Dual Functional Replacement Syntans for Leather

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Abstract

In the present study we have synthesised thermoresponsive syntan using phase changing material (PCM) encapsulated into a replacement syntan. Syntan was analysed for their particle size, thermal response was verified using Differential scanning calorimetry (DSC) and surface morphology was analysed using scanning electron microscopy (SEM). These syntans were applied to leathers for making leather thermoresponsive. The thermal comfort range achieved on leathers prepared using the experimental syntan was about 2.5°C, compared to control of about 0.5°C with an error of ±0.5°C. The physical and strength properties of experimental leathers were superior compared to control.

Introduction

Skin of a live animal is capable of adjusting towards heat/cold by the mechanism of thermoregulation. This property of skin is lost when the animal is flayed. Hence, to regain this unique functionality to certain extent, smart materials need to be added to skin while converting it to leather.[1] Skin/hides are termed as leather once the tanning material is treated to them. Tanning is basically conversion of putrescible (degrading) into non-putrescible material.[2]

Leather is a viscoelastic material, which has the unique property of breathability. Unlike other synthetic materials, leather and leather products are capable of absorbing and releasing air, heat and water vapour. These advantageous properties also come with a few drawbacks, such as leathers limited capability to adjust towards extreme climatic conditions such as heat/ cold.[3] In order to overcome these limitations leather needs to be treated with certain speciality chemicals which can impart those functionalities. Phase changing materials (PCM) are one such smart materials which can absorb and release heat over a particular temperature range.

The PCMs are the materials with high heat of fusion, which has the capability to transform its physical form from liquid to solid and vice versa upon absorbing and releasing heat. There are numerous phase changing materials available in the market, but our interest was with materials which can respond at human body comfort range of 28-34°C.[4] The PCM are hydrophobic in nature and leather processing is entirely carried out in aqueous medium. Hence, the compatibility issues are the major concern. In order to overcome this limitation, PCM are encapsulated into polymeric materials such as phenol or melamine-based condensate polymers.[5,6] These polymers are generally used as syntans in leather processing as filling agents, hence in this study we aim to prepare PCM encapsulated syntans. Thus, synthesised materials not only fill the leather matrix like conventional syntans but also impart the thermoregulation properties to leather.

In the present study we have synthesised PCM based thermoresponsive syntan which not only can fill the leather matrix like conventional syntan but also help in thermoregulation. The syntans were analysed using different techniques such as particle size measurement, scanning electron microscopy, differential scanning calorimetry and the syntan treated leathers were analysed for infrared thermal imaging, physical strength and organoleptic properties.

Materials and Methods

Materials

Phenol (>99% pure), formaldehyde (37%), n-Octadecane, from MERCK India, sodium hydroxide (NaOH, >99% pure), sodium lauryl sulphate (99% pure) from Himedia India.

Syntan Preparation

Phenol (0.2125mol) was stirred with equal molar sulphuric acid for 2h at 105°C. Followed by addition of 100g deionised water, formaldehyde (0.425mol) and stirred at 95°C for 2h (PF- at pH 3.5). PF solution pH was adjusted to 6 using 40% strength sodium hydroxide and stirring was continued for another 1h. Separate solution containing 1g of n-Octadecane (PCM), 0.5g anionic surfactant dissolved in 50ml deionised water and was homogenised for 15 min at 4000 rpm. To prepare the microcapsules, the emulsion containing PCM was gradually added to polymer solution and stirring was continued for 2h. The final solution pH was adjusted to 3.5. The small quantity of the resultant product obtained was dried in a hot air oven at 80°C for analysis. (PF-PCM)

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Leather Application

Table I
Detail description of leather processing

Material: Goat wet blue leather
Number of pieces: 4 (2-control, 2- experiment)
Article: Softy upper
Total Weight: 3.6 kg

Process	Chemical	Percentage (%)	Time	Remarks
Neutralisation	Water	100		
	Sodium Formate	0.5	20	
	Sodium bicarbonate	0.5	10+ 30	10min run time, check pH-5.6 and additional 30min run time
				Drain/wash/drain
Post tanning	Water	100		
	Acrylic Syntan	2	30	In dilution with 10% water
	Syntan (C, E)	20	45+45	In two intervals of 45min each
	Synthetic Fatliquor	16	60	In dilution with 10% water
	Formic Acid	3	60	Dilution with 10% water. In 3 feeds of 10min and 30min additional run time

