Stimuli Responsive Leathers using Smart Retanning Agents

by

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Abstract

The main use of leather is to protect the body against external environment and to provide comfort. However, leather may be used for additional functions specific to 1) an adverse or extreme climate and 2) job-ambience or profession so as to enhance adaptability and productivity of the user. When such an application arises, the leather is termed as "smart material". Making leather perform the functions it did as a skin on a live animal renders it as smart leather. Hence, the futuristic objective is to make the processed skin termed "leather" retain its memory so as to result in "smart or intelligent leather". In this paper, it has been attempted to incorporate thermo responsive function into leathers using smart materials such as phase changing materials (PCM). PCMs are capable of absorbing or releasing large amount of heat during phase transitions between two solid states and/or liquid and solid states. Manufacture of syntans using PCM based on two different prepolymers viz, melamine formaldehyde and naphthalene sulfonic acid has been attempted in this paper. The retanning agents synthesized have been characterized using various techniques like FT-IR, DSC, TGA and SEM analysis. Leathers made using PCM incorporated retanning agents have been tested for various properties viz. strength properties, thermal stability, organoleptic properties to study the influence of the PCM incorporated retanning agents.

Resumen

El uso principal del cuero es proteger el cuerpo del ambiente exterior y así proveer confort. Sin embargo, el cuero puede emplearse también en funciones adicionales específicas a 1) un clima adverso y extremo y 2) ambiente laboral o profesión para incrementar adaptabilidad y productividad en el usuario. Cuando esta situación surge, el cuero se denomina como un "material inteligente" Haciendo al cuero desempeñarse como la piel lo hizo en un animal vivo lo convierte en cuero inteligente. Entonces, el objetivo futuro es conferir a la piel denominada "cuero" retener su memoria para tal resultar en "inteligente o cuero sabio". En esta publicación, se ha tratado de incorporar una función termo responsiva a cueros utilizando materiales inteligentes tales como materiales cambiantes de fase (PCM). PCMs son capaces de absorber o generar grandes cantidades de calor durante transiciones entre fases entre dos estados sólidos y/o entre estados líquidos y sólidos. Fabricación de recurtientes usando PCM basados en dos prepolímeros diferentes Vg., melamina formaldehído y ácido naftalen-sulfónico han sido intentados en esta obra. Los recurtientes sintetizados han sido caracterizados usando varias técnicas como FT-IR, DSC, TGA y SEM analisis. Los cueros producidos utilizando recurtientes de PCM incorporados han sido testeados por varias propiedades Vg. Resistencias físicas, estabilidad térmica, propiedades organolépticas, para estudiar las influencias de recurtientes con PCM incorporados.

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Introduction

Materials have always been of great significance to humans. In earlier times, materials only had a support function. Today's materials are of a different calibre, containing the addition of special properties, mainly electrical, optical, magnetic and chemical. The modern functional materials have forms such as membranes, catalysts, thin films, semiconductors and sensors. Similarly, the main traditional use of leather is to protect against external environment. If the leather is made to sense conditions in environment it becomes 'smart' and respond to them then it becomes 'intelligent'. Smart or intelligent materials are those that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields.[1]

The human body is an automatic thermoregulating engine. The main function of skin is to keep the body warm when outside temperature is cold and vice versa. Development of properties found in skin when the animal was alive to be made available in the leather, as well viz. 'making leather function as a living skin', is the way forward to be explored. This opens up not only new areas of application for leather such as developing value added products but also enhances the value of present areas of application including upholstery leather, where if the smart leather keeps the outside heat away, it prevents the interiors from getting heated up when the car is parked under the sun.

Thermo responsive function of the leather could be incorporated using new materials like phase change materials (PCM). PCM possess the ability to change their state with a certain temperature range.[2] PCM takes advantage of latent heat that can be stored or released from a material over a narrow temperature range. In recent years, a range of techniques have been developed to make temperature regulating textiles and smart garment products.[3-6] Although smart textiles are being attempted, the same for smart leathers needs innovations in product and process development due to the inherent 3-dimensional matrix of leather. The wide distribution of pore structure of leather makes it challenging.

Before applying PCM's to leather, they need to be contained within microspherical containers. Hence, the microencapsulation of PCM becomes essential. Various methods of encapsulation have been reported.[7-9] The challenge in applying PCMs for leather arises due to the intrinsic nature of the material. Recently, thermoregulated natural leather using phase change materials has been attempted.[10] However, the mode of application was coating the surface with binder made using PCM. The major drawbacks of the current stimuli-sensitive polymer-gel structures are their weak mechanical properties and poor transitional response. Processing of these materials into thin shapes and their integration to leather will lead to development of stimuli responsive leathers for smart applications. This paper attempts to develop thermoresponsive leathers by incorporating the PCM through retanning process.

