to maintain thermal comfort, temperature of the surrounding also needs to be maintained. Thermal comfort provided by the leathers was assessed by infrared imaging technique. Images of control and experimental leathers were taken at different temperature starting from 31 to 42°C in order to simulate the comfort of the wearer as the temperature fluctuation below 35 (Hypothermia) and above 37.5°C (Hyperthermia) and may lead to discomfort. Leathers were strapped to a chilling or heating unit and temperature measurements were carried out. Current studies showed control leathers comfort range

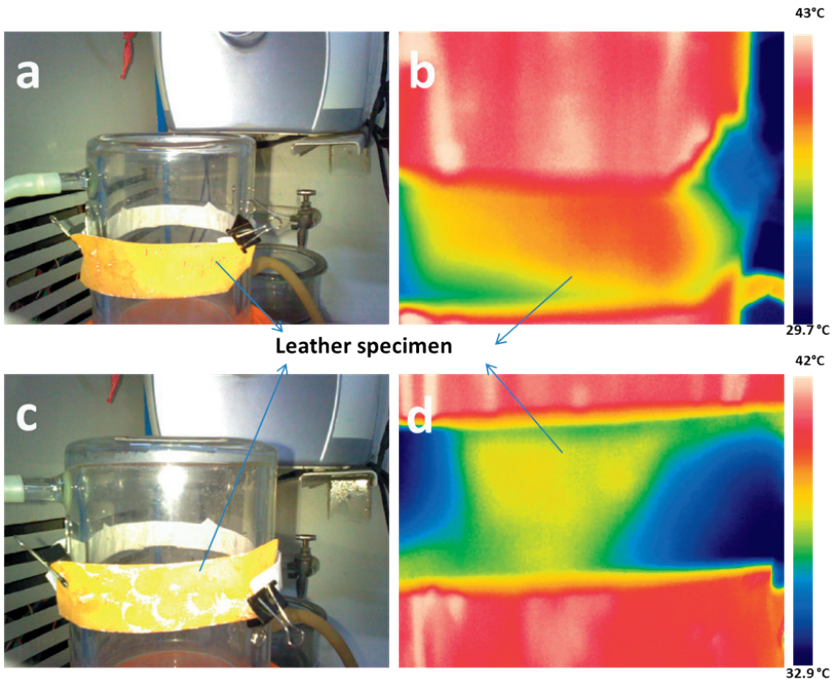

Figure 5. Digital images of **a)** control **c)** experimental, infra-red images of **b)** control **d)** experimental syntan treated leather

Table II

Temperature difference exhibited by control and experimental leathers

Control			Experiment		
	Grain surface temperature, °C	Flesh surface temperature, °C	Grain surface temperature, °C	Flesh surface temperature, °C	
Comfort Zone	32.5	32.2	32.7	31.7	Comfort Zone
	34.6	34.5	34.2	32.3	
	35.4	34.6	35.6	33.4	
	36.5	35.7	36.8	34.4	
	37.8	37.4	37.4	35.2	
	38.6	37.9	38.6	35.8	
	39.5	38.7	39.1	36.2	
	40.4	39.6	40.6	37.5	
	41.5	40.6	41.7	38.4	
	42.3	41.4	42.5	39.1	
Average Change		1±0.5		3±0.5	

