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Phase change materials for smart textiles – An overview

S. Mondal *

Department of Chemical and Biological Engineering, Colorado State University, Fort Collins, CO 80523-1370, USA

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Abstract

Phase change materials (PCM) take advantage of latent heat that can be stored or released from a material over a narrow temperature range. PCM possesses the ability to change their state with a certain temperature range. These materials absorb energy during the heating process as phase change takes place and release energy to the environment in the phase change range during a reverse cooling process. Insulation effect reached by the PCM depends on temperature and time. Recently, the incorporation of PCM in textiles by coating or encapsulation to make thermo-regulated smart textiles has grown interest to the researcher. Therefore, an attempt has been taken to review the working principle of PCM and their applications for smart temperature regulated textiles. Different types of phase change materials are introduced. This is followed by an account of incorporation of PCM in the textile structure are summarized. Concept of thermal comfort, clothing for cold environment, phase change materials and clothing comfort are discussed in this review paper. Some recent applications of PCM incorporated textiles are stated. Finally, the market of PCM in textiles field and some challenges are mentioned in this review paper.

Keywords: Phase change materials; Clothing comfort; Microencapsulation; Smart temperature adaptable fabrics

1. Introduction

Fundamental principles of science are now increasingly employed for the manufacturing of innovative textile products. One such principle is 'Phase Change', the process of going from one physical state to another i.e. from a solid to a liquid and vice versa. Fibre and textile which have automatic acclimatising properties have recently attracting more and more attention. This effect could be achieved by using phase change material (PCM) [1]. The technology for incorporating PCM microcapsules [2] into textile structure to improve their thermal performance was developed in the early 1980s under NASA research programme. The original intent was to use these fabrics in the astronauts' space suits to provide improved thermal protection against the extreme temperature fluctuations in outer space. From the original application of astronauts suits, the PCM incorporated textiles taking the market place of consumer apparel products.

Thermal energy storage (TES) is the temporary storage of high or low temperature energy for later use. It bridges the time gap between energy requirements and energy use [3]. Among the various heat storage techniques of interest, latent heat storage is particularly 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

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* Fax: +1 970 491 7369.
E-mail address: subratamondal@yahoo.com

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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 application 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. Phase change processes

Latent heat storage is one of the most efficient way of storing thermal energy. Unlike the sensible heat storage method, the latent heat storage method provides much higher storage density, with a smaller temperature difference between storing and releasing heat [10]. Every material absorbs heat during a heating process while its temperature is rising constantly. The heat stored in the material is released into the environment through a reverse cooling process. During the cooling process, the material temperature decreases continuously. Comparing the heat absorption during the melting process of a phase change material (PCM) with those in normal materials, much higher amount of heat is absorbed if a PCM melts. A paraffin-PCM, for an example, absorbs approximately 200 kJ/kg of heat if it undergoes a melting process [10]. High amount of heat absorbed by the paraffin in the melting process is released into the surrounding area in a cooling process starts at the PCM's crystallization temperature. After comparing the heat storage capacities of textiles and PCM, it is obvious that by applying paraffin-PCM to textiles their heat storage capacities can substantially enhanced [6].

During the complete melting process, the temperature of the PCM as well as its surrounding area remains nearly constant. The same is true for the crystallisation process; during the entire crystallisation process the temperature of the PCM does not change significantly either. Phase change process of PCM from solid to liquid and vice versa is schematically shown in Fig. 1. The large heat transfer during the melting process as well as the crystallization process without significant temperature change makes PCM interesting as a source of heat storage material in practical applications. When temperature increases, the PCM microcapsules absorbed heat and storing this energy in the liquefied phase change materials. When the temperature falls, the PCM microcapsules release this stored heat energy and consequently PCM solidify [10].

The phase diagram of the binary system of tetradecane–hexadecane (Fig. 2) has been thoroughly discussed by He et al. [11,12]. Because the pure tetradecane ($C_{14}H_{30}$) and hexadecane ($C_{16}H_{34}$) solid have similar structure (triclinic crystals), the binary system contains all conditions for formation a solid solution [12]. Phase diagrams (equilibrium diagrams) depict the concentration–temperature–pressure relationships of a chemical system at equilibrium and are used to visualise how these relations change with temperature and chemical composition. The upper curve $(T - x_{i(1)})$ in Fig. 2 is the liquidus or freezing point curve. The lower curve $(T - x_{i(s)})$ is the solidus or melting point curve. Any system represented by a point above the liquidus is completely molten, and any point below the solidus represents a completely solidified mass. A point within the area enclosed by the liquidus and solidus curve indicates an equilibrium mixture of liquid and solid solution. These two curves approach and touch at point M, which is the minimum-melting point. The phase transition occurring on the cooling of a given mixture has been described by He et al. [11,12]. The phase transition temperature range for each homogenous liquid can be obtained directly from the phase diagram. The storage density of mixtures,

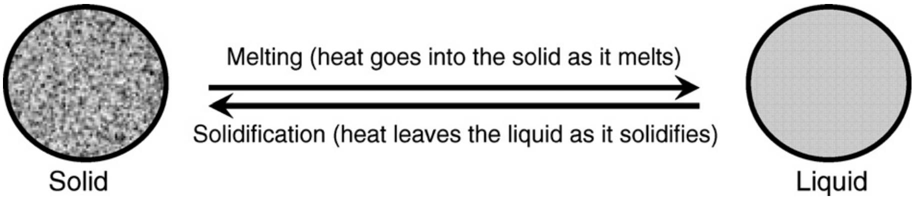

Fig. 1. Schematic representation of phase change process.

