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Review Article

Application of Phase Change Materials in Textiles: A Review

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ABSTRACT

Phase change materials or PCMs are compounds which store and release latent heat by changing chemical bonds through a phase alteration. These materials absorb energy during the heating and release energy to the surroundings through a reverse cooling process. The integration of PCM in textiles by coating, encapsulation or any other means has grown concentration to the scientist. In this paper; characteristics, classification, working principle of PCMs and its versatile application in textiles are mainly discussed.

Keyword: Phase Change Material, Microencapsulation, Clothing Comfort, Heat Storage

INTRODUCTION

'Phase Change' refers to go from one physical state of a material to another i.e. from a solid to a liquid and vice versa. Phase change materials are used to achieve automatic acclimatizing properties of fiber and textile materials. [1] The technology for incorporating PCM microcapsules [2] into textile construction to increase their thermal performance was established in the early 1980s under NASA investigation programme.

Thermal energy storage bridges the time gap between energy requirements and energy use.[3] Latent heat storage is very attractive due to its ability to provide a high storage density at nearly isothermal conditions. Phase-change thermal energy storage systems offer other advantages, such as a small temperature difference between storage and retrieval cycles, small unit sizes and low weight per unit storage capacity. [4-5]

Phase change materials possess the ability to change their state with a certain temperature range. These materials absorb energy during the heating process as phase change takes place, otherwise this energy can be transferred to the environment in the phase change range during a reverse cooling process. [6] The insulation effect reached by the PCM is dependent on temperature and time; it takes place only during the phase change (in the temperature range of the phase change) and terminates when the phase change in all of the PCMs would complete. Since, this type of thermal insulation is temporary; therefore, it can be referred to as dynamic thermal insulation. Numerous engineering applications has made the topic of melting of phase change material in enclosures one of the most active fields in heat transfer research today. [7]

Textiles containing phase change materials react immediately with changes in environmental temperatures, and the temperatures in different areas of the body. When a rise in temperature occurs, the PCM microcapsules react by absorbing heat and storing this energy in the liquefied phase change materials. When the temperature falls again, the microcapsules release this stored heat energy and the phase change materials solidify again. [8] The thermal insulation capabilities of cold protective clothing materials may be significantly improved by the incorporation of Micro PCM, these capsules containing small amounts of PCM. Manufacturer can now use phase change material to provide thermal comfort in wide variety of garments. The use of phase change materials, which absorb energy during heating and release energy during cooling, improve the thermal insulation capacity which differs significantly from the insulation properties of any other material. [9] Currently this property of PCMs is widely exploited in various types of garments. PCM microcapsules could be directly incorporated into fibres, and foams, or typically applied to fabrics as a coating. In this article an account of PCM, working principle with textile structure and the application PCM incorporated textiles are reported.

2. Characteristics and Classification of PCMS

A phase-change material (PCM) is a substance with a high heat of fusion which, melting and solidifying at a certain temperature, is capable of storing and releasing large amounts of energy. Heat is absorbed or released when the material changes from solid to liquid and vice versa; thus, PCMs are classified as latent heat storage (LHS) units. [10]

PCMs latent heat storage can be achieved through solid–solid, solid–liquid, solid–gas and liquid–gas phase change. However, the only phase change used for PCMs is the solid–liquid change. Liquid-gas phase changes are not practical for use as thermal storage due to the large volumes or high pressures required to store the materials when in their gas phase. Liquid–gas transitions do have a higher heat of transformation than solid–liquid transitions. Solid–solid phase changes are typically very slow and have a rather low heat of transformation.

Initially, the solid–liquid PCMs behave like sensible heat storage (SHS) materials; their temperature rises as they absorb heat. Unlike conventional SHS, however, when PCMs reach the temperature at which they change phase (their melting temperature) they absorb large amounts of heat at an almost constant temperature. The PCM continues to absorb heat without a significant rise in temperature until all the material is transformed to the liquid phase. When the ambient temperature around a liquid material falls, the PCM solidifies, releasing its stored latent heat. A large number of PCMs are available in any required temperature range from −5 up to 190°C. [11] Within the human comfort range between 20–30°C, some PCMs are very effective. They store 5 to 14 times more heat per unit volume than conventional storage materials such as water, masonry or rock. [12]

