Review on Micro-encapsulated Phase Change Materials (MEPCMs): Fabrication, Characterization and Applications

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Abstract

The use of latent heat storage, microencapsulated phase change materials (MEPCMs), is one of the most efficient ways of storing thermal energy and it has received a growing attention in the past decade. However, there is no complete overview of its utilisation in thermal energy storage systems, and the information is widely spread in the literature. In this paper, a comprehensive review has been carried out for MEPCMs. Four aspects have been the focus of this review: fabrication and characterization of MEPCMs, applications of MEPCMs to the textile and building, fundamental properties of microencapsulated phase change material slurry (MPCS) and application of MPCS to the thermal energy storage system. Over 140 recent publications are referenced in this paper.

Keywords: MEPCMs; MPCS, Fabrication; Characterization; Heat transfer

Contents

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Nomenclature

C_p	specific heat capacity (kJ/ (kg ^oC))
c	volumetric concentration of slurry (%)
d, D	diameter (m)
De'	modified Dean number
h	heat transfer coefficient (W(m^2K))
ΔH_c	heat of crystallization (kJ/kg)
ΔH_f	heat of fusion (kJ/kg)
L	latent heat (kJ/kg)
k	permeability coefficient
m	mass (kg)
Nu_e	Nusselt number
P_e	Peclet number
R	radius (m)
R_e	Reynolds number
S_{te}	Stefan number
rmp	stirring rate
T	temperature (^oC)
T_m	melting temperature (^oC)
T_c	crystallizing temperature (^oC)

Greek letters

π	the ratio of a circle's circumference C to its diameter
ρ	density (kg/m^3)
Φ	the encapsulation efficiency (%), volume faction.
μ	viscosity (Pa s)

1. Introduction

In recent years, sustainable and renewable energy has been a factor of importance ever since the energy crisis of the 1970s. Thermal energy storage (TES) systems provide the potential to attain energy savings, which in turn reduce the environmental impact related to energy use; these systems actually provide a valuable solution for correcting the mismatch that is often found between the supply and demand of energy [1, 2]. Latent heat storage is one of the most efficient ways of storing thermal energy. Unlike the sensible heat storage method, the latent heat storage method provides much higher storage density, with a smaller temperature difference between storing and releasing heat.

Phase change materials (PCMs) are "latent" heat storage materials. Normally, the thermal energy transfer occurs when a material changes from solid to liquid, or liquid to solid. Organic and inorganic materials are two most common groups of PCMs [3]. Organic materials are further described as paraffin and non-paraffin. Most of organic PCM are non-corrosive and chemically stable, performance little or no sub-cooling, are compatible with most building materials and have a high latent heat per unit weight and low vapour pressure. They have disadvantages in low thermal conductivities, high changes in volume on phase change and flammability, though extensive investigations are carried out to enhance their heat transfer rate [4-11]. In contrast, inorganic materials (salt hydrate and metallic) have a high latent heat per unit volume and high thermal conductivities, and are non-flammable and low in cost in comparison to organic materials. However, they are corrosive to most metals and suffer from decomposition and sub-cooling, which can affect their phase change properties. Therefore, In order to overcome these problems, a new technique of utilising microencapsulated phase change material (MEPCM) in thermal energy storage system has been developed. The main merits of MEPCM over PCM are as follows: (1) increasing heat transfer area; (2) reducing PCMs reactivity towards the outside environment and controlling the changes in the storage material volume as phase change occurs.

Since MEPCM was developed, it had been mainly used in the textile and building applications. It can increase the thermal mass of buildings and even clothing without increasing their real mass very much [12]. When MEPCM dispersed into the carrier

fluid, e.g. water, microencapsulated phase change material slurry (MPCS) is fabricated. They are potentially applicably to the secondary refrigeration and air conditioning loops for improving the energy efficiency and to reduce the quantity of refrigerant [13].

