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Thermal Energy Storage Materials (PCMs) for Textile Applications

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ABSTRACT

Phase change materials (PCMs) can absorb, store and release energy in the form of heat. Latent heat storage is one of the most efficient ways of storing thermal energy and it provides much higher storage density with smaller temperature difference between storing and releasing heat. These materials change its phase and absorb energy during the heating process and release the same to the environment during the reverse cooling process. This paper reviews the work on thermal energy storage materials, development of PCMs, classification, working principle of PCMs and working of PCMs in clothing. The review also summarizes the evaluation of textiles containing PCMs and different applications.

Keywords: Phase change materials (PCMs), Latent heat, microencapsulation, storage systems

1. INTRODUCTION

Latent heat method was recognized for thermal storage as an alternative source for sensible heat storage to improve the thermal performance clothing during the changes of environmental temperature conditions[1]. Latent heat storage uses organic phase change materials (PCMs) for this purpose and the recent literature shows the direct incorporation of PCMs into the fibers or coated on the substrate[2-4]. Phase change materials have traditionally been used in low temperature thermal energy storage for residential heating and industrial heat exchanger units[5-7]. The process of going from one physical state to another i.e. from a solid to a liquid and vice versa and the substances that undergo the process of phase change are called as Phase Change Material's [8-11]. They are capable of absorb, storing and releasing large amounts of heat energy in the form of latent heat over a defined temperature range while change in phase, heat energy absorbed by the PCM when its melting point is reached. The absorbed energy is stored in the PCM during the heating process while cooling process the decrease in temperature is delayed due to the released energy. So, the temperature of the material remains constant during the phase change and they use chemical bonds to store and release heat [10, 12]. The thermal energy transfer occurs when a material changes from a solid to a liquid or from a liquid to a solid. Ice is an excellent phase change material that changes phase when heated at 100°C and is converted to water during this process it absorbs a large amount of heat and this result in cooling of the surroundings[13]. Due to its outstanding functional property they are using in scientific and industrial sectors [14].

Phase Change Materials melts and solidify at certain temperature and change in phase of a substance is their melting or freezing point and the boiling or condensation point. These phase changes have highest values in enthalpy during phase change [15]. Some of the PCMs change their state within a temperature range just above and below human skin temperature can be used for making protective clothing for abruptly changing climatic conditions. Phase change materials have the unique ability to absorb heat energy and release heat energy without changing temperature themselves. Different phase change materials viz. Eicosane, Octadecane, Nonadecane, Heptadecane and Hexadecane will have different freezing and melting points and when combined in a microcapsule will store heat energy and emit heat energy and maintain their temperature range of 30-34°C which is comfortable for the body [9].

2. DEVELOPMENT OF PHASE CHANGE MATERIALS

Ghali K *et.al* [16] explained the technology of using PCMs in clothing developed for improving the thermal insulation of textile materials during the changes in the environment temperature. Phase change materials were developed by the National Aeronautics and Space Administration's (NASA) in the late 1970 for development of new materials that could protect delicate instruments in space from the extreme temperatures. NASA identified more than 100 PCMs, including pure lithium chloride that is used for heat management of electronics, telecommunications and microprocessor equipment and used on the Lunar Rover and Skylab projects in 1970s. The Triangle Research and Development Corp. (Triangle R&D), Raleigh, N.C., worked on the feasibility of incorporating PCMs within textile fibers by using paraffinic hydrocarbons during 1987. In the mid-1980s, US Department of Agriculture's Southern Regional Research Center (SRRC) worked on the “Polytherm” fabric that is a temperature adaptable fabric based on the durable binding of polyethylene glycol to cotton and cotton/polyester blends using poly functional cross linking agents and acid catalysts. In 1999, Frisby launched its cooling vests. These vests provide at least four hours of cooling[17]

3. CLASSIFICATION OF PCMS

PCMs are classified based on their melting temperature. The materials with melting temperature below15ºC are used in air conditioning applications and materials with melting temperature above 90ºC are used for absorption refrigeration. All other materials that melt between these two temperatures can be applied in solar heating and for heat load leveling applications [18]. It was in 1980s a general classification of phase change materials given by Abhat [19] and also by Lane [20-21], Dinser and Rosen[22], Atul *et.al*[23] gave the further details about the classification and characteristics of phase change material. Zalba *et.al*[24] listed the properties of different phase change materials and classified the substances used for thermal energy storage. The general classification of phase change material shown is Fig. 1.