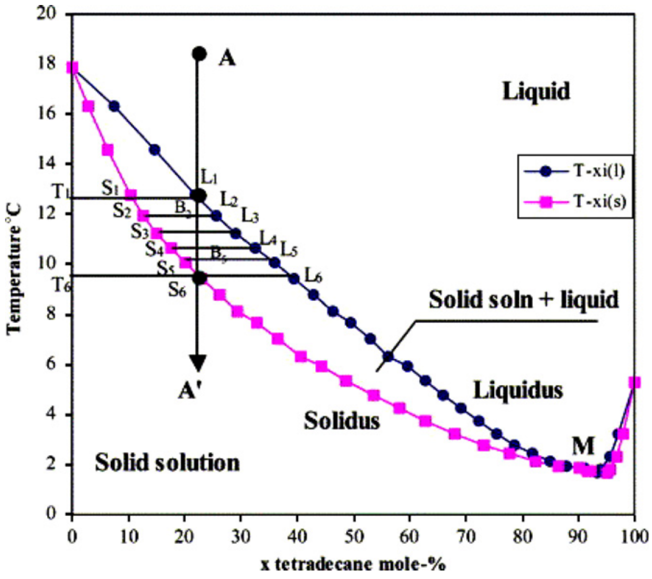

Fig. 2. The liquid–solid phase diagram of binary mixtures system of $C_{14}H_{30}$ and $C_{16}H_{34}$ (reproduced with permission from [11]).

corresponding to a certain temperature range within the phase transition temperature range, can be obtained by using the "lever principle" from the phase diagram. The phase transition temperature range of mixtures is the function of the composition of mixtures, and the storage density in any temperature range is the function of composition and temperature change.

3. Working principle of phase change materials (PCMs)

Thermal energy storage is an essential technique for thermal energy utilization [13]. 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 [14] on the phase of the substances involve in the heat transfer processes. For substances that are solid, conduction is the predominate 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 [15,16]. 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) [6,16]. 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

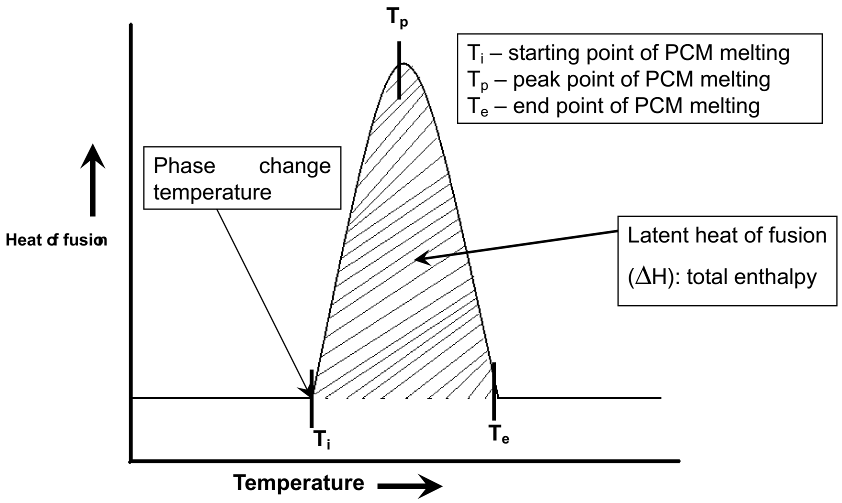

Fig. 3. Schematic of DSC heating thermogram of PCM.

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 celcius.

4. Different types of PCMs

Phase change materials are able theoretically to change state at nearly constant temperature and therefore to store large quantity of energy [17]. Using the thermal energy storage (TES) of phase change material (PCM) which has a melting point from 15 to 35 °C is one of the most effective ideas for effective utilization of this kind of materials in textiles field. In addition to water, more than 500 natural and synthetic PCMs are known [18]. These materials differ from one another in their phase change temperature ranges and their heat storage capacities. The required properties for a PCM for a high efficiency cooling system with thermal energy system (TES) for specific application [19] such as in textile fields are as follow:

(i) melting point between 15 and 35 °C;
(ii) large heat of fusion;
(iii) little temperature difference between the melting point and the solidification point;
(iv) harmless to the environment;
(v) low toxicity;
(vi) non-flammable;
(vii) stability for repetition of melting and solidification;
(viii) large thermal conductivity, for effective heat transfer;
(ix) ease of availability;
(x) low price.

A wide spectrum of phase change material is available with different heat storage capacity and phase change temperature. A simple and classical example of phase change materials is the paraffin wax leads ranging from 15 to 40 μm in size, which can be microencapsulated and then either integrated into fiber or used as a coating. Some of the PCMs are describes in the following paragraphs:

4.1. Hydrated inorganic salt

Hydrated inorganic salt with ‘*n*’ water molecules, can be used in the manufacturing of heat storage and thermo-regulated textiles and clothing which usually, has a heat-absorbing and -releasing temperature interval of about 20–40 °C. Physical and chemical properties of Glauber’s salts are very attractive for thermal storage: the salt has a convenient melting temperature (32.4 °C) and melting latent heat of 254.00 kJ/kg which gives high energy at its melting point [20]. In the thermal energy system (TES), using sodium sulfate water solution as the PCM, heat produced or absorbed by the following chemical reaction between the decahydrate crystal and the water solution [21]:

$$Na_2SO_4 + 10H_2O \Longleftrightarrow Na_2SO_4 \cdot 10H_2O.$$

The mode of a crystallizing process, which occurs by cooling the TES capsule continuously, differs significantly depending on the initial temperatures being higher or lower than 32 °C. When the capsule is cooled down from a temperature higher than 32 °C to a temperature lower than 32 °C, a process of crystal nucleation in a supersaturated solution appears. When the initial temperature is lower than 32 °C, the heat removal process is explained by a phenomenon of crystal growth where crystal nuclei or small crystals already existing in the solution increase in size. Hydrated salts are attractive materials for use in thermal energy storage due to their high volumetric storage density ($\sim$350 MJ/m^3), relatively high thermal conductivity ($\sim$0.5 W/m °C) and moderate costs compared to paraffin waxes. Glauber salt ($Na_2SO_4 \cdot H_2O$), which contains 44% Na_2SO_4 and 56% H_2O by weight has been studied [22,23].

Manganese(II) nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$) has 125.9 kJ/kg heat of fusion. Its density is nearly 1.8×10^3 kg/m^3, and this means a latent heat per unit volume of 226.6×10^3 kJ/m^3. It contains 68% that of water, and the melting point is 25.8 °C. The temperature difference between the melting and the solidification point was found to be quite large. Further, the $Mn(NO_3)_2 \cdot 6H_2O$ is characterized by general availability, low toxicity and non-flammability [19].

