

Microencapsulation of PCMs in Textiles: A Review

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ABSTRACT

Phase change materials (PCMs) are used to achieve latent heat storage or release from a material. The storage of latent heat or thermal regulation is based on the transition of material undergoes phase changes from solid to liquid, liquid to gas or vice versa. PCM has the ability to absorb and release heat from surroundings in dynamic heat exchange processes. A wide range of PCMs can be classified into two types such as organic PCMs and inorganic PCMs with different storage heat capacity and temperature. A most example of PCMs is the paraffin wax. The PCMs cannot be integrated in to textile materials directly due to some extent disadvantages. The PCMs are enclosed in microcapsules for textile application. In recent years, the use of PCMs in heat transfer application incorporated with textile substrates is quantitatively enormous. Therefore, in this paper, the principle of PCMs, microencapsulation techniques and areas of applications in textiles are discussed.

Keywords: Phase change materials, Paraffin, Microencapsulation, Textile materials

Introduction

Phase change is the process of changing from one physical state to another i.e., solid to liquid or vice versa. The process of phase change can be done by phase change materials. Phase change materials are used to storage and release latent heat during their phase transition at a defined temperature range. Thermal energy storage (TES) is considered as one of the most important advanced energy technologies, and an increasing attention has

been paid in thermal applications (Fang, Kuang, Gao, & Zhang, 2009). Thermal energy storage is the process of storage of high or low temperature temporarily for later use (Mondal, 2008; Hailot, Bauer, Kroner & Tamme, 2011). TES can be stored as change in internal energy of material as sensible heat, latent heat and thermo-chemical or combination of these (Figure 1). Among the various thermal storage techniques, latent heat storage is often interest due to its ability to produce a high storage density at nearly isothermal conditions. Latent

heat storage (LHS) is based on the heat storage or release when a material undergoes a phase change from solid to liquid, liquid to gas or vice versa (Demirabas, 2006). Figure 2

presents the different stages involved in bring out on the market such a commercial product as latent heat storage materials on the basis of phase change materials.

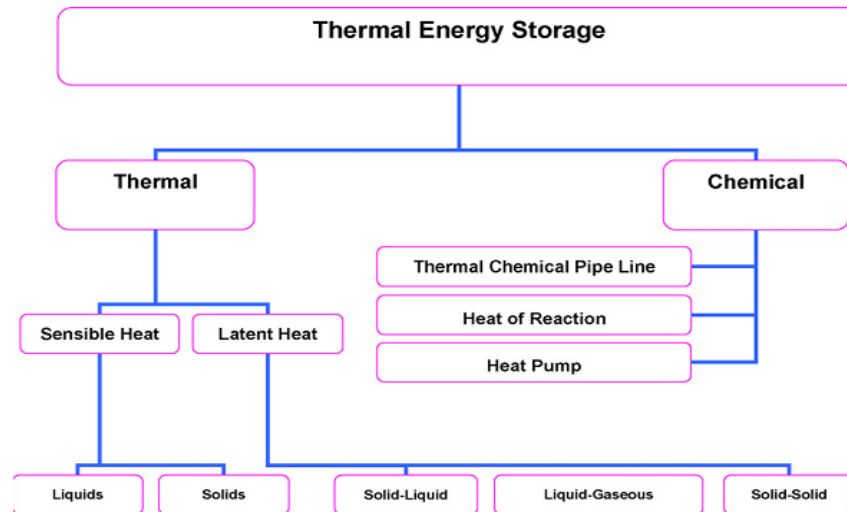


Figure 1. Classification of Thermal Energy Storage

Phase Change Materials and its Processes:

Phase change materials are used to stored or released heat energy during the phase transition of the materials. This is called as latent heat storage systems (Fang et al, 2009; Mondal, 2008; Sharma, Tyagi, Chen & Buddhi, 2009; Golemanov, Tcholakova, Denkov & Gurkov, 2006; Choi, Lee, Kim & Yang, 2001). During heating process, every material absorbs some heat by constantly rising temperature and released into the environment by reverse cooling process as temperature decreases continuously. Compare

heat absorption of a phase change materials with normal materials during heating process, PCMs can absorbs high amount of heat if melts (Oner, Sarier & Cimen 2008). During the melting/crystalline process, the temperature of PCM as well as its surrounding area remains nearly constant. PCM is often interested as in many particular applications due to large heat transfer during the melting/crystallization process with sufficient temperature change makes interesting as a source of thermal storage material.