3.1. Organic phase change materials

Organic PCMs are expensive and they have average Latent Heat per unit volume and low density. Most PCMs are combustible in nature and also have a wider range of Melting Point [24-26]. They are classified into two groups, namely paraffin (alkane) and fatty acids. Paraffinic hydrocarbons are widely used in textiles than other PCMs due to its outstanding properties as non-corrosiveness, chemical and thermal stability and low under cooling. Polyethylene glycol (PEG) is an alternative organic compound used as a PCM and its melting point and heat depend on its molecular weight[27-28]. Paraffinic hydrocarbons, fatty acids and fatty alcohols are substances which have low solubility in water. Therefore they are highly used in building materials and they exhibit melting enthalpies between 150 and 220 KJ/kg. Mixtures of paraffin can be prepared to have melting temperatures of 15°C to 30°C that include all needs of building applications[15].

3.2. Inorganic phase change materials

Inorganic materials are generally Hydrated Salt based materials that have a number of hydrates and an anhydrous form leading to stratification of material and loss of Latent heat recovery with time[26]. Thermal Salt manufacturers used to add performance enhancing agents for delaying the degradation of the thermal salt for say 100 cycles. But they did not explain the reason for sub cooling and degradation. Further, they also suggested using impurities grade based material as it promotes the nucleation and prevent sub cooling. Experts on crystallography have managed to identify the preferred crystal nucleation method. It consists of a cold finger that nucleates and promotes the growth of desired crystals and Detoxification whereby any impurity that promotes the growth of undesirable crystals is removed[24-25]. Kalaiselvam *et.al* [29] worked on the production of PCMs in various chemical formulations, which were designed to melt and freeze at as selected temperature.

4. PROPERTIES OF PHASE CHANGE MATERIALS

Ravi Kumar and Srinivasan[13] listed the most important properties required for phase change materials. Mondal[11] and Nagano *et.al*[30] gave the phase change materials for a high efficiency cooling system and thermal energy storage for specific applications such as

- High latent heat of fusion per unit mass
- High specific heat that provides additional sensible heat storage effect and also avoid sub cooling.
- High thermal conductivity
- High density, so that a smaller container volume holds the material.
- A melting point in the desired operating temperature range.
- The phase change material should be non-poisonous, non-flammable and non-explosive.
- No corrosiveness to construction material

5. PHASE CHANGE PROCESSES

Mondal.S[11] explained the process of phase change in a substrate according to the environment. Each and every material absorbs heat and stores in it while heating process, the stored heat is released to the environment through reverse cooling process. PCM materials absorbs higher amount of when compared with normal materials paraffin PCM absorbs approximately 200 kJ/kg of heat during the melting process and is released into the surroundings in a cooling process. The heat storage capacity of textile materials can substantially enhanced by applying of PCMs. Fig.2 shows the phase change process

PCM microcapsules can produce temporary heating and cooling effects in garment layers when the temperature of the layers reaches the phase change material transition temperature. The effect of phase change material on the thermal comfort of protective clothing systems will be maximized when the wearer is repeatedly going through temperature or intermittently touching or handling cold objects. The temperature of the PCM garment layers must change over with buffering effect to continue [9]

6. WORKING PRINCIPLE OF PHASE CHANGE MATERIALS (PCMS)

Atul Sharma *et.al*[23] and Mondal[11] explained the working principle of phase change material for thermal energy storage systems. There are four methods for thermal energy storage system[31] they are

- Sensible heat utilization
- Latent heat utilization
- Utilization of reversible chemical heat
- Utilization of heat of dilution.

The mode of heat transfer highly depends on the phase of the substances involve in the heat transfer processes[32]. 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. In case of textile applications, the phase changes from solid to liquid and vice versa will be considered. Therefore, the principle of solid to liquid phase change and vice versa would be explained. Water is an excellent phase change material can be always used for comparisons. When Ice changes its state to water it absorbs a latent heat 335kj/kg and when it is further heated, a sensible heat of only 4kJ/kg is absorbed[27]. The typical differential scanning calorimetry heating thermogram for Phase change material shown in Fig. 3.