C-control (PF), E-Experiment syntan (PF-PCM)

Analysis of Syntan

The total solid content present in the liquid solution of the prepared polymeric syntan was estimated using APHA - 2540 B.[7] Particle size measurements were carried out using particle analyser (Zetasizer Nano series- ZS, Malvern) Scanning electron microscopy analysis was carried out using Hitachi S-3400 SEM microscope. The surfaces of the samples were studied with the microscope operating at 10-30 kV. The specimens were sputter coated with a thin layer of gold prior to examination. Differential Scanning Calorimeter (DSC)-Q200 TA Instruments was used for analysing the phase changes of the PCM. The samples were analysed at the heating rate of 5°C/min between 25°C to 200°C.

Analysis of Leather

Infra-red thermal imaging of leather surfaces was analysed using thermal imaging camera which has IR and visible systems (FLIR system E60). The leather analysis technique was developed in house using a double walled glass jacket with provision for circulating water. This jacket is connected to a temperature controller unit. The leathers were mounted onto the glass jacket and the temperature was increased. Leather surface images were taken by thermal imaging camera which has IR and visible systems (FLIR system E60) having a thermal sensitivity of < 0.05°C with a measurement range of -20°C to +650°C and images were taken with a resolution of 320 × 240 pixels. The samples were observed from a distance of 30 cm at room temperature of 25°C and 50% relative humidity.

Strength Property Analysis

Samples for physical testing were cut from control and experimental leathers. The samples were conditioned to the required relative humidity of 65±2% at 20±2°C for 48 h as per standard procedure.[8] The tensile,[9] tear strength[10] and grain crack index[11] were measured as per the standard procedures. Values reported were average of four samples.

Organoleptic Property Analysis

Crust leathers from the conventional as well as the experimental process were assessed for run, softness, fullness, grain smoothness and general appearance by standard hand evaluation technique. Four experienced leather technologists rated the leathers on a scale of 0-10 points for each functional property. Where higher points indicate better properties exhibited. An average of four samples were evaluated.

Results and Discussion

Solid Content and Particle Size Analysis

Solid content present in syntan gives information about the total solid matter present which actually binds/ fills the leather matrix. Solid content was measured for both control and experiment syntan, it was calculated to be 35 and 39%. The size of the particles was analysed using particle size analyser, the size distribution of the syntans were plotted in the Fig 1. It can be observed that the particle size of the PF syntan are in the range of 1700 to 3600 nm while the PF-PCM encapsulated syntan possessed larger diameter in the range of 1400-5600 nm. The bigger particle size of experimental syntan may be due to the encapsulation of PCM.

Scanning Electron Microscopy Analysis of Syntan

From Fig 2, scanning electron microscopy analysis of control (a) and experimental syntan (b) shows the surface morphology. It can be seen that the experimental syntan has formed microcapsules containing PCM material, while the control sample contain

