

Manufacturing Technology of Shape-Stabilized Phase Change Materials

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ABSTRACT

Phase change materials (PCMs) can absorb, store or release latent heat when undergoing through phase transition in predetermined narrow temperature range and hence used in thermal energy storage applications. But PCMs might leach out due to increase in volume during phase transition process. Shape stabilization techniques of PCMs are developed to mitigate this problem. The shape-stabilized PCMs are made by preparing composite PCMs and encapsulation. Shape stabilization improves handling and applicability of PCMs. The increasing demand for energy-saving, ecologically sustainable and user-friendly techniques of energy storage has drawn attention to shape-stabilized PCMs. In this article, we reviewed shape stabilization techniques of PCMs.

Keywords: PCM; thermal energy storage; shape-stabilization; encapsulation; composite PCM

1. INTRODUCTION

Earth's natural non-renewable energy resources such as fossil fuels, natural gas, etc. have been used in ways that are uneconomic and inefficient. The profligate use of these resources has created the threat of their extinction. To meet the need of energy requirements for today's population and future generations, efficient use of available energy resources is essential. Greener and sustainable methods that have the ability to capture waste or free thermal energy can be a possible way to alleviate this problem. Thermal energy can be stored in various forms such as chemical energy (reversible reactions), sensible heat and latent heat. [1] Thermal energy storage (TES) is difficult with complicated chemical processes which are arduous to control. Sensible heat storage devices give low energy density and have variable discharging temperatures. PCMs are advantageous over other TES methods because they store latent heat greater energy

storage density at a constant temperature. PCMs are used in applications such as building materials, thermoregulating textile materials, solar energy storage devices, electronic equipments, space and water heating devices, smart packaging and other areas. [2-8]

The concept of latent heat storage is based on the phase transition of the materials. We know that materials can have three phases that are solid, liquid and gas. The strength of intermolecular forces defines the state of the material. The concept of phase transition can be explained with the help of Figure 1. T_{ENV} and T_{PCM} are temperatures of environment and phase transition temperature of PCM respectively. When $T_{ENV} > T_{PCM}$, heat is supplied to the PCM from outside environment. PCM absorbs heat to break internal chemical bonds. [9] It undergoes phase transition after absorption of latent heat of phase transition. This energy triggers phase transition of the material while retaining constant

temperature. Size of the molecule as well as structural molecular configuration decides the amount of thermal energy stored during phase transition. [10] Small molecules give highly packed structure and stores a large amount of heat. As shown in Figure 1, when the temperature of the PCM is above or below T_{PCM} , heat absorbed or released is sensible heat. Reverse cooling cycle initiates when $T_{ENV} < T_{PCM}$. The drop in temperature aids in nucleation of the second phase. This is known as sub-cooling which is an important concern for determining the suitability of PCMs in particular applications. The phase reversal process releases back latent heat of fusion to the environment. Thus, the temperature of PCM rises.

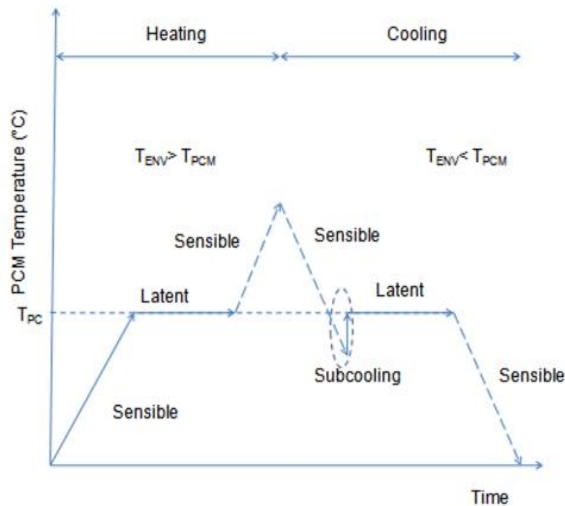


Figure 1. PCM functioning

PCMs can be classified according to the type of the phase change involved. The possible phase transitions include solid–solid, solid-liquid, solid–gas and liquid–gas phase changes. The phase transformations involving gas phase possess problems due to high pressure and high-volume change which makes their use impractical. Solid–solid phase change materials (SSPCM) involve transformation from one crystal lattice configuration to other crystal lattice configuration or from crystalline state to amorphous state. The solid-liquid PCMs exhibit greater volume expansion during phase transition process. The low viscosity

