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Enhancement of Thermo-Regulating Textile Materials Using Phase Change Material (PCM)

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Abstract

The overall challenge for "smart textiles" is to enhance the PCMs and making the thermal effects last longer. Many experimental tests were used to analyzing the PCMs effects on clothing, comparing to those without PCMs, have been studied in last years. The conclusions of these investigations have confirmed that while thermal protection using PCMs is enhanced, its warming impact is only impermanent. Since use of PCMs in textiles is generally new, there is still much potential for development on how PCMs are made and their general execution. In any case, the future searches splendid for PCMs. There have even been proposed possible uses in the therapeutic medical field and in the cooling/heating of buildings. The uses of PCMs appear to be various and definitely extend beyond textiles. “Smart textiles” is starting to expect a critical part in day-by-day life and the comfort of consumers.

Keywords: Smart textiles; PCMs; Analyzing; Warming

Abbreviations: THS: Thermal Heat Storage; PCM: Phase Change Materials; POM: Polarized Optical Microscopy; DSC: Differential Scanning Calorimetry; DI: Duration Index.

Introduction

Protection from outdoor environmental conditions is one of the crucial requirement in textile industry. Smart textiles are a functionalized textile with some integrated materials into the textile structure, which make the textiles able to sense or response to the environment, such as intensive heat, extreme cold, magnetic, nuclear radiations, electrical, chemical etc.. [1]. During heating process with increasing temperature, all materials are absorb heat through its structure. Stored heat will be released to environment during cooling process. Normal textile can be absorb 1 kj/kg by increasing temperature 1°C [2,3].

Many years ago, researchers were developed a new technology for the incorporation the microencapsulated phase change materials (PCMs) into textile materials to improve their thermal performance [4]. PCMs store and release heat through changing their phase from solid to liquid. Producing functional or smart textile products was occurred using many techniques. One of these techniques is incorporation of microcapsules to textile finishing

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processes. Thermal storage of latent heat was development using many phase change materials (PCMs) such as organic and/or inorganic materials.

Phase-Change Heat Storage

Thermal heat storage materials (THS) allow the storage of heat to retrieve the heat/cold after some time. Thermal heat storage materials can be proceeding by storage of Latent or Sensible Heat. They however can be costly and combustible at high temperatures (Figure 1).

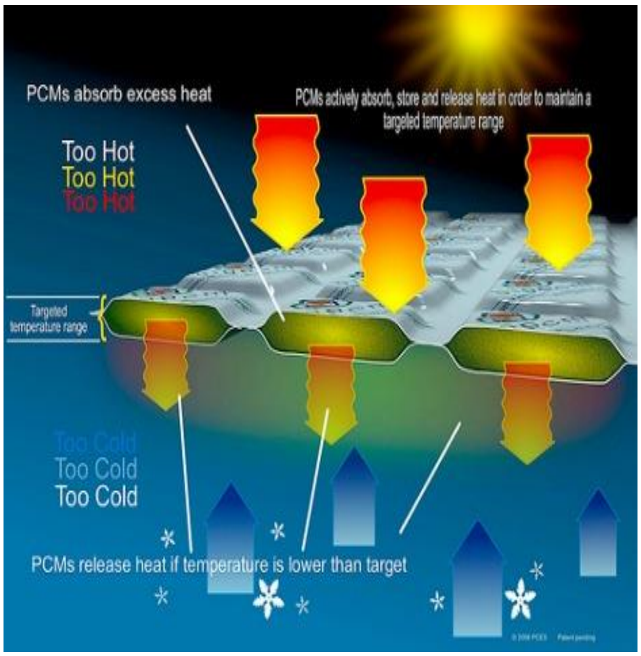

Figure 1: Thermal heat storage materials (THS).