This paper provides a review of studies dealing with microencapsulated phase change materials. The material in this review has been arranged within the main areas of work:

- Fabrication and characterization of MEPCM
- Applications of MPECM to the textile and building
- Fundamental properties of MPCS
- Application of MPCS to the thermal energy storage system

2. Microencapsulated phase change material (MEPCM)

2.1. Definition of microencapsulated phase change material (MEPCM)

Microencapsulation is defined as a process in which tiny particles or droplets are surrounded by a coating, or embedded in a homogeneous or heterogeneous matrix, to give small capsules with many useful properties [14]. All three states of material (solids, liquids, and gases) can be microencapsulated. This allows liquid and gas phase materials to be handled more easily as solids, and can also provide a physical barrier between the core material and the shell material. Depending on the physico-chemical properties of the core, the wall composition, and the used microencapsulation techniques, different type of particles can be obtained (see Fig.1 [15]): simple sphere surrounded by a coating of uniform thickness; particle containing an irregular shape core; several core particles embedded in a continuous matrix of wall material; several distinct cores within the same capsule and multi-walled microcapsules [14]. Among them, simple sphere particle is the most common one being fabricated and utilised. The microencapsulated phase change material is defined as composing of phase change materials (PCMs) core and a polymer or inorganic shell to maintain the shape and prevent PCM from leakage during the phase change process [16]. Fig. 2 showed the typical structure of MEPCM [17]. Microencapsulated

phase change material overcomes the following problems in comparison to the convectional PCM: corrosive to metal, decomposition, sub-cooling and leakage.

2.2. Fabrication and characterization of MEPCM

Microencapsulation processes are usually categorized into two groups: chemical processes and physical processes. The use of some methods has been limited to the high cost of processing, regulatory affairs, and the use of organic solvents, which are a concern for heath and the environment [18]. Physical methods are mainly spray drying or centrifugal and fluidized bed processes, which are inherently not capable of producing microcapsules smaller than 100 μm. The chemical processes include the interfacial polymerization, in situ polymerization, the sample or complex coacervation, phase separation, suspension-like polymerization and other fabrication methods. MEPCM are mainly fabricated by chemical methods due to its properties and applications.

2.2.1. In situ polymerization

In situ polymerization generally involves bringing together two immiscible liquids, e.g. water and organic solvent, respectively; containing complimentary, direct-acting, organic intermediates that will react with each other to establish a solid pre-condensate [18]. Fig. 3 showed the processes of in situ polymerization [19]. In situ polymerization is very similar to interfacial polymerization; the distinguishing characteristic of in situ polymerization is that there are no reactants in the core material. All polymerization occurs in the continuous phase, rather than two phases, as in interfacial polymerization. Due to its good chemical stability and mechanical strength, melamine-formaldehyde (M/F) and urea-formaldehyde (U/F) had been widely used as the shell material. However, ineluctable remnant formaldehyde may exist after forming the shell, which causes the environmental and health problem during the polymerization process. The in situ processes have the ability to yield microcapsules with the best quality in terms of diffusion-tightness of their walls and of a size ranging between 5 and 100 μm[12]. Therefore, in situ polymerization method had been widely used in fabricating microencapsulated phase change materials.

Hong and park [20] fabricated melamine resin microcapsules with long self-life using fragrant Margin oil as core material and melamine formaldehyde as shell material, sodium lauryl sulphate as emulsifier and poly(vinyl alcohol) (PVA) as protective colloid by in situ polymerization. The size of all the resulted particles was below 10 μm by stirring at the rate of 3000 rpm, and their size distribution was narrower. They concluded that the microencapsulation efficiency (%) was about 87 % and the loading amount of Migrin oil in the microcapsules was about 53 wt. %. Choi et al. [21] prepared microcapsules with Tetradecane as the core material and melamine formaldehyde as the shell material. A 5 wt. % Strene-maleic anhydride-monomethyl (SMA) was used as the emulsifier. They indicated that the rpm of the homomixer in the emulsifying step was one of the most important factors affecting both the size and the size distribution of the capsules, the optimum rpm was up to 8000. The results showed that the size of the capsules was decreased and the uniformity is improved with an increasing rpm in the emulsifying. Zhang et al. [22] fabricated microcapsules and nanocapsules using 70 wt. % *n*-octadecane with melamine formaldehyde shell. The stirring rate, emulsifier content and cyclohexane content have effects on the diameters and morphology of the microencapsulated *n*-octadecane, as shown in Fig. 4 [22]. The diameter distribution becomes narrower with the increase of stirring rate and emulsifier content. The diameters have no effects on the melting behaviours of microcapsules; however, they have significant effects on the crystallization behaviours. The thermal stable temperature rises with the increase of stirring rate, emulsifier content; however, it keeps unchanged with the increase of cyclohexane content. Zhang et al. [23] demonstrated that the thermal stability of MEPCM can be improved by using different mole ratios of urea-melamine-formaldehyde copolymers as shells. The highest thermal stable temperature of MEPCM with diameters in the range 0.4—5.6 μm is approximately 163 °C and the urea-melamine-formaldehyde mole ratio is 0.2:0.8:3. The thermal stability of 160 °C heat treated microcapsules adding 8.8 % cyclohexane can be further enhanced up to approximately 37 °C. Zhang et al. [24] also indicated that melamine-formaldehyde microcapsules containing *n*-octadecane synthesized with 30.0–40.0 vt % of cyclohexane have the highest thermal stabilities, with 230 °C and 289 °C in air and nitrogen atmosphere, respectively; and approximately 5-28 vt % of expansion space was formed inside the microcapsules. Fan et al. [25] also proved that microcapsules containing 18-19 % reserved expandable space are synthesized at 30-