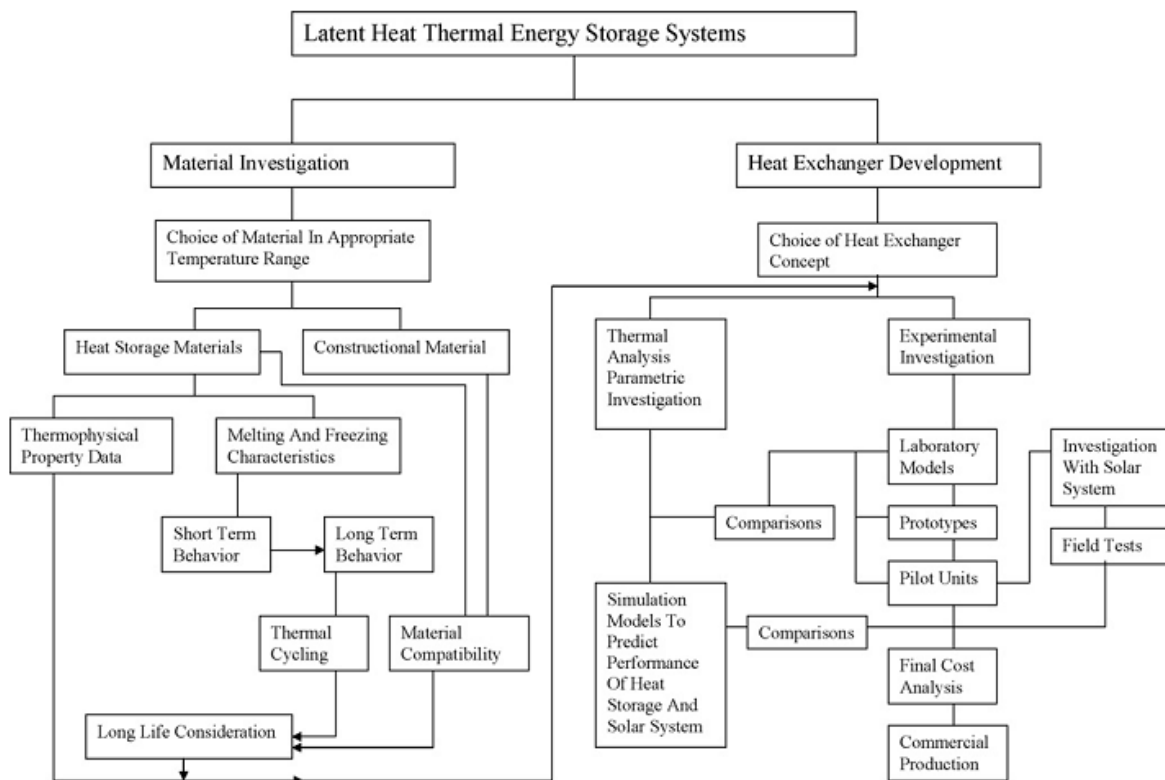


Figure 2. Different stages of Latent Heat Thermal Storage Energy Systems

Classification of PCMs

PCMs mainly classified into two groups such as organic PCMs and inorganic PCMs, as shown in the Figure 3 (Sharma, et al, 2009). A large number of PCMs available with different temperature range but only a few commercially used. Inorganic PCMs and organic PCMs have a wide range of melting temperature of between 8.1°C and 130°C (Erkan, 2004). In most cases, the density of PCM is less than 10^3 kg/m^3 and thus smaller than the density of most inorganic materials like water and salt hydrates. The result is that with exception per volume than inorganic materials. PCMs have the structure of covalent bond of carbon based compounds, hydrocarbons and their derivatives are said to be organic PCM. The materials classes cover the temperature range between 0° C and about 200° C. This is because covalent bonds in organic materials, most of them are not stable

at higher temperature. Paraffin wax as phase change material has broad applications due to their own characteristics such as non-toxic, chemically inert, low cost and high storage energy capacity (Choi et al, 2001). Paraffin is a technical name of alkane, but often it's specifically used for linear alkanes with general formula C_nH_{2n+2} . Paraffin are good storage of thermal energy with respect to mass and melt and solidify congruently with little one or no sub cooling. Their stability of confines their vapor pressure is usually not significant. Their volume increase upon melting is in the order of 10 vol%. This is similar to that of many inorganic materials, but less critical as paraffin are softer and therefore build up smaller forces upon expansion. Paraffins are insoluble in water as they are water repellent. They do not react with most common chemical agents. Inorganic PCMs are hydrated inorganic salts. They have a wide range of melting temperatures of

between 8.1° C and 130° C. but their heat absorbing and releasing temperature interval is usually between 20-40° C. However they require a great deal of heat of fusions and have limited lifecycles. Salt hydrates are the most important group of PCMs, which is mostly studied for their use in latent heat thermal energy storage systems. Most salt hydrates have poor nucleating properties resulting in

super cooling of the liquid before crystallization begins (Huang, Noeres, Petermann & Doetsch, 2010; Kenisarin, 2009; Qingwen, Li Yi, Xing Jianwei, Hu J.Y, & Marcus Yuen, 2007; Aktal, Tanme, Stenhagen, 2008). But, it is controlled by adding nucleating agent, which provides the nucleon which crystal formation is initiated.