Experimental Section

Reagents

Melamine, naphthalene and urea were purchased from Himedia laboratories Pvt. Ltd. Sulfuric acid, formaldehyde, triethanol amine, sodium hydroxide, citric acid were procured from SD fine chemicals Pvt. Ltd. Triton X-100, sodium lauryl sulfate, *n*-octadecane, styrene-maleic anhydride copolymer were purchased from Sigma Aldrich, India. All the chemicals were used as obtained without further purification.

Microencapsulation of *n*-octadecane

Synthesis of Prepolymer Solution

Synthesis of melamine-formaldehyde prepolymer: The prepolymer solution is prepared by treating 0.1 mole of melamine with 0.9 moles of formaldehyde in water at a temperature of 70°C under stirring for 1 h. The pH of the solution was adjusted to 8.5 using triethanolamine. The stirring was carried further until the solution becomes transparent. Synthesis of naphthalene sulfonic acid prepolymer: 0.1 mole of naphthalene was treated with 0.2 moles of concentrated sulfuric acid in a 250mL round bottomed flask at 120ºC for 3 h under constant stirring. The resultant 2–naphthalene sulfonic acid was then transferred into a beaker with a subsequent addition of 0.02 moles of formaldehyde and stirred at 60ºC for 30 min. A mixture of urea-formaldehyde (1:1) was then added gradually to the above solution and stirring carried for further 2 h, followed by adjusting the pH to 7.0 using 5N sodium hydroxide solution, which resulted in the naphthalene sulfonic acid prepolymer.

Synthesis of Oil Phase

1.0 g of triton X-100 was added drop-wise to 200 mL of water under vigorous stirring. After 15 min, 0.1 g of sodium lauryl sulfate was added and stirring continued for further 30 min. To this solution, 2.0 g of *n*-octadecane was gradually added and stirred for 90 min.

Synthesis of Water Phase

0.035 g of styrene-maleic anhydride and 0.002 g of sodium hydroxide mixed with 2 mL of de-ionized water, emulsified mechanically at 50°C under a stirring rate of 2000 rpm for 120 min. The solution was adjusted to pH 4.5 using 10% weight of citric acid.

Emulsion Preparation

To the clear water phase solution, oil phase was added drop-wise under vigorous stirring, which resulted in a white emulsion.

Fabrication of Microcapsules (PCM)

To prepare the microcapsules, the emulsion was initially stirred at the rate of 4000 rpm at 50°C, to which prepolymer was added gradually. After the addition of the prepolymer, the temperature was raised to 80°C and the stirring was continued for further 120 min. The resultant product obtained was dried in an air oven at 80°C for 12 h. The abbreviations used to denote the smart retanning agents made using different prepolymer solution and the leathers made from the same are given in Table 1.

TABLE I
Sample Names Used in This Paper With Their Description

Sample Name	Description
MF-SM	PCM encapsulation using melamine-formaldehyde prepolymer
NSA-C	Control sample without PCM using naphthalene sulfonic acid prepolymer
NSA-SM	PCM encapsulated sample using naphthalene-sulfonic acid prepolymer
L-MF-C	Retanned leather using conventional retanning agent with melamine base
L-MF-SM	Retanned leather using MF-SM as retanning agent
L-NSA-C	Retanned leather using conventional retanning agent with naphthalene base
L-NSA-SM	Retanned leather using NSA-SM as retanning agent

Characterization of Smart Retanning Agents

FT-IR Analysis

Functional group analysis for MF-SM (Melamine formaldehyde based smart material) and NSA-SM (naphthalene sulfonic acid based smart material) was carried out using Nicolet Impact 400 FT-IR spectrophotometer. The samples were pelletized by mixing with KBr.

Differential Scanning Calorimetry

The thermal stability of smart retanning agents and the leathers made using them were determined using Differential Scanning Calorimeter (DSC)-Q200 TA Instruments. The temperature was calibrated effectively using indium as standard. The samples were analyzed at the heating rate of 5ºC/min between 25 to 200ºC.

Thermo-Gravimetric Analysis

The thermo-gravimetric analysis of smart retanning agents and the leathers made using them were determined using Thermo Gravimetric Analyzer (TGA) – Model Q50, TA Instruments. The samples were analyzed at the rate of 10 ºC/min from 25 to 800ºC.