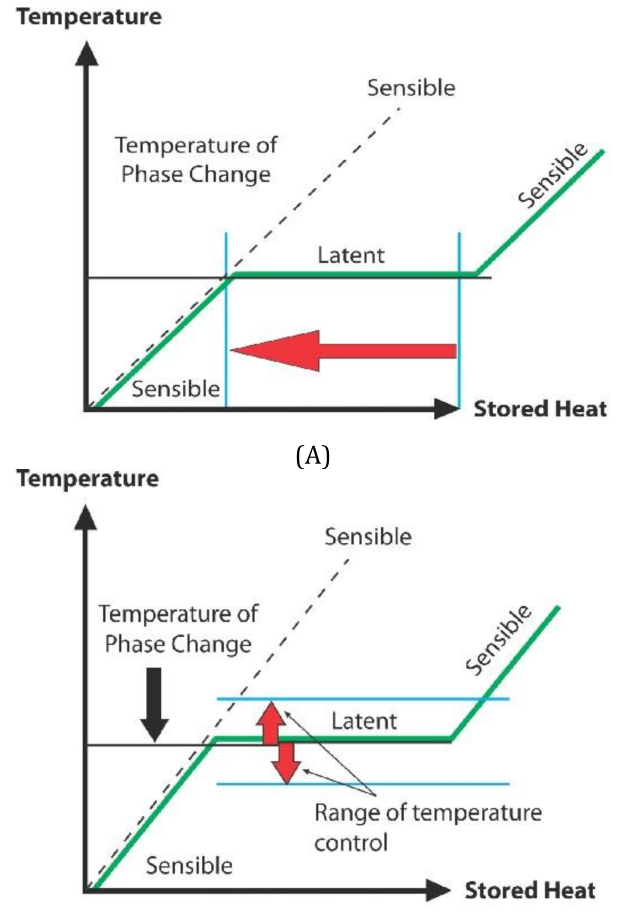

Figure 2: A. sensible heat vs. latent heat and B. Temperature control during phase-change energy storage

Latent or sensible heat storage

The most widely recognized method for thermal heat storage is as *sensible heat*. As appeared in Figure 2, heat was transferee to the storage medium prompts to a temperature increment of the storage medium.

The phase change materials can store high quantity of heat (melting process) or cold (solidification process). Upon melting storage material was absorb heat and keep its temperature constant during melting process. In the event that the melting process is completed, further transfer of heat results again in sensible heat storage. The heat provided upon melting called "*latent heat*", and the process called "latent heat storage".

Sensible heat is a heat contributes to the change of temperature of the heated material. If the heat transferred to the object, the temperature of this object will increased and if the heat removed from the object, the temperature of this object will decreased [5]. Furthermore, the transferred heat (H) is proportional with temperature change (ΔT), and the relationship can be describe as follow: [1]

$$H \alpha \Delta T \quad \Rightarrow \quad H \alpha (T_f - T_i) \quad \text{Equation 1}$$

Where T_f is the final temperature and T_i is the initial temperature. The proportionality constant is (C) which named "the heat capacity". The heat capacity is the heat amount needed to raise the object or substance temperature by one degree with units of energy per degree.

$$H = C\,(T_f - T_i) \quad \text{Equation 2}$$

Specific heat or specific heat capacity (C_P) is the heat amount needed to change the substance temperature of one unit of mass by one degree. Therefore, it is an intensive variable with a unit of energy per mass per degree [5]. So it can be calculated using the following equation:

$$H = m\,C_p\,\Delta T \quad \text{Equation 3}$$

Where C_P is the material specific heat, m is the material mass and ΔT is the change of temperature by the heat.

Latent heat is the not sensed heat by temperature change, and sensed by the change of the phase of material. During the phase change, the temperature of the material does not change. Furthermore, latent heat can be calculated using the following equation: [1]

$$H = m\,L_p \quad \text{Equation 4}$$

Where L_p is the specific latent heat of the phase change materials (melting or crystallisation or condensation process). Specific heat for any unknown materials can be calculated using standard specific heat values of sapphire (alumina, Al_2O_3) using the following equation:

$$C_{P\,Sample} = \frac{H_{Sample}}{H_{Alumina}} \times \frac{m_{Alumina}}{m_{Sample}} \times C_{P_{Alumina}}$$

Equation 5

Which C_p is the specific heat ($J{\cdot}K^{-1}{\cdot}g^{-1}$), m is the mass of material (g) and H is the heat flow (mW). Sapphire (Al_2O_3) is used for determination the heat capacity as a calibrant. The specific heat values C_p of this alumina can calculate by the following equation: [6]

$$C_p(T) = \alpha + \beta T + \delta T^2 + \varepsilon T^3 + \eta T^4 + \lambda T^5 + \varphi T^6 + \gamma T^7$$

Equation 6

Where T is the temperature in K, the coefficient values for sapphire (Al_2O_3) calculated for two temperature ranges was written in Table 1 [6].

