Phase Change Materials (PCMs) technology for leather wearing industry

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Abstract: Textiles containing microencapsulated phase change materials (microPCMs) are considered intelligent because they react immediately to changes in environmental temperature and adapt to prevail on hot or cold conditions.

In this work microPCMs technology has been applied to natural leathers and the methods of application were investigated by morphological analysis; the thermal performances of samples were evaluated by differential scanning calorimetry and infrared vision camera, their physic characteristics were examined by mechanical properties.

Key words: leathers, microcapsules, phase change materials, infrared thermography

1 Introduction

Intelligent textiles are able to sense stimuli from the environment, react and adapt to them by integration of functionalities in textile structure. According to this definition, textiles containing phase change materials (PCMs) are considered intelligent, because they react immediately to changes in environmental temperature and adapt to prevail on hot or cold conditions.

In the present applications of PCMs technology in the textile industry, the crystalline alkyl hydrocarbons are used exclusively. The alkyl hydrocarbons are non toxic, non corrosive and non hygroscopic. In order to realise the desired temperature range in which the phase change takes place, the hydrocarbons can be mixed.

To prevent the liquid hydrocarbons from migrating within a fibrous substrate, they need to be microencapsulated. A variety of chemical and physical techniques for manufacturing different types of microcapsules exists and can be employed for forming microencapsulated PCMs. The key parameters of microPCMs are particle size and its uniformity, core-to-shell ratio (with PCM content as high as possible), thermal and chemical stability, resistance to mechanical action.

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In the last decade several methods of incorporating microPCMs into fibrous structures were developed to produce fabrics having enhanced thermal properties. Most work in this field can be found in patent literature and only a few papers in published literature report the formulation of PCM microcapsules, finishing of fabrics and the evaluation of their characteristics, including their thermal properties and durability, especially if referred to the use of this technology in the leather industry.

2 Experimental

2.1 Materials

Ovine natural leather with a thickness range of 0.6±0.1mm was supplied by Carisma (Italy), microencapsulated PMCs characterized by phase transition temperatures at 18°C (Ty65) and 28°C (MPCM28) were supplied by Microtek Laboratories (Ohio-USA).

Chemicals for wet leather impregnation: commercial Bioplen V6 (acrylic resin solution – Biokimica SpA-Pisa-Italy), Baytan N (fungicide - Bayer), Cromitan B (Chromic Sulfate Cr2(SO4)3 - Basf).

Chemicals for dry coating: Baygen Compact Bottom AP (aqueous preparation of covering polyurethane and acrylic dispersions), Baysin LN (dispersant and thickener), Bayderm Prebottom APV (polyurethane dispersions), all purchased from Bayer.

2.2 Methods for PCMs application to leather

In this study two coating methods were experimented for the application on leather of microPCMs, the efficiency of the wet and dry coating process were compared as microPCMs adhesion on leather samples.

2.2.1 Preparation of microPCMs solution for leather impregnation process

The tanning bath solution was formed by water, formic acid, NH₃, Baytan N, pigment, Cromitan B, Bioplen V6, 4 and 40% wt of microPCMs referred to sample weight; chemicals were left in contact for 2h and then samples were washed by cold water.

2.2.2 Preparation of the microPCMs solution for leather coating

To prepare the coating mixture, 4 and 40% wt of microPCMs whit respect to leather weight were dispersed in the aqueous preparation of covering polyurethane and acrylic agents. The coating solution were deposited on the leather sample by means of a manual roll and then dried at room temperature.

2.3 Characterization

2.3.1 Morphology test

The surface morphology of the microcapsules-treated leathers was observed by a scanning electron microscope (SEM, Philips XL 20 Series) after the samples had been sputter coated with a layer of gold.

2.3.2 Thermal performance test
The thermal heat capacity of the samples was analyzed using a differential scanning calorimeter (DSC, TA Instruments Q20 DSC) cooled with RCS system. The heating and cooling rate was 10°C/min up to 80°C.

The temperature distributions of the microPCMs-coated samples were measured using an infrared (IR) and visible vision system (FLIR SYSTEMS, Thermo Vision™ A40 M Researcher), having a thermal sensitivity of 0.08°C, a wavelength of 7.5–13 μm, a measurement range of -40 - 2000°C, a frame rate of 1/50 s, and an imager with a resolution of 320 x 240 pixels. The monitoring distance is of 30 cm at 25°C, 50% relative humidity.

2.3.3 Mechanical test

Tensile strength and percentage extension have been determined using the tensile testing machine Instron 5564 with a uniform cross head speed of 50 mm/min; the elastic modulus, E, were calculated by the initial slope of tensile curves.