4.2. Linear long chain hydrocarbons

Hydrophobic linear hydrocarbon is by product of oil refining having general formula of C_nH_{2n+2}. These are non-toxic, inexpensive, and have extensive source of raw materials, would be suitable for varied usage as they have wide range of melting temperature depending on their carbon atoms (Fig. 4). The melting and crystallization of hydrocarbon with $n = 13$–18 are in the range from -5.5 to 61.4 °C [24]. By selecting the number of carbon atom of hydrocarbon, the phase transition temperature could be tailored for specific applications. From Fig. 4, we can see that *n*-Eicosane have melting temperature is about human body temperature. They might be the most important PCMs in the manufacture of heat storage and thermo-regulated textiles and clothing. The performance of thermoregulation would depends on the heat adsorption and heat emission of the hydrocarbons. The heat adsorption and heat emission of some linear hydrocarbons are listed in Table 1.

4.3. Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is another important PCMs for textile applications. Commercial paraffin waxes are cheap with moderate thermal storage densities ($\sim$200 kJ/kg or 150 MJ/m^3) and a wide range of melting temperatures [10]. The repeating unit of PEG is oxyethylene ($-O-CH_2-CH_2-)_n$, with either end of chains comprising with

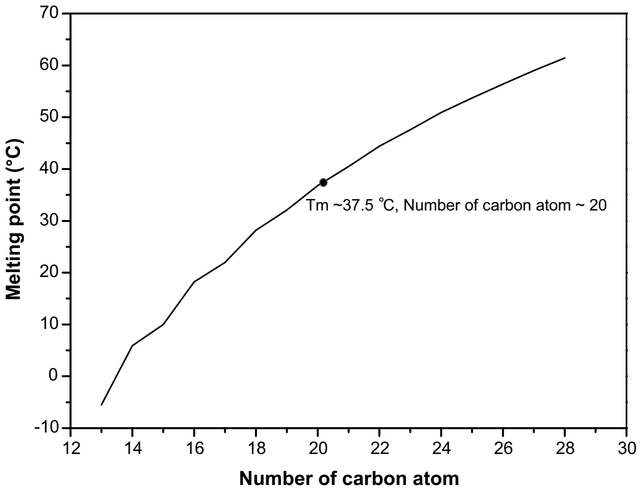

Fig. 4. Paraffin hydrocarbon and their melting temperature [24].

hydroxyl group. The melting temperature of PEG is proportional to the molecular weight; when it's molecular weight is lower than 20,000. Differential scanning calorimetry can be used to evaluate PEG for latent heat thermal energy storage. The formation of crystalline phase would influences by the molecular weight of PEG; there is an increased tendency of higher-molecular-weight PEGs towards the formation of crystalline phase owing to their lower segmental mobility and more convenient geometrical alignment. During the freezing cycle, an increase in the molecular weight of PEG causes an increase in the solidification temperature and heat of crystallization. It influences also the course of solidification by lowering the crystallization temperature (T_c). An additional effect observed in the case of the blend's freezing is associated with larger supercooling, probably due to morphological constraints and entanglements in interlamellar regions. The possible advantage of using PEG blends to replace pure components is connected with the possibility of changing the temperature range and heat associated with melting/freezing [27]. The melting point temperature of PEG would depend on the molecular weight of polymer (Table 2).

Table 2
Molecular weight and melting point of polyethylene glycol (PEG)

Materials	Molecular weight	Melting point (°C) (approx. value)	Ref.
PEG 1000	1000	35	[28]
PEG 1500	1500	50	[29,30]
PEG 3400	3400	59	[29,30]
PEG8000	8000	60	[31]
PEG10000	10,000	62	[29,30]
PEG20000	20,000	63	[29,30]

4.4. Others

Feldman and Shapiro [32] have analyzed the thermal properties of fatty acids (capric, lauric, palmitic and stearic acids) and their binary mixtures. The results have shown that they are attractive candidates for latent heat thermal energy storage in space heating applications. The melting range of the fatty acids was found to vary from 30 to 65 °C, while their latent heat of transition was observed to vary from 153 to 182 kJ/kg. These properties are of prime importance in the design of a latent heat thermal energy storage system. In their natural form, fats and vegetable oils melt at temperatures useful for thermal energy storage. Incremental improvement of their heat release characteristics could pave the way for commercial applications as phase change materials (PCM). These chemicals could provide a biomaterial alternative to a technology dominated by paraffin and salt products [33].

Thermal phase change properties of some other PCM are as follows: butyl stearate, melting point (m.p.) = 19 °C, f.p. = 21 °C, heat of fusion (ΔH_m) = 120 kJ/kg, vinyl strearate, m.p. = 27 °C, f.p. = 29 °C, ΔH_m = 122 kJ/kg, isopropyl stearate, m.p. = 14 °C, f.p. = 18 °C, ΔH_m = 142 kJ/kg seem promising [34].

5. Thermal conductivity enhancer for PCM

One of the most commonly used PCMs in storing thermal energy is the paraffin. The advantage of PCM storage compared to sensible heat-storage systems, is its potential to store large amounts of heat with only a small temperature swing. However, PCMs have some disadvantages, such as the low heat-conductivity of the material [35]. The thermal conductivities of most PCMs are too low to provide a required heat exchange rate between the PCM and substrate. Therefore, thermal conductivity enhancer would be useful to efficiently use the thermal energy stored in the PCM [36]. The thermal conductivities of PCM could be enhanced by using metal filler, carbon nanofiber/fiber fillers etc [36–39]. Carbon fibers have a strong resistance to corossion and chemical attack, which make

Table 1
Latent heat of adsorption and emission [24–26]

Hydrocarbons	No of C atoms Ref. [24]	Latent heat of adsorption (ΔH) in J/g	Latent heat of emission ($-\Delta H$) in J/g	Crystallization temperature (T_c, °C)	Ref.
n-Hexadecane	16	235.2	236.6	12.2	[25]
n-Heptadecane	17	176.4	182.6	16.5	[25]
n-Octadecane	18	244.8	246.4	22.0	[25]
n-Nonadecane	19	177.6	182.6	26.4	[25]
n-Eiscosane	20	242	230	30.4	[26]

them compatible with most PCMs. The thermal conductivities of carbon nano-fibers are considerably high and their densities are less that 2260 kg/m^3, which is lower than those of metals that are usually used as additives [37]. Therefore, carbon nanofiber (CNF)/fiber could be used as efficient thermal conductivity enhancer for PCM useful for textile applications. The CNF could be introduced into the PCM by using shear mixing and melting techniques. It is common knowledge in heat transfer that when lateral surface area increases, the heat transfer rate increases. The thermal properties of the modified PCM could enhanced significantly by dispersing CNFs into it [37]. As a result of this enhancement, the cooling rate during the solidification process of the new nanocomposite increased significantly by increasing the mass ratio of the CNFs.