PCMs mainly classified into two groups such as organic PCMs and inorganic PCMs, as shown in the Figure 1. [13] A large number of PCMs available with different temperature range but only a few commercially used. Inorganic PCMs and organic PCMs have a wide range of melting temperature of between 8.1°C and 130°C. [14] In most cases, the density of PCM is less than 103 kg/m^3 and thus smaller than the density of most inorganic materials like water and salt hydrates. The result is that with exception per volume than inorganic materials. PCMs have the structure of covalent bond of carbon based compounds, hydrocarbons and theirs derivatives are said to be organic PCM. The materials classes cover the temperature range between 0°C and about 200°C. This is because covalent bonds in organic materials, most of them are not stable at higher temperature. Paraffin wax as phase change material has broad applications due to their own characteristics such as non-toxic, chemically inert, low cost and high storage energy capacity. [15] Paraffin is a technical name of alkane, but often it's specifically used for linear alkanes with general formula C_nH_{2n+2}. Paraffin are good storage of thermal energy with respect to mass and melt and solidify congruently with little one or no sub cooling. Their stability of confines their vapor pressure is usually not significant. Their volume increase upon melting is in the order of 10 vol%. This is similar to that of many inorganic materials, but less critical as paraffin are softer and therefore build up smaller forces upon expansion. Paraffins are insoluble in water as they are water repellent. They do not react with most common chemical agents. Inorganic PCMs are hydrated inorganic salts. They have a wide range of melting temperatures of between 8.1°C and 130°C. But their heat absorbing and releasing temperature interval is usually between 20-40°C. However they require a great deal of heat of fusions and have limited lifecycles.

Salt hydrates are the most important group of PCMs, which is mostly studied for their use in latent heat thermal energy storage systems. Most salt hydrates have poor nucleating properties resulting in super cooling of the liquid before crystallization begins. [16-19] But, it is controlled by adding nucleating agent, which provides the nucleon which crystal formation is initiated.

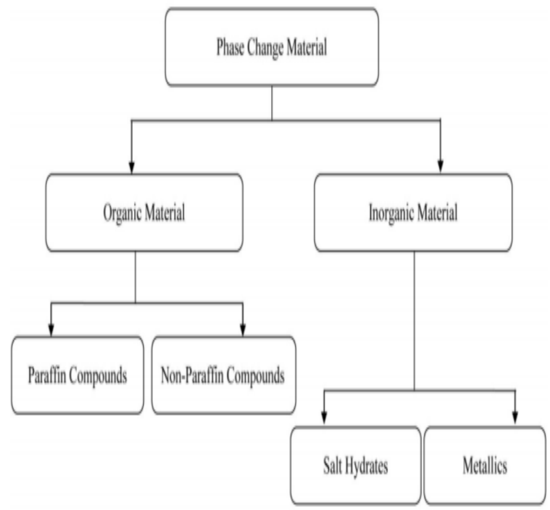


Figure. 1. Classification of PCMs

3. Phase Change Processes

Phase change materials are used to stored or released heat energy during the phase transition of the materials. This is called as latent heat storage systems. [13, 15, 20-22] During heating process, every material absorbs some heat by constantly rising temperature and released into the environment by reverse cooling process as temperature decreases continuously. Compare heat absorption of a phase change materials with normal materials during heating process, PCMs can absorbs high amount of heat if melts. [23] During the melting/crystalline process, the temperature of PCM as well as its surrounding area remains nearly constant. PCM is often interested as in many particular applications due to large heat transfer during the melting/crystallization process with sufficient temperature change makes interesting as a source of thermal storage material. Phase change process of PCM from solid to liquid and vice versa is schematically shown in Fig. 2.

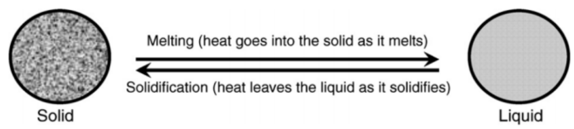


Fig. 2. Schematic representation of phase change process.