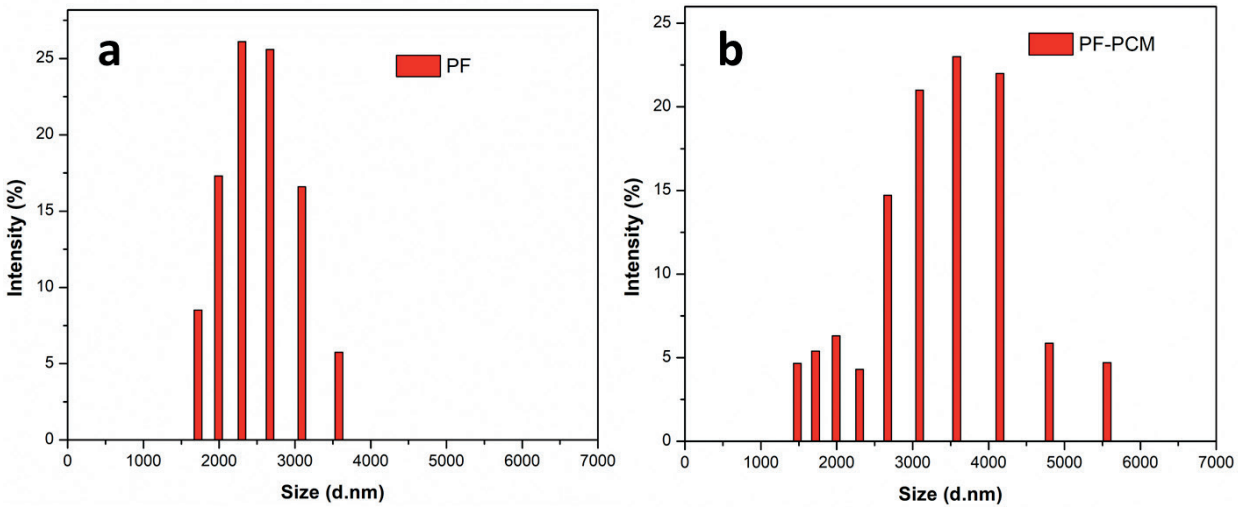

Figure 1. Particle size distribution of PF and PF-PCM syntan

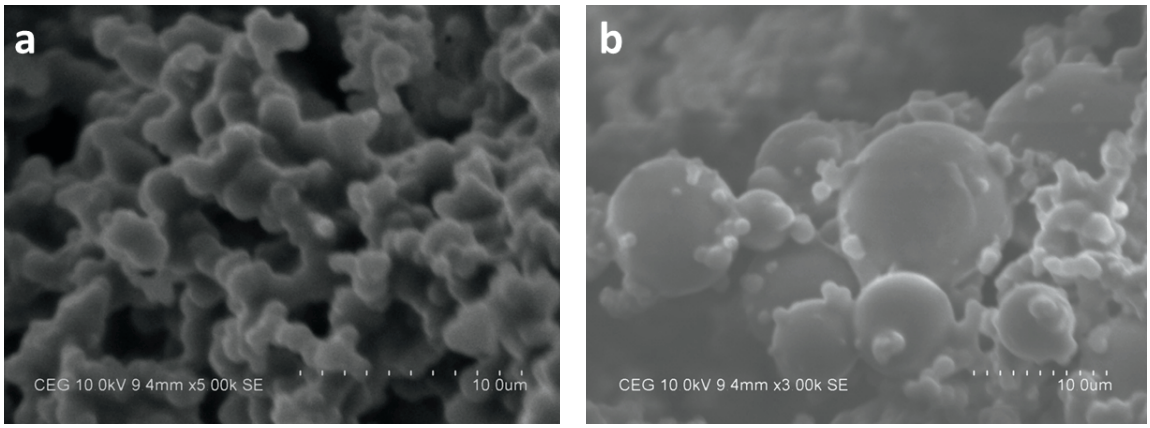

Figure 2. Surface morphology analysis of PF **(a)** and PF-PCM **(b)** syntan

clusters of syntan without PCM. The particle size data showing the variations can be validated from SEM, the size of the experimental syntan with microcapsules were larger in size compared to the control syntan.

Differential Scanning Calorimetry Analysis of Syntan

Differential scanning calorimetry analysis of syntan gives the information about the phase transformation of the material. From Fig 3, DSC thermographs of control (PF) and experimental (PF-PCM) syntan were plotted to understand the thermal changes exhibited by these syntans. It can be observed that the experimental syntan encapsulated using PCM (n-Octadecane) shows phase change at 27°C confirming the presence of PCM. The peaks above 100°C attributes to the polymers phase transformation.

