BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Tomul LVI (LX), Fasc. 2, 2010
Secţia
TEXTILE. PIELĂRIE

TEXTILES INTEGRATING PCMS – A REVIEW

BY

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Abstract. Phase change materials (PCMs) used in textiles are combinations of different types of paraffin - each with different melting and crystallization points. The PCMs are enclosed in a microcapsule to prevent leakage of the material during its liquid phase. PCM microcapsules can be incorporated into the spinning polymer of manufactured fibers (*e.g.*, acrylic, viscose), incorporated into the structure of foams and these foams applied to fabric in a lamination process, or embedded in a coating compound and coated onto fabrics. Filling hollow fibres is another method to incorporate PCMs in textiles.

Textile structures with incorporated PCMs have the following interactive functions: absorption of surplus body heat; an insulation effect caused by heat emission of the PCM into the textile structure; a thermo-regulating effect – which keeps the microclimate temperature nearly constant.

Differential Scanning Calorimetry measurements can be used to determine the thermal capacities, melting temperature of PCM, and crystallization temperature of the phase changes of PCM microcapsules embedded in textile structures. Thermal Insulation Properties can be determined using a Dynamic Heat Transfer Measurement.

On the other hand thermo-regulated properties of PCM containing textiles could be measured by an instrument that is called the Fabric Intelligent Hand Tester (FIHT). The indices of thermal regulating capability (Id and Δtd), static thermal insulation (Is), and the thermal psychosensory intensity (TPI) of textile incorporating phase change materials are measured.

The manufacture, properties and applications of heat-storage and thermo-regulated textiles have been extensively studied since the 1980s but their development is still of present interest.

In this review paper the areas of application in textiles, the methods of PCMs integration in textiles and the methods of evaluation of their thermal properties are presented.

Key words: phase change materials, smart textiles, thermo-regulating effect.

1. Introduction

According to the Textile Glossary smart textiles are defined as textiles that can sense and react to changes in the environment, such as changes from mechanical, thermal, chemical, magnetic and other sources [1].

Depending on their functional activity smart textiles can be classified in three categories [2]:

1. *Passive Smart Textiles* – the first generations of smart textiles, which can only sense the environmental conditions or stimulus.

2. *Active Smart Textiles* – the second generation of smart textiles, which sense and react to the conditions or stimulus.

3. *Ultra Smart Textiles* − the third generation of smart textiles, which can sense, react and adopt themselves to environmental conditions or stimuli.

Textiles with Phase Change Materials (PCMs) are one example of Active Smart Textile.

Phase Change Materials are inorganic or organic compounds which store and release latent heat by changing chemical bonds through a phase transformation, unlike sensible heat storage materials such as water, which change structure mechanically. Examples of inorganic compounds are the following salts: Glauber's salt (sodium sulfate decahydrate) and calcium chloride hexahydrate; organic compounds are paraffin wax and carboxylic acid. These materials store, release or absorb heat as they oscillate between solid and liquid form. They release heat as they change to a solid state and absorb as they return to liquid state [2].

The inorganic PCMs have a wide range of melting temperatures, between 8.1ºC and 130ºC, high volumetric storage density, relatively high thermal conductivity and moderate costs compared to paraffin waxes. Moreover, they need careful preparation, can be corrosive to some metals and have limited life cycles (ex. Lithium nitrite trihydrate lasts 25 cycles, calcium chloride hexahydrate lasts only a few cycles, and sodium sulfate decahydrate only one cycle [3]).

Organic PCMs have more uses due to their outstanding properties, even if they are generally more expensive. When compared with other PCMs, paraffin hydrocarbons have outstanding properties such as no corrosiveness, chemical and thermal stability, recyclability, simplicity of use and low or no undercooling. Linear chain hydrocarbon is a by-product of oil refining. The formula is C_nH_{2n+2}. The melting and crystallization points of hydrocarbons having between 16 and 21 carbon atoms are in the temperature range 10ºC to 40ºC. Polyethylene glycol (PEG) is an alternative organic compound for use as a PCM. Its melting point and heat depend on its molecular weight when its molecular weight is lower than 20000. The PEGs with molecular weight from 800 to 1500 have melting points of about 33ºC [2],…,[5].