4. Working Principle of Phase Change Materials (PCMS)

Thermal energy storage is an essential technique for thermal energy utilization. [24] For thermal energy storage there are four alternatives viz. sensible heat utilization, latent heat utilization, utilization of reversible chemical heat, and utilization of heat of dilution. Material has four state viz. solid, liquid, gas and plasma. When a material converts from one state to another, this process is called phase change. There are four kinds of phase change, such as (a) solid to liquid (b) liquid to gas (c) solid to gas and (d) solid to solid. Heat is absorbed or release during the phase change process. This absorbed or released heat content is called latent heat. PCM which can convert from solid to liquid or from liquid to solid state is the most frequently used latent heat storage material, and suitable for the manufacturing of heat-storage and thermo-regulated textiles and clothing. Modes of heat transfer are strongly depends [25] on the phase of the substances involve in the heat transfer processes. For substances that are solid, conduction is the pre dominate mode of heat transfer. For liquids, convection heat transfer predominates, and for vapors convection and radiation are the primary mode of heat transfer. For textile applications, we will only consider the phase change from solid to liquid and vice versa. Therefore, the principle of solid to liquid phase change and vice versa would be discussed. When the melting temperature of a PCM is reached during heating process, the phase change from the solid to the liquid occurs. Typical differential scanning calorimetry (DSC) heating thermogram for PCM melting is schematically shown in Fig. 3. During this phase change, the PCM absorbs large quantities of latent heat from the surrounding area. PCM may repeatedly converted between solid and liquid phases to utilize their latent heat of fusion to absorb, store and release heat or cold during such phase conversions. Phase change materials as such are not new. [26-27] They already exist in various forms in nature. The most common example of a PCM is water at 0°C, which crystallizes as it changes from liquid to a solid (ice). [6,27] A phase change also occurs when water is heated to a temperature of 100°C at which point it becomes steam. In order to compare the amount of heat absorbed by a PCM during the actual phase change with the amount of heat absorbed in an ordinary heating process; water can be used for comparisons. When ice melts into water it absorbs approximately a latent heat of 335 kJ/kg. When water is further heated, a sensible heat of only 4 kJ/kg is absorbed while the temperature rises by one degree Celsius.

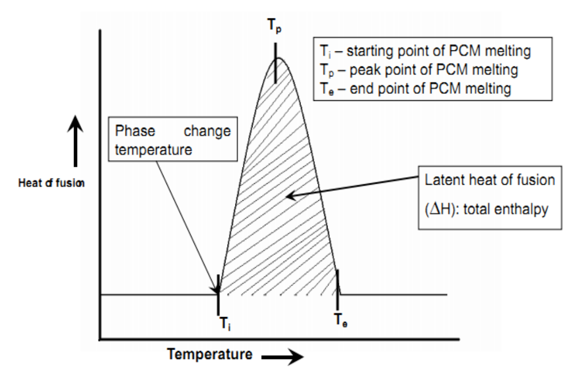


Fig. 3. Schematic of DSC heating thermogram of PCM. [21]

5. How Pcms Works In Textiles

Before applying PCM's to textile structure, the PCM's would be encapsulated in very small spheres to contain them while in a liquid state. These microcapsules have approximate diameters of between 1 lmand30 lm. The microcapsules are resistant to mechanical action, heat and most types of chemicals. [21]

Usually PCM microcapsules are coated on the textile surface. Microcapsules are embedded in a coating compound such as acrylic, polyurethane and rubber latex, and applied to a fabric or foam. Capsules can also be mixed into a polyurethane foam matrix, from which moisture is removed, and then the foam is laminated on a fabric. [28] In Fig. 4 it is seen that PCM microcapsules (Outlast) in fabric and in Fig. 5 how it works. [43] PCMs-containing microcapsules can be incorporated also into acrylic fibre in a wet spinning process. In this case the PCM is locked permanently within the fibre. The fibre can then normally be processed into yarns and fabrics. [28-29]

In treating textile structures with PCM microcapsules for garment applications, the following thermal benefits are realized: a 'cooling' effect, by absorbing surplus body heat, an insulation effect, caused by heat emission of the PCM into the textile structure; the PCM heat emission creates a thermal barrier which reduces the heat flux from the body to the environment and avoids undesired body heat loss, a thermo regulating effect, resulting from either heat absorption or heat emission of the PCM in response to any temperature change in the microclimate; the thermo-regulating effect keeps the microclimate temperature nearly constant. [30]