molten PCMs can leak out of the structure in which they are incorporated due to increase in volume during phase transition. The rigorous research and investigation carried out to solve this problem have put forward shape stabilization techniques of PCMs. The aim of these techniques is to prevent leakage of PCMs with the help of supporting structure or container. These are means by which PCMs retain their shape during phase transition. As shown in Figure 2, the shape-stabilized techniques of PCMs are categorized as composite preparation and encapsulation. Shape-stabilization improves cost-effectiveness and applicability of PCMs. Properties of shape-stabilized PCMs can be tailored as per requirements of applications. This has expedited their use in widespread applications. This paper is intended to review various manufacturing techniques employed for producing shape-stabilized PCMs.

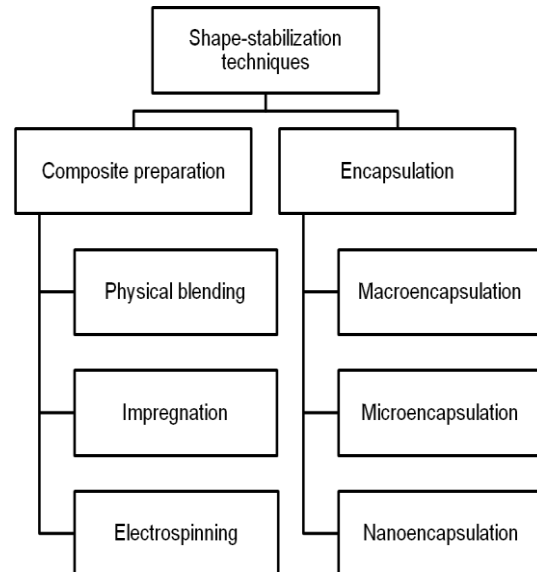


Figure 2. Shape stabilization techniques of PCMs

2. MANUFACTURING TECHNIQUES OF SHAPE-STABILIZED PCMS

Shape-stabilized PCMs consist of PCM and at least one other material. The other constituent act as supporting material for PCMs. Deliberate choice of the supporting material helps in modifying phase change enthalpy, thermal cycling

stability, thermal conductivity and thermal degradation characteristics. The PCMs are incorporated into other materials with the intention of improvement in their handling, cost-effectiveness and readiness for applications with tunable dimension. There are two kinds of shape-stabilization techniques of PCMs which are composite preparation and encapsulation.

2.1 Composite preparation

A composite material constitutes different materials. Thus, it has properties of constituent materials. Composite PCMs integrate heat storage properties of PCMs as well as structural properties of supporting material. Composite PCMs maintain the shape-stabilized form in the course of the entire phase change process. These materials are known as form-stable PCMs. Form-stable PCMs retain maximum percentage of PCM and do not allow PCM to leak when the temperature of the composite is above the melting point of PCM. The word shape-stabilized can be used interchangeably with form-stable. Form stable PCMs are synthesized by blending the PCM and the supporting material. Leakage of molten PCM is prevented by means of hydrogen bonding, polar force, van der Waals force, capillary effect and surface tension. [11] Composite PCMs can be manufactured in different shapes and sizes. These materials are also advantageous since there is no special container to support PCM which can leak out due to mishandling. The form-stable PCMs are produced by physical blending, vacuum impregnation and electrospinning.

2.1.1 Physical blending

The PCM and supporting polymer are mixed together by melt blending method or solvent casting method. In melt blending, PCM and supporting polymeric material, which has significantly higher melting point, are mixed and melted together. The mixture is then cooled to ambient temperature. In solvent casting, solution of PCM, solvent and polymer are mixed

together. The mixture is then subjected to solvent removal by evaporation. In both the methods, the polymeric matrices tether leakage of PCM by engulfing it. Polymer matrices present opportunity to select mechanical and chemical properties as per requirement. The PCM polyethylene glycol (PEG) can be blended with many chemically different polymers such as cellulose acetate, [12-14] polyacrylic acid, [15] polymethyl methacrylate (PMMA), [16,17] cellulose, [18,19] agarose, [20] chitosan, [20] polyvinyl alcohol (PVA), [21] polyvinyl chloride (PVC). [22] The polymer gets entangled in lamellar structure of PEG. Thus, PEG is prevented from leaking out of the composite system. Paraffin can be incorporated into high density polyethylene (HDPE), [23-25] low density polyethylene (LDPE), [26-28] styrene-butadiene-styrene copolymer (SBS) [29-30] and polypropylene (PP). [31,32] Acrylate polymers impart impact strength, chemical resistance, as well as optical clarity and can be used as structural support for fatty acid PCMs. [33-35]