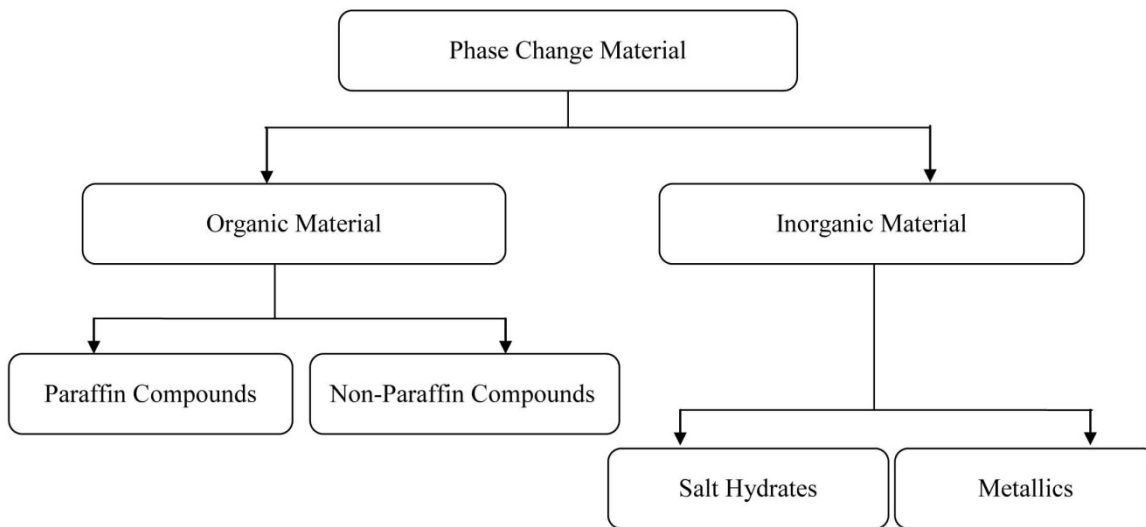


Figure 3 Classifications of PCMs

Microencapsulation

Microencapsulation is the process of enclosing micro sized particles of solids or liquids droplets or gases in the shell structure called microcapsules that have many interesting features (Yoshizawa, 2004; Jothi, Prasanna, Prabha, Ramaiah, 2009). Particle size is below 1µm are known as nanoparticles, whereas particles size between 3-800µm are known as microparticles or microcapsules or microspheres. Particles larger than 1000µm are known as macroparticles. Microcapsules that have wall less than 2 µm in thickness and 20-40µm in diameter is useful in textile application. The Figure 4 shows the classification of microparticles according to their morphology as mono-cored, poly-cored and matrix-types. Microparticles have a number of interesting advantages (1) to protect

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the encapsulated substances from the external environment, (2) to mask encapsulated particles like color, odor and taste, (3) to obtain controlled release of the encapsulated PCMs materials, (4) to ease handling of powder-like materials, (5) to gets targeted release of the encapsulated substances, (6) to ease handling of toxic materials. The microcapsules are produced by depositing a thin layer of polymers on small solid or liquid particles, or dispersions of solids in liquids. The core materials in the shell structure may be released by friction, by pressure, by diffusion through the polymer wall, by dissolution of the polymer wall coating. Today's textile industry makes use of microencapsulated materials to enhance the properties of finished goods. Paraffin's are largely used in textile applications either solid or liquid state encapsulated into any polymer

materials to improve the thermo regulating properties (Zang & Wang, 2010). Microencapsulated materials containing PCM are called encapsulated PCM-microcapsules.

The encapsulated paraffin is coated or finished on the surface of the textile material using conventional or unconventional methods (Onofrei, Rocha & Catarino, 2010).