7. WORKING OF PHASE CHANGE MATERIALS IN CLOTHING

The textile material treated with PCM can absorb heat energy and changes its state form solid to liquid and produces a temporary cooling effect in the clothing layers, the heat energy may be produced by the wearer or from the environment[9]. If the PCM garment is worn in a cold environment where the temperature is below the PCM's freezing point and the fabric temperature drops below the transition temperature, the microencapsulated liquid PCM will change back to a solid state, generating heat energy and a temporary warming effect[17]. All PCM microcapsule may not go through the transition when the wearer moves in different activities and there is a temperature gradient from the skin surface through the clothing layers to the environment[25]. The interaction of textile with PCM microcapsules offers the following advantages[33]

- 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.

Add- on percentage of microcapsules decides the heat absorbing capacity. 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) on the fabric undergo a melting process[30]. Wang *et al*[34] studied the effect of PCM on intelligent thermal protective clothing and they found when the PCM layer's temperature increases above the PCM's melting point ($28^{o}C$), the PCM melts and becomes liquid and when the PCM layer's temperature reaches to $29^{o}C$ the conductive fabrics were powered off. During this process, thermal energy is absorbed and stored. Once the PCM becomes liquid, the temperature continuously increase and the then decrease after a short time and when the temperature of the PCM layer decreases below $27^{o}C$, the liquid PCM becomes solid and releases heat energy. In this process, the PCM acts as a thermal buffer material by releasing stored heat.

8. EFFECT OF PCMS ON TEXTILE PROPERTIES

Addition of phase change material to the textile material will have significant changes in physical properties and that will vary on the add-on percentage. A textile material treated with PCM result in increasing weight of the textile material and decreases the strength and elongation of the fabrics[25].

9. THERMAL CONDUCTIVITY ENHANCER FOR PCM

Most of the phase change materials have low thermal conductivity to provide a required heat exchange rate between the PCM and substrate. Therefore, thermal conductivity enhancer used for efficient use of thermal energy stored in the PCM [18, 35]. It could be enhanced by using metal filler, carbon nanofiber/fiber fillers etc. Carbon fibers offers great advantages like strong resistance to corrosion and chemical attack, which make them compatible with most PCMs. 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 well known that heat transfer rate increases when lateral surface area increases[11, 36-38]

10. THERMAL ENERGY STORAGE SYSTEMS

The thermal energy storage defined as the temporary storage of heat energy at high or low temperatures[29]. Heat energy can be stored in three ways viz. sensible, latent, and chemical reaction. Sensible heat storage is based on increasing the temperature of any substance without changing its phase. The storage of heat via chemical reactions is based on the thermo physics of the reactions[27, 39]. Latent heat storage is one of the most efficient ways of storing thermal energy[40]. It provides much higher storage density, with a smaller temperature difference between storing and releasing heat and it depends on the transition of material between two phases[11]. The following are the methods of thermal energy storage systems:

- Sensible heat: Heating a liquid or a solid without changing phase. The amount of energy stored depends on the temperature change of the material.
- Latent heat: Heating a material, this undergoes a phase change. The amount of energy stored in this case depends upon the mass and latent heat of fusion.
- Chemical reactions: This method requires certain physicochemical reaction to produce heat and then stored. Absorbing and adsorbing are two examples for the bond reaction. Overview of thermal energy storage methods are given in Table1.

Among all the methods, sensible and latent heat storage systems are in use, while bond energy storage systems are being proposed for use in the future for medium and high temperature applications. The specific application for which a thermal storage system is to be used determines the method to be adopted and the following are the some of the considerations, which determine the selection of the method of storage and design of Phase change material. Fig. 4 shows the changes in temperature and heat during the change in phase[27].