	(T = 70 - 300 K, -203.15 - 26.85°C)	(T = 290 - 2250 K, 16.85 - 1976.85°C)
α	3.63245×10^{-2}	-5.81126×10^{-1}
β	-1.11472×10^{-3}	8.25981×10^{-3}
δ	-5.38683×10^{-6}	-1.76767×10^{-5}
ε	5.96137×10^{-7}	2.17663×10^{-8}
η	-4.92923×10^{-9}	-1.60541×10^{-11}
λ	1.83001×10^{-11}	7.01732×10^{-15}
φ	-3.36754×10^{-14}	-1.67621×10^{-18}
γ	2.50251×10^{-17}	1.68486×10^{-22}

Table 1: the coefficient values (A to H) for sapphire (Al_2O_3) [6].

Phase change materials (PCMs)

Phase Change Materials (PCM) is a materials having large heat of fusion able to store large amount heat at a certain temperature (≈ 32°C, the melting point) once the state changing from solid to liquid. Also able to release the stored heat at a certain temperature (≈ 32°C, the melting point) once the state changing from liquid to solid. Therefore, PCM microcapsules help the garment to keep its temperature constant by absorbing/releasing the heat [7,8].

PCM temperature regulation performance

When the fabrics goes into sunshine suddenly from an air conditioned room, the microcapsules present on the fabric absorbs the radiant heat from sun and change their phase from solid to liquid state at constant temperature and the heat absorbed is used to keep their state as liquid. In addition, when the fabrics goes into an air conditioned room suddenly from sunshine, the microcapsules present on the fabric release the absorbed heat to go back to the stable solid state [9-11].

PCMs working principle mechanism

Heat transfer has different modes, which depends on the phase of materials [12]. Materials in solid state is predominate mode of heat transfer, materials in liquid state is convection heat transfer and materials in vapours state is convection and radiation heat transfer.

In textile applications, it is considering the material with phase change from solid to liquid and vice versa. Therefore, a typical differential scanning calorimetry (DSC) for PCM melting is shown in Figure 3. Figure 3 shows that, the PCM absorbs large amount of latent heat, and converted between solid and liquid phases during phase conversions.

In addition, phase change materials are commonly known and not new, they are present in different forms in nature. One of the most common examples of a phase change materials is water, which crystallizes at 0°C as it changes from liquid to a solid phase [8,13]. Moreover, at 100°C, it becomes steam and the phase was change.

Meaning that, once the ice converted to water it absorbs a heat approximately 335 kJ/kg. By further heating by one degree Celsius, a sensible heat of about 4 kJ/kg only is absorbed.

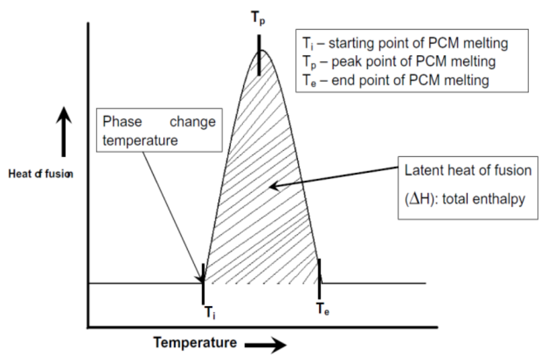

Figure 3: Scheme of DSC heating of phase change material.

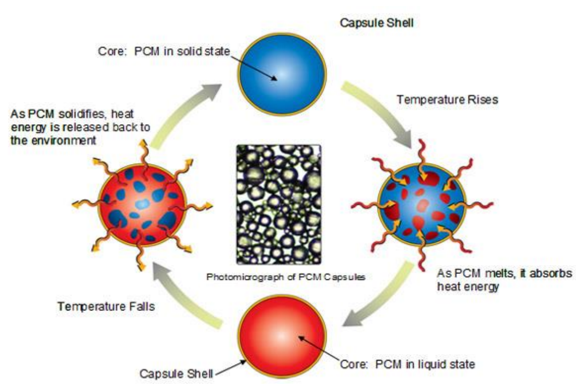

Figure 4: PCMs working mechanism [14].