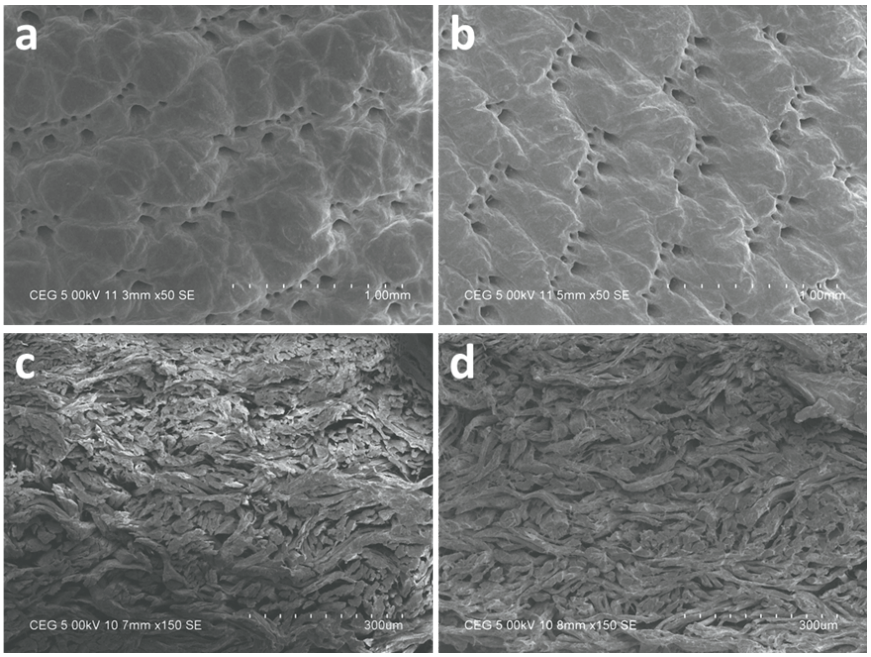

Figure. 6. Scanning electron microscopy images showing grain surface of **a)** control **b)** experimental leathers at 50X, cross section images of **c)** control and **d)** experiment at 150× magnification

(grain surface temperature) was limited to 37.8 and 40.6°C for control and experimental leathers. (Table II)(Fig. 5) Experimental leathers exhibited a higher comfort temperature range of 3 ± 0.5°C compared to control syntan treated leathers.

Scanning electron microscopy of leathers

Scanning electron microscopy images of experimental and control syntan treated leathers were analysed to understand the morphology of the leather surface and compactness of fibers by observing the cross section. Experimental leathers were compared to control leathers (Fig. 6) and it was observed that both leathers were flat with no surface deformities. Cross section view of experimental leathers indicated more compact structure than control leathers. This might be due to higher reactivity of experimental syntan, which may have enhanced uptake of other post tanning chemicals.

Physical testing of leather

Tensile strength property of MTP02 syntan treated leather was comparable to that of control, with no major difference on percentage elongation at break values indicating that both experiment and control leathers have similar stretching property (Table III). Experimental leathers exhibited higher tear strength property, which might be due to higher cross linking of the experimental syntan with collagen fibers. Grain crack index values were almost similar to that of control leathers. Water vapour permeability gives the measure of leathers ability to allow water vapour to permeate through and through over a period of time, experimental leathers exhibited the value slightly lesser than control syntan treated leathers, which indicated that the experimental leathers retained the moisture without permeating, which in turn increased the leather capability to retain heat. Water absorption values were 0.8072 and 1.0726 mg/cm^2 for control and experiment leathers. This clearly shows that the experimental leathers have higher water absorption and high water retention capability.

Softness analysis of leather helps to understand the ability of fatliquor absorbed, control and experimental leathers showed value of 5.4771 and 6.1328. This indicates that the experimental leathers absorbed higher amounts of post tanning chemicals than compared to control. Higher softness means more sliding of fiber bundles in leather matrix, which also mean higher absorption of fatliquor.

Table III

Physical strength properties of control and experimental syntan treated leather

				Grain crack index		
	Tensile strength (N mm^{-2})	**Elongation at break (%)**	**Tear strength (N mm^{-1})**	**Mean load (kg)**	**Mean distension (mm)**	**Water vapour permeability (mg cm^{-2} hr^{-1})**
Control	12±5	60±5	34±2	26	9.30	13.60
Experiment	14±3	61±5	50±2	25	9.25	12.50