2.1.2 Impregnation

Impregnation of PCMs into porous supporting materials can be done with or without application of vacuum. While selecting a porous structure, characteristics of pore configuration such as porosity, pore diameter distribution and pore profile are examined. [36] The pores hinder leakage of PCM in melted form. But small pore size may also interfere in the molecular motion of PCMs leading to decrease in latent heat. Hence the selection of optimum porous structure is important. The PCM impregnated porous structure thus act as form-stable composition. [37] The process of impregnation can be better explained with Figure 3. As shown in the figure, PCM and porous materials are introduced in a furnace equipped with a vacuum pump. This assembly melts PCM and removes air from both the components with the help of vacuum. In the course of operation, firstly PCMs are melted. Then the melted PCMs are physically mixed with porous materials.

After this, vacuum supply is cut off to allow entrance of air in the furnace. The final product obtained in this process is the

porous material impregnated with the PCM. This product is dried before use.

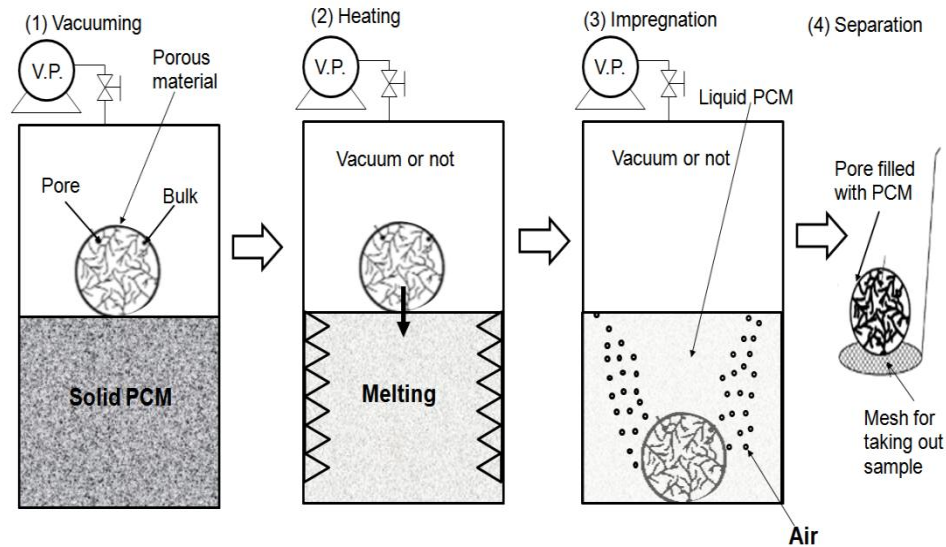


Figure 3. Vacuum impregnation of PCMs into porous material

Many researchers used EG, [38-39] expanded perlite (EP), [36,40] diatomite, [11] graphene oxide, [41,42] montmorillonite, [43] attapulgite, [44] silica, [45] carbon matrix, [46] carbon nitride matrix [47] and kaolin [48] as supporting materials for engulfing PCMs. Porous and highly thermally conductive materials like graphite matrix, metal foams increase the thermal conductivity of the PCMs effectively.

2.1.3 Electrospinning

Electrospinning is a simple and impressive technique to synthesize composite PCMs. It produces ultrafine fibers of various polymers which are incorporated with PCMs. Electrospun composite PCM is a promising member of TES materials because of its high latent heat storage capacity, large specific surface areas and good mechanical strength. PCM/polymer core/sheath structure can be obtained by coaxial spinning with core component as PCM and shell component as polymer. Core-sheath type nanofibers were synthesized with PEG as core and sheath of

polyvinylidene fluoride (PVDF) [49,50] and cellulose acetate. [51-55] Single phase electrospinning produces composite fibrous structure. So, researchers manufactured ultrafine fibers with PEG as PCM and different polymer matrices such as cellulose acetate, [52,55] poly(DL-lactide), [56] PVDF [50] and nylon 6,6. [57] Polymer composite nanofibers were made with fatty acids/ fatty acid esters as PCM with polymer matrix poly(styrene-co-acrylonitrile), [58] polyethylene terephthalate (PET) [59-62] and PVA. [63]

