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Effect of micro phase-change materials on the thermal behavior of leather

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ABSTRACT

Today, scientists are interested in the manufacturing and invention of smart textiles such as phase change materials (PCMs). The process of phase change from solid to liquid and vice versa takes place in such materials. Using materials such as PCM could change the properties of leather for better performance, and could be applied to many places such as the shoe industry. The background of the study is that using PCMs could increase thermoregulating properties of materials. For finishing leather with PCMs, several methods were suggested such as spraying, tanning, laminating, etc. In this study, first impregnated leather with 5% and 10% of PCM by spray technic are prepared and characterized using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). Finally, water vapor permeability and physical properties of the samples were analyzed for an understanding of leather comfort. The results reveal that after impregnating with 10% PCMs, significant effects on the thermal behavior of samples were observed, and this finishing had no effect on the comfort of leather.

Keywords
PCMS,
thermal comfort,
leather finishing,
thermoregulating

1 Introduction

Recently, the use of phase change materials (PCMs) has gained more attention due to their function, which provides an interesting benefit to the customer. PCMs consist of a core and a shell, where various materials are used for the core component, e.g. paraffin, n-eicosane, n-octadecane, butyl stearate, etc., which absorbs heat and changes its phase from solid to liquid. This phase change slows down the temperature rise. It could be applied to different types of industries such as footwear, high-tech clothing, construction, sustainable energy as well as refrigerant fluids. More generally, it can be used to design a wide range of thermal transient regimes [1].

Pollution of the environment and limited energy sources caused new problems for humans, leading to a variety of studies around possible ways of reducing energy consumption, as well as finding new materials for smart use of energy.

In the footwear and garment industry, the way of using energy and the amount of them is an important factor, customer and production line are two different sides of the industry, and for both parts, wise energy consumption is important, for the customer, especially athletics and the specific user such as laborers in difficult conditions which are energy challenging for them, also for production line for more profit and less pollution of the environment the way of using energy is on priority.

The PCMs are encapsulated in small spheres to be contained in a liquid state (Fig. 1). The microcapsules have an approximate diameter of 1-10 μm and are resistant to abrasion, pressure, heat and chemicals according to the shell chemical compounds. Micro-sized capsules are required to provide a large contact area with the environment and ensure optimal efficiency of the phase change [2].

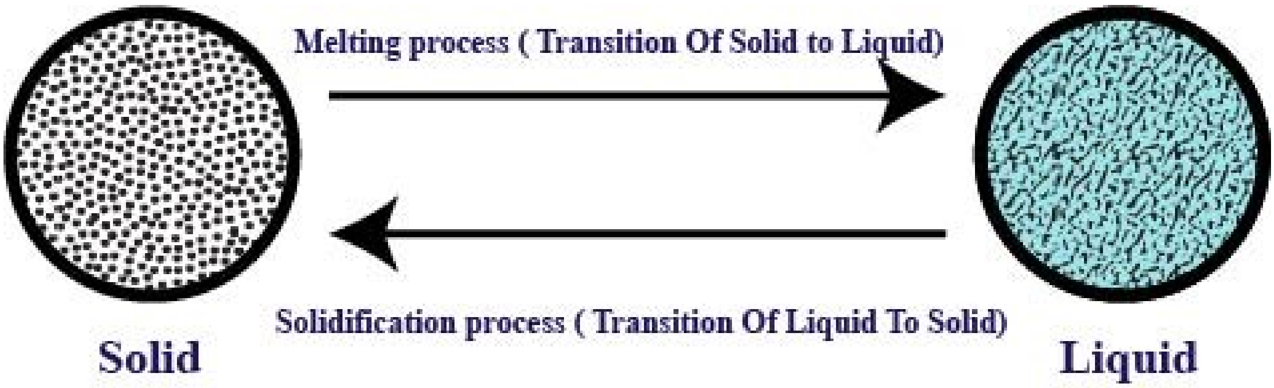

Fig. 1 Phase change phenomena. Adopted from http://www.venture-chemical.co.jp/technical/technical_leaflet.html.

Among a variety of possible wall materials for microcapsules, amino resins, in particular melamine-formaldehyde, play a major role in the patent literature. Amino resins represent an interesting economic alternative, as these polymeric raw materials have been produced on a large scale for many years and have already been used in many processes such as phase separation and interfacial reactions (e.g. dicarboxylic acid dichlorides and di- or triamines). Furthermore, melamine-formaldehyde microcapsules prepared by in situ polymerization have impermeable shells [3].