Scanning Electron Microscopy

The scanning electron micrographs of the smart retanning agents and the leathers made using them were taken by means of a Hitachi S-3400 SEM microscope. The surfaces of the powder samples were studied with the microscope operating at 10-30 kV. The fracture ends of the specimens were sputter coated with a thin layer of gold prior to examination.

Retanning and Characterization of Leathers Made Using Smart Retanning Agents

Retanning of leather using the smart retanning agents was carried out by partially replacing the syntan by encapsulated PCM. Control leathers were made using 14% retanning agents and experimental leathers were made using 10% retanning agents along with 4% of smart retanning agent. A post tanning recipe given in Table II was followed for making upper leathers from wet blue goat skins using the smart retanning agents, MF-SM and NSA-SM. A conventional post tanning process was also carried out as a control with commercial retanning agents with melamine base and naphthalene base separately. The samples for physical testing were obtained as per IULTCS method.[11] The samples were conditioned at 26.7±2ºC and 65±2% R.H. for 48 h. Physical properties such as tensile strength, % elongation and tear strength were investigated.[12,13] Each value reported is an average of four experiments. Crust leathers were assessed for grain smoothness, softness, grain tightness and fullness by standard tactile evaluation technique. Experienced tanners rated the leathers in a scale of 0-10 points for each functional property.

RESULTS AND DISCUSSION

Characterization of Retanning Agents Made Using PCM

FTIR Analysis

The incorporation of PCM into melamine-formaldehyde and naphthalene sulfonic acid prepolymer was confirmed using FT-IR analysis. The FT-IR spectrum for melamine formaldehyde based PCM (MF-SM) (Fig. 1a) has a broad band around 3402 cm^{-1}, which indicates the presence of –OH group, which was formed after the condensation of melamine with formaldehyde. Due to the symmetric stretch of $-CH_2$- sharp bands arise around 2810 cm^{-1} and 2929 cm^{-1}, which clearly indicates that *n*-octadecane was incorporated along with the melamine formaldehyde prepolymer. The presence of C=N bond in melamine was observed around 1597 cm^{-1}. After the condensation of melamine-formaldehyde, the C=O in melamine was reduced to C-O in the prepolymer, which gives a band around 1039 cm^{-1}. The FT-IR spectrum of naphthalene sulfonic acid based PCM (NSA-SM) (Fig. 1b) shows the presence of –OH groups in the prepolymer with a broad band

TABLE II
Post-tanning process for the manufacture of upper leather from wet blue

Process/chemicals	%	Duration (min)	Remarks
Washing			
Water	100	10	Drained
Neutralization			
Water	150		
Sodium formate	1.0	10	
Sodium bicarbonate	1.0	3x15+45	pH – 4.5 - 5.0, Drained.
Washing			
Water	200	15	Drained
Retanning, Dyeing and Fat liquoring			
Water	100		
Grain tightening acrylic syntan	2.0	30	
Synthetic fatliquor	2.0	45	
Acid dye	2.0		
Phenol-naphthalene syntan	8.0	60	
Synthetic fatliquor	6.0	30	
Semi-synthetic Fatliquor	4.0	60	
Melamine resin syntan	4.0		
Vegetable tanning agent	2.0	60	
Formic acid	1.5	4x10+20	The exhaustion of the bath was checked. Drained.
Washing	100	15	The leathers were set twice, hooked to dry, conditioned, and staked.

around 3437 cm^{-1}. Small peaks around 2930 cm^{-1} determine the presence of $-CH_2$- symmetric stretch, which in turn proves the incorporation of *n*-octadecane in the prepolymer. Slight deformation in the $-CH_2$- shows band around 1427cm^{-1}. The C-C and C-N bond stretching frequencies appears around 1034-1220 cm^{-1}. The band at 1620 cm^{-1} provides the evidence for the presence of C=O, which is present in urea.