40 wt. % cyclohexane in the oil phase, which have a highest thermal resistant temperature 270 °C, and a lower permeability, less than 1.2 %. Song et al. [26] prepared microcapsules with aminoplast as the shell and bromo-hexadecane (BrC_{16}) as the core. The results showed that silver nano-particles significantly increased strength and solved the common problem of particle agglomeration. In addition, new microcapsules demonstrated higher thermal stability performance and capable of enduring higher temperature

The microcapsules containing *n*-octadecane and nucleating agents encapsulated in melamine-formaldehyde shell with about 1μm in average diameter were fabricated by Fan et al. [27]. They proved that adding approximately 20 wt. % paraffin in core material was able to prevent *n*-octadecane from super-cooling, and had no effect on the morphology and dispersibility of microcapsules. Zhang et al. [28] demonstrated that the degree of super-cooling of microencapsulated n-octadecane is decreased by adding 10.0 wt. % of 1-octadecanol as a nucleating agent. Wang et al. [29] fabricated Urea-formaldehyde (UF) microcapsules containing two-phase core materials in which phthalocyanine blue BGS particles were homo-dispersed in tetrachloroethylene (TCE). The dispersibility and migration speed of fine particles in TCE were found to be strongly influenced by the type of surface modifier. The results showed that using octadecylamine (ODA) to modify MEPCM particles resulted in a significant increase of the dispersing extent (DE) and the electrophoresis velocity of the particles in TCE (about 4 and 20 times more than that of unmodified). Shin et al. [30], [31] prepared melamine-formaldehyde microcapsules containing Eicosane for textile materials. They concluded that the treated fabrics had heat storage capacities of 0.91-4.44 kJ/kg and retained about 40 % of their heat storage capacity after five launderings. The results suggested that microcapsules with higher core/shell ratios need to be made to improve the thermal-regulating efficiency of fabrics. They also indicated that a treated fabric with 22.9 % add-on is capable of absorbing 4.44 kJ/kg of heat if the microcapsules on the fabric undergo a melting process. The air permeability and moisture vapour permeability decrease by 28 and 20 %, respectively, at 22.9 % add-on. Boh et al. [32] fabricated microcapsules using higher hydrocarbon phase change material as the core and amino-aldehyde resins as the shell. They indicated that the high molecular weight of emulsifier was better than low molecular weight and by increasing the amount of emulsifier; it is possible to produce microcapsules with

better thermo-physical properties. Su et al. [33] prepared a series of melamine formaldehyde microcapsules containing composite PCMs as core material. They concluded that the optimal shell material dropping rate 0.5 mL/min-1, double-shell, and temperature elevating speed 2°C/10 min. The surface morphologies and the shell structure of microcapsules are crucial to thermal properties, the melt point of PCM in the shell does not change and the heat transfer is obvious. Fig. 5 showed that the best samples is the microcapsules of two layers, 0.5 mL/min-1 dropping rate, 2 °C/10 min temperature elevating speed [33]. The lost weight temperature of two layers microPCMs is higher than that of one layer. Kim et al. [34] fabricated the microcapsule containing titanium dioxide (TiO_2) and halocarbon oil was synthesized via in situ polymerization. They concluded that the microcapsule walls polymerized with urea, melamine, and formaldehyde (UM/F) were found to be rigid and smooth.