A recent study shows that textiles containing PCMs respond to environmental changes to perform their function and provide greater comfort to their users [4].

For a garment that needs to be protected against cold, thermal insulation by attracting microcapsules is a solution. These capsules contain a small amount of PCMs. The industry uses PCMs to produce clothing with different comfort and thermal properties. Nowadays, with the application of thermal properties, absorption and release of energy of PCMs in textiles, patching is done by different methods: direct bonding, bonding by foam or other coating methods [5].

Heat exchange with the environment plays a key role in the heat balance of the human body. Thermal comfort can be defined differently, but one of the accepted definitions is the psychological satisfaction of humans according to their body temperature and their environment. General dissatisfaction is caused by coldness or warmth [6].

Yang et al. published a review paper summarizing different techniques for the application of textiles with PCMs, they divided into three different areas, PCMs for fiber, yarn and fabric [7].

Kumar et al. worked on the application of PCM for thermal energy storage in recent years. They found that latent heat storage systems can store more energy density with less temperature difference between storing and releasing heat compared to the sensible energy storage system. They mainly focused on providing PCM thermal energy storage applications and providing an understanding to develop new PCMs with improved performance and safety [5].

Kumar and Gupta study application of PCM in solar thermal energy shows that it can help to store excess solar energy for future use. One of the best ways to store thermal energy from the sun is to use PCMs, as a large amount of latent heat can be captured and isothermal nature of PCMs during heat expansion and release during phase change [6].

Jima et al. worked on a cool leather garment suitable for hot weather, they used *N*-octadecane, a microcapsule with spherical shell containing melamine-formaldehyde polymer with 226 nm average and 142 J/g heat storage capacity. They concluded that the preparation of leather with 20% mass of microcapsule was suitable for hot weather [3].

Nazemi et al. worked on different finishes and the effect of finishes on the physical properties of textiles and used them in the sports industry to improve athletic performance, they also simulated and modeled athletic behavior by software and showed that finishes may be important for different users [8,9].

Huang et al. studied the thermal properties and application of microencapsulated PCMs for thermal energy storage, they reviewed different processes and techniques of encapsulation and concluded that the encapsulation method of PCM is an approach to alleviate leakage, phase separation and volume change problems. Microencapsulated phase change materials are one of the most popular techniques to increase the efficiency of resource use for thermal energy storage [10].

Butuc et al. published a paper on the different applications of thermo-regulating textile and the way of applying this in the future to textile materials, their results show the advantage of PCMs on knitted fabric.

Huang et al. studied on the microcapsule with properties of thermoregulating was made of polyethylene glycol (PEG) on leather and concluded that this finishing can improve the thermal behavior of leather [11].

Salaün et al. investigated polymer nanoparticles reducing the thermal conductivity of phase change materials and proved that the polymer nanoparticles do not affect the latent heat and even improved the phase change behavior as well as the mechanical properties [2].

In this study, micro-PCM technology was applied to raw leather and the application methods were investigated by morphological analysis; the thermal performance of the samples was evaluated by differential scanning calorimeter (DSC) and the surface by scanning electron microscopy (SEM).

2 Materials and process

PCMS with hexadecane core and melamine-formaldehyde shell was purchased from Razi chemical Co. Iran, sulfonate ester as surfactant was provided by Simab Rezin Ltd. Iran, sodium hexametaphosphate (SHMP) as dispersing agent was purchased from Simab Rezin Ltd. Iran, cross-linked acrylic emulsion copolymer as thickener was provided by Simab Rezin Ltd. Iran, polyurethane binder was provided by Simab Rezin Ltd. Iran, respectively. In addition, anti-foaming agent was supplied by Simab Rezin Ltd. Iran, chrome tanned cowhide was purchased from Maral Leather Ltd. Iran (called raw leather).