TABLE III
DSC analysis for the retanning agents

Sample Name	Onset temperature (°C)	Peak (°C)	Enthalpy (J/g)
MF-SM	77.9 ± 0.3	116.7 ± 0.2	378 ± 2
NSA-C	169.5 ± 0.1	202.1 ± 0.3	47 ± 3
NSA-SM	198.1 ± 0.1	209.7 ± 0.1	115.1 ± 1

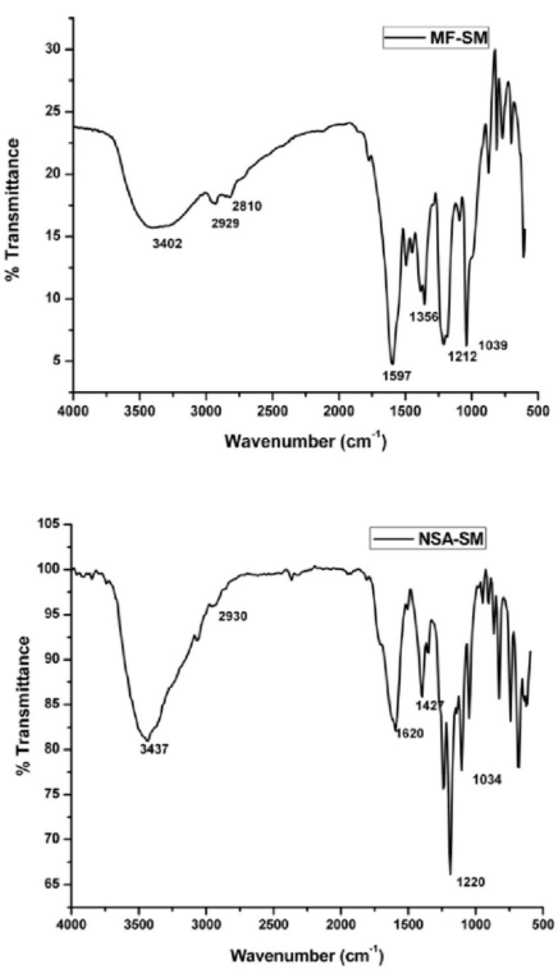

Figure 1. FT-IR spectra of PCM incorporated retanning agents a) MF-SM and b) NSA-SM

DSC-TGA Analysis

In order to study the thermal properties of the retanning agents made after incorporating PCM (*n*-octadecane), DSC analysis of both the melamine formaldehyde and naphthalene sulfonic based retanning agents was carried out. Table III shows that the peak temperature for PCM incorporated retanning agents is higher than that of the control. The enthalpy of transition is 115.1 J/g for NSA-SM, which is higher than that of NSA-C, whose enthalpy of transition is 47 J/g. It can also be seen that NSA based retanning agents have better thermal stability as against MF based retanning agents. DSC analysis clearly indicates that PCM incorporation increases the thermal stability of the retanning agents. The thermogravimetric analysis (TGA) of PCM incorporated retanning agents was also carried out and the thermograms are given in Fig. 2. It can be seen that between MF-SM and NSA-SM, naphthalene sulfonic acid based retanning agent has better stability against thermal degradation, which is about 219°C as against 112°C of melamine formaldehyde based retanning agent.

Scanning Electron Microscopy Analysis

The encapsulation of PCM into the prepolymer was confirmed also using scanning electron microscopy (SEM) analysis. SEM micrographs shown in Figure 3 clearly show that the PCM, *n*-octadecane is successfully encapsulated into both melamine-formaldehyde and naphthalene sulfonic acid based prepolymers.

Thermo Responsive Function Analysis

A methodology to determine the surface temperature of the leather was developed in-house. For this the leathers treated with PCM material were exposed to natural sunlight at an angle of 45°C to the sun and the surface temperature of the leather monitored using a non-contact thermometer over a period of 60 min.

Properties of Leather Made Using PCM

Thermal Stability (DSC and TGA) of Leathers

The thermal stability of the control leathers and leathers made using PCM incorporated retanning agents was studied using DSC. Table IV gives the onset, denaturation temperature and enthalpy of denaturation for control and leathers made using PCM incorporated retanning agents both melamine formaldehyde and naphthalene sulfonic acid based. The PCM incorporated retanning agents show better thermal stability than the control samples. Fig. 4 shows the TGA thermograms of control leathers and leathers made using PCM incorporated retanning agents. The results indicate that leathers made using PCM incorporated retanning agents have better thermal degradation stability than the control leathers. Also, it can be seen that L-NSA-SM has better stability than L-MF-SM.