3 Results and discussion

3.1 SEM observations

Figures 1, 2 and 3 show the surface of neat leather and 40%wt treated leathers by means of impregnation and coating process respectively. It can be noted that, by means of impregnation method, just a few numbers of microPCMs are countable, while in the other case most of microPMCs adhere on the leather. As a matter of fact, thermal properties of coated samples are higher but the surface morphology of the leather is changed by microcapsules addition, affecting its overall properties. In fact it is difficult to maintain durability, moisture vapour permeability, elasticity and softness of samples when a discrete content of microPMCs is loaded. In the following, for industry applications, the coating process will be adopted using a 4%wt of microPCMs in the coating solution to preserve leather characteristics.

![Figure 1 neat leather (magnification 755X)](image-url)
Figure 2 leather treated by impregnation method at 40\% wt microPCMs (magnification 755X)

Figure 3 leather treated by coating method at 40\% wt microPCMs (magnification 200X)

3.2 DSC analysis

The DSC curves of leather samples are shown in figures 4 and 5. It is possible to evaluate the thermal performances as a function of microPCMs content, for both 18\(^\circ\)C and 28\(^\circ\)C transition temperature, respectively.

With increasing microPCMs Ty65 content, the thermal capacity slowly increased from 0.449 J/g at 4\% wt to 8.03 J/g at 40\%wt%; with increasing microPCMs MPCM28 content, the thermal capacity slowly increased from 1.03 J/g at 4\% wt to 20.44 J/g at 40\%wt%. Neat leather and leather treated with coating solution without microPCMs do not show any thermal transition.
3.3 Mechanical properties

Tensile behaviour of samples containing 4wt% of PCMs were recorded. The tensile properties indicate the extensibility and recoverability of leather samples from external stress: as a consequence of the coating process, the elastic modulus decreases (table 1) and a plasticization effect of additives can be confirmed, promoting the more soft feeling.
Table 1 Elastic Modulus of coated samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elastic Modulus [MPa]</th>
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<tbody>
<tr>
<td>Neat leather</td>
<td>46±10</td>
</tr>
<tr>
<td>Coated leather without microPCMs</td>
<td>22±4</td>
</tr>
<tr>
<td>Coated leather containing 4%wt MPMC28</td>
<td>25±7</td>
</tr>
<tr>
<td>Coated leather containing 4%wt Ty65</td>
<td>18±10</td>
</tr>
</tbody>
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The tensile strength of treated samples are lower than that of neat leather, since the polyurethane and acrylic agents reduce the entanglements among collagen fibers and consequently the strength resistance of material.

Table 2 Tensile strength of coated samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength at maximum [MPa]</th>
</tr>
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<tbody>
<tr>
<td>Neat leather</td>
<td>26±8</td>
</tr>
<tr>
<td>Coated leather without microPCMs</td>
<td>15±3</td>
</tr>
<tr>
<td>Coated leather containing 4%wt MPMC28</td>
<td>19±7</td>
</tr>
<tr>
<td>Coated leather containing 4%wt Ty65</td>
<td>12±6</td>
</tr>
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3.4 Infrared thermography

Infrared (IR) thermographic systems, or IR imagers, provide images that represent surface temperatures, or thermograms, by measuring the magnitude of infrared radiation emanating from the surface of an object. Because IR imagers see the radiation naturally emitted by objects, imaging may be performed in the absence of any additional light source. Modern IR imagers resolve surface temperature differences of 0.1°C or less. With this high sensitivity, they can make non-destructive evaluation of thermal phenomena, which are only revealed in the form of slight temperature gradients. Infrared thermography can be used as both a qualitative and a quantitative tool.

In fig.6 is reported the typical thermogram recorded by the instrument obtained by comparing the reference sample (coated leather without microPCMs) and the additivated one with 40%wt microcapsules. The left side of the peak is related to the heating step, the right side is related to the cooling step. At around 18°C and 12.5°C are evident two shoulders on the signal of the additivated sample that are caused respectively by the melting and crystallization process of microPMCs. These transitions are responsible of the delayed thermal response of leather additivated samples, since part of the heat generated is used to melt and crystallize the paraffin inside the microcapsules.
4 Conclusions

In this work microPCMs technology has been applied to natural leather in order to improve its thermal performance without modification of standard finishing procedure. The coating method is more efficient than the impregnation one as confirmed by SEM observations. Mechanical properties are slightly modified by chemical treatments. The thermal characteristics of additivated leathers have been studied by infrared thermography: samples containing 40wt% of microPMCs show a significant thermal effect, but for commercial uses the 4wt% is preferred, obviously in this case the thermal response is less pronounced.

References