An SEM microscope (model: KYKY-EM3200) was used to evaluate the morphology of the leather, and also a DSC instrument (NETZSCH DSC 200F3) was used to compare the heating behavior of the coated leather and a raw leather, an AM120Z-H laboratory stirrer was used to stir the mixture, an Isotherm® Forced Convection laboratory oven was used as a drying machine, the tensile strength was measured using a universal material testing machine (model H10K-S, Tinius Olsen, America) according to ASTM D5034-09(2013). Rubbing fastness was measured using a Taber Instrument Corporation North Tonawanda, N.Y. USA Model 174 MFG in accordance with AATCC Test Method 8-2007. ASTM Standard Test Method E96 was used for water vapor permeability, which involved three different steps to test the dish, the test environment and the test mass.

3 Methods

Jima et al. used the spray technique for finishing leather in 2019. This study also used their technique as mentioned here, microcapsules were coated on one side of leather by spray technique during leather finishing [10]. The prepared microcapsules were first dissolved in water under stirring at 2000 rpm for 10 min and added to the finishing solution at 5 or 10 wt% of the leather used to treat the leather. The solution was sprayed onto the leather in 4 cross-coats. After 3 cross-coats, the leathers were baked at 70 °C and 150 Pa and another cross-coat was applied. The leathers were dried between each coat to allow for better absorption. After drying for 3 hours, a 1:1 lacquer/water mixture with a small amount of hand modifier was sprayed on the surface of the leather through 2 cross-coats to give a glossy appearance and protection to the finished film. The coated leather was buffed at 80 °C and 150 Pa to ensure cross-linking of the finishing chemicals with the leather and to further shine the surface. Finally, the treated leathers were dried at 30 °C before characterization [10].

After finishing, SEM, DSC, tensile strength, rub fastness and water vapor permeability tests were used to characterize the finished leather.

4 Results and discussion

Figure 2 shows the comparison of raw leather and leather finished with 5 and 10% of PCMs. The result shows that after finishing, the pores of the raw leather are filled with PCMs and this phenomenon caused a loss of breathability. In addition, the size of the PCMs is visible in this figure, showing that micro- and nanoparticles were covering the leather.

As it can be seen in Figure 2, there is no sign of haring process on the hide and PCMs have completely covered each pore.

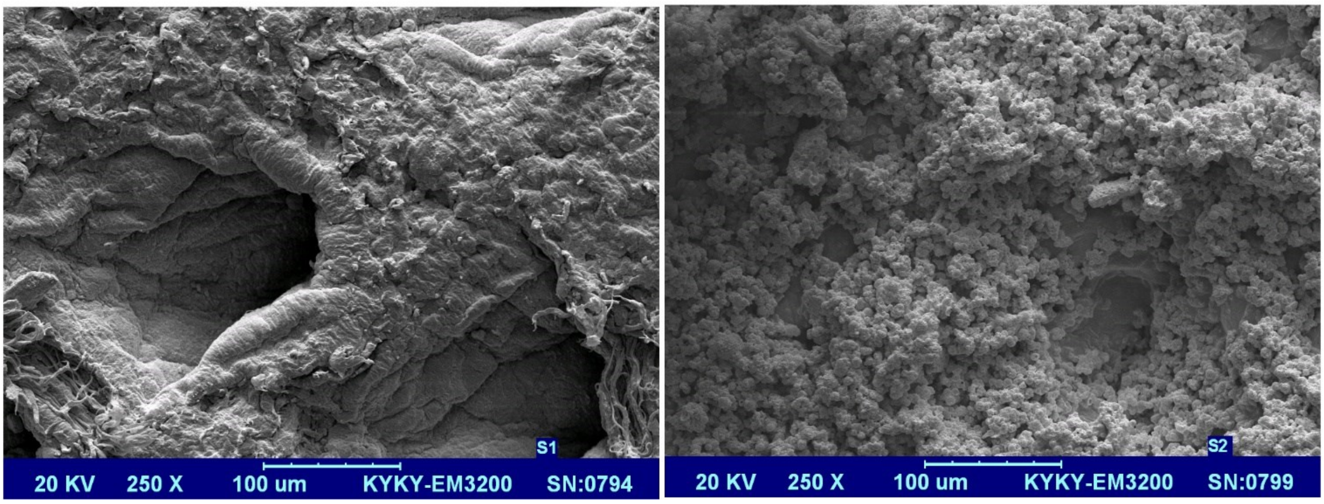

Fig. 2 (S1) raw leather; (S2) leather finished by PCMs.