Scanning Electron Microscopic Studies of Leathers

The scanning electron microscopic analysis of the experimental leather was carried out to study the influence of

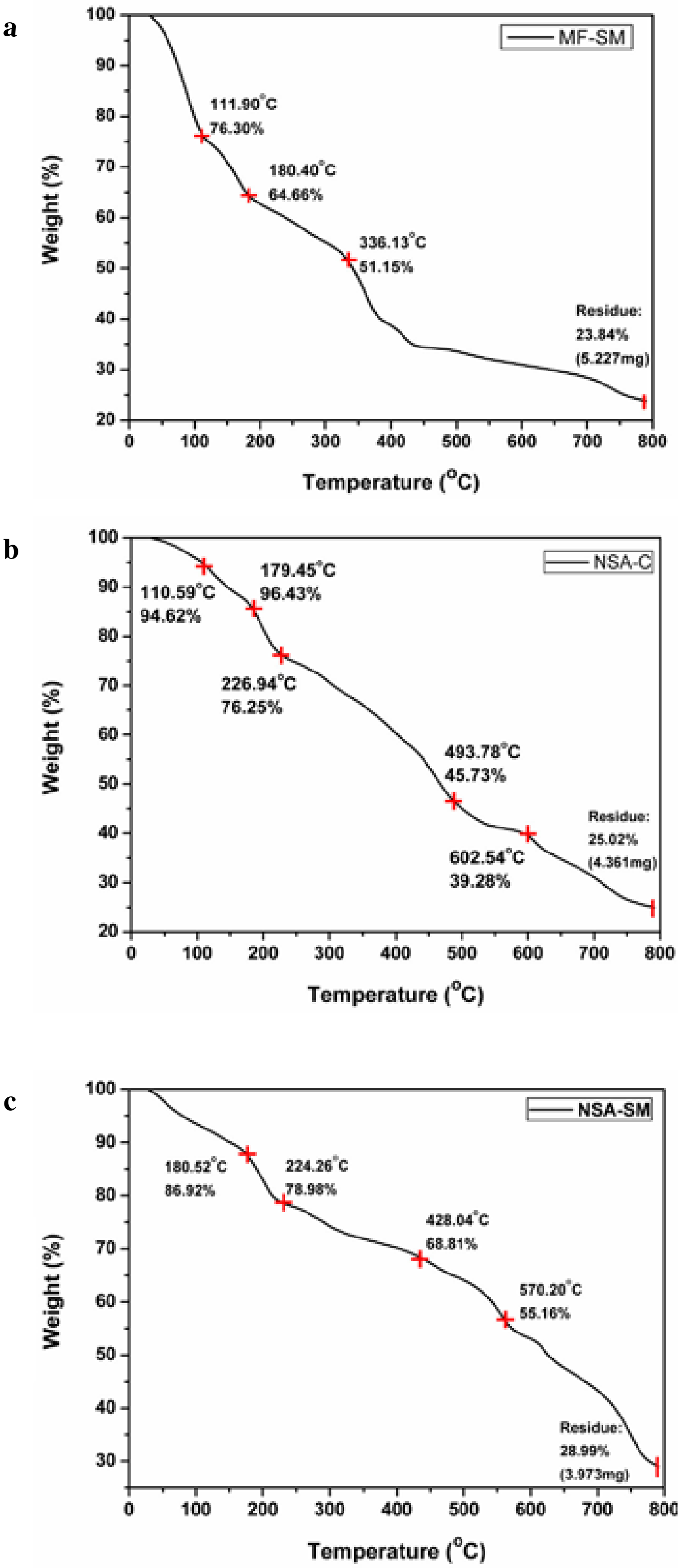

Figure 2. Thermogravimetric analysis (TGA) of PCM incorporated retanning agents a) MF-SM, b) NSA-C and c) NSA-SM

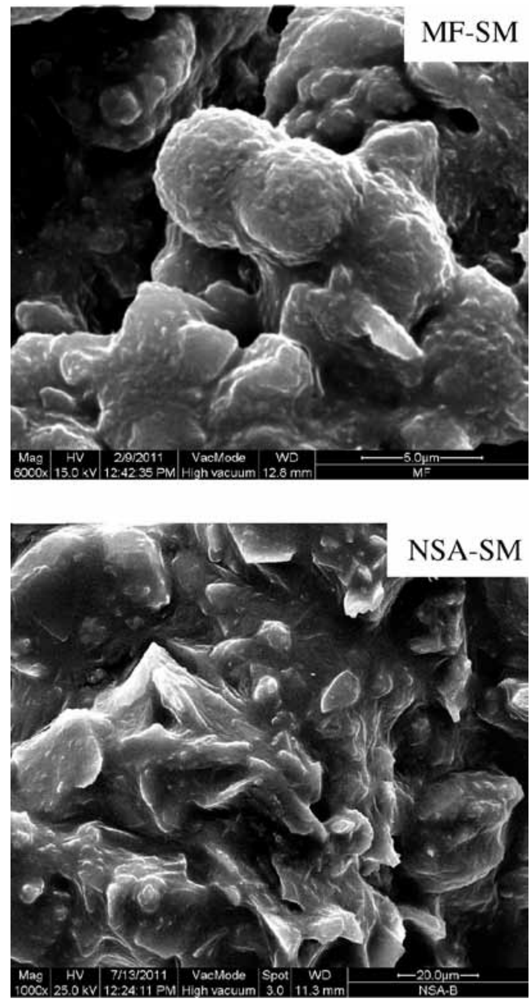

Figure 3. SEM micrograph of PCM incorporated retanning agents a) MF-SM and b) NSA-SM