2.2 Encapsulation

To prevent leakage of PCMs during the phase change, encapsulation techniques are employed. There are three principal types of encapsulation which are macroencapsulation, microencapsulation and nanoencapsulation. [64] In macroencapsulation, PCMs are encapsulated in some form of containers such as tubes, pouches, spheres, cylinders, panels, tin-plated metal cans, mild steel cans or other receptacle. [2,64] Some geometries of encapsulation are shown in Figure 4.

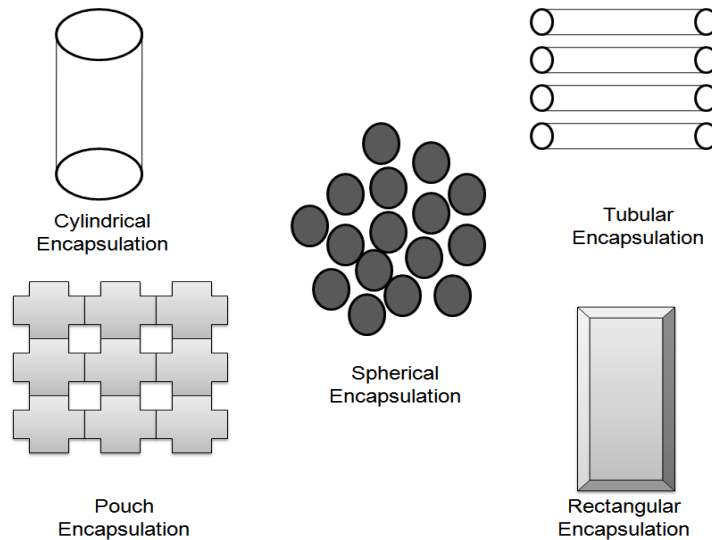


Figure 4. Different types of encapsulations

The diameter range of capsule shells is given in Table 1.

Table 1. Diameter range of capsules [65]

Type of capsule	Range of diameter
Macrocapsule	>1mm
Microcapsule	1µm to 1mm
Nanocapsule	<1µm

2.2.1 Macroencapsulation

Zukowski [66] manufactured short-term TES assembly by preparing macroencapsulated paraffin wax in polyethylene film bags. These bags were arranged in three layers separated by steel net. It can be used in building applications where short-term energy storage is needed. Memon et al. [67] prepared macroencapsulated PCM by incorporation of paraffin–light weight aggregate (p-LWA) into normal weight aggregate concrete. Oro et al. [68] used PCMs encapsulated in thin stainless steel containers inside food storage chambers. Sun et al. [69] prepared macroencapsulated PCM pouches which can be incorporated in fabric to improvise warmth retention of fabric. These pouches were inserted into layered fabric assembly as shown in Figure 5.

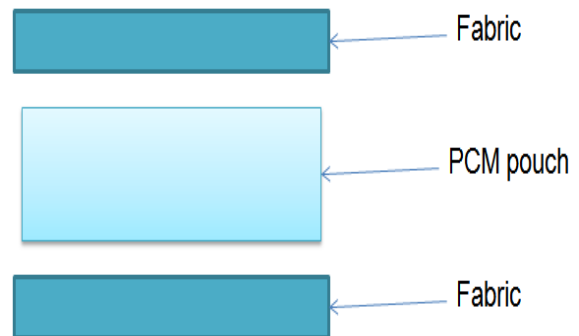


Figure 5. Schematic diagram of the multi-layer fabric assembly

2.2.2 Microencapsulation

The microencapsulation method is the exhaustively used technique for PCM incorporation. This has been most pervasively used technique in broad spectrum of applications such as building, medical, electronics, food, etc. Microencapsulation is a simple and effective process of protecting PCMs from outside reactive environment. The encapsulation process also improves the specific area of heat transfer of PCMs. [70] Borreguero et al. [71] synthesized microcapsules containing paraffin RT27. The shell material was prepared from polyethylene/ethylene vinyl acetate. Liang et al. [72] synthesized microcapsules with butyl stearate as PCM by interfacial polycondensation of ethylene diamine and TDI. Boh et al. [73,74] prepared