For a better analysis, Figure 3 shows the compression of raw leather, leather finished with 5% PCMs, and leather finished with 10% PCMs. Figures 3b and 3c show the correct distribution and a greater number of microcapsules. The first point relates to the correct method of dispersion and the second shows the presence of more PCMs on the leather. Another conclusion that can be drawn from the figure is the dimensions of the PCMs.

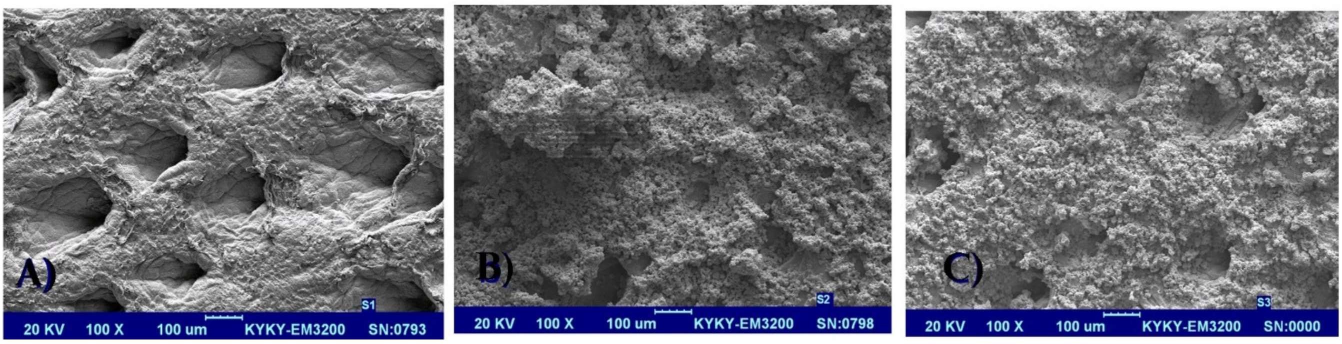

Fig. 3 Comparison of a) raw leather; b) leather finishing by 5% PCMs; c) leather finishing by 10% PCMs.

Once the SEM test has proven that the PCMs has been properly applied to the leather with the correct dispersant, the DSC test is carried out to observe the thermal behavior of the PCMs before they are applied. With the figures as the result of this experiment, this research can prove how much energy is saved before and after the laying of PCMs.

Firstly, the finished sample was examined using microcapsule powders to observe that the PCMs used in this process had an effective performance on the heat absorption properties and energy utilization of the sample. The results are shown below.