the encapsulated PCM on the fibre structure as compared to the conventional retanning agents. The micrographs showing the grain of experimental leather are given in Fig. 5. The grain surface of the leather is smooth without any deposits, which is in agreement with the assessment of the organoleptic properties of leathers that the experimental leathers exhibit better grain smoothness compared to control leather.

Physical Strength Characteristics of Leathers

The leathers made using PCM were characterized for the physical and organoleptic properties. Tensile, % elongation and tear strength for the control leathers and leathers processed with PCM incorporated retanning agents are given in Table V. It is seen that the physical properties of leathers retanned with encapsulated PCM are better than the control leathers. It is also seen from the table that experimental leathers exhibit better tensile and tear values to that of UNIDO norms.[14] The incorporation of PCM through surface coating had resulted in decrease in physical strength characteristics.[10] Thus, the incorporation of PCM as a retanning agent overcomes this disadvantage and results in leathers with better physical strength properties.

TABLE IV
DSC Analysis for Retanned Leathers

Sample Name	Onset temperature (°C)	Peak (°C)	Enthalpy (J/g)
L-MF-C	47.1 ± 0.3	91.9 ± 0.1	266 ± 2
L-MF-SM	51.2 ± 0.1	97.2 ± 0.1	280 ± 3
L-NSA-C	45.9 ± 0.3	82.5 ± 0.2	313 ± 2
L-NSA-SM	47.3 ± 0.2	85.1 ± 0.1	315 ± 4

Hand Evaluation of Leathers

The bulk properties of the control and leathers retanned with PCM incorporated retanning agents were assessed by standard tactile evaluation by experienced tanners. The comparative ratings for each property are given in Fig.6. It can be seen from the figure that leather retanned using the encapsulated PCM exhibits better bulk properties than control leathers. It is also seen that leathers made using naphthalene sulfonic acid based smart retanning agent exhibit better organoleptic properties than melamine formaldehyde based leathers.

Thermo Responsive Function

The determination of thermo responsive function is based on infra-red imaging techniques. For application in leather, this method needs to be simplified and hence an in-house method to evaluate the same and compare it with control leather was developed. The expectation out of such leathers is that they should have a lower grain surface temperature when compared to the surrounding environment. To test this property, the leathers were exposed to natural sunlight. The incident light was optimized at an angle of 45° to the sun. With a mid-summer temperature of 40±2°C in Chennai, India, after exposure for about 60 min, the control leathers had grain surface temperature of 39±1°C, while that of PCM treated leathers were 35±3°C. No major difference was observed between the two types of retanning agents investigated in this study. The ability of thermo responsive leathers to attain 4±2°C lower temperature than control leather could be attributed to the phase transition of the *n*-octadecane incorporated in the retanning agent.