The effectiveness of thermal conductivity enhancers (TCEs) in improving the overall thermal conductance of phase change materials (PCMs) has been studied by Nayak et al. [40]. For the case of PCM with porous TCE matrix, it was observed that inserting aluminum matrix into Eicosane can offer an order-of-magnitude increase in thermal conductivity and melting rate. Melt convection has a considerable effect on the evolution of the solid–liquid interface. However, the effect of convection becomes insignificant beyond a certain volume fraction of TCE. For the case of PCM with TCE fins, too, convection in the melt plays a significant role in temperature uniformity. The performance of the heat sink improves if the TCE material is distributed in the form of thinner fins. It is also found that rod-type fins perform better than plate-type ones, as they are able to maintain better uniformity of temperature within the PCM leading to less chip temperature [40].

The numerical approach makes it possible to calculate the processes that occur inside the solid PCM (conduction), liquid PCM (convection), and air (convection) simultaneously, and to account for the phase-change, moving boundary due to the variation of the PCM volume, and solid phase motion in the melt [41]. The paraffin (*n*-docosane)/expanded graphite (EG) composite PCMs can be easily prepared by impregnation of liquid paraffin into the porous structure of EG. The paraffin/EG composite PCM with mass fraction of 10% EG would accepted as form-stable composite PCM as it allowed no leakage of melted paraffin from the pores of EG when subjected to a solid–liquid phase change process. In particular, the use of form-stable composite PCM can reduce the weight of the latent heat thermal energy storage (LHTES) system due to its low density besides its direct usability in energy storage systems without a requirement of an extra storage container. Increasing the mass fraction of EG from 2% to 10% gradually increased the thermal conductivity of paraffin/EG composite PCM. A very high correlation ($r = 0.9986$) occurred between thermal conductivity and mass fraction of EG, indicating a strong association between the two attributes [5].

6. Fire hazard treatment of paraffin

One of the problem we are still facing is the burning behavior of the PCM layer, as the microcapsules are mostly made of paraffin. Flame propagation can be stopped by adding a flame retardant treatment to the coating but there was still a hole formation at the place where the flame was applied. Possible solutions of this problem are the improvement of the flame retardant treatment or the use of the PCM in a sandwich construction between two fabrics [42]. Cai et al. prepared stable phase change material (PCM)-high density polyethylene (HDPE)/paraffin hybrid with different flame-retardant systems by using twin-screw extruder technique. The weight of char residues of flame-retardant form-stable PCMs are markedly higher than that of the form-stable PCM. Although, its latent heat is given by differential scanning calorimetry (DSC) method, which showed the latent heat of PCM had not distinct change with the addition of flame retardant. In other words, the property of thermal energy storage has not been affected by the addition of flame retardants [43]. A kind of form stable phase change material (PCM) based on high density polyethylene (HDPE), paraffin, organophilic montmorillonite (OMT) and intumescent flame retardant (IFR) hybrids is reported by Cai et al. [44]. The synergy between OMT and IFR leads to the decrease of the heat release rate (HRR), contributing to improvement of the flammability performance. The DSC analyses indicate the latent heat of the form stable PCM has no distinct change with the loading of the IFR and OMT. A kind of shape stabilized phase change nanocomposites materials (PCNM) based on high density polyethylene (HDPE)/ethylene–vinyl acetate (EVA) alloy, organophilic montmorillonite (OMT), paraffin and intumescent flame retardant (IFR) are prepared using twin-screw extruder technique [45]. The paraffin acts as a phase change material and disperses in the three-dimensional network structure. The TGA analysis results indicate that the flame retardant shape stabilized PCNM produce a larger amount of char residue at 800 °C than that of shape stabilized PCNM, although the onset of weight loss of the flame retardant shape stabilized PCNM occur at a lower temperature. The formed multicellular char residue contributes to the improvement of thermal stability performance.

7. Concept of thermal comfort

The heat exchange with the environment plays a key role in the thermal state of the human body [46]. Thermal comfort is defined as that condition of mind which expresses satisfaction with the thermal environment. Dissatisfaction may be caused by warm or cool discomfort for the body in general, as expressed by the predicted mean vote (PMV) and predicted percentage of dissatisfied (PPD) indices [47]. However, thermal dissatisfaction may also be caused by an unwanted heating or cooling of one particular part of the body (local discomfort). The PMV and PPD indices express warm and cool discomfort for the body as a whole. Due to individual differences, it is impossible to specify a thermal environment that will satisfy everybody. A percentage of the occupants can always be expected to be dissatisfied. Nevertheless, it may be possible to specify environments predicted to be experienced as acceptable by a certain percentage of the occupants. In the new standard, comfort requirements are specified predicted to be acceptable for at least 80% of the occupants [48]. The indoor air quality is quite mediocre in many air-conditioned or mechanically ventilated buildings, even though existing standards may be met. The aim should be to provide indoor air that is perceived as fresh, pleasant and stimulating, with no negative effects on health, and thermal environment perceived as comfortable by almost all occupants [49]. The impact of enthalpy on acceptability or on perceived air quality expressed in percentage dissatisfied or decipol is strong. Humans obviously like a sensation of cooling of the respiratory tract each time air is inhaled. This causes a sensation of freshness which is felt pleasant. If proper cooling does not occur, the air may feel stale, stuffy and unacceptable. A high enthalpy means a low cooling power of the inhaled air and, therefore, an insufficient convective and evaporative cooling of the wet mucous membranes in the respiratory tract, and in particular the nose. Heat loss through respiration is only around 10% of the total heat loss from the body, and humidity and temperature of the inhaled air has, therefore, only a small impact on the thermal sensation for the human body as a whole [49]. Therefore, clothing would play prominent role as far comfort to the wearer is concern. The transport of dry heat through a fabric is a complex process involving conduction, convection and radiation. Transport of sensible heat flow from the skin of a dressed subject to a cooler environment is even more complicated. Warm air can be pressed through the fabric layers of the clothing and through small and large openings of the clothing to the surrounding environment, and cold air can be sucked into the clothing. Within the clothing, mixing of air layers of different temperatures can be caused by compression and extension of air-filled cavities. An additional influence of wind may further enhance the complexity of heat exchange [50]. The dry heat loss, H_{dry}, from the skin can be calculated from the heat balance equation as:

$$H_{\mathrm{dry}} = M - W - C_{\mathrm{res}} - E_{\mathrm{res}} - E - S.$$

where M is the metabolic rate, W is the external work, C_{res} is the convective respiratory heat loss, E_{res} is the evaporative respiratory heat loss, E is the evaporatory heat loss from the skin and S is the change in body heat content. With, all values are expressed in $\mathrm{W\,m^{-2}}$.

During activity, body movements lead to circulation of air trapped in the clothing and thus to increased convective heat transfer and lower I_{cl} (intrinsic clothing insulation) values. Also, surface air insulation I_{a} is reduced by body movements. This reduction is caused by changes in the heat transfer coefficient, h, because the convective heat transfer coefficient, h, is increased [50]. Thermal neutrality for a person is defined as a condition in which he prefers neither a higher nor a lower ambient temperature level. Thermal neutrality is a necessary condition for a person to attain thermal comfort but this condition is not always sufficient. A further requirement is that no local warm or cool discomfort is experienced on any part of the body; asymmetric radiation may create such local discomfort [51].

Personalized ventilation can improve occupants' thermal comfort, perceived air quality and decrease the intensity of sick building syndromes (SBS) symptoms compared to mixing ventilation. Occupants will use the provided individual control of airflow rate and positioning of the air terminal device to obtain preferred microenvironment in rooms where the air temperature is within the range recommended by indoor climate standards. Under mixing ventilation the thermal sensation approached the slightly warm level for both whole body and local ratings. In the second condition, personalized ventilation systems (PVS) provided local cooling that resulted in a whole body thermal sensation close to neutral. The cooling was even more visible for the head region, for which the thermal sensation was almost neutral. The difference between local thermal sensation with mixing ventilation and PVS was significant throughout the whole experiment ($P < 0.01$). The thermal sensation felt with PVS was in general perceived as more acceptable than the sensation with mixing ventilation ($P < 0.05$) [52]. The improvement in perceived air quality with PVS depends on the room air temperature and the temperature difference between room and personalized air. The greatest improvement was observed when the temperature of the personalized air was lower than the room air [52].

8. Clothing for cold environments

For predicting or evaluating the indoor thermal environment, clothing is an important factor. In most cases clothing is selected individually by the occupants. In some cases, however, the type of clothing is prescribed by the workplace (e.g., clean room, uniforms and dress codes). The indoor air temperature may affect also the clothing adjustment, i.e. the attitude of people to change their clothes in a workplace [53]. Because of the limitations of their physiological defenses against cold, humans are generally obliged to supplement those defenses by clothing and shelter, which reduce the thermo-regulatory challenge to an endurable and usually comfortable level. Reduced discomfort from cold is accompanied by increased discomfort from heat. A nude person in the cold experiences sustained vasoconstriction, shivering, and sometimes a fall in deep body temperature. Fully clothed people in the Antarctic occasionally suffer these responses (mainly during light work, or when their clothing is wet or cannot be adjusted), but their most characteristic thermo-regulatory experience is alternating vasoconstriction and vasodilatation [54]. The bioheat human model is capable of predicting accurately nude human transient physiological responses such as the body's skin, tympanic, and core temperatures, sweat rates, and the dry and latent heat losses from each body segment. The nude body model is integrated to an existing clothing model based on heat and mass diffusion through the clothing layers and takes into consideration the moisture adsorption by the fibers [55]. In cold environments, appropriate assessment of working time limits is important to avoid unacceptable body cooling during work. At low temperatures both general body cooling and local cooling can limit the working time because of discomfort, deteriorated extremity performance and, in more extreme cases, due to cold injury. Duration limited exposure (DLE) index, which provides a method to determine acceptable time limits when, in a cold environment, clothing insulation is not sufficient to protect wearer from body cooling [56]. DLE is defined as the maximal exposure time with the existent clothing insulation and can be determined at two levels strain, a lower level starting from thermo-neutral conditions (DLEneu) and a higher level starting from the body slightly cooled (DLEmin). Heat balance, defined as preservation of the initial core temperature was maintained at all ambient temperatures at the time limits predicted by DLE, although at the expense of different levels of peripheral cooling. The energy expenditure (EE) of the subjects was higher with the lighter clothing than with the heavier clothing during the mild cold exposure and male subjects were satisfied thermally with the environment. Since the EE was affected by clothing thermal insulation in mild cold (19 °C air), clothing thermal insulation should be taken into consideration. During the mild cold exposure, a slight decrease in rectal temperature (T_{re}) was observed in both sexes but there were no significant differences related to clothing types and sex. During the mild cold exposure, T_{sk} (skin temperature) decreased by an average of male 2.0 °C (female 1.9 °C) and male 1.1 °C (female 1.5 °C) in the S- (short sleeves and knee trousers) and L-type (long sleeves and long trousers) clothing, respectively [57].

9. 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 μm and 30 μm. The microcapsules are resistant to mechanical action, heat and most types of chemicals. They react to temperature fluctuations in the following way [16]:

The temperature rises: when temperature rises due to a higher ambient temperature, the microcapsules react by absorbing heat. The PCMs in the microcapsules melt. They draw heat from their surroundings and store the surplus energy.