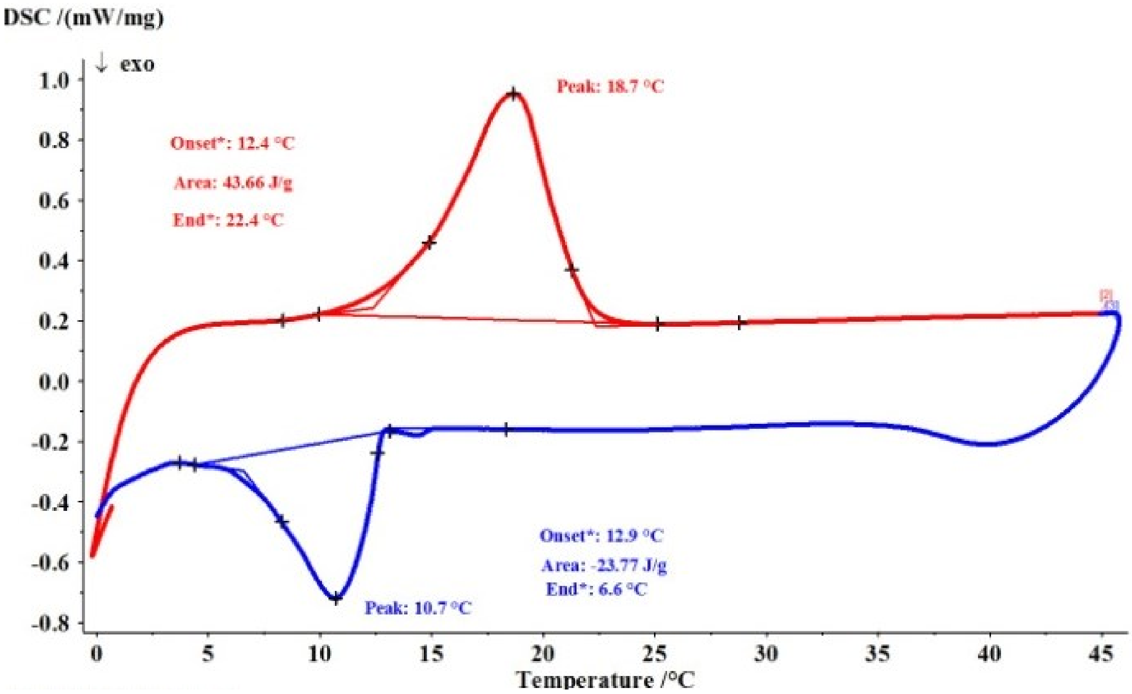

Fig. 4 DSC measurement of PCMs.

As shown in Figure 4, the melting point of PCMS is 18.7 °C. The area under the curve represents the amount of energy absorbed, which is 43.66 J for 1 g of PCMs. The reverse plot shows the crystallization point at 10.7 °C. The area under the curve shows that PCMs releases 23.77 J of energy for 1 g of PCMs. This proves that the materials are properly absorbing and releasing the target properties. With the application of the above data, for a better state of comparison, natural leather was also examined by DSC. The results are depicted in Figure 5.

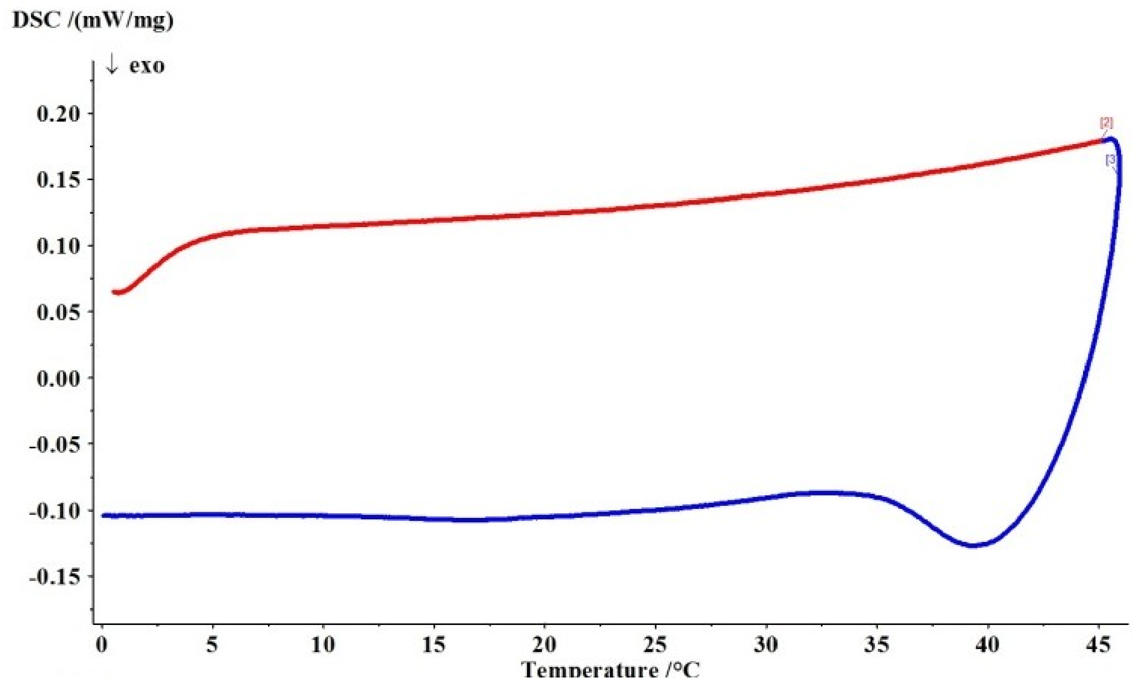

Fig. 5 DSC measurement of raw leather.

As can be seen from Figure 5, there is no peak in the thermal region, proving that leather has no energy absorption or release in this region. And if PCMs were applied to a sample, it must have their thermal properties, i.e. energy absorption and release.

Figure 6 shows the thermal behavior of leather impregnated with 5% PCMs, which shows that the amount of PCMs was not enough for the expected efficient thermal behavior of leather.