PCMs have been used in many engineering applications, especially in the fields of thermal storage and insulation (industrial refrigeration and ice production). Some of these PCMs change phase within a temperature range just above and below human skin temperature. Fibres, fabrics and foam with built-in PCMs store the warmth of body and then release it back to the body, as it needs it. Since the process of phase change is dynamic, the material are constantly changing from a solid to liquid and back depending upon level of physical activity of the body and outside temperature [2].

For clothing applications, the melting heat-absorbing temperature interval is from 20ºC to 40ºC, and the crystallization heat-releasing temperature interval is from 30ºC to 10ºC. The phase change temperature of hydrated inorganic salts, polyhydric alcohol-water solution, polyethylene glycol (PEG), polytetramethylene glycol (PTMG), aliphatic polyester, linear chain hydrocarbon, hydrocarbon alcohol, hydrocarbon acid, etc., is in this interval [3].

Filling or impregnating the fibres with PCMs is a process of obtaining PCMs inside textiles. Vigo and Frost (1989) filled hollow rayon and polypropylene fibres with inorganic PCMs but the decrease on fibre heat capacity was greater after more heat-cool cycles [4]. In 1983, Vigo and Frost filled hollow rayon and polypropylene fibres with PEG for an average molecular weight of 400, 600, 1000 and 3350. The heat-absorbing and heat-releasing capacity of filled hollow polypropylene fibre is 1.2-2.5 times that of untreated fibre, and that of filled hollow rayon is 2.2-4.4 times that of untreated rayon [3].

Paraffin hydrocarbons are widely used in textiles, either in solid or liquid state. Paraffin waxes with phase-transition temperature near the required range are hexadecane, heptadecane, octadecane, nonadecane and eicosane. They can be mixed in order to obtain the desired temperature ranges for which the phase change takes place [6]. In order to prevent the paraffin's dissolution while in the liquid state, it is enclosed into small plastic spheres with diameters of only a few micrometers (5-60 µm). These microscopic spheres containing PCM are called PCM-microcapsules [7].

PCM-microcapsules can be incorporated into textiles in different ways [2], [4]:

1. The PCM microcapsules of different shapes – round, square and triangular are permanently locked within the fibre structure at the polymer stage, during the wet spinning process of fibre manufacture. This process was developed in the 1990s. Micro encapsulation provides a softer hand, increased stretch, more breathability and air permeability to the fabrics.

2. The PCM microcapsules are embedded in a coating compound like acrylic, polyurethane, etc. and applied to the fabric. There are various coating processes available such as knife-over-roll, knife-over-air, pad-dry-cure, gravure, dip coating and transfer coating.

3. Microcapsules are mixed into water-blown polyurethane foam and these foams are applied to fabric in a lamination process; water is taken out of the system through drying process.

Outlast® Technology is the most common and used technique of integrating PCMs in textiles. The origins of Outlast® Technology go back to 1988 when US National Aeronautics and Space Administration (NASA) implemented a program to develop thermally adaptive phase-change materials that could be applied to astronauts' suits and gloves. They encapsulated phase-change materials (PCMs) (*e.g.* nonadecane) with the hope of reducing the impact of extreme variations in temperature encountered by astronauts during their missions in space [8], [9].

© *Outlast Technologies, Inc.* was founded in 1990 in Boulder, Colorado. In 1991 the company founders acquired from *Triangle Research and Development Corporation* the exclusive patent rights for incorporating this innovative technology into commercial fibres and fabrics. The first brand promotion of commercial gloves and footwear incorporating Outlast® technology was in 1998 [10].

The microcapsules have walls less than 1 μm thick and are typically 20–40 μm in diameter, with a PCM loading of 80–85%. *Accordis*, formerly *Courtaulds Fibres*, in Bradford, UK, developed the technology of in-fibre incorporation of the Outlast microcapsules, loading the fibre with 5–10% of microcapsules. In this way the PCM is permanently locked within the fibre (Fig. 1); there is no change necessary in subsequent fibre processing (spinning, knitting, dyeing, etc.) and the fibre exhibits its normal properties of drape, softness and strength [8]. Also, the microcapsules can be applied on different textile materials through coating (Fig. 2). For many products (*e.g.* sleeping bags) nonwovens are coated. In jackets coated linings are used, but it can also be applied to mid layers put between the first layer and the lining [9]. Outlast® currently uses two grades of phase change materials in order to fit to different applications. One application is for cold weather/extremity wear designed to operate from 18.3ºC to 29.4ºC. The other grade is used in four season applications designed to operate from 26.7ºC to 37.8ºC. A mixture of paraffin waxes having between 15 and 24 carbon atoms is used in order to cut production costs [9], [11].