Sarier and Onder [18] used three types of paraffin (C_nH_{2n+2}), *n*-hexadecane, *n*-octadecane and *n*-Eicosane, were preferred for the encapsulation since they are nontoxic, non-corrosive, chemically inert, easily available and have no unpleasant odor. They indicated that to enhance the thermal capacities of fabrics or to enlarge their phase transition intervals, it was better to use a combination of microcapsules containing different types of PCMs or paraffin waxes rather than those including a mixture of them. An in-situ polymerization microencapsulation process was used to prepare the MEPCM with melamine resin as the shell material and n-Docosane ($C_{22}H_{46}$) as the core material [35]. The results concluded that to obtain a MEPCM particle size of ca. 10 μm, the corresponding stirring rate is 6000 rpm and to get a better microencapsulation efficiency of the core material in the preparation experiment, the core mass fraction in a single MEPCM particle is lower than 70 %. DSC thermal analysis showed that the prepared MEPCM with a core mass fraction of 60 % had a high heat of fusion of 150 kJ/kg. The thermal stability of the MEPCM behaved well over the temperature range of 0 °C to 180 °C. Su et al. [36] developed a two-step coacervation (TSC) method to fabricate *n*-octadecane microcapsules using M/F shell to increase life time of MEPCM (See Fig. 6 [36]). The results showed that the new method reduced the cracks on shells and increased the compactness of shells, and the average thicknesses of shells were 0.1 μm. They also demonstrated that the shell resistance permeability is increased by TSC from values of permeability coefficient *k*. Li et al. [37] prepared microcapsules using n-octadecane as core and

M/F as shell with low remnant formaldehyde content. The employed MF pre-polymer was prepared by incorporating formaldehyde once and melamine for three times. The results indicated that with the dropping rate of the MF pre-polymer decreasing, the flocculation phenomenon of microcapsules decreases and the globular surface becomes smoother; and the thermal stability increases regularly. The average diameter of the microcapsules is about 2.2 μm and the diameter distribution is narrow.

M/F microcapsules containing with active ingredients for intumescent flame retardant system were fabricated [38]. They found out that the thermo-physical properties of MEPCM were strongly dependant on the nature of core content and the synthesis conditions; especially, thermal conductivity depended on the chemical structure of the polymeric shell whereas heat capacity is related to the core material. Yuan et al. [39] successfully prepared microcapsules containing curing agent for epoxy with poly(melamine-formaldehyde) (PMF) as the shell material and high-activity polythiol (pentaerythritol tetrakis (3-mercaptopropionate), PETMP) as the core material. They indicated that the appropriate reaction time was about 40-60 min. The reaction temperature at about 50 ^{o}C, otherwise the microcapsule might collapse and shrink. The pH value was about 2.9-3.2. The feeding weight ratio of core/shell monomers should be set at about 2.3. The sizes of microcapsules were mainly depended on the dispersion rate and emulsifier content. Yu et al. [40] fabricated microcapsules containing *n*-dodecanol using M/F resin as shell and styrene-maleic anhydride copolymer (SMA) as emulsifier. The results showed that thermo and physical properties of MEPCM were affected greatly by the types and the amounts of SMA. They also demonstrated that when the mass ratio of emulsifier to *n*-dodecanol was 4.8 %, the phase change latent heat and encapsulation efficiency reached to the maximum value of 187.5 kJ/kg and 93.1 %, respectively. A series of microencapsulated phase change materials (micro-PCMs) based on n-octadecane core and resorcinol-modified melamine-formaldehyde shell were synthesized using different emulsifiers [19]. They indicated that the SMA as emulsifier was optimal for fabrication of the microcapsules. Microcapsules with core/shell weight ratio of 75/25 by using SMA had a compact surface of the shell and a mean particle size of below 20 μm. This sample indicated much better phase change properties and 92 % encapsulation efficiency. Alkan et al. [16] fabricated microcapsules using docosane as the core material and PMMA as the shell material. The results showed that

microcapsules had smooth and compact surface with average diameter of 0.16 μm. Thermal gravimetric analysis (TGA) proved microcapsules had good chemical stability and the thermal cycling tests indicated that it had good thermal reliability.

2.2.2. Interfacial polymerization

Interfacial polymerization (IFP) involves dispersing an organic phase (containing poly-functional monomers and/or oligomers) into an aqueous phase (containing a mixture of emulsifiers and protective colloid stabilizers) along with the material to be encapsulated [41]. Fig. 7 [41] showed the manufacture of microcapsules by interfacial polymerization. Interfacial polymerization can be used to prepare bigger microcapsules, but most commercial IFP processes produce smaller capsules in the 20-30 μm range for herbicides and pesticide uses, or even smaller 3-6 μm range for carbonless paper ink.