The temperature falls: when the temperature falls due to a lower ambient temperature, they release the previously stored heat. Interacting textiles structure with PCM microcapsules for garment applications, the following thermal benefits are realized [16]:

- 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).

The treated fabric with 22.9% add-on of microcapsules is capable of absorbing 4.44 J/g of heat if the microcapsules (melamine–formaldehyde microcapsules containing eicosane were manufactured by *in situ* polymerization) on the fabric undergo a melting process. The heat of absorption by the microcapsules delays the microclimate temperature increase of clothing. This leads to enhanced thermo-physiological comfort and prevents heat stress [58].

The impact of phase-change materials (PCM) on intelligent thermal-protective clothing has been investigated by Wang et al. [59]. In the heating process, when the PCM layer's temperature increases above the PCM's melting point (28.0 °C), the PCM melts and becomes liquid. During this process, thermal energy is absorbed and stored. After all the PCM becomes liquid, the temperature continually increases. When the PCM layer's temperature reaches 29.0 °C, the conductive fabrics were powered off. The temperature of the PCM layer then decreases after a short time. When the temperature of the PCM layer decreases below 27.0 °C, the liquid PCM becomes solid and releases heat energy. In this process, the PCM acts as a thermal buffer material by releasing stored heat. The electrical energy consumed by the clothing assembly (nonwoven fabric coated with PCM and having conductive layer) with PCM is about 30.9% less than that consumed by the clothing assembly without PCM (nonwoven fabric, having conductive layer). Therefore concluded that a conductive fabric can significantly increase the temperatures of the different layers of the assembly and make the assembly warmer.

10. PCM and clothing comfort

Comfort is a term created by psychologists; nevertheless it has a physiological basis which is far from clear [60]. 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 [61]. 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 [62]. 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 [63].

11. How to incorporate PCMs in textiles

The PCMs change phases within a temperature range just above and below human skin temperature would be suitable for application in textiles. This interesting property of PCMs would be useful for making protective textiles in all-season. Fiber, fabric and foam with PCMs could store the heat body creates then release it back to body, as it needs. Since the process of phase change is dynamic; therefore, the materials are constantly changing from a state to another depending upon level of physical activity of the body and outside temperature. The thermo-regulating characteristic is possible in manmade fiber by adding PCM microcapsules to a polymer solution prior to fiber extrusion. In the process, PCM microcapsules are integrated inside the fiber itself. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, foam techniques are some of the convenient processes for PCMs' incorporation into the textile matrix.

11.1. Fiber technology

The incorporation of PCM within a fiber requires first that the PCM be microencapsulated. PCMs would be added to the liquid polymer, polymer solution, or base material and fibre is then spun according to the conventional methods such as dry or wet spinning and extrusion of molten polymer. The microencapsulated PCM fibers could store heat over long periods. If the environmental temperature drops, the fiber slowly radiate heat.

The composition and properties of a series of sheath/core composite polypropylene fibres nonwovens with different phase change material (PCM) contents in the core have been studied using SEM, DSC and temperature sensors [64]. It is observed that the PCM content in the fibre, sheath/core ratio and the content of 4-hole spiral crimp PET fibre affect the temperature regulating ability of the nonwoven. The temperature regulating ability has no truck with the fibre titer in the experimental scale. There can be a maximum temperature difference of 9.3 °C between the nonwovens made from composites and control (polypropylene) fibres during temperature rising, and 10.2 °C between control and composite samples during temperature dropping. Photothermal conversion and thermo-regulated fibres (PCTFs) have been prepared using the fibre-forming polymer containing photothermal conversion ceramic as sheath and the fibre-forming polymer containing microPCMs as core. It is observed that the photothermal conversion and thermo-regulated fibres have better temperature-regulating abilities when compared with the control. The maximum heat absorbing and heat releasing temperature differences are found to be 4.5 °C and 6.5 °C respectively when the PCTF nonwoven is compared with PP nonwoven [65].

11.2. Coatings

A coating composition for textiles includes wetted microspheres containing a phase change material dispersed throughout a polymer binder, a surfactant, a dispersant, an antifoam agent and a thickener. Preferred phase change materials include paraffinic hydrocarbons. The microspheres may be microencapsulated. To prepare the coating composition, microspheres containing phase change material are wetted and dispersed in a dispersion of water solution containing a surfactant, a dispersant, an antifoam agent and a polymer mixture. The coating would be then applied to a textile substrate. In an alternative embodiment, an extensible fabric would be coated with an extensible binder containing microencapsulated phase change material to form an extensible, coated fabric [24]. PCM could be incorporated into the textiles by coating using polymer such as 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.

11.3. Lamination

In order to improve thermo-physiological wearing comfort of protective garments, PCM would be incorporated into a thin polymer film and applied to the inner side of

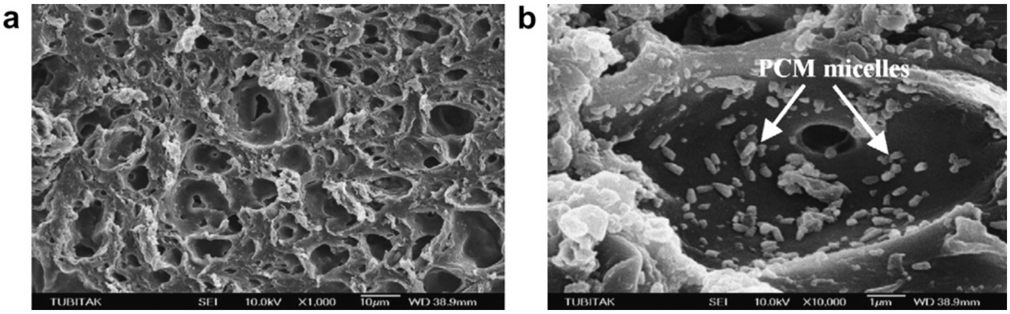

Fig. 5. PU1 containing *n*-hexadecane: (a) magnification 1000×; 10.0 kV and (b) magnification 10,000×; 10.0 kV (reproduced with permission from [68]).