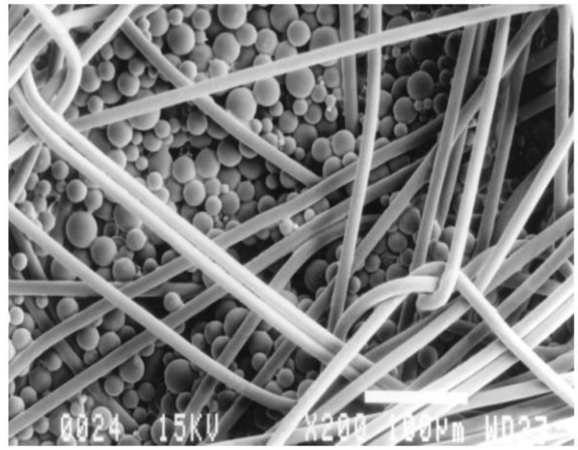
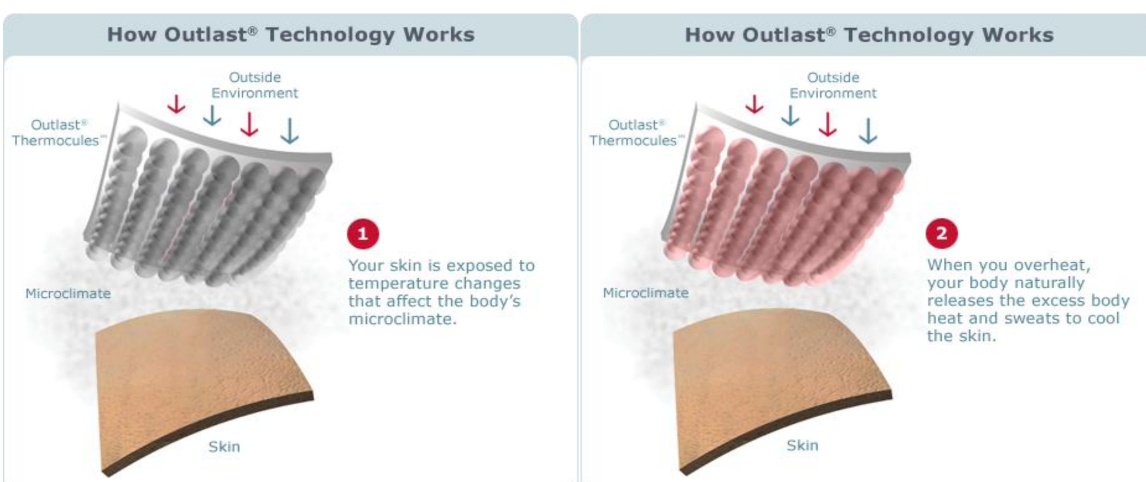


Fig. 4 PCM microcapsules in a fabric (Outlast Europe).

6. Microencapsulation and Its Technique

Microencapsulation is the process of enclosing micro sized particles of solids or liquids droplets or gases in the shell structure called microcapsules that have many interesting features. [31-32] Particle size is below 1µm are known as nanoparticles, whereas particles size between 3-800µm are known as microparticles or microcapsules or microspheres. Particles larger than 1000µm are known as macroparticles. Microcapsules that have wall less than 2 µm in thickness and 20-40µm in diameter is useful in textile application. Microencapsulation of core materials can be done by various techniques.