Yadav et al. [42] carried out an early theoretical study on the microencapsulation of butachlor in polyurea shell by interfacial polymerization. They concluded that the time of encapsulation depended on the size of the microcapsule and by monitoring the pH of the continuous phase, and the capsule size was weakly dependent on the rpm. Another study by Yadav et al. [43] found out the permeability of the polyurea microcapsules was strongly influenced by the degree of crystallinity of the polymer shell, the release of cyclohexane from polyurea shell was determined by diffusion across the polymeric membrane. Hong and Park [44] indicated that a decrease in the molecular weight of stabilizing agent polyol could give sharper, more porous an permeable micro-membranes due to an increase of the hydrophobic hard segment and their thinner wall. Hong and Park [45] fabricated polyurea microcapsules containing ovalbumin with good thermal stability. Urea-formaldehyde microcapsules were prepared with lemon oil as the core material using four kinds of emulsifier, gelatin, span 80, polyvinyl alcohol, and sodium dodecyl sulphate (SDS) [46]. The results showed that the particle sizes of the microcapsules were greatly dependent on the stirring rate, stirring time and the viscosity of the core material. The SDS was the most suitable emulsifier for preparing urea-formaldehyde microcapsules and the particle sizes were the smallest at 5% emulsifier content.

Shulkin and Stöver [47] fabricated microcapsules using hydrophilic oil as core materials and styrene-maleic anhydride (SMA) copolymers as the shell material. They demonstrated that microcapsules contained more core material by either increasing the ratio of styrene to maleic anhydride groups in the copolymer, or by incorporating *t*-butyl styrene instead of styrene into the copolymer. The microcapsules contained octadecane showed a phase change at 29-30 °C [48]. They indicated that the core content of their microcapsules measured ΔH_f was less than that calculated based on the feed amount of octadecane. The efficiency of octadecane encapsulation increased as the core content decreased. Zou et al. [49] prepared polyurea microcapsules with 2.5 μm in diameter using hexadecane as the core material and OP [poly(ethylene glycol) octylphenyl ether] as an emulsifier. The DSC results showed that the melting point and the heat of fusion of microcapsules were 18 ^{o}C and 66 kJ/kg. Tseng et al. [50] fabricated MEPCM without emulsifier while polymerizing the pre-polymer at the interface by acid-catalyst for at least 2 h at a pH value of 3.5. The weight ratio of core PCM to the whole capsule was related to the sizes by the equation below [50]:

$$\frac{m\mathrm{PCM}}{m\mathrm{PCM}+m\mathrm{Shell}}=\frac{(4/3)\pi\cdot R^3\mathrm{PCM}\cdot\rho\mathrm{PCM}}{(4/3)\pi\cdot R^3\mathrm{PCM}\cdot\rho\mathrm{PCM}+(4/3)\pi(R^3-R^3\,\mathrm{PCM})\cdot\rho\mathrm{Shell}}$$

A series of PU-shell microcapsules containing *n*-octadecane were successfully synthesized using diethylene triamine (DETA) as a chain extender reacting with toluene-2, 4-diisocyanate (TDI) [51]. Styrene-maleic anhydride (SMA) was used as an emulsifier. They proposed a formula for calculating the efficiency of MEPCM, where $\Delta H_{f,\ MicroPCM}$ *and* $\Delta H_{c,\ MicroPSM}$ are the latent heat of fusion and the heat of crystallization of MEPCM [51]:

$$\Phi=\frac{\Delta Hf,\mathrm{MicroPCMs}+\Delta Hc,\mathrm{MicroPCMs}}{\Delta Hf,\mathrm{PCMs}+\Delta Hc,\mathrm{PCMs}}$$

The results showed that molar ratio of DETA/TDI was found to be a factor for the shell thickness and the dry weight of microcapsules and the PU-shell microPCMs samples fabricated by 3000 rpm emulsion rate with DETA/TDI molar ratio of 1.01 (DETA=3.6 g) were suitable for thermal energy storage. In addition, SMA had great effects on the shell structure and its amount may be related to the microcapsule

release properties. A similar study was carried out by Siddhan et al. [52], cyclohexane was used as the solvent for TDI and *n*-octadecane. They concluded that emulsification stirring speed of >2000 rpm for the initial experiments was necessary for forming a good emulsion; however, the stirring speed should be reduced to allow formation of continuous wall and the speed should not be reduced immediately after adding the DETA, to solve both problems of capsule agglomeration and their poor stability to heat. In addition, they also demonstrated that the effect of core-to-monomer (CM) ratio and PCM-to-cyclohexane (PC) ratio was found to have great effect on the core content, encapsulation efficiency, and microcapsule stability. A maximum encapsulation efficiency of 92 % was achieved; along with the core content of 70 % was obtained with CM ratio of 3.7 and the PC ratio of 6. The microcapsules were found to be stable at 150 ^{o}C for 8 h.