the fabric system by lamination. The cooling effect of the PCM can delay the temperature rise and, hence, the moisture rises in the microclimate substantially. As a result, the wearing time of the garments can be extended significantly without the occurrence of heat stress as a serious health risk. The longer wearing times will further lead to a significantly higher productivity. The more comfortable wearing conditions will also result in a reduced number of accidents and lower error rates. Beside chemical protective suits the PCM can also improve the thermo-physiological wearing comfort of other protective garments made of nonwovens such as surgical gowns, uniforms, or garments worn in clean rooms [66,67]. Microcapsules would be mixed into a water-blown polyurethane foam mix and these foams are applied to a fabric in a lamination process, where the water is taken out of the system by drying process. The excellent honeycomb structure obtained during foam formation made considerable amount of still air trapping possibility, thus, leading to an increased passive insulation. Although the presence of PCM micelles in cells can easily be distinguished (Fig. 5) [68].

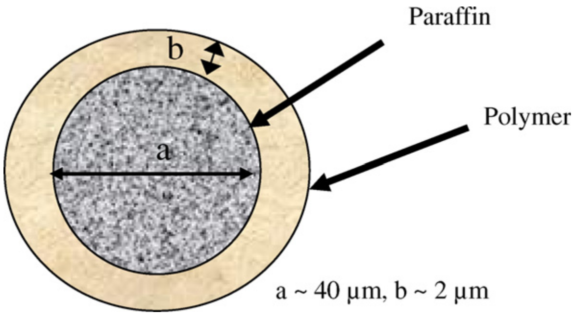

Fig. 6. Microencapsulation: Paraffinic PCM core material individually with a hard polymeric shell.

12. Microcapsulation

Microencapsulation of liquids and solids is an innovative micropackaging technology which is opening up new technical textiles which can provide textiles with new properties and added value [69,70]. Microencapsulation involves the production of microcapsules which act as tiny containers of solids. Microcapsules that have walls less than 2 μm in thickness and 20–40 μm in diameter (Fig. 6) is useful in fiber applications [2]. These containers release their core contents under controlled conditions to suit a specific purpose. The microcapsules are produced by depositing a thin polymer coating on small solid particles or liquid droplets, or on dispersions of solids in liquids. The core contents–the active substance–may be released by friction, by pressure, by diffusion through the polymer wall, by dissolution of the polymer wall coating, or by biodegradation. In their application in textiles, the paraffins are either in solid or liquid state. 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. These microscopic spheres containing PCM

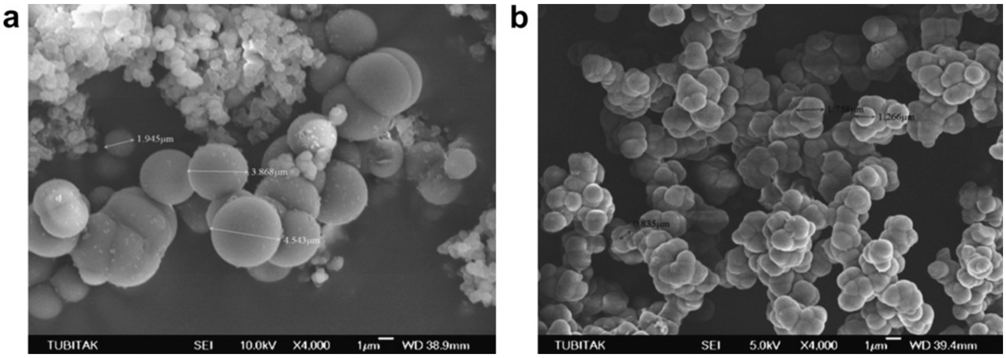

Fig. 7. (a) Polyurea–formaldehyde microcapsules containing *n*-octadecane core; magnification 4000×; 10.0 kV. (b) Polyurea–formaldehyde microcapsules containing the mixture of *n*-octadecane and PEG 600 core; magnification 4000×; 5.0 kV (reproduced with permission from [71]).

are called PCM-microcapsules. The microencapsulated paraffin is either permanently locked in acrylic fibres or in polyurethane foams or coated onto the surface of a textile structure.

Microcapsule production may be achieved by means of physical or chemical techniques. The use of some techniques has been limited to the high cost of processing, regulatory affairs, and the use of organic solvents, which are concern for health and the environment. Physical methods are mainly spray drying or centrifugal and fluidized bed processes which are inherently not capable of producing microcapsules smaller than 100 μm. The most suitable chemical processes are associated with the simple or complex coacervation and interfacial (or in situ) polymerization techniques [71]. The microencapsulation method based on in situ polymerization technique, was quite successful to produce microcapsules (Fig. 7) with an enhanced thermal capacity in relation to the PCM content. Seventy-seven percent of microcapsules were obtained ⩽100 μm in diameter and 90% of them were smaller than 185 μm by using in situ polymerization techniques.