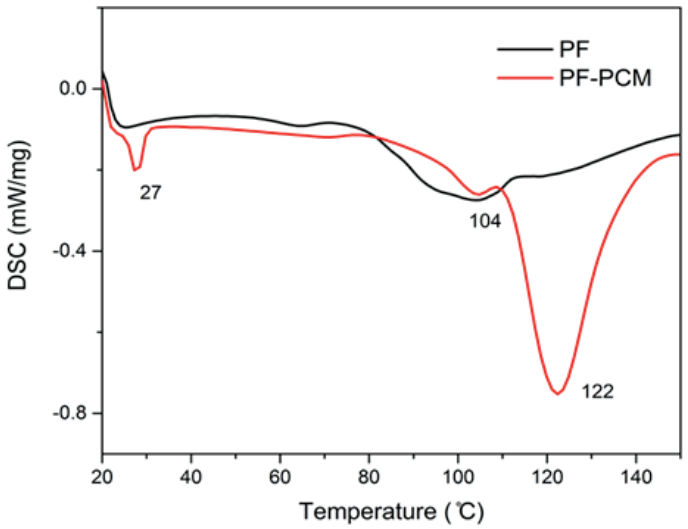

Figure 3. Differential scanning calorimetry analysis of PF and PF-PCM syntan

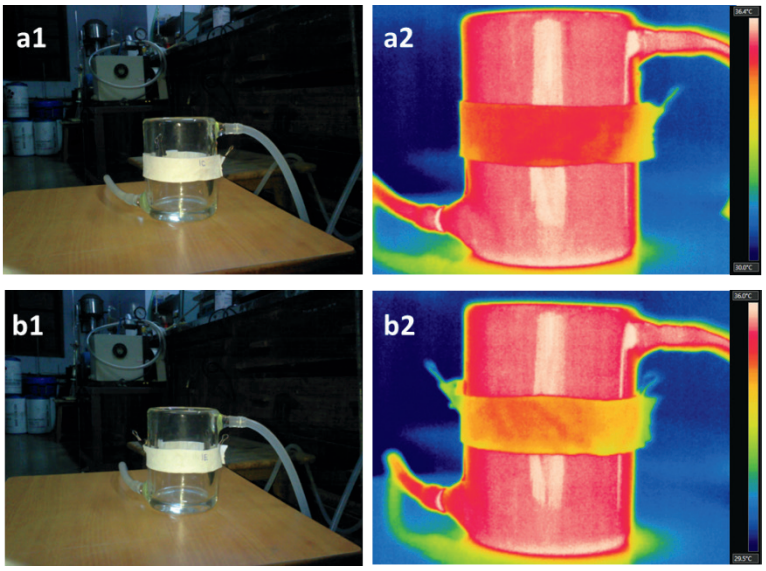

Figure 4. Digital and Infra-red thermal imaging of **(a1, a2)**PF and **(b1, b2)**PF-PCM syntan treated leathers

Infra-Red Thermal Imaging Leathers

Infra-red thermal imaging of leathers was performed to analyse the leathers ability for the absorption or release of heat. From Fig 4, digital image of control (a1), experiment (b1) and their corresponding thermal images (control-a2 and experiment-b2) are shown. The temperature of the glass jacket and the temperature on the leather surface were tabulated in table II. The flesh surface temperature values were noted after 60 sec exposure of heat on the grain surface. It can be observed that the experimental leathers absorbed more heat compared to control leathers. The thermal image of leather Fig 4: b2, the variation in color (yellow) compared to control (red) when exposed to similar conditions proves that the experimental leathers absorbed more heat compared to control. The difference in temperature can be compared with the temperature scale.

Scanning electron microscopy analysis of leather

In order to understand surface and cross-sectional morphology of leathers, scanning electron microscopy analysis was performed on the leathers. From Fig 5, surface and cross sections of leathers were imaged. Fig 5 (a,b) shows surface image of control and experimental leathers, it can be seen that both leathers show no surface deformities and cross sectional images of control and experimental leathers Fig 5 (c,d) shows the fiber structure, both leathers show compact fiber alignment.

Table II

Thermal analysis of control and experimental leathers

	Control		Experiment	
	Grain surface temperature °C	**Flesh surface temperature °C**	**Grain surface temperature °C**	**Flesh surface temperature °C**
	24.0	23.7	24.0	21.8
	25.1	24.5	25.0	22.7
	26.1	25.4	26.0	24.1
	27.2	26.2	27.1	24.8
	28.0	27.3	28.0	25.6
	29.1	28.7	29.1	26.4
	30.1	29.5	30.0	27.5
	31.0	30.4	31.1	29.0
	32.0	31.6	32.2	29.4
	33.1	32.4	33.1	31.1
	34.0	33.7	34.0	31.6
Average Change	**0.5±0.4**		**2.5±0.5**	