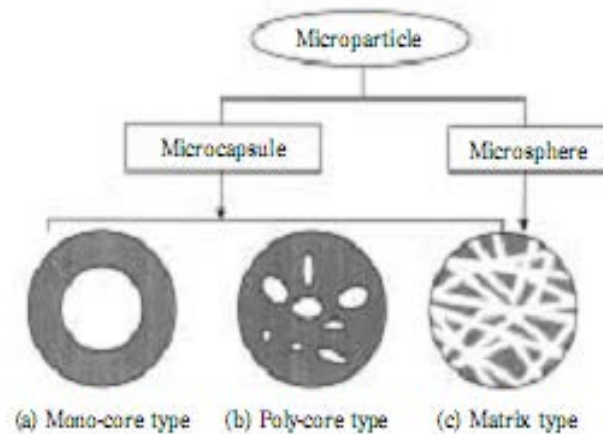


Figure 4. Classifications of Microparticle

Microencapsulation Techniques

Microencapsulation of core materials can be done by various techniques. Broadly the methods are divided into two type's namely chemical and physical methods. Some of the preparation methods are described in Table 1.

Interfacial polymerization method

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

In situ polymerization method

In this polymerization method, the direct polymerization of a single monomer is carried

out on the particle surface. In this process, the reactive agents are added to the core material, polymerization occurs exclusively continuous phase. Polymerization method consisted of the synthesis of pre-polymer solution, preparation of emulsion and formation of solid shell material. For example, encapsulation of various water immiscible liquids with shells formed by the reaction at acidic condition of urea-formaldehyde with aqueous media (Gong, Zhang & Wang, 2009; Zhaoguo, Wang, Liu & Yang, 2008; Fang, Chen, & H.Li, 2010). Microencapsulated material prepared based on in situ polymerization techniques shows enhanced thermal property in relation to the PCM content.

Chemical coacervation method

Bungenberg 1932, investigated in water, organic chemicals do not necessarily remain uniformly dispersed but may separate out into layers or droplets. If the droplets which form contacts a colloid, rich in organic compounds and are surrounded by a tight skin of water molecules are known as coacervates (Onder, et al, 2008; Bansode, Banarjee, Gaikwad, Jadhav and Thorat, 2010). Two methods for

coacervation are available, namely simple and complex coacervation processes. The mechanism of formation of encapsulated PCM microcapsules for both processes is identical, except in which the phase separation is carried out. In simple coacervation, a desolvation agent is added for phase separation. Complex coacervation refers to the phase separation of a liquid precipitate, when solutions of two hydrophilic colloids are mixed under suitable conditions. The basic steps involved in complex coacervation methods are (1) first the core materials, usually an oil is dispersed into a polymer solution, (2) polymer solution is then added to the prepared dispersion, (3) deposition of the shell material onto the core particles occurs when the two polymers form a complex, (4) triggered by the addition of salt or by dilution of the medium, (5) finally, prepared microcapsules are stabilized by cross linking, desolvation or thermal treatment.

Solvent evaporation method

In this method, microcapsule coating material is dissolved in a volatile solvent, which is immiscible with the liquid manufacturing vehicle phase (Bansode et al, 2010; Alex, & Bodmier, 1990). A core material is to be encapsulated to be dissolved or dispersed in the coating polymer solution. With the help of agitator, this mixture is added to the manufacturing vehicle phase, and then heated to evaporate the solvent for the polymer. After evaporated, leaving solid microspheres, the liquid vehicle temperature is reduced to ambient temperature with continued agitation.

The microspheres can then be washed and dried. The solvent evaporation method produce microcapsules are applicable to a wide variety of liquid or core materials.

Spray drying method

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

Fluidized bed method

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

Table 1. Preparation methods of Microencapsulation of PCMs

Polymerization	Procedure of Preparation	Ref.
In-situ Polymerization	Paraffin 25gm solid(core)/0.66 mol/L melamine in water was prepared and 14.5% formalin of 41.5% (wall), 2.9 g/L sodium dodecyl sulphate(SDS) added as an emulsifier, then pH was reduced to 8.5-9 with aqueous solution of 10% sodium hydroxide at 250 rpm at 70-75°C for 1hr, then the temperature was reduced to collect microcapsules.	[29,32]
Interfacial Polymerization	<i>n</i> -octadecane (core)/ melamine formaldehyde (wall), oil solution was prepared by mixing 2,4-diisocyanate. Prepared oil solution pored drop wise into an aqueous solution with 5wt% sodium salt of styrene melamic anhydride as an emulsifier. Amine-terminated polyoxypropylene was dissolved in an aqueous solution containing 0.1wt% SMA. Then the solution was continuously stirred at 600 rpm at 60°C for 3 hr. The resultant microcapsules were washed and filtered.	[31]
Complex coacervation	<i>n</i> -hexadecane (core)/ 1 unit gum Arabic, gelatin (wall) was dissolved in 10 units of distilled water above 45°C. then, stirred at 1000 rpm for 10 min. To this, a few drops of 10% sodium carbonate solution were added to dissociate the polyelectrolyte. The pH was adjusted to 9-10. Then the coacervate was recovered.	[8]
Spray dryer	Paraffin wax (core)/ 10% w/w gelatin and acacia (wall) were prepared to form emulsion solution. Then the prepared solutions were fed into the spray dryer. Emulsions were atomized with a feed rate of 20 ml/min by a centrifugal atomizer operated at 25,000 rpm at temperatures were between 130°C and 80°C. The microcapsules were collected at the bottom.	[30,33-35]