Phase change materials (PCM) can absorb and/or release thermal heat to control and regulate the temperature (Figure 4). At the point when PCMs is in its solid phase it will assimilate warm as the outside temperature rises (absorb heat as the temperature increases). The PCM's temperature will reflect the outside temperature until reach the melting point of PCMs. Then, the PCMs will start melting, i.e. "phase changing". During phase change process, the PCMs will absorb heat with large amounts without changing in temperature and the PCMs giving a cooling effect. The required time for the PCMs to provide the cooling effect determined by the PCM's latent heat of fusion of melting or enthalpy of melting and the enthalpy measured in J/g. as the enthalpy is higher the time providing for cooling effect is longer.

Requirement and Classification of PCMs

In textiles field, the effective utilization of smart textile is occurs by using the phase change material (PCM) with a melting point between 15 and 35°C. There are more than 400 natural and/or synthetic PCMs differ from one to each other in their melting temperature and heat storage capacities are already known [15,16]. Choosing of phase change materials is depending on their utilization, the required properties for a PCM to be used in textile fields are as follow: [17].

Their melting point ranged from 15 to 35°C;
Have high heat of fusion; Low temperature difference between melting and the crystallization point; Eco-friendly to the environment; Low toxicity and non-flammable; Stable upon repeated processes; High thermal conductivity and Low price.

Many of the PCMs are available with different heat storage capacity and temperature. These PCMs are classified to many groups.

Hydrated inorganic salt as PCMs

Hydrated inorganic salt containing water molecules used in the thermo-regulated textiles and clothing. Usually, it has a heat absorbing/releasing temperature about 20–40°C. The main advantages of this type of PCM are good thermal conductivity, high latent heat of fusion, non-flammable and cheap.

On the other hand, they cause corrosion to most metals and suffer from loss of hydrate. Furthermore, super cooling is the biggest problem. Impurities give a strong effect on its curves. The common examples of this type of PCMs are calcium chloride hexahydrate ($CaCl_2.6H_2O$), Manganese nitrate hexahydrate ($Mn(NO_3)_2.6H_2O$), barium carbonate $BaCO_3$, sodium sulphate decahydrate ($Na_2SO_4.10H_2O$) and sodium carbonate decahydrate ($Na_2CO_3.10H_2O$) [17-19]. Heat of fusion and temperature of some inorganic hydrated salt are listed in Table 2.

Salt	Formula	Melting temperature (°C)	Enthalpy of fusion (kJ/mole)
Calcium nitrate tetrahydrate	$Ca(NO_3)_2{\cdot}4\,H_2O$	42	31.05/132 [20]
Calcium chloride hexahydrate	$CaCl_2{\cdot}6H_2O$	29.5	43.40/200 [20]
Sodium sulphate decahydrate	$Na_2SO_4{\cdot}10H_2O$	32	78.20/240-245 [21]
Disodium hydrogen phosphate dodecahydrate	$Na_2HPO_4{\cdot}12H_2O$	34.5	94.9/265 [21]
Ferric nitrate nonahydrate	$Fe(NO_3)_3{\cdot}9H_2O$	48.5	77.0/190 [22]
Manganese (II) nitrate hexahydrate	$Mn(NO_3)_2{\cdot}6H_2O$	24.8	40.26/140 [23]

Table 2: Heat of fusion and temperature of some inorganic hydrated salt [1,18].

Linear long chain hydrocarbons

Linear hydrocarbons are the by-products of the oil refinery with general formula C_nH_{2n}+2. These materials are non-toxic, inexpensive, and available with different melting temperature ranges depending on the number of carbon atom (chain length). Selecting the chain length causes different application according to the melting point. This type of PCM is the most important one, which can be uses as thermo-regulated textile having high efficiency in many textile field such as sportswear. Therefore, it is the most important materials to produce thermo-regulated fabrics. The functionality of these fabrics depends on the heat adsorption and emission by hydrocarbons. Values for heat adsorption and emission of linear hydrocarbon are listed in Table 3 [1,7,24,25].