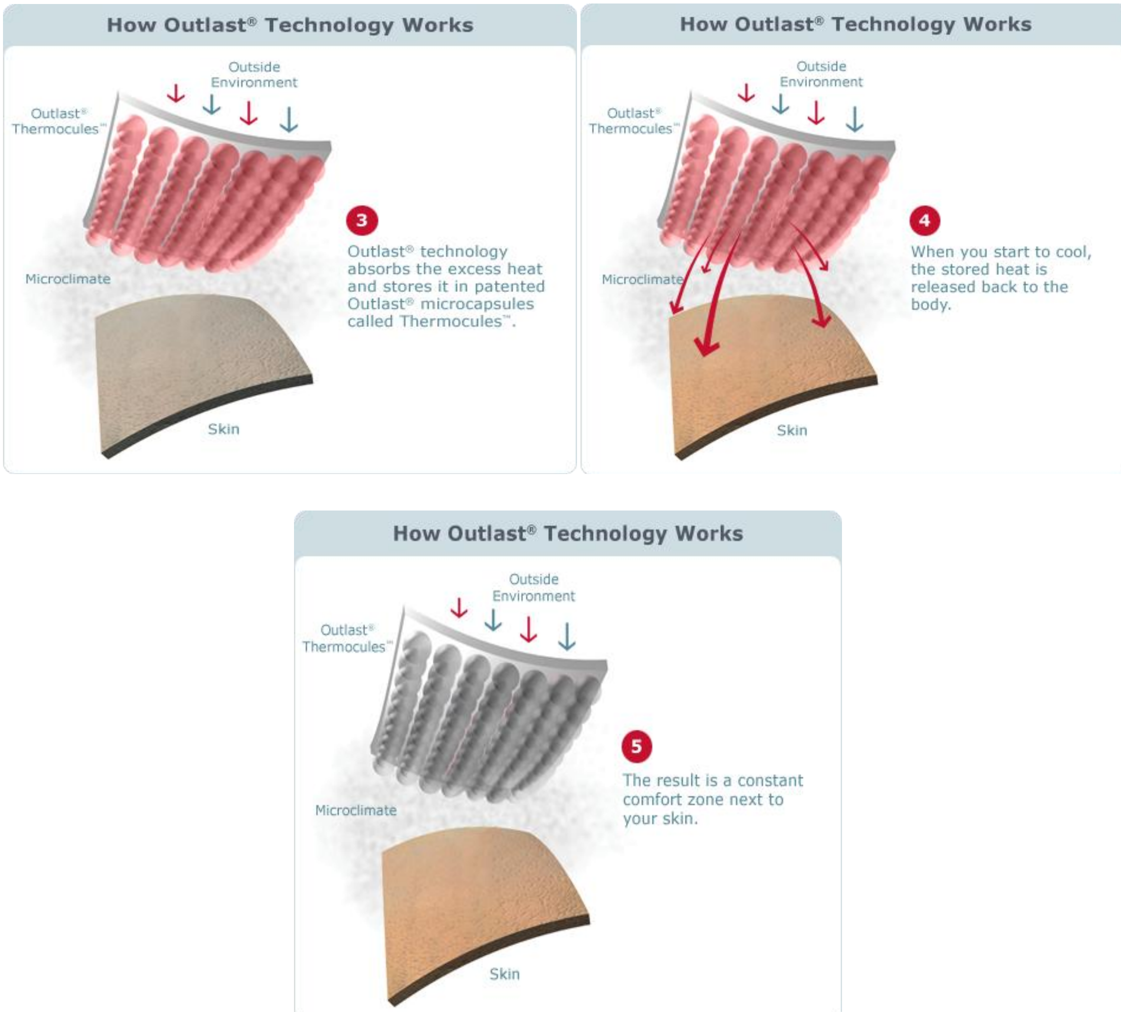


Fig. 5 functioning principle of PCM in a fabric (Outlast Europe).

6.1 Interfacial polymerization method

In interfacial polymerization methods, the shell wall is formed at or on the surface of the droplet or particle by polymerization of reactive monomers. The substances used for polymerization are multifunctional monomers. The multifunctional monomer is dissolved in core material and dispersed in aqueous phase containing dispersed agents. These reactants diffuse to undergo polymerization at interface and generation of capsule shell achieved. This kind of polymerization is mechanically determined different from the usual step polymerization.

6.2 In situ polymerization method

In this polymerization method, the direct polymerization of a single monomer is carried out on the particle surface. In this process, the reactive agents are added to the core material, polymerization occurs exclusively continuous phase. Polymerization method consisted of the synthesis of pre-polymer solution, preparation of emulsion and formation of solid shell material. For example, encapsulation of various water immiscible liquids with shells formed by the reaction at acidic condition of urea-formaldehyde with aqueous [33-35] Microencapsulated material prepared based on in situ polymerization techniques shows enhanced thermal property in relation to the PCM content.