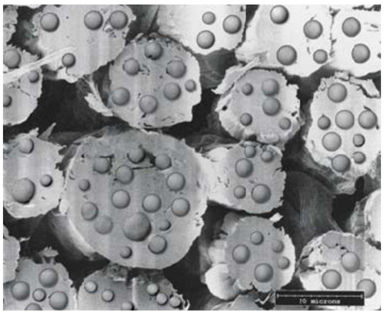

Fig. 1 – Outlast® Thermocules® in acrylic fiber [9] (with © Outlast Technologies, Inc. permission).

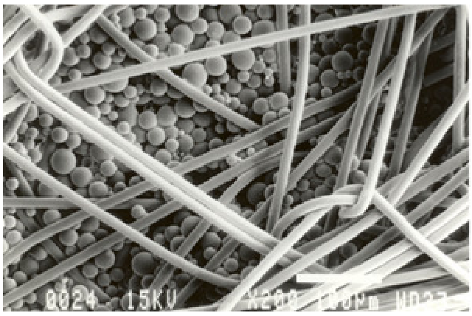

Fig. 2 – Outlast® Thermocules® as coating on textiles [9] (with © Outlast Technologies, Inc. permission).

When the encapsulated PCM is heated to the melting point, it absorbs heat as it moves from a solid state to a liquid state. This phase change produces a temporary cooling effect in the clothing layers. The heat energy may come from the body or from a warm environment. The storage of heat stops once the PCM has completely melted.

If the PCM garment is worn in a cold environment where the temperature is below the PCM's freezing point and the fabric temperature drops below the transition temperature, the micro encapsulated liquid PCM will change back to a solid state, generating heat energy and a temporary warming effect.

Intensity and duration of the PCM's active thermal insulation effect depend mainly on the heat storage capacity of the PCM-microcapsules and their applied quantity. The textile substrate construction also influences the efficiency of the active thermal insulation effect of the PCM. For instance, thinner textiles with higher densities readily support the cooling process. In contrast, the use of thicker and less dense textile structures leads to a delayed and therefore more efficient heat release of the PCM. Furthermore, the phase change temperature range and the application temperature range need to correspond in order to realize the desired thermal benefits [7].

2. Applications of PCMs Incorporated Textiles

Applications of phase change textiles include the following domains, illustrated in Fig. 3.

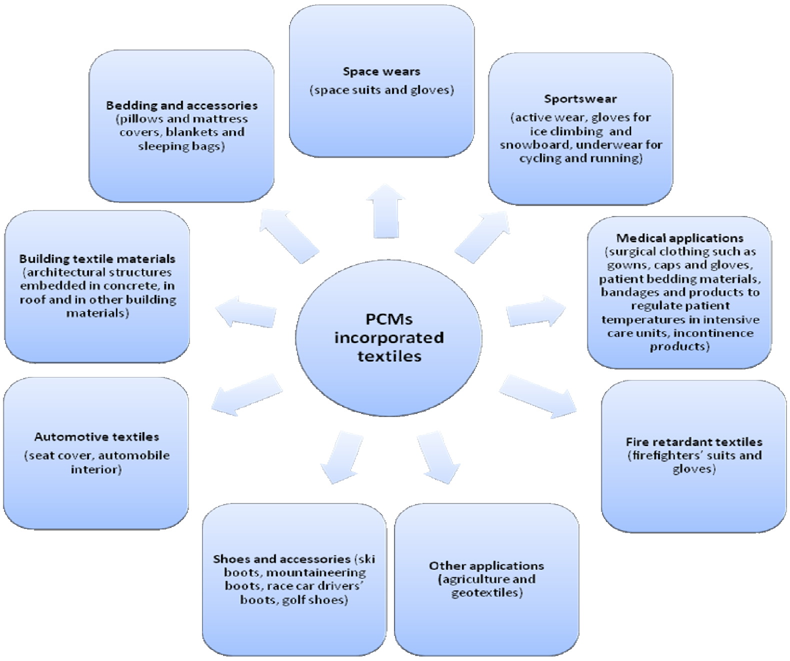

Fig. 3 – Applications of PCMs incorporated textiles.