Paraffin Type	2nd Heating		
	T_o (°C)	T_p (°C)	ΔH (J/g)
C_{10}: *n*-decane	-12.3	-16.7	11.69
C_{12}: *n*-dodecane	-9.1	-11.2	11.73
C_{14}: *n*-tetradecane	6.3	8.8	77.9
C_{16}: *n*-hexadecane	12.2	22.6	235.2
C_{17}: *n*-pentadecane	16.5	25.5	176.4
C_{18}: *n*-octadecane	22.0	33.4	244.8
C_{19}: *n*-nonadecane	26.4	33.6	177.6
C_{20}: *n*-eicosane	30.4	42.8	242.0

Table 3: Peak temperature and enthalpy of second heating for different paraffin compounds.
T_o: crystallisation temperature, T_p: Peak Temperature, ΔH: Enthalpy

Polyethylene glycol (PEG)

One of the important PCMs for textile application is Polyethylene glycol (PEG). Oxyethylene is the repeating unit of PEG with terminal hydroxyl group. When the PEG molecular weight is lower than 20000, the melting temperature is proportional to its molecular weight. Increasing the PEG molecular weight will led to formation of crystalline phase and convenient geometrical alignment. In addition, increasing the molecular weight of PEG led to increasing in the crystalline heat and temperature. One of the advantage uses of PEG blends is the possibility of changing the heat and temperature range for freezing and melting [26, 27].PEG melting point is depending on its molecular weight, Table 4 explain melting point of some PEGs [28].

PEGs Molecular weight	Melting point (°C)
PEG 1000	35 [29]
PEG 1500	50 [30,31]
PEG 3400	59 [30,31]
PEG 8000	60 [32]
PEG 10000	62 [30,31]
PEG 20000	63 [30,31]

Table 4: Molecular weight and melting point of polyethylene glycol (PEG).

Others

Thermal behaviour of different fatty acids like palmitic, lauric, capric, stearic and palmitic acids have been studied and confirmed that, they have good latent heat storage ranged between 153 and 182 kJ/kg with varying melting point from 30 to 65°C [33].

Fats and vegetable oils is another important type of PCMs. Heat of fusion of this type are good which make them applicable for textile industry. These materials in salt form are biomaterial, which make them more attractive for biotechnology application [34].

Heat of fusion, melting and freezing temperature of some paraffin salt are listed in Table 5 [35].

Oils	Melting point (°C)	Freezing point (°C)	heat of fusion (ΔH) (kJ/kg)
butyl stearate	19	21	120
vinyl stearate	27	29	122
isopropyl stearate	14	18	142

Table 5: melting point of some Fats and vegetable oils.

How to Incorporate PCMs in Textiles

The PCMs change stages inside a temperature extend simply below and above body skin temperature would be reasonable for application in textile materials. This fascinating property of PCMs would be helpful for making defensive materials overall season. Foam, fiber and fabric texture with PCMs could store the heat body makes then release it as it needs back to body. Since the procedure of stage change is progressive; in this way, the materials are always showing signs of change from a state to another contingent on level of physical action of the outside temperature and body. Thermo-regulating properties are also possible in artificial fiber by adding PCM microcapsules during fiber extrusion. All the while, PCM microcapsules are coordinated inside the fiber itself. There are many processes to incorporate PCMs into the textile texture such as coating, melt spinning, lamination, synthetic fiber extrusion, injection molding etc…

Fiber technology

Incorporation of PCM inside a fabric requires microencapsulated PCM, which added to the polymer solution, and then the fiber is spinning using a dry or wet spinning or extrusion of melted polymer. The thermo-regulated fiber with microencapsulated PCM could store heat for long time. The shell/core composite of polypropylene nonwovens fibers with various PCMs contents in the core have been examined through DSC, SEM and it has confirmed that, the temperature regulating affected by the shell/core ratio [36].

The Photo-thermal conversion thermo-regulated fibers have been synthesis using the fiber-forming polymer as shell and the micro-PCMs as core. It is showing that, it has better regulation temperature compared to control [37].