6.3 Chemical coacervation method

Bungenberg 1932, investigated in water, organic chemicals do not necessarily remain uniformly dispersed but may separate out into layers or droplets. If the droplets which form contacts a colloid, rich in organic compounds and are surrounded by a tight skin of water molecules are known as coacervates. [36-37] Two methods for coacervation are available, namely simple and complex coacervation processes. The mechanism of formation of encapsulated PCM microcapsules for both processes is identical, except in which the phase separation is carried out. In simple coacervation, a desolvation agent is added for phase separation. Complex coacervation refers to the phase separation of a liquid precipitate, when solutions of two hydrophilic colloids are mixed under suitable conditions. The basic steps involved in complex coacervation methods are (1) first the core materials, usually an oil is dispersed into a polymer solution, (2) polymer solution is then added to the prepared dispersion, (3) deposition of the shell material onto the core particles occurs when the two polymers form a complex, (4) triggered by the addition of salt or by dilution of the medium, (5) finally, prepared microcapsules are stabilized by cross linking, desolvation or thermal treatment.

6.4 Solvent evaporation method

In this method, microcapsule coating material is dissolved in a volatile solvent, which is immiscible with the liquid manufacturing vehicle phase. [37-38] A core material is to be encapsulated to be dissolved or dispersed in the coating polymer solution. With the help of agitator, this mixture is added to the manufacturing vehicle phase, and then heated to evaporate the solvent for the polymer. After evaporated, leaving solid microspheres, the liquid vehicle temperature is reduced to ambient temperature with continued agitation. The microspheres can then be washed and dried. The solvent evaporation method produce microcapsules are applicable to a wide variety of liquid or core materials.

6.5 Spray drying method

In this method, liquid or slurry rapidly converted dried powder with a hot gas. The main advantage is the ability to handle labile materials because of the short contact time in the dryer. Microcapsulation by spray drying is a low cost, economical operation which is mostly used for the encapsulation of fragrance, oils and flavors. The basic steps involved in preparation of microcapsules using spray dryer are (1) core materials are dispersed in a polymer solution and sprayed into the hot chamber; (2) heated air is supplied to remove the solvent from the coating material, thus forming the microencapsulated product.

6.6 Fluidized bed method

This method of different types of fluid coaters include top spray, bottom spray and tangential spray used for encapsulating solid or liquids absorbed into porous particles. The three basic steps involved in fluidized bed method are (1) solid particles to be encapsulated are suspended on a jet of air and then covered by a spray of liquid coating material, (2) rapid evaporation of solvent helps in the formation of an outer layer on the particles, (3) process is continued until the desired thickness and weight is obtained.

7. Methods of Incorporation of PCMs into Textiles

Textiles containing PCMs have different thermal properties from conventional textiles. PCMs microcapsules can be applied to a wide variety of textile substrates in order to improve thermo-regulation and insulation properties. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, foam techniques are some of the convenient processes for incorporation of PCMs into textile substrate.

7.1 Spinning method

In this method, liquid polymer, polymer solution and fiber can be added with PCMs is then spun according to the spinning methods such as melt, dry or wet spinning and extrusion of molten polymers. The extruded fibers/polymers could store and release heat according to the temperature of the environment. During this period of activity, the encapsulated fibers store or release the excess heat generated by the body. PCMs fibers have high latent heat, but easily lost their properties in use. [39] In addition, it is observed that the particle size and size distribution of the microencapsulated PCMs affect the spin ability and mechanical properties of thermal regulating fibers.

7.2 Coating method

In this method, microspheres containing in phase change material dispersed in water solution and coated into textile substrate includes a surfactant, a dispersant, an antifoam agent, a thickener and a polymer binder. There are various coating processes available such as knife-over-roll, [40] knife-over-air, pad-dry-cure, [41] gravure, dip coating and transfer coating.

7.3 Lamination method

PCMs would be incorporated into a tiny polymer film and applied to the inner side of the textile substrate by lamination in order to improve the thermo-regulating properties of the wearing garments. The heat stress of chemical and non-woven protective garments is decreased by incorporating PCM into a tiny film and applied into a fabric system. [42] The PCMs fibers by lamination have the following advantages: a high PCM concentration per unit area, low cost of the production processes and low weight of the textile is minimized.