From original applications in space suits and gloves, nowadays phase change materials (PCM) are in consumer products.

The textiles with PCMs present the following thermal benefits [5], [12]:

– a cooling effect, caused by heat absorption of the PCM;

– a heating effect, caused by heat emission of the PCM;

– a thermo-regulating effect, resulting from either the heat absorption or heat emission of the PCM which is used to keep the temperature of a surrounding substrate nearly constant.

– an active thermal barrier effect, resulting from either heat absorption, or heat emission of the PCM which regulates for instance, in a garment system the heat flux from the human body into the environment and adopts it to the thermal needs (*i.e.* activity level, ambient temperature).

However, the thermo-regulating function offered against extremes of cold and/or heat is available only for a limited period and could be maximized if the wearer were repeatedly going through temperature transients. This fact reduces the application range of phase change textiles. A suitable thermo-regulating effect can only be realized when specific design principles are applied in the development process of such textile products. For example, in a garment application further requirements on the textile substrate include sufficient breathability, high flexibility and mechanical stability. Furthermore, the phase change temperature range and the application temperature range need to correspond in order to realize the desired thermal benefits.

3. Common Techniques for Measuring PCMs Thermal Properties

In the case of traditional fabrics, the thermal properties are investigated by standard steady-state procedures involving the use of guarded hot plate apparatus. For evaluation of the thermal performances of textiles containing PCMs the standard methods are not suitable, because long, continual thermal stress could activate the change in phase that would lead to measurements that deviate significantly from those that should be obtained [3].

Differential Scanning Calorimeter (DSC) is a technique which measures the thermal effects on materials as they are heated or cooled, and undergo thermal transitions. DSC makes it possible to analyze and quantify the material’s energy absorption and release in appropriate temperature use ranges. The equipment heats and cools a sample in a controlled manner and records the material’s temperature of its phase transitions (melting and crystallization). The instrument also records the amount of energy required to melt the sample and amount of energy released when the sample crystallizes upon cooling. The DSC thereby provides quantitative information on the materials temperature buffering use ranges and, by integrating the melt and crystallization peaks, the amount of latent energy capacity or temperature buffering capacity in Joules that are absorbed, stored and released [9].

The diagram in Fig. 4 illustrates a typical phase change material. The top curve is the heating or energy increase and melting curve and the bottom curve is the cooling and crystallization data.

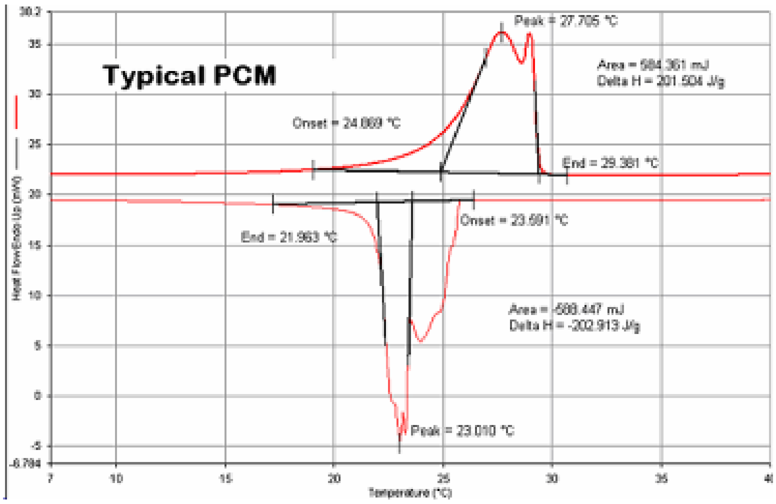

Fig. 4 − DSC plot of a typical PCM [9]
(With © Outlast Technologies Inc. permission).

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum. The resulting spectrum represents the molecular absorption and transmission, creating a sample molecular fingerprint. It can identify unknown materials, determine the quality or consistency of a sample and determine the amount of components in a mixture [13].

Thermal Gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. The test results are a graph of the TGA signal (actual weight loss or gain converted to percent weight loss) on the Y-axis plotted versus the sample temperature in ºC on the X-axis [14].