Pascu et al. [53] used an epoxy resin and carboxylic acids for the synthesis of microcapsules. They concluded that experiments performed at lower stirring rates led to larger microcapsules, in the range 100–400 µm, while higher stirring rates resulted in microcapsules in the range 10–50 µm. The presence of a crosslinked affects the morphology of the external microcapsule surface; the microcapsule external surface appeared smooth with a crosslinked. Zhang and Wang [54] synthesized microencapsulated *n*-octadecane with polyurea shells. Polyurea was considered as an optimal shell material due to its good physical properties and chemical stabilities, and it also does not cause environmental and health problems in comparison of melamine-formaldehyde resin and urea-formaldehyde resin. The results showed that the microcapsules synthesized using Jeffamine as the amine monomer were better than those synthesized by ethylene diamine and diethylene triamine in terms of surface, particle size, phase change properties, encapsulation efficiency and anti-osmosis property. They also indicated that the microcapsules fabricated with a core/shell weight of 70/30 were optimal. See table. 1 for details [54]. Another recent study by Liang et al. [55] used butyl stearate as a phase change material and polyurea shell as the shell material, they indicated that the emulsifier had an important influence on the uniform size distribution of microcapsules, but it had little influence on the size value of the microcapsules.

2.2.3. Suspension-like polymerization

Sánchez et al. [56] developed a method based on a suspension free radical polymerization process to fabricate microencapsulated non-polar PCMs. They used different PCMs (paraffin wax PRS, Tetradecane, Rubitherm RT27, Rubitherm 20, nonadecane) as the core materials and polystyrene as the shell material. They indicated that PEG could not be encapsulated due to its hydrophilic nature. Microcapsules were obtained with the 50 % by weight of capsules is PCM. The average diameter of microcapsules was 237 μm which were quite large in the application. Another study by Sánchez et al. [57] investigated the influence of reaction temperature, stirring rate, and the mass ratio of paraffin wax to styrene on the thermal properties of microcapsules. They concluded that reaction temperature had no significant effect on the size of the microcapsules and when the core/shell mass ratio was higher than 2.00, it was difficult to encapsulate the paraffin. They found a relationship between the stirring rate and the mean particle diameter in number. Sánchez et al. [58] designed a pilot plant that used on the laboratory scale with the aim of preparing microcapsules with a similar particle size and with the same phase change material (PCM) content as those obtained in the laboratory in their previous studies. The resulted showed that the experimental values were fitted to the theoretical expression for the average dissipation rate as a function of the mean particle size.

Chang et al. [59] microencapsulated n-octadecane using a PMMA network-silica hybrid as the shell material. The results showed that the most suitable condition for producing high latent heat and PCM content in microcapsules was by the introduction of 5 % SiO_2 in microcapsules. Silica here was used to improve the PCM content in microcapsules. The highest latent heat (180 kJ/kg) and PCM content (74 %) of microcapsules were obtained when the inorganic/organic ratio of the microcapsule was 5 %. You et al. [60] fabricated microcapsules using n-octadecane (MicroPCMs) with a styrene (St)–divinybenzene (DVB) co-polymer shell. The average diameter of the microcapsules was about 80 μm and the heat of fusion was about 126 kJ/kg. In a recent study, they [61] also indicated that the thermal decomposition temperature of microencapsulated *n*-Octadecane was about 230 °C which was higher than that of MicroC18 using melamine-formaldehyde shell. Microencapsulated n-Octadecane were synthesized by suspension-like polymerization [62], and styrene-1,4-butylene glycol diacrylate copolymer(PSB), styrene-divinylbenzene copolymer(PSD), PSDB,

and polydivinylbenzene (PDVB) were used as shell materials, respectively. The results showed that both of the different copolymer shells and various PCM contents had little influence on the thermal stability of MicroPCMs.

2.2.4. Complex coacervation

Complex coacervation was defined as a phenomenon taking place in colloid systems, where macromolecular colloid rich coacervate droplets surround dispersed microcapsule cores, and form a viscous microcapsule wall, which is solidified with cross-linking agents [63].