Methods of Incorporation of PCMs into Textiles

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

Spinning method

In this method, liquid polymer, polymer solution and fiber can be added with PCMs is then spun according to the spinning methods

such as melt, dry or wet spinning and extrusion of molten polymers. The extruded fibers/polymers could store and release heat according to the temperature of the environment. During this period of activity, the encapsulated fibers store or release the excess heat generated by the body. PCMs fibers have high latent heat, but easily lost their properties in use (X.X.Zhang, K.Zhang & J.J.Niu, 2004). In addition, it is observed that the particle size and size distribution of the microencapsulated PCMs affect the spin ability and mechanical properties of thermal regulating fibers.

Coating method

In this method, microspheres containing in phase change material dispersed in water

solution and coated into textile substrate includes a surfactant, a dispersant, an antifoam agent, a thickener and a polymer binder. There are various coating processes available such as knife-over-roll (Zuckerman, Pushaw, Perry & Wyner, 2003), knife-over-air, pad-dry-cure (Shing, Yoo & Son, 2005), gravure, dip coating and transfer coating.

Lamination method

PCMs would be incorporated into a tiny polymer film and applied to the inner side of the textile substrate by lamination in order to improve the thermo-regulating properties of the wearing garments. The heat stress of chemical and non-woven protective garments is decreased by incorporating PCM into a tiny film and applied into a fabric system (Pause, 2005). The PCMs fibers by lamination have the following advantages: a high PCM concentration per unit area, low cost of the production processes and low weight of the textile is minimized.

Applications of PCMs in Textiles

The main challenge in developing textile-PCM structure is their application method.

Microencapsulation of PCMs in a polymeric shell is an obvious choice but it adds weight to the garments. The possible applications of PCMs in textile are listed in Table 2 (Zhang et al, 2004).

PCMs found in aerospace textiles such as space suits and gloves to protect astronauts from extreme temperature fluctuations while performing extra-vehicular activities in space. Textile containing PCMs could use in medical filed in order to increase the thermo-physical comfort of surgical clothing such as gowns, caps and gloves. Textile-PCMs applications also found in bedding materials such as mattress covers, sheers and blankets. Active wear garments need to provide a thermal balance between the heat generated by the body while engaging in a sports and the heat released into the environment. Normal active wear garments do not always fulfill this requirements, hypothermia is likely to occur due to heat stress. Microencapsulation of PCMs into textile structure helps in regulating the thermal shocks and thus, thermal stress to the wearer, and helps in enhancing of work under extreme conditions (Demirbas, 2006; Zhang2001).

Table 2. Applications of PCMs in Textiles

Applications	Brief description
Casual clothing	Underwear, Jackets, Sports garments
Professional clothing	Fire fighters protective clothing, Bullet proof fabrics, Space suits, Sailor suits
Medical uses	Surgical gauze, Bandage, Nappies, Bed linings, Gloves, Gowns caps, Blankets
Shoe linings	Ski boots, Golf shoes
Building materials	In proof, In concrete
Life style apparel	Elegant fleece vests, Men's and women's hats, Rain wear
Other uses	Automotive interiors, Battery warmers

Conclusion

This paper reviews mainly focusing on the phase change materials and microencapsulation techniques in textile application. PCM is a smart material enhances the thermal properties from conventional

textiles due to PCMs have the ability to store or release the energy during the phase transition of materials occurs. Textiles materials containing PCMs are extensively being developed and investigated. Microencapsulation is studied as the process of enclosing micron sized particles in a

polymeric shell. Because of these properties, Microencapsulated textile materials become huge range of applications includes space, apparel, blanket, medicine, insulation, protective clothing and many others. Thus this paper also discussed different types of microencapsulation of PCMs into textile materials.

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