Infrared Thermography is a type of infrared imaging science. Thermographic cameras detect radiation in the infrared range of the electromagnetic spectrum and produce images of that radiation, called thermograms. Since infrared radiation is emitted by all objects near room temperature, thermography makes it possible to “see” one's environment with or without visible illumination. The amount of radiation emitted by an object increases with temperature; therefore thermography allows one to see variations in temperature [15].

4. Research on PCMs Thermal Properties when Used in Textiles

The endothermic and exothermic behaviour of fabrics and fibres was studied by Vigo and Frost using Differential Scanning Colorimeter (DSC) [16],…,[18]. In 1995, Barbara Pause suggested a measurement method and an apparatus to measure the basic and dynamic thermal resistance [19]. Hittle and Andre (2002) suggested a measurement method that is nearly the same as Pause's method. In order to characterise thermoregulation effect they have proposed to use the Temperature Regulating Factor (TRF). The TRF is a dimensionless number of the range (0, 1).The TRF value of 1 means the fabric has no capacitance and poor temperature regulation. The TRF equals zero means that the fabric has infinite capacitance and that a body being in contact with it will remain at constant temperature [4]. Based on years of research and testing textiles containing "phase change materials" (PCMs) by Outlast Technologies, Inc., and Prof. Dr. Douglas Hittle the first "Test Method for Steady State and Dynamic Thermal Performance in Textile Materials" (ASTM D7024-04) was established by the ASTM in June 2004. This test method covers the determination of the overall thermal transmission coefficient due to conduction for dry specimens of textile fabrics, battings, and other materials and the determination of the temperature regulating factor (TRF) [9].

Vigo and Bruno preliminary measured the thermal regulating properties of textiles with PCMs using Infra-Red Thermography [20].

The thermal performances and phase change properties of the PCMs suitable for textile thermal isolation have been evaluated by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared (FTIR) and Thermal Gravimetric Analysis (TGA) by Fabien Salaün *et al.* [6]. The manufacture and properties of intelligent textiles, containing PCM, have been extensively studied at the Textile Research Institute (Łódz) since 1999 by Bendkowska and a test instrument has been designed and built based on the model of heat transfer through textile containing the PCMs, formulated by Hittle and Andre. The instrument can be used for testing steady-state and transient state characteristics of the apparel fabrics containing the PCMs [21]. Also, a new method for evaluating the thermal conductivity for smart textiles made of phase change or temperature depended compounds has been developed at Technical University of Łódz, Department of Textile Metrology. It is based on thermovision measurements of temperature simultaneously on both sides of the material during heating or cooling process [22]. YING BO-AN *et al.* from The Hong Kong Polytechnic University, Institute of Textiles and Clothing**,** proposed three indexes for the PCM treated fabrics: Index of thermal buffering capability (Id and Δtd) - can be used to describe the thermal regulating/buffering performance of PCM fabrics during phase change process, which are strongly dependent to PCM add-on level. The meaning of index Id is the mean of the heat flux which occurred during phase change and Δt_d is duration time of phase change. From the aspect of thermal comfort of textile and clothing, the index of the thermal psychosensory intensity (TPI) − is defined to express the thermal perception by body. The index of static thermal insulation I_s presents the static thermal insulation effects of the fabrics, and I_s is given in units of heat flux (W/m^2). These indexes can be measured by the instrument of the Fabric Intelligent Hand Tester [23].

At the University of Naples “Federico II” Italy, the thermal performance of natural leather coated and impregnated with MicroPCMs have been analyzed using Differential Scanning Calorimeter and the temperature distribution on the MicroPCMs-coated samples were measured using an Infrared (IR) Thermographic System. The results demonstrate that the coating method is more efficient than the impregnation one, and the thermal effect is significant for the samples containing a higher percent of microPCMs (40% wt). Also, the mechanical properties (elastic modulus and tensile strength) are slightly modified by chemical treatments [24].

At The Institute for Environmental Research, Kansas State University, Manhattan, Huensup Shim and Elizabeth A. McCullough have studied the effect of PCMs in fabric-backed foams on heat loss from a thermal manikin’s surface to the environment during environmental temperature transients and on human subjects’ physiological responses and comfort perceptions during environmental temperature transients and changes in activity. They concluded that the effect of PCMs in clothing could be maximized if the wearer were repeatedly going through temperature transients or intermittently touching hot or cold objects with PCM gloves [25].

5. Conclusions

Textiles containing PCMs are considered smart because they react to changes in environmental temperature absorbing and releasing latent heat and provide a thermo-regulating effect.