- Heat losses from the storage have to be kept to a minimum and they are particularly important for long term storage.
- The rate of charging and discharging.
- The temperature range, over which the storage has to operate.
- The capacity of the storage has a significant effect on the operation of the rest of the system. A smaller storage unit operates at a higher mean temperature. This results in a reduced heat transfer equipment output as compared to a system having a larger storage unit. The general observation which can be made regarding optimum capacity is that "short-term" storage units, which can meet fluctuations over a period of two or three days, have been generally found to be the most economical for building applications.
- Cost of the storage unit, this includes the initial cost of the storage medium, the containers and insulation, and the operating cost[41]

Table 1 - Summary of thermal energy storage methods

Type of Thermal Energy Storage	Functional principle	Phases	Examples
Sensible Heat	temperature change of the medium with highest possible heat capacity	Liquid	Hot water, Organic liquids molten salts, liquid metals
		Solid	Metals, minerals, ceramics
Latent heat	Essentially heat of phase	Liquid-solid	Nitrides, chlorides,
	Change	Solid-solid	Hydroxides
Bond energy	Large amount of chemical Energy is absorbed and	Solid-Gas	$Cao/H_2O, MgO/ H_2O, Fecl_2/NH_3$
	Released due to shifting of Equilibrium by changing	Gas-Gas	CH_4/ H_2O
	Pressure and temperature	Liquid-Gas	$LiBr/H_2O, NaOH/ {}_2O, H_2SO_4$

The amount of heat that is required to melt solids at a constant temperature is called the melting enthalpy or heat of fusion. The latent heat of fusion is greater than the sensible heat capacities of the materials[27]. Different phase change materials and their melting enthalpy are given in Fig. 5.

11. INCORPORATION OF PCMS INTO 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. The thermo regulating characteristics can be obtained by adding PCM microcapsules to textile by some convenient processes [11, 43, 44].

11.1. Fiber technology

PCM are directly added to the polymer solution and is then spun according to conventional methods and it was developed in the1990s. This process enhances the protection of microencapsulated PCMs with a dual wall, the first being the wall of the microencapsulated and the second being the fiber itself[27]. The PCM microcapsules are permanently locked within the fiber structure during the wet spinning process of fiber manufacture[9]. The microencapsulated PCM fibers could store heat over long periods[11, 15, 43].

11.2. Coatings

The microspheres containing phase change material are wetted and dispersed in a dispersion of water solution containing a surfactant, a dispersant, an anti-foam agent and a polymer mixture. The coating would be then applied to a textile substrate[12]. There are various coating processes available such as knife-over-roll, knife-over-air[10] pad-dry-cure, gravure, dip coating, and transfer coating [9, 11, 27, 43, 45]

11.3. Lamination

This method offers great advantages over other application methods and this process involves directly incorporating PCMs into a polymer film (0.3 mm thickness) that is then laminated to the non-woven fabric system. Pause[46] has claimed that when lamination is compared with the other PCM applications in garments, the method offers the following advantages:

- A high PCM concentration per unit area is obtained,
- The expensive micro- encapsulation procedure of the PCM can be avoided
- Any increase in the weight of the garment is minimized [27].

Microcapsules would be mixed into a water-blown polyurethane foam mix and these foams are applied to a fabric in a lamination process[9], where the water is taken out of the system by drying process. 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 the fabric system by lamination[11, 43]

11.4. Microencapsulation

There are many benefits of microencapsulated phase change materials, such as increasing heat transfer area, reducing PCMs reactivity towards the outside environment and controlling the changes in the storage material volume. Lane[47, 48] has identified over 200 potential phase change heat storage materials melting from 10 to 90ºC to be used for encapsulation. The micro encapsulated PCM can be applied on to woven, non-woven or knitted fabrics. It provides a softer hand, increased stretch more breathability and air permeability to the fabrics and enhanced thermal properties[9, 49]. Microencapsulation of liquids and solids is an innovative micro packaging technology which is opening up new technical textiles which can provide textiles with new properties and added value. Microencapsulation involves the production of microcapsules which act as tiny containers of solids have approximate diameters of between 1 µm and 30 µm [18, 33, 50]. 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. Microcapsule production may be achieved by means of physical or chemical techniques. The use of chemical 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 100µm[11].

12. EVALUATIONS OF TEXTILES CONTAINING PCMS

Atul *et.al*[23] explained the techniques used for latent heat of fusion and melting temperature of phase change materials and Gokhan [27] was reported a method to evaluate the behavior of fabrics containing PCM by using differential scanning colorimeters for both basic and dynamic thermal resistance. Traditional thermal resistance is measured by standard stationary methods involving the use of a guarded hot plate apparatus. The performances of textiles containing PCMs can be determined under three categories:

i. Thermal resistance
ii. Thermo-regulated properties
iii. Other properties

Further, thermal resistance can be divided into two subcategories:

a. Traditional thermal resistance
b. Dynamic thermal resistance.