An early study by Wen et al. [64] fabricated microcapsules through complex coacervation and used them as potential prostheses for organ transplantation. Hawlader et al. [65] microencapsulated paraffin wax with average particle sizes of 50-100 μm. The results showed that higher coating to paraffin ratio led to a higher encapsulation ratio of paraffin and the hydrophilicity value of microcapsules depended mainly on the paraffin wax to coating ratio. Hawlader et al. [66] used both experiments and simulation to evaluate the characteristics of microcapsules based on their previous research. They concluded that thermal cyclic test showed that encapsulated paraffin kept its geometrical profile and energy storage capacity even after 1000 cycles of operation, (see Fig. 8 for details [66]). Hawlader et al. [67] indicated that the optimal homogenizing time was 10 min and the amount of cross-linking agent was 6-8 ml in the coacervation method; and they also demonstrated that microencapsulation efficiency depended upon the process parameters, such as core to coating ratio, emulsifying time and the amount of cross-linking agent. Alvarado et al. [68] investigated super-cooling suppression of microencapsulated *n*-tetradecane. They indicated that super-cooling of MEPCM could be effectively suppressed when combined with 2 or 4 % of tetradecanol. Özonur et al. [69] microencapsulated natural coco fatty acid mixture for thermal energy storage. The results showed that coco fatty acid mixtures have kept their geometrical profiles even after 50 thermal cycles for melting and freezing operations in temperature range from 22 to 34 °C and it was also found that gelatin+gum Arabic mixture was the best wall material. Onder et al. [70] used three types of paraffin waxes, namely *n*-hexadecane, *n*-octadecane and *n*-nonadecane as the core materials and gum arabic-gelatin mixture as the shell material. The results showed that microcapsules with *n*-octadecane gave the highest enthalpy

value of 166 kJ/kg. They concluded that more precise pH value, amount and concentration of surfactants and higher stirring rates were crucial for fabricating good microcapsules.

2.2.5. Other fabrication methods

Loxley and Vincent [71] fabricated microcapsules by phase separation method using PMMA as the shell material. They indicated that small ionic surfactants were unsuitable emulsifiers for forming microcapsules and polymeric emulsifiers worked well. The shell thickness of capsules was affected by the concentration of polymer in the oil phase before emulsification. Yang et al. [72] microencapsulated n-tetradecane with different shell materials, acrylonitrile-styrene copolymer (AS), acrylonitrile-styrene-butadiene copolymer (ABS) and polycarbonate (PC) by phase separation method. The results showed that microcapsules with melting enthalpy > 100 kJ/kg, encapsulation efficiency 66-75 %, particle size <1 μm were obtained for all three shell materials. Polyaniline particles were synthesized by the convectional oxidation polymerization with M/F resins[73]. Sun and Zhang [74] investigated the mechanical strength of microcapsules of three different wall materials, melamine-formaldehyde resin, urea-formaldehyde resin and gelatin-gum arabic coacervate. The results showed that gelatin microcapsules had better mechanical strength than M/F resin and U/F resin. Su et al. [75] studied the mechanical properties of the M/F shell of a series of microcapsules. They concluded that when the mass ratio of the core and shell material was 3:1, a yield point of about $1.1*10^5$ Pa was found and when the compression was increased beyond this point the microcapsules showed plastic behaviour. It also found that double shell showed better mechanical properties. Sawada et al. [76] prepared M/F resin microcapsules by the batch method and micro-reactor method with telomeric surfactant. The results showed that micro-reactor gave a smaller diameter and a narrower size distribution than those prepared by the batch method. Kim and Kim [77] manufactured microencapsulated octadecane with waterborne polyurethane using the pre-polymer mixing process method. The results showed that the size of microcapsules (1-6 μm) decreased with increasing emulsifier contents. The heat of fusion, the heat of crystallization, and their encapsulation efficiencies of octadecane were found to increase with increasing microencapsulated blends, thickener, and hardener contents. Alkan et al. [78] demonstrated that 80 %PEG / 20 %PMMA, 80 %PEG / 20%Eud S, and 80%PEG / 20%Eud E blends were suitable materials for