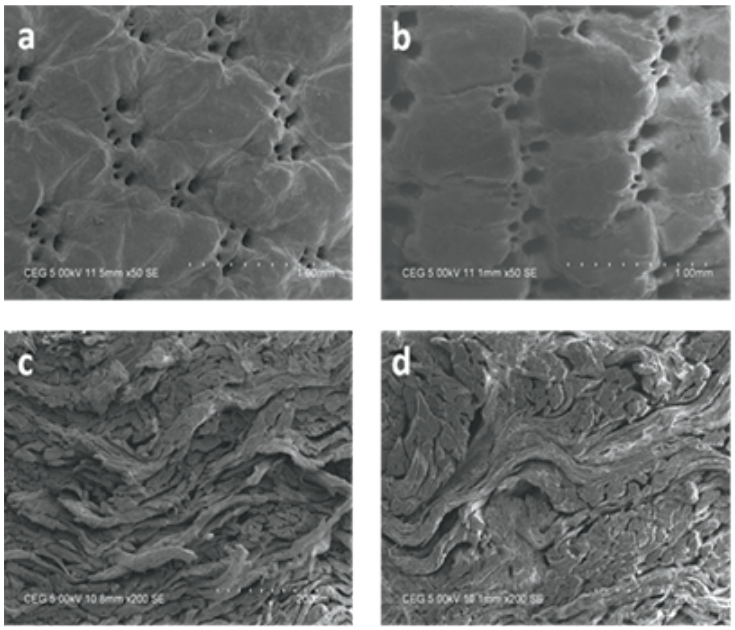

Figure 5. Scanning electron microscopy analysis of PF (**a**-surface, **c**- cross section) and PF-PCM (**b**-surface, **d**- cross section) syntan treated leathers

Physical Strength Analysis of Leathers

Strength properties such as tensile, tear and grain crack index were measured for control and experiment leathers. From table III, tensile strength and the percentage elongation values of experimental leathers were slightly increased compared to control leathers. Similarly, tear strength values of both the leathers were almost equal, while grain crack index value improved in case of experimental leathers. This shows that the experimental syntan improved grain tightness of the leather.

Organoleptic Property Analysis of Leathers

Organoleptic properties of leathers were assessed for softness, fullness, belly filling and grain tightness. From Fig 6, softness and fullness of both experimental and control leathers were similar, while experimental syntan treated leathers showed better belly filling and grain tightness compared to control leathers, the data is in agreement and can be confirmed from the grain crack index values.

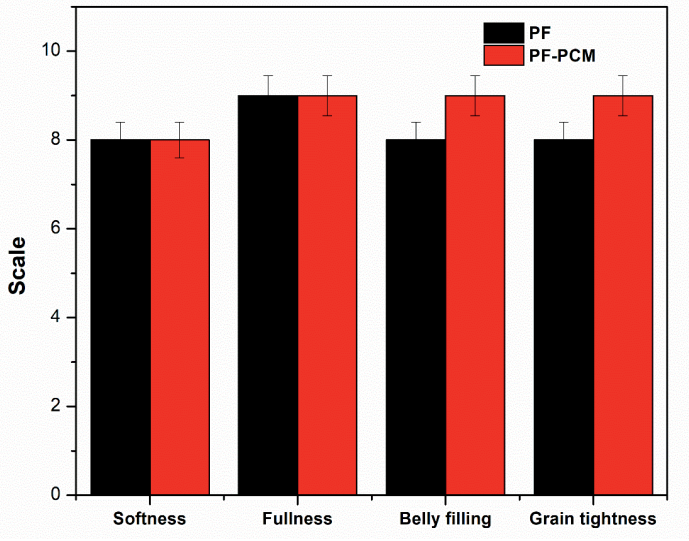

Figure 6. Organoleptic properties of PF and PF-PCM syntan treated leathers

Table III

Strength property analysis of control and experimental leathers

	Tensile Strength (N/mm^2)	Percentage elongation (%)	Tear strength (N/mm)	Grain crack index	
				Load (N)	Distance(mm)
Control	24±0.5	63±4	55±3	25±1	11±0.5
Experiment	26±0.5	68±3	53±3	29±2	17±0.9

Conclusions

We have shown the synthesis, application and analysis of thermoresponsive syntan. Leathers made using the syntan exhibited thermoresponsive behaviour. From the SEM images, PF-PCM syntan showed perfect capsule formation. The differential scanning calorimetry analysis confirmed the presence of PCM inside the capsules. The thermal comfort range achieved on leathers prepared using the experimental syntan was about 2.5°C, compared to control of about 0.5°C. The physical and strength properties of experimental leathers were superior compared to control. From this study we have prepared syntan which not only helps in filling the leather matrix but also exhibits thermoresponsive character. Thus, these dual functional syntans find application in preparation of thermal comfort leathers. These leathers also find applications in preparation of shoes, garments and gloves which can be used at high altitudes and extreme climatic conditions.

Acknowledgements

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