8. PCM and clothing comfort

Comfort is a term created by psychologists; nevertheless it has a physiological basis which is far from clear. [44] Comfort is usually considered to be identical with the term optimum temperature, but even this term is identified differently by physiologists, behavioral scientists and those using biophysical techniques. Thermal comfort and discomfort rely upon both internal (core) and external (skin) temperature sensitivity and the central integration of these two loops. When dealing with textile and allied assemblies, as in clothing or bedding, we are dealing with the factors contributing mainly to the external loop of the thermal comfort sensation. Skin has a special role, as it is not only the source of information by virtue of comfort sensors, but the interface between the thermal core of the body and the environment. The human body attempts to maintain core body temperature around 37°C. The balance between perspiration and heat productions by the body and loss of the same is the comfort factor. [45] The body would be in a state of comfort when the body temperature is about 35°C and there is no moisture on the skin. Heat loss by evaporation is the only way to dissipate heat from the body when environment temperature is greater than skin temperature. [46] PCMs can be incorporated in a numerical three-node fabric ventilation model to study their transient effect on body heat loss during exercise when subjected to sudden changes in environmental conditions from warm indoor air to cold outdoor air. The results indicate that the heating effect lasts approximately 12.5 min depending on PCM percentage and cold outdoor conditions. Heat released by PCMs decreases the clothed-body heat loss by an average of 40–55 W/m^2 for a one-layer suit depending on the frequency of oscillation and crystallization temperature of the PCM. The experimental results reveal that under steady-state environmental conditions, the oscillating PCM fabric has no effect on dry resistance, even though the measured sensible heat loss increases with decreasing air temperature of the chamber. [47]

9. Applications of PCMs incorporated textiles

Phase change materials (PCMs) in textiles adapt to the thermal regulating functional performance of PCM garments [48-49] by altering their state of aggregation in a defined temperature range. Applications of phase change textiles include apparel, blankets, medical field, insulation, protective clothing and many others. The following is a brief summary of the application of PCM in textile fields.

9.1 Space

The technology uses phase change materials, which were first developed for use in space suits and gloves to protect astronauts from the bitter cold when working in space. Phase-change materials keep astronauts comfortable at space. [21]

9.2 Sports wear

From original applications in space suits and gloves, phase change materials (PCM) are nowadays using in consumer products as well. In order to improve the thermal performance of active-wear garments, clothing textiles with thermo-regulating properties are widely used. The thermo-regulating effect provided by these textiles could be based on the application of PCM. It is necessary to match the PCM quantity applied to the active-wear garment with the level and the duration of the activity for the garment use. Active wear needs to provide a thermal balance between the heat generated by the body and the heat released into the environment while engaging in a sport. The heat generated by the body during sports activity is often not released into the environment in the necessary amount thus increasing thermal stress. When phase change materials would incorporate in sportswear, during physical activity, the wearer's excessive body heat increases and is absorbed by the encapsulated phase change materials and released when necessary. Snowboard gloves, underwear, active wear, ice climbing and underwear for cycling and running are few more examples of applications of PCMs in sports wear. [21]

9.3 Medical applications

As the phase change materials interact with the microclimate around the human body, responding to fluctuations in temperature which are caused by changes in activity levels and in the external environment. Therefore, the textiles treated with PCM microcapsules have potential applications in surgical apparel, patient bedding materials, bandages and products to regulate patient temperatures in intensive care units. [50] PEG-treated fabric may be useful in medical and hygiene applications where both liquid transport and antibacterial properties are desirable, such as surgical gauze, nappies and incontinence products. Heat-storage and thermo-regulated textiles can keep the skin temperature within the comfort range, so they can be used as a bandage and for burn and heat/cool therapy. [39]

9.4 Casuals

Heat storage and thermo regulated textiles can be used as face fabrics, liner fabrics, batting etc.