microcapsules containing paraffinic PCM by in-situ polymerization of trimethylol melamine and hexamethoxymethylol melamine. Jin et al. [75] synthesized microcapsules with paraffin core materials and the shell material made from urea-formaldehyde prepolymer by in-situ polymerization. Onder et al. [76] prepared microcapsules containing paraffin as core material and biodegradable gum arabic-gelatin mixture as shell material. Su et al. [77] fabricated non-permeable shell material by two-step coacervation method. The octadecane core material was encapsulated by melamine formaldehyde shell material.

2.2.3 Nanoencapsulation

The microencapsulated PCMs are prone to rupture during processing. Microcapsules synthesized are generally larger than 10 μm . For flawless processing, the expected size of the microcapsule is lower than 3 μm . The diameter of nanocapsule is smaller than 1 μm which have better processability than microcapsule. Cho et al. [78] prepared nanocapsules in the range of 100 to 2000 nm. The shell material was prepared by interfacial polycondensation reaction. Ichikawa et al. [79] prepared nanocapsules in the range of 500 to 600 nm. The nanocapsules were formed by interfacial polycondensation reaction. Fang et al. [80] synthesized nanocapsules in the range of 100 nm. PCM tetradecane was encapsulated by urea formaldehyde coating by in-situ polymerization.

3. CONCLUSIONS

PCM melts from crystalline phase while the temperature of the substrate is prevented from rising. Similarly, during the crystallization process, the dropping of the temperature of the substrate is prevented. PCMs can leach out due to increase in volume during phase transition process. Shape stabilization techniques of PCMs are developed to mitigate this problem. Techniques of shape-stabilization of PCMs include composite preparation and

encapsulation. The preparation methods of composite PCMs with different polymers and porous structures are reviewed. Different types of encapsulated PCMs and their fabrication methods were discussed. The following conclusions are drawn.

(1) The composite PCMs can be synthesized by incorporating PCMs into supporting structure by physical blending, impregnation and electrospinning. Composite PCMs don't require capsulation hence heat resistance provided by the capsule is eliminated and make the product cost-effective. To improve long-term performance and compatibility with heat transfer agent, PCMs can be integrated with supporting polymeric material by physical blending. The PCMs and polymer are mixed together in molten form or in solution form in order to entangle PCM uniformly into the lamellar structure of the polymer. PCMs can also be shape stabilized by impregnating into the porous supporting material. High PCM impregnation ratio is improved with vacuum-assisted impregnation. Also, the use of the highly thermally conductive porous material is an effective way of producing a phase change composite with high thermal stability. The PCMs are form-stabilized into polymeric support by electrospinning mixture of PCMs and polymer. Coaxial electrospinning produced shape-stabilized PCMs with core of PCMs and shell of polymeric material. Single-phase electrospinning fabricated fibrous structure with PCM moiety dispersed in the polymer matrix. Composite electrospun PCM lock PCM into polymeric skeleton. The electrospun mat has large heat-transfer surface area, high porosity, high aspect ratio, and superior mechanical flexibility.

(2) The encapsulation techniques are classified on the basis of the size of the capsules into macroencapsulation, microencapsulation and nanoencapsulation. Encapsulation protects PCMs from the outer reactive environment improving their shelf life. These capsules can be incorporated into different building materials and polymers to improve thermoregulating properties easily.

The frequently used microcapsules fabrication technologies of spray drying process, fluidized-bed process, interfacial polycondensation, in situ polymerization and phase coacervation are summarized in this review.

PCMs make admirable contribution towards energy harvesting by storing thermal energy in the form of latent heat. PCMs can leach out due to increase in volume during phase transition process. Shape stabilization techniques of PCMs are developed to mitigate this problem. Development of shape-stabilized PCM products is in the initial stage and it is necessary to conduct a lot of applied investigations directed to provide acceptable production technologies and demonstrate the profitable spheres of their application. The prospective industrial applications of PCMs achieved by selection of proper PCM from the wide spectra of PCM, considering its storage capacity and temperature range of operation in the end application. Growing concerns over energy conservation have been the stimulant for the flourishing PCM market.

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