13. Smart temperature adaptable textiles

The required thermal insulation of clothing systems primarily depends on the physical activity and on the surrounding conditions, such as temperature and relative humidity. The quantity of heat produced by human being depends very much on the physical activity and can vary from 100 W while resting to over 1000 W during maximum physical performance [62]. Particularly during the cooler seasons (approx. 0 °C), the recommended thermal insulation is defined in order to ensure that the body is sufficiently warm when resting. At a more intensive activity, which is often the case with winter sports, the body temperature increases with enhanced heat production. To keep this increase within a certain limit, the body perspires in order to withdraw energy from the body by evaporative cooling. If the thermal insulation of the clothing is reduced during physical activity, a part of the produced heat can be removed by convection thus the body is not required to perspire so much. The quality of insulation in a garment against heat and cold will be extensively governed by the thickness and density of its component fabrics. High thickness and low density improve insulation due to the presence of lots of air gaps. However, a garment made from a thick fabric will have greater weight, and the freedom of movement of the wearer will be affected. The effectiveness of the insulation is also affected by the external temperature. The more extreme the temperature, be it very high or very low, the less effective the insulation becomes. Clearly then a garment made from an intelligent fabric whose nature can vary depending on the external temperature can provide superior protection. Thermo-regulated textiles are a kind of smart new textile product that contains low temperature phase-change materials (PCM). When a substrate containing PCM is heated, the increases in temperature of the substrate is interrupted at the melting point of the phase change material, due to absorption as latent heat. The temperature will rise only when the entire solid has melted. Conversely, during the cooling process at low ambient, the drop in temperature is interrupted at the solidification temperature. The heat flux through a material containing PCM is thus delayed in both heating as well as cooling, during the process of phase change. This thermal insulation is dependent on temperature and time; and being temporary in nature, it can be termed dynamic thermal insulation [61]. Fabrics have been given enhanced thermal properties by coating the fibers with phase change material and plastic crystals. Temperature adaptable textile fibers [72] which store heat when the temperature rises and release heat when the temperature decreases, in which phase change or plastic crystalline materials would be enclosed within hollow fibers, or impregnated upon non-hollow fibers. At the phase change temperature, a characteristic of phase change material during the heating cycle is to absorb and hold a quantity of thermal energy at almost a constant temperature while changing to the next phase. Thus, the material can be precooled and used as a barrier to heat, since a quantity of thermal energy must be absorbed by the phase change material before its temperature can rise. The phase change material may also be preheated and used as a barrier to cold, as a quantity of heat must be removed from the phase change material before its temperature can begin to drop.

Nonwoven protective garments are used in a variety of applications such as asbestos and lead abatement, pest control, and treatment of hazardous waste. The construction of the nonwovens used in such garments provides a high barrier function against the penetration by dust, liquids, or gases. However, in the same way the fabric system prevents the transfer of hazardous materials into the garment, it also limits the outward passage of body heat and moisture. As a result, under strenuous activities, the core temperature of the wearer's body may rise quickly above the comfort level into the heat stress zone. The problem can be solved by applying phase change material. The incorporation of phase change material in a nonwoven fabric system adds a thermo-regulating feature to it. By using such nonwoven fabric systems with incorporated phase change material for protective garments, the wearer's comfort can be enhanced substantially and the occurrence of heat stress could be prevented [67].

14. Testing of PCM incorporated textiles

The melted and unmelted morphology of PCM could be identified by polarized optical microscopy (POM) [73]. POM revealed that before copolymer's transition temperature, with the increase of temperature, the spherulites had no change; when the temperatures approached transition point, the spherulites faded away and eventually disappeared. Differential scanning calorimetry measurements would 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. On the other hand thermo-regulated properties of PCM containing textiles could be measured by surface cooling rate measurements. The indices of thermal regulating capability (I_d and Δ_{td}), static thermal insulation (I_s), and the thermal psychosensory intensity (TPI) of textile incorporating phase change materials can be measured by an instrument that is called the Fabric Intelligent Hand Tester (FIHT) [74]. The index of static thermal insulation (I_s) can be obtained from the test data by calculating the mean heat flux at the equilibrium state. The indices of the thermal regulating capability (I_d and Δ_{td}) can be obtained by calculating the differences between the heat flux changes of PCM and non-PCM fabrics.

15. Applications of PCMs incorporated textiles

Phase change materials (PCMs) in textiles adapt to the thermal regulating functional performance of PCM garments [75,76] 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.

15.1. 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.

15.2. 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 sports wear, 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.

15.3. Bedding and accessories

Embedded microcapsules into quilts, pillows and mattress covers ensure active temperature control in bed. When the body temperature rises, the additional heat energy is absorbed and the body cools down. When the body temperature drops, the stored energy is released and the body is kept warm.

15.4. 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 [74]. 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 [77].

15.5. 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 [77].

15.6. Other

PCMs are used in automobile textile such as seat cover. Automobile interior applications use paraffins due to their high capacity for heat storage; lack of toxicity, corrosiveness, or hygroscopic properties; low cost; and amenability to mixing to realize the desired temperature range. The paraffins are microencapsulated and applied to a textile matrix. PCM treated fabric in headliners and seats provided superior thermal control. Helmets, fishing waders, firefighters' suits, are some other examples of application of PCMs in textiles.

16. Market for PCM in textile applications

From original applications in space suits and gloves, phase change materials (PCM) are in consumer products, nowadays. Microencapsulation of liquids and solids is an innovative micropackaging technology which is opening up new marketing opportunities for performance apparel markets for making smart thermo-regulated textiles. In textile processing, specially in the nonwovens business, microencapsulated PCM are on the market already [66]. A narrow interpretation of smart textiles or smart materials is when it shows a clearly defined reaction as a result of a clearly defined stimulus. This namely holds good for all smart textiles. Solutions were generated from the conclusions drawn from innovation management and marketing. The only appropriate definition says that something is new if it has been categorized as something new by the market [78]. Such textiles have integrated technology or have new junctions or capabilities. Applications range from the highly complex life support systems to the convenient or fun, and from life saving military uniforms to stain resistance or entertainment. The main areas of focus for smart and interactive textiles are the military, healthcare, and performance sportswear. Definitely, PCM incorporated textile would take a major role in future smart textiles segments. In today's competitive market situation in world, the demand of today's customer is to get comfort in cloth, which is to be worn in different situations from daily wear to functional wear. Phase change materials are the source to be incorporated in textile material to add value i.e. comfort to wearer [79].

17. Challenges and opportunities

Phase change materials found in today's consumer products originally were developed for use in space suits and gloves to protect astronauts from extreme temperature fluctuations in space. There are many challenges facing the use of this new innovative material. The use of innovative new materials and integration of PCM into garments requires, for example, the development of new types of testing methods and standards. Furthermore, the development of materials, such as their mechanical properties, durability or functionality in various conditions, may take a long time. The main challenge in developing textile-PCM structures is the method of their application. Encapsulation of PCMs in a polymeric shell is an obvious choice but it adds dead weight to the active material. Efficient encapsulation, yield of encapsulation, stability during use and integration of capsules onto fabric structure are some of the technological issues would be considered. Another important challenges lies to the textile community for this innovative textile in practical use is the durability of PCM incorporated textiles in repeated uses.

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