Thermal underwear, jackets, sports garments and skiwear are the latest products in markets based

On phase change technology. [51]

9.5 Home textiles

Interior decorations, curtains, bed clothes, blankets, mattresses, pillows, sleeping bags etc. are some of the potential applications of thermo regulated textiles. Outlast® are the major players in producing products based on these intelligent textiles. [51]

9.6 Automotive textiles

The scientific theory of temperature control by PCMs has been deployed in various ways for the manufacturing of textiles. In summer, the temperature inside the passenger compartment of an automobile can increase significantly when the car is parked outside. In order to regulate the interior temperature while driving the car, many cars are equipped with air conditioning systems; though, providing adequate cooling capacity needs a lot of energy. Hence the application of Phase Change Material technology in various uses for the automotive interior could offer energy savings, as well as raising the thermal comfort of the car interior. [52]

9.7 Shoes and accessories

Currently, PCMs are also used in footwear, especially ski boots, mountaineering boots, race car drivers' boots etc. The phase change technology reacts directly to changes in temperature of both the exterior of the garment and the body. Phase change materials (paraffins) contained in microcapsules are linked to a specific temperature range depending on end use (36°C for a motor cycle helmet and 26°C for gloves). Heat-storage and thermo-regulated textiles can absorb, store, redistribute and release heat to prevent drastic changes in the wearer's head, body, hands and feet. In the case of ski boots, the PCM absorbs the heat when the feet generate excess heat, and send the stored heat back to the cold spots if the feet get chilly. This keeps the feet comfortable. Ski boots, footwear and golf shoes are some of the products where PCM could be used. [39]

9.8 Air-conditioning buildings with PCM

Recently PCMs have been studied for application to solar thermal storage and air conditioning in domestic buildings. By PCM applications in coatings for textiles used in roof covering, the thermal insulation value may be greatly enhanced. After the PCM has absorbed the surplus heat during the day it can be recharged by the overnight cooling effect. Pause described [53] a special panel system with PCM, which can be used for increasing the thermal resistance of lightweight construction walls. The main element of this panel is the cell structure, which is made of a textile reinforced material and filled with PCM. The quantity of the PCM contained in the panel is equivalent to a thermal storage of 700 kJ. Computer simulations have indicated that application of this panel can provide energy savings of about 20%.

10. Test Methods of PCM incorporated textiles

Traditional thermal insulation materials rely upon trapped air for their performance. The non-physiological testing procedures for quantifying the performance of such materials have therefore been designed accordingly. Trapped air insulation is a static system, which relies upon the convection/conduction of heat through air voids and fibre. The TOG and CLO tests therefore are designed to measure this effect. Fabrics containing PCM form a dynamic system that responds to changes in skin temperature and external conditions. It is therefore quite logical that the traditional non-physiological testing procedures for the old trapped air technology do not quantify the benefits of PCM. [54] The best type of testing for all of these materials is of course human physiological testing, but as always these are very time consuming and costly and could never be used for routine quality control testing. The American Society for Testing and Materials (ASTM) approved a new standard test procedure to measure the amount of latent energy in textile materials in June 2004. Based on years of research and testing textiles containing 'phase change materials' (PCMs) by Outlast Technologies, Inc., and Prof. Dr Douglas Hittle, Director Solar Energy Applications at Colorado State University (http:// welcome.colostate.edu), the first 'Test Method for Steady State and Dynamic Thermal Performance in Textile Materials' (ASTM D7024) was established by the ASTM. Phase-change technology in temperature-regulating textiles with increased latent energy represents an entirely new approach to providing increased comfort and performance. Standard testing procedures used for determining the insulating value of traditional fabrics do not measure the stored energy in these new, innovative 'smart' fabrics. Therefore a new test method and apparatus was required as ASTM D1518 'Standard Test Method for Thermal Transmittance of Textile Materials' determined only the R-value (or CLO value as used in the garment industry) in a steady state. This new test method measures dynamic temperature changes and differentiates and quantifies the temperature-buffering properties of a material in a dynamic environment. It measures the effects of changing temperature and a fabric's ability to absorb, store and release energy. This test provides the measurement to separate PCM technology from unsubstantiated claims of temperature regulation through moisture management, wicking or straight thermal insulation properties of a fabric. A differential-scanning calorimeter (DSC) is used to measure the heat capacity or enthalpy of the microcapsules and the fibre containing the microcapsules. This is a well-established procedure that has been used for many years to quantify the melting and crystallization points, or ranges, of materials as well as the heat absorption and release potential of the same material. The same technique is used to measure the heat capacity of the finished article. [54] Another technique known as thermo-gravimetric analysis (TGA) is used to assess the thermal strength of the micro PCMs. This is important because the process used to manufacture the fibre and the processes through which the fibres containing the microcapsules are subjected to in conversion to yarns and fabrics use heat. [54]

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