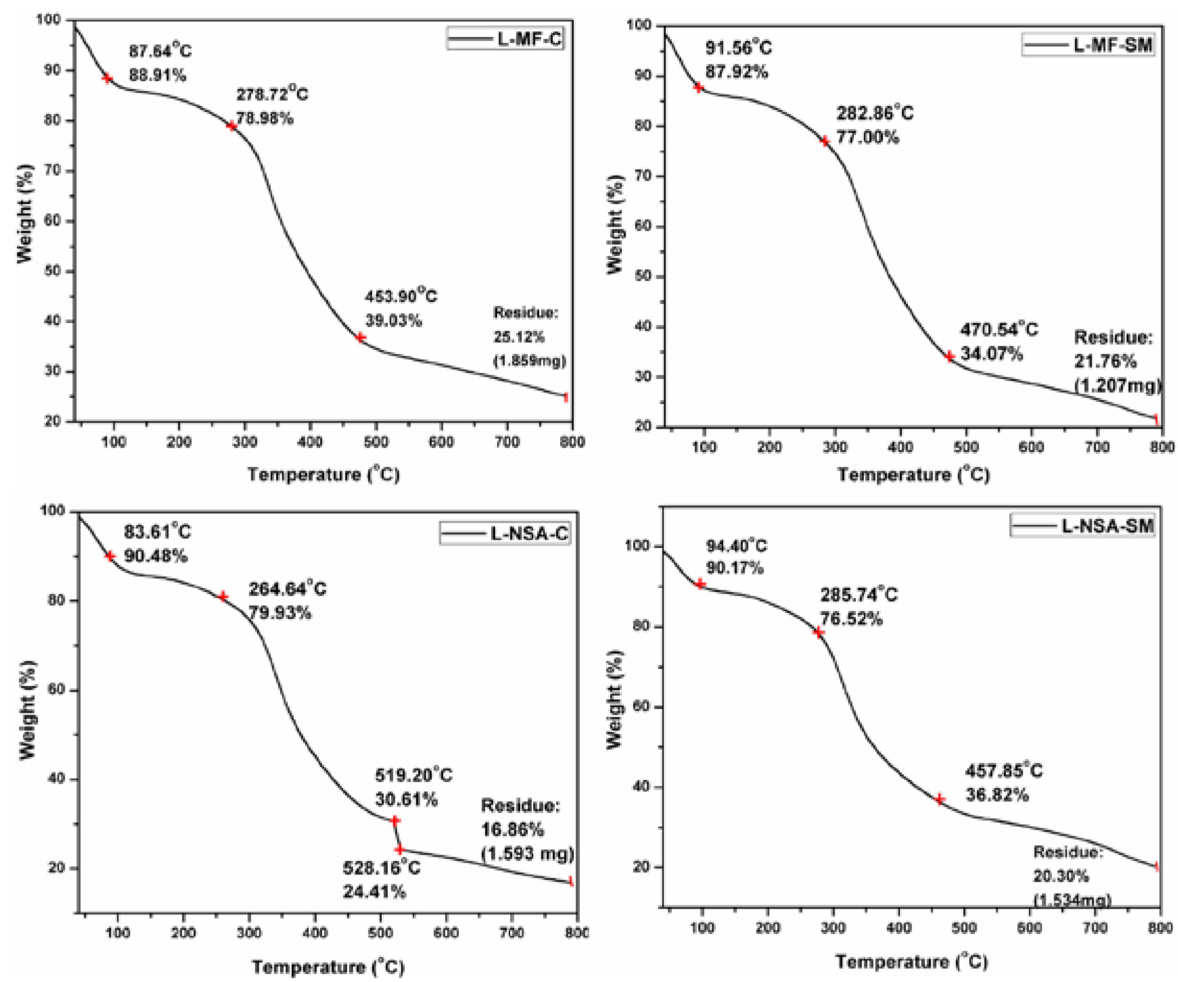

Figure 4. Thermogravimetric analysis (TGA) of leathers a) L-MF-C, b) L-MF-SM, c) L-NSA-C and d) L-NSA-SM