Coatings

Coating process allows to dispersion the microcapsule PCMs through polymer solution, water solution containing a surfactant and a thickener. After that, it has applied to textile materials to form an extensible, coated fabric [24]. In addition, PCMs could be incorporated into textile materials throughout coating process-using polymers for example; polyurethane, acrylic etc. pad-dry-cure, knife-over-air, knife-over-roll, transfer and dip coating are the applicable processes for coating.

Lamination

Keeping in mind the end goal to enhance thermo-physiological wearing comfort of protective clothing, PCM would be imparted into a thin film and using in the internal side of the textile by lamination.

The cooling impact of the PCM can postpone the increasing temperature and, henceforth, the increasing moisture ascends in the microclimate generously. Accordingly, the wearing time of the pieces of clothing can be developed fundamentally without the event of heat stress as a genuine health hazard. The more drawn out wearing circumstances will additionally prompt to an essentially higher productivity. The more open to wearing conditions will likewise bring about a reduced number of mischances and lower error rates [38,39]. Microcapsules would be blended into a polyurethane foam blend and applied to a textile using lamination process, where the water is removed from the treated fabric by drying process [40].

Microencapsulation

One of most advantageous technique for producing smart fabric is to incorporate encapsulated PCMs to textile [41]. Incorporation of PCMs into textiles materials as a shell/core matrix brings large scope for example, protection of PCM from leaking, decrease evaporation and interaction with the environment, long time span of usability on a clothing for usual fabric-care forms, and no antagonistic impact on the textile properties. Another way to deposit the organic PCM materials onto textiles materials is to encapsulate the organic PCMs into another organic material to prevent the flow ad leaking from the surface. The simplest way is to synthesis a polymer composite with side chains contain a PCM. So, the gaps between each two-side chains able to keep a crystal of PCM through it.

Inorganic PCMs are widely used for heat storage in different applications such as building insulation and thermo-regulated fabrics. Inorganic PCMs have an important advantage for example, high storage capacity. On the other hand, because the corrosive properties of the inorganic salts, the microencapsulated of the PCM is not easily. Therefore, a silica-based material has used to produce capsules with hydrated inorganic salt in the core [41-43].

Textile With Smart Adaptable Temperature

The required thermal protection of clothing essentially depends on the physical actin and environmental conditions, for example, relative humidity and temperature. The amount of heat delivered by body depends especially on the physical action and can change from 100 to more than 1000 W amid most extreme physical execution [44]. In cold seasons (0°C), the recommended heat protection is characterized with a specific end goal to guarantee that the body is adequately warm while resting. At a more serious action, which is regularly the case with winter sports clothing, the body temperature increments with improved heat generation.

Once the thermal protection of garment is decreased during physical activity, part of heat will expelled. The nature of protection in clothing against cold and heat will be broadly administered by the external temperature, thickness and density of the fabrics. Therefore, a thick fabric with low density will have large weight but improve the insulation. In addition, intelligent fabrics are depending on external temperature and provide a good thermal insulation. This heat protection is reliant on time and temperature; and being impermanent in nature, it can be named as dynamic heat protection [45].

Textiles have improved thermal heat properties by fiber coating with PCMs. Textile with smart adaptable temperature [46] can be impart inside hollow fibers or deposited upon non-hollow fibers. A characteristic of PCMs during heating cycle is to absorb and store a thermal heat at a constant temperature while changing to the other phase. Nonwoven protective clothes are used in a many applications such as treatment of hazardous waste. Therefore, the construction of these fabrics must be provides a high barrier function against the dust, liquid and/or gas penetration. Nonetheless, the fabric should prevent the transfer of hazardous materials into the fabric. Impregnation of PCMs into a nonwoven fabric adds thermo-regulating properties to it. Utilizing these nonwoven fabrics with incorporated PCMs for protective clothes, the users comfort will be improved substantially and the feeling of heat stress will be counteracted [38].