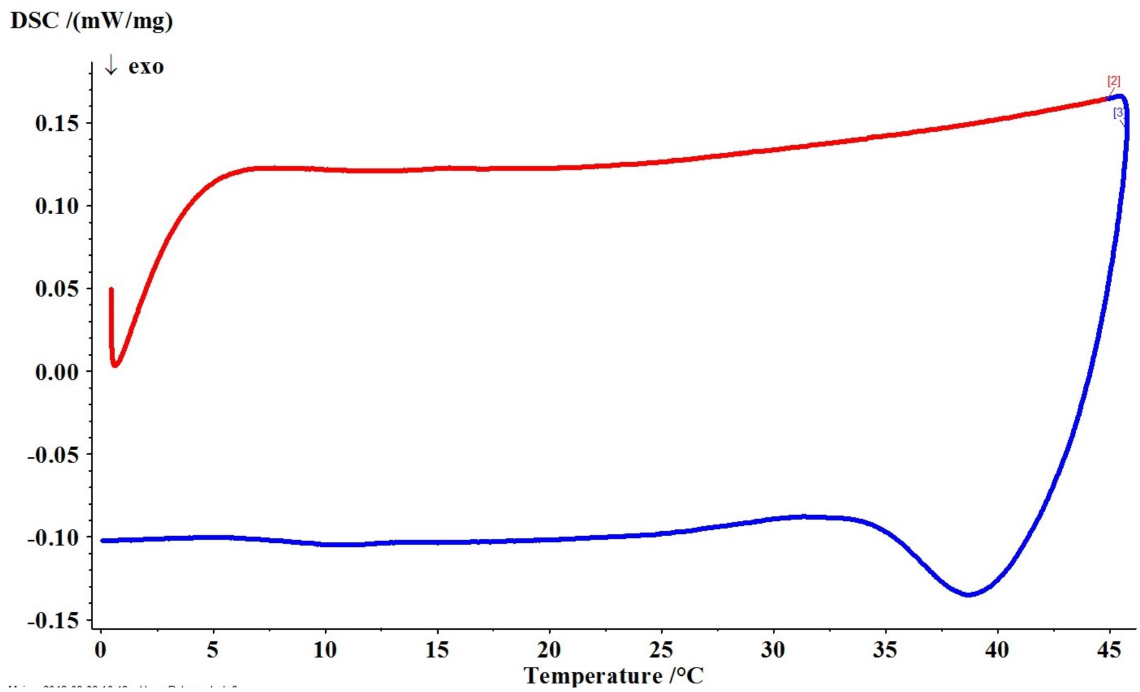

Fig. 6 DSC measurement of leather sprayed with 5% PCMs.

The same procedure was used to impregnate the samples with the 10% PCM sprayed onto the leather. The DSC results are shown in Figure 7.