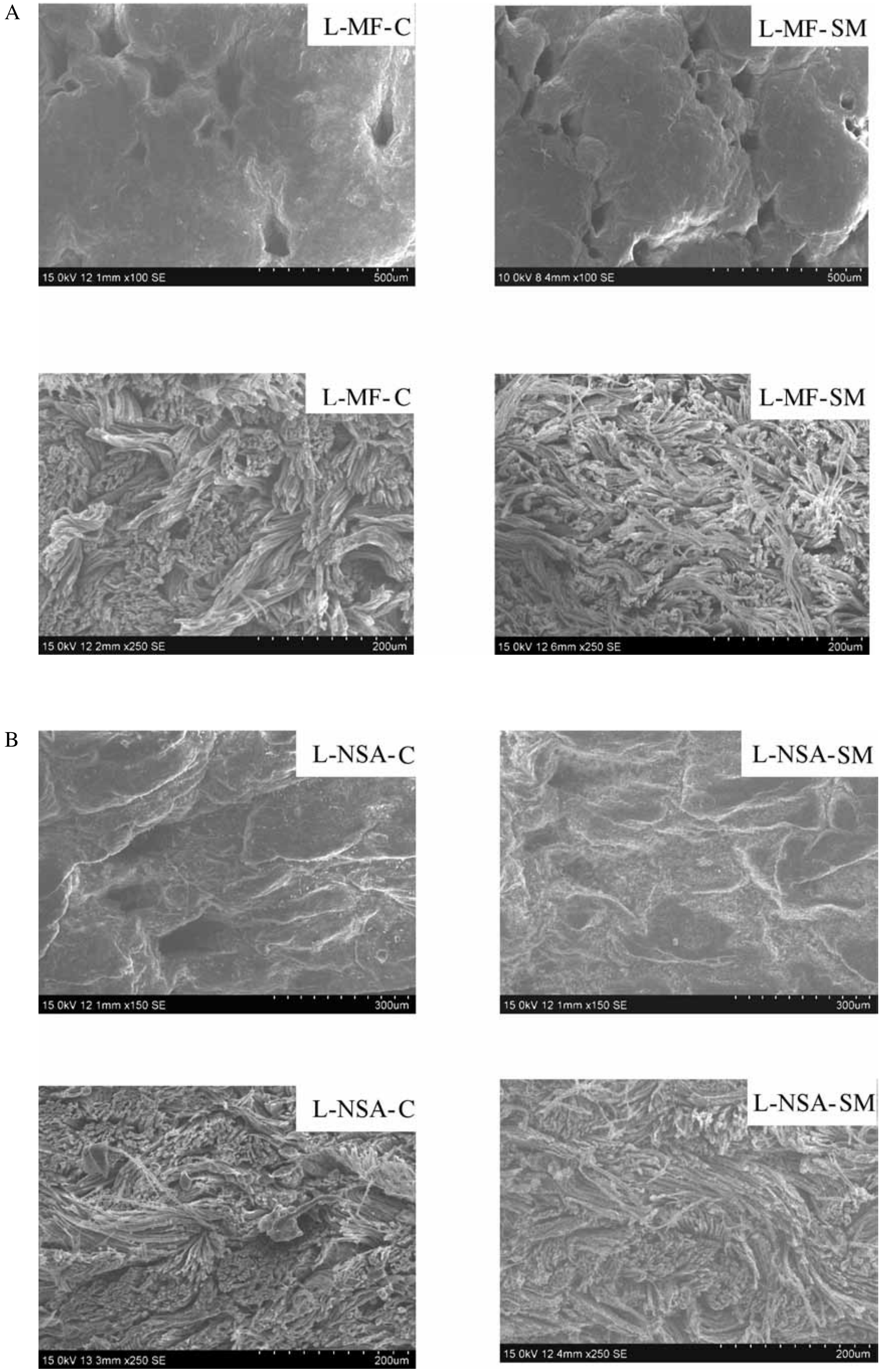

Figure 5. SEM micrographs showing the grain (x150) and cross section (x250) of control leathers and leathers made using PCM incorporated retanning agents.

TABLE V
Physical strength characteristics of control leathers and leathers made using retanning agents incorporated with PCM

Sample	Tensile Strength (Kg/cm^2)	% elongation at break	Tear strength (Kg/cm)
L-MF-C	211±3	65±1	67±3
L-MF-SM	235±4	74±2	75±2
L-NSA-C	205±2	85±2	40±1
L-NSA-SM	226±3	102±2	46±2
UNIDO norms	200		40

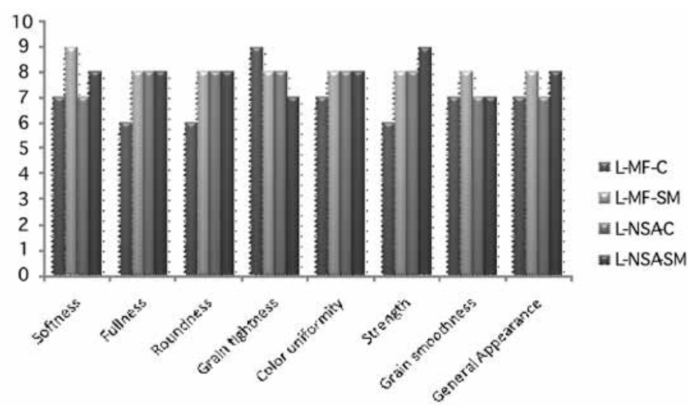

Figure 6. Organoleptic properties of leathers made using PCM incorporated retanning agents

CONCLUSIONS

In the present study, thermo responsive leathers were developed by incorporating phase change materials (PCMs) into leather through retanning operation. The retanning agents made using PCM were characterized using FT-IR and SEM to confirm the encapsulation of PCM into the prepolymer. The leathers made using these smart retanning agents have been characterized for their physical strength and organoleptic properties and have been shown to exhibit better properties than control leathers. The above describer in-house test method suggests that these leathers do exhibit the thermo responsive function.

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