Testing and Evaluation of PCM Incorporated Textiles

Polarized optical microscopy (POM) can be used to identify the morphology of melted and unmelted of PCM [47]. Differential scanning calorimetry (DSC) used to determine the melting/freezing temperature and thermal capacities of PCMs microcapsules and treated fabric with PCMs. Therefore, it is clear that, PCMs are characterized by measuring fusion/crystallization temperature (T_p and T_f) and enthalpy (ΔH). Furthermore, there are other indexes, which calculate to helping in the choosing of material for a specific use. For textile, it is duration index (DI) [48] and total resistance to dry heat transfer, *R* [49].

Duration index (DI; J/cm^3/K) allows knowing the time for PCM to be working at a constant temperature during the phase change. Duration index can be calculated using the following equation: [48]

$$DI = \frac{\Delta H \times \rho}{\Delta T}$$ Equation 7

where ΔH is the PCM enthalpy, ρ is the density of PCM and ΔT is the temperature difference between those of change of phase (T_p) and the temperature of interest (body temperature).

Resistance to dry heat transfer is related to the textile material on which PCM will applied. The computerized thermal manikin was used to make a simulation of losing the heat from a human body to the environmental atmosphere and measure the insulation value of the textile [49,50]. The total resistance to dry heat transfer can be calculated using the following equation:

$$R = \frac{\Delta T \times A}{H}$$ Equation 8

Which A; is area of material, ΔT; is the temperature difference between two sides of the material (T_F – T_R; R, rear and F, face of the material) and H; is heat flow. The R-value for textile materials is given in ''clo'' (the unit for clothing insulation) [49,50]. Furthermore, clo is measured in (m^2·°C/W; 1 clo = 0.155 m^2.°C/W, in addition, 1 clo corresponds to a human with a typical business suit and 0 clo corresponds to a naked person.

Applications of PCMs textiles fields

Thermo-regulated fabric is one of the important functional finishes. Applications of phase change materials to textiles to impart thermal behavior have been occurred in several fields include medical field, apparel, protective clothing, insulation and many others.

Sports wear

Sports-wear garments and clothing with thermo-regulating properties using PCMs are widely used. Because that the heat emission from the body during sports activity not released with necessary amount which increasing the thermal stress, so, sports-wear need to enhance the thermal balance between the body and the released heat during sporting time. Therefore, the thermo-regulated wear was absorbed the body heat and release it in needed.

Space

The first using of PCMs has been done for gloves and space suits to protect astronauts from the cold when working in space and keep them comfortable.

Bedding

Mattress covers, quilts and pillows with microencapsulated PCMs confirm the temperature control. Increasing the body temperature will activate the PCMs to absorb the excess heat led to cooling the body. Then, once the body temperature is drop, the stored heat will released to the body and worm it.

Medical applications

Thermo-regulated fabrics with heat storage capacity can keep the skin temperature in the comfort form; therefore, they used as a bandage for heat/cool and burn therapy [51].

Textiles with PCMs microcapsules have important applications in-patient bedding materials, bandages, surgical apparel and regulate patient temperatures especially in intensive care units [52]. One of the most usually PCMs in this field is PEG.

Others

Automobile fabric like seat covers with incorporated PCMs are exist now in the market using paraffins as PCM due to its high storing capacity of heat, low coast, nontoxic. Thermo-regulated fabric in headliners and seats confirmed thermal control.

Market for PCM in Textile Applications

Nowadays, phase change materials (PCM) are uses in many fields, and it is in consumer products. Micro-packaging technology using microencapsulation of phase change materials extend a new marketing for advanced thermo-regulated fabric. Textile with microencapsulated PCM is in the market already [38]. The market only can conclude something as a new, [53] like fabric with integrated technology or have new functionalities.

Incorporated textile with PCM would take an important role in future smart textile segments because interactive smart textiles are use generally in the healthcare, performance sportswear and military. These days, the markets situation in the world is in the demand of customer to get comfortability in clothes to be uses in different situations from daily wear. Phase change materials (PCMs) are the materials to add values to textile (thermo-regulated fabric) [54, 55].

Economic and Environmental Benefits

Storing of natural thermal heat for facility heating and/or cooling needs. Storing the thermal heat during off demand hours and use it during peak demand to save on heat cost Moving of heating and cooling load also reduces peak time stress of heating and cooling equipment that can lead to reduced operating & maintenance cost.

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