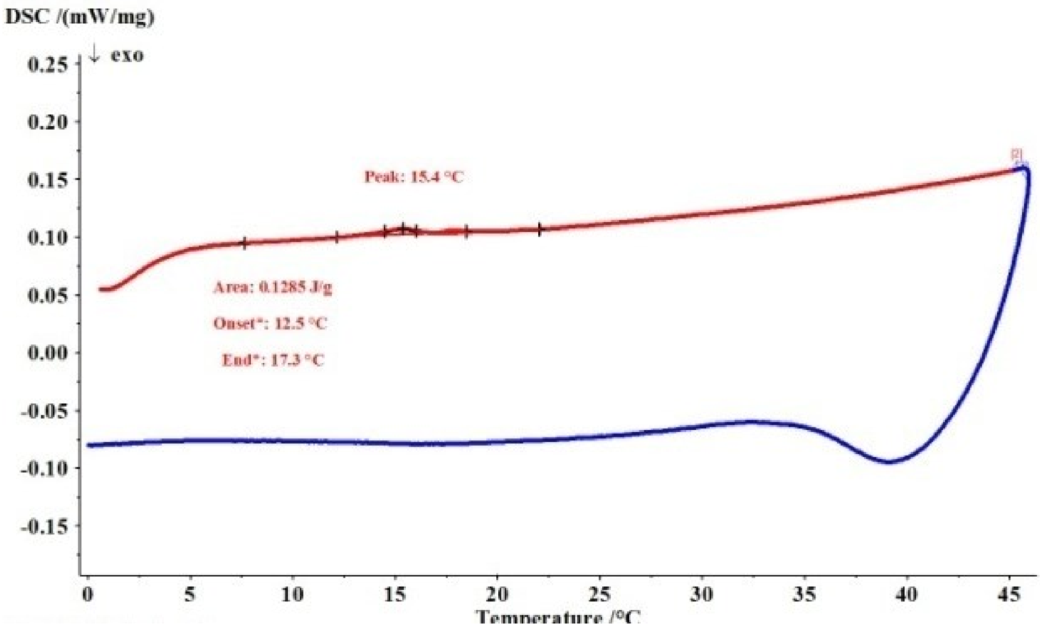

Fig. 7 DSC measurement of leather sprayed with 10% PCMs.

The figure shows that PCMs have resulted in a temperature peak at 15.4 °C, which is the melting point of the PCMs. The area under the curve shows that for each gram of PCMs, 0.1285 J of energy is stored in the leather. This energy can be released as the environment gets colder. This can make the consumer feel warmer.

To analyze the comfort of leather after finishing, water vapor permeability tests were carried out. Table 1 shows the water vapor permeability results of raw leather, leather finished with 5% PCMs and leather finished with 10% PCMs. Table 1 shows that PCMs had an effect on the breathability of the leather, but this effect was negligible. Most researchers agree that the transition between air and water through the garment is the most important factor for the comfort of the user, but according to these characteristics the definition of garment comfort was so complex because the sense of feeling of the users is different from each other [12]. If the transition of air and water through the garment is reduced by any process, the user will feel uncomfortable due to air being trapped between the body and the garment, in this study water vapor permeability was used as a simple test to understand the effect of PCMs finishing on the transition of water through the samples.

Table 1. Results of water vapor permeability examination.

Title	**Raw leather**	**Leather finished by 10% of PCMs**	**Leather finished by 5% of PCMs**
Mass of sample before experiment	4.09 g	4.14 g	4.55 g
Total mass of sample (sample + water) before experiment	207.91 g	204.87 g	201.19 g
Total mass of sample (sample + water) after experiment	199.26 g	197.36 g	193.17 g
Mass of sample (sample + water absorption) after experiment	4.03 g	4.42 g	4.77 g
Total transition	8.65 g	7.51 g	8.02 g
Absorption	0.21 g	0.28 g	0.22 g
Water vapor permeability (WVP**)**	437.26 g/(m² day)	379.63 (g/m² day)	405.41 (g/m² day)

To understand the effect of PCMs on the rub fastness of leather, Table 2 shows the physical properties of the samples. Table 2 shows that finishing leather with PCMs had a negligible effect on the rubbing fastness of leather, indicating that this technique could be an efficient performance for customers.

The tensile strength of the unfinished leather was 16 MPa and after finishing with PCMs the tensile strength increased slightly, which means that the porous leather filled with PCMs makes the finished leather stronger than the unfinished leather.

Table 2. Physical properties of samples.

Title	Leather finished by 10% of PCMs	Leather finished by 5% of PCMs	Raw leather
Dry rubbing fastness	3	3.5	5
Wet rubbing fastness	2.5	2	5
Tensile Strength (MPa)	17.5	17.2	16

5 Conclusions and outlook

Comparing samples coated with 5% and 10% PCMs, 10% samples were the better choice, but even this concentration was not perfect for ideal properties. In addition, after finishing the leather with PCMs, the physical properties of the samples were reduced, but by less than 1%, which was negligible. The rubbing fastness of the samples was high, indicating that the finishing technique was accurate without any significant changes in the rubbing fastness of the samples. Also, from the results of this study, it can be understood that PCMs in certain concentrations could improve the thermal behavior of leather, this phenomenon could affect the comfort of the garment, but the designer could use this type of leather on an important part of the garment that has less direct contact with the user's body.

Taking into account the experiments carried out in this study for similar projects, the proposal is to use PCMs in the lining of textiles and to use PCMs in the tanning process. The last point is to consider the financial possibilities to optimize the use of PCMs in the processing of leather and other textiles.

Author Contributions

S. Nazemi: Investigation, resources, data curation, writing – original draft preparation; R. Bagherzade: writing – review and editing; M. Gorji: conceptualization, methodology. The authors declare no conflict of interest.

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