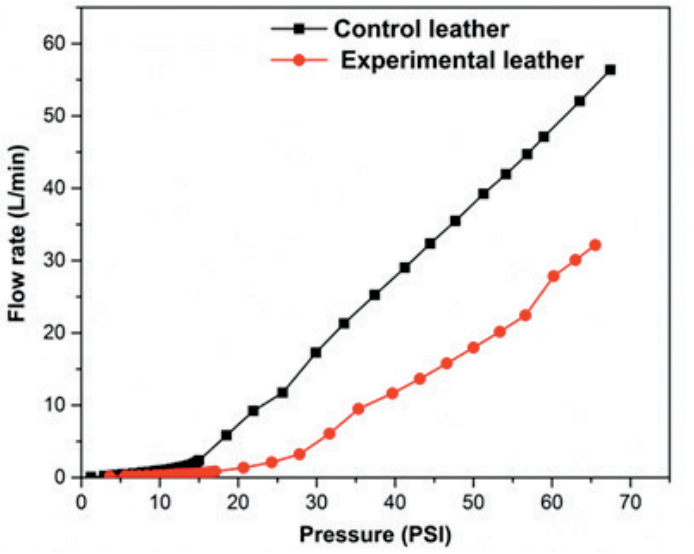

Figure 7. Permeability analysis of leather

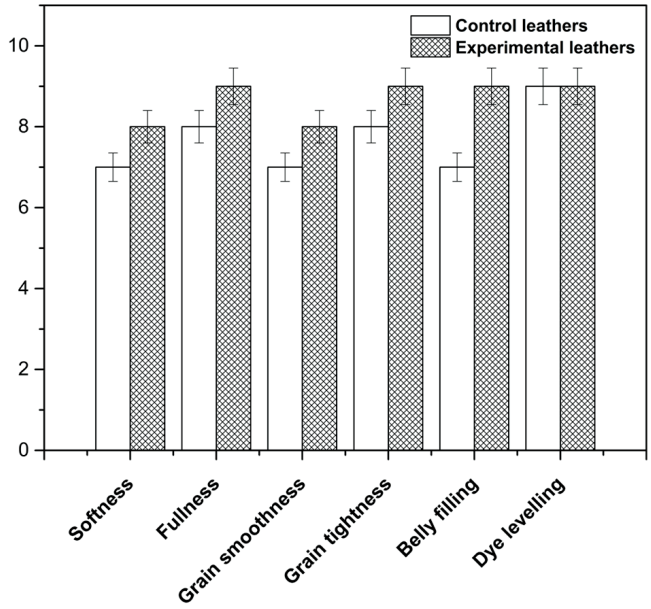

Figure 8. Organoleptic properties analysis of leather

Porosity analysis of leather

Air permeability and porosity of leather were analysed to understand the breathability of leather, which is one of the essential characteristics of leather. The air permeability of experimental leather is lower than the control leather (Fig. 7), which indicate no void spaces present in the leather matrix. Lower air permeability can also influence the heat flow as indicated by the infra-red image of experimental leathers. Experimental syntan might be filling the leather and absorbing water vapour due to its hygroscopic nature. It was found that the largest pore present in control and experimental leathers is 5.3258 and 1.8185 µm.

Color measurement of leather

Color values confirmed that the experimental syntan treated leathers showed increase in color strength compared to control leathers. (Table IV) This was confirmed by the increase in ΔE value by 3.91, this gives the measure of just noticeable difference (JND),[29] it can be concluded that experimental syntan treated leathers exhibited an increase in intensity of color.

Organoleptic properties

Organoleptic properties of leathers made from control and experimental syntan are shown in Fig. 8. The ratings were plotted by taking an average of four samples evaluated with an error margin of 5%. Properties such as softness, fullness, grain smoothness, grain tightness, belly filling and dye levelling were compared with control syntan treated leathers. Syntan was uniformly distributed, as there was no evidence of looseness in belly regions of the experimental syntan treated leathers, dye uniformity and levelling properties were excellent, dye intensity was slightly enhanced in case of experimental leathers. Overall, leathers made using experimental syntan exhibited better properties than the control counterpart.

Wastewater analysis

Effluent from leather processing is analysed for COD, BOD and Total solids to understand the pollution characteristics. From Table V, there is a reduction in COD, BOD and TS content. There was reduction of COD and TS values by 25 and 35%. This might be due to the higher uptake of leather chemicals making the experimental syntan not only efficient but also eco-friendly in nature.

Conclusions

It can be observed from the present study that the prepared polymer MTP02 exhibited better pH and temperature response. From the clouding behavior analysis, it can be observed that the temperature response of polymer can be altered by changing pH. Collagen-polymer interaction studies provided insights about the stability

Table IV

Color values of control and experimental leathers

Sample	L*	a*	b*	ΔE
Control	72.543	9.151	24.352	-
Experiment	73.048	10.315	28.051	3.91

L* represents lightness, a* represents redness-greenness and b* represents blueness-yellowness of the color

Table V

Analysis of waste water

	COD (mg/L)	BOD (mg/L)	TS (mg/L)
Control	1800±50	175±5	5760±50
Experiment	1350±50	168±5	3750±50

and functional groups were analyzed using FTIR. After treating leather with syntan, thermoresponsive behaviour was analysed and a temperature difference of 3±0.5 compared to 1±0.5 °C of control leathers. Improved tensile and tear strength values was observed and also organoleptic properties such as softness, fullness, grain tightness and belly filling were better than control counter parts. Scanning electron microscopy analysis provided information about leather surface and fiber alignment. Water vapor and air permeability of leathers were tested to understand the filling behaviour of syntan. Color values were measured to understand the dye uptake and covering. Synthesized acrylic syntan can be used for production of stimuli responsive leathers, which can respond to temperature and pH. Thus experimental leathers find its applications in developing environment and pH adjustable leathers.

Acknowledgements

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