Due to the thermal properties of PCMs, such textiles have become important for use in many applications such as: medical applications, sport, automotive, building materials, aerospace textiles, agriculture, geotextiles etc.

Paraffin is the preferred kind of PCMs for textile applications because the melting point of paraffin is very close to the temperature of the body, which can be fine tuned by mixing paraffins with different number of carbon atoms. The melting point of paraffin depends on the number of carbon atoms, *i.e.* the melting point increases with increase number of carbon atoms in molecule.

The PCMs are enclosed in microcapsules to prevent leakage of the material during its liquid phase.

PCM microcapsules can be incorporated into the spinning polymer of manufactured fibres (*e.g.*, acrylic, viscose), incorporated into the structure of foams and these foams applied to fabric in a lamination process, or embedded in a coating compound and coated onto fabrics. Filling hollow fibres is another method to incorporate PCMs in textiles.

For evaluation of the thermal performances of textiles containing PCMs the traditional methods are not suitable. The most generally used methods are:

Differential Scanning Calorimetry – for Thermal storage/Release Properties; Storage Property - Measurement of melting temperature & heat of fusion; Release Property - Measurement of crystallization temperature & heat of crystallization;

Dynamic Heat transfer measurement – for Thermal Insulation Properties and

Thermo-Gravimetric Analysis (TGA) − is used to assess the thermal strength of the micro PCMs.

The manufacture, properties and applications of heat-storage and thermo-regulated textiles have been extensively studied since the 1980s but their development is still of present interest.

The effect of the structural parameters on the thermo-regulating properties of the textiles which incorporate PCMs will be investigated in a future study.

Acknowledgments. This work was conducted under support of the FCT - Fundação para a Ciência e a Tecnologia, within the framework of “Ciência 2008” Program and the 2C2T – O Centro de Ciência e Tecnologia Têxtil, Universidade do Minho, Portugal.

Received: May 21, 2010

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MATERIALE CU SCHIMBARE DE FAZĂ INCORPORATE ÎN TEXTILE

(Rezumat)

Materialele cu schimbare de fază (PCM) utilizate în textile sunt combinații între diferite tipuri de parafină, fiecare cu puncte de topire şi cristalizare diferite. Materialele cu schimbare de fază sunt micro-încapsulate pentru a preveni curgerea materialului pe durata fazei lichide. Aceste materiale pot fi incorporate direct în soluția de filare în procesul de obținere a fibrelor (fibre acrilice, viscoză) sau pot fi incorporate

în structura unor spume (ex. poliuretanică) care se aplicată pe stucturile textile prin laminare. Inserarea materialelor cu schimbare de fază în hollow fibre este o altă metodă de utilizare a acestora în domeniul textil.

Textilele care conțin materiale cu schimbare de fază prezintă următoarele funcții interactive: absorbția căldurii eliberată de corpul uman; un efect de izolare determinat de emiterea căldurii de către materialul cu schimbare de fază în structura textilă; un efect de termo-reglare care menține microclimatul la o temperatură aproape constantă.

Calorimetria cu scanare diferențială (Differential Scanning Calorimetry) poate fi utilizată pentru determinarea proprietăților termice, a punctului de topire şi a punctului de cristalizare a materialelor cu schimbare de fază din structurile textile. Capacitatea de izolare termică poate fi determinată prin măsurarea transferului de caldură în condiții dinamice (Dynamic Heat Transfer).

Pe de altă parte, proprietățile de termo-reglare ale textilelor care conțin materiale cu schimbare de fază pot fi determinate cu ajutorul unui instrument denumit “Fabric Intelligent Hand Tester” (FIHT). Cu acest instrument se măsoară indicii capacității de reglare termică (Id şi Δtd), indicele izolării termice statice (Is) şi indicele intensității termice psihosenzoriale (TPI).

Realizarea, proprietățile şi aplicațiile textilelor care sunt capabile să stocheze căldură şi să asigure termoreglarea au fost studiate începând cu anii 1980, dar domeniul încă prezintă interes şi realizarea unor noi produse este de mare actualitate.

În această lucrare sunt analizate domeniile de aplicație ale materialelor cu schimbare de fază în textile, metodele de integrare a materialelor cu schimbare de fază în produse textile şi metodele de evaluare a proprietăților lor.