Pause[46] has claimed that the dynamic thermal resistance measurement involve in two steps, the first one involves pre cooling the sample to below the range of the phase change and, at the same time, preheating a metal plate to above that range and the second, the sample is brought into contact with the preheated metal plate. The increase in temperature on the other side of the specimen is then recorded over time. The measurement ends when the temperature exceeds that of the range for the phase change. The test is repeated with a control sample. Usually the time taken is directly related to the basic thermal resistance of the sample without PCM and for the sample with PCM, the time recorded depends on this basic thermal resistance as well as on the dynamic thermal resistance. So, the dynamic thermal resistance can be calculated by comparing the results with reference to the basic thermal resistance.

13. APPLICATIONS OF PCMS INCORPORATED TEXTILES

Phase change material treated textiles shows better thermal regulating functional performance by changing their state of aggregation at defined temperature range. This special property make them to finds lot of applications in various fields include apparel, blankets, medical field, insulation, protective clothing and many others. The following are the few application of PCM in textile fields[11, 27].

13.1. Space

Phase change materials were developed for use in space suits and gloves to protect astronauts from the extreme temperatures in space and it keep astronauts comfortable at space[9, 11]. Fig 6 shows the space suit.

13.2. Sports wear

PCM treated garments used as active wear for provide a thermal balance between the heat generated by the body and the heat released into the environment. Usually heat generated by the body during sports activity is often not released into the environment in the necessary amount thus increasing thermal stress. In order to improve the thermal performance of active wear garments with thermo regulating properties are widely used. The quantity of PCM applied to the active wear garments depends on the level and the duration of the activity[9, 11] Active sport wear garment shown in Fig. 7

13.3. Bedding and accessories

It can also be used in quilts, pillows and mattress covers to 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[9, 11] Phase change bedding fabrics shown in Fig. 8

13.4. Medical applications

PCM treated textiles have potential applications in surgical apparel, patient bedding materials, bandages to regulate patient temperatures in intensive care units. 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[9, 11] Phase change material treated surgical gown is shown in Fig. 9.

13.5. Shoes and accessories

Especially PCM incorporated textiles are used in footwear, especially ski boots, mountaineering boots, race car drivers boots etc. Heat-storage and thermo-regulated textiles can absorb, store, redistribute and release heat to prevent drastic changes in the wearers head, body, hands and feet[11, 27] Phase change material treated Ski boots is shown in Fig. 10

13.6. Cold Storage

Specially it is used as a backup for refrigerator and cold storage power failure and used to keep frozen food, beverages, packed foods, ice creams, flowers. These PCM profiles can be put into a refrigerated vehicle to prevent food from spoiling during transportation or extended storage without power[51] Transported trucks containing PCM is shown in Fig. 11

13.7. Building applications

In building applications, the impregnation of phase change material into the porous construction to increase thermal mass. The use of PCMs to store coolness have been developed for air conditioning applications, where cold is collected and stored from ambient air during night, and its relieved to the indoor ambient during the hottest hours of the day. Another application is the integration of a phase change material in the thermal diode to improve effectiveness of the heat sink. PCMs also used in wall curtain. This window is double sheeted with a gap between the sheets and an air vent at the top corner, the gap can be filled with PCM that upon freezing would prevent the temperature of the internal ambient from decreasing[11,18,23-24]. Wall curtains containing PCM is shown in Fig. 12

14. CONCLUSIONS

A review of phase change material has been carried out. The information obtained is presented. PCMs are categorized into two classes' viz. organic PCMs and Inorganic PCMs. Paraffinic hydrocarbons are widely used in textiles than other PCMs due to its outstanding properties as non-corrosiveness, chemical and thermal stability and low under cooling. Addition of PCMs to the textile material will significantly decrease the strength and elongation of the fabric. Latent heat of storage system was found to be efficient way of thermal storage and to enhance the thermal conductivity of PCMs, a metal or carbon nanofiber fillers are used. Many applications of PCMs are divided in building applications, space, active sportswear, medical application.

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