solar energy storage space heating. Alkan and Sari [79] also encapsulated the fatty acids into PMMA as much as 80 wt.% and demonstrated that they were candidate PCMs for space heating. Jiang et al. [80] fabricated microcapsules with phenolic resin (PFR) shell and n-hexadecane (HD) core using Gum arabic and SDS as emulsifier by internal phase separation method. The resulted showed that the shell thickness was easily adjusted by varying the ratio of shell to core and the mechanisms of weight loss are completely different in dissimilar environment. Tahuchi et al. [81] prepared microcapsules with n-pentadecane as the core material and MMA as the shell material. They indicated that with the increase in the volume of MMA absorbed, the diameters and mechanical strength of microcapsules were increased and the amount of PCM leaking from the microcapsules was decreased with the volume of MMA absorbed. Zhang et al. [82] prepared microcapsules by encapsulated n-tetradecane with polymethyl methacrylate (PMMA), polystyrene (PS) and blend of them by internal phase separation method to form microcapsule of 1- 2μm in size. The results indicated that optimal microcapsules were obtained with a core/shell ratio 3:1 and the heat of fusion of 151 kJ/kg. Sarl et al. [83] also prepared PMMA/Octacosane microcapsules by using a miniemulsion methods and they proved that the microencapsulated Octacosane had good energy storage potential. A series of PUF microcapsules containing epoxy resins were synthesized by Yuan et al. [84]. They indicated that the formation of microcapsules was affected by the surfactant type. The size of microcapsules can be controlled by the surfactant concentration and the surface morphology of microcapsules can be adjusted by the surfactant concentration, the adjusting time for pH and the heating rate. The microcapsules prepared with surfactant sodium dodecylbenzene sulfonate (SDBS) showed good storage stability, excellent solvent resistance and appropriate mechanical strength. Two recent studies carried out by Sarl et al. [85] and Alkan et al. [86] both used emulsion polymerization method to prepare MEPCM. The PMMA/Heptadecane microcapsules and the PMMA/eicosane microcapsules were fabricated, respectively. The microcapsules prepared by both studies have good energy storage potential.

2.3. Applications of MEPCM

2.3.1. Textile applications

Application of microencapsulated phase change materials in the textile industries had been developed and continued to grow particularly in the Western Europe, Japan and North America [87]. Many studies had been done on MEPCM textile materials. Fig. 9 showed an example of MEPCM technology in textile fibres [87].

Giraud et al. [88] developed a new concept of phosphate encapsulated by polyurethane (PU) shell in flame retarded coated cotton to resist heat and flame. Giraud et al. [89] investigated two types of microcapsules with polyether-polyurethane shell and polyester-polyurethane shell respectively to resist heat and flame. They indicated that both types of microcapsules in the polyurea coatings on cotton fabric gave an efficient flame retardant and coatings containing microcapsules with polyester-polyurethane shells evolve the smallest quantity of smoke and CO. Kim and Cho [90] investigated thermostatic fabrics using a 100 % polyester fabric treated with octadecane-containing microcapsules. The treated fabrics were quite promising in terms of its thermal storage/release, durability, and temperature sensing properties. Kim and Kim [77] indicated that the heat of fusion of waterborne polyurethane (WBPU) /octadecane-coated nylon fabrics were much higher than those of the control nylon fabric and WBPU-coated nylon fabrics; and the nylon fabrics coated with WBPU/octadecane blends have cooler touch sensation compared with nylon fabrics and WBPU-coated nylon fabrics. Shin et al [30] fabricated M/F microcapsules with eicosane for textile application. The microcapsules had high latent heat and the treated fabrics retained 40 % of their heat storage capacity after five launderings. They also suggested that microcapsules with higher core/shell ratios needed to be made to improve the thermo-regulating efficiency of fabrics. Shin et al. [31] evaluated the MEPCM treated fabrics and found out that a treated fabric with 22.9 % add on was capable of absorbing 4.44 kJ/kg heat with a melting process; the air permeability and moisture vapour permeability decreased by 28 and 20 %, respectively. Thermo-regulated shell/core composite fibres containing 4-24 % of microencapsulated n-octadecane were investigated [91]. The results indicated that the enthalpy of the fibres was approximately 11 kJ/kg and the fibres also presented acceptable mechanical strength; as the content of MEPCM was not exceed 20 wt %,

which could be used for fabric materials production. Sarier and Onder [18] used four types of polyurea-formaldehyde microcapsules containing different waxes for the design of thermally enhanced fabrics. They demonstrated that a combination of microcapsule containing different types of PCMs were better than those including a mixture of them. Onder et al. [70] investigated three different microcapsule in terms of their thermal properties, durability when integrated into woven fabrics. *N*-hexadecane, *n*-octadecane, *n*-nonadecane were used as PCMs due to their desire melting point for fabrics materials production. The experiments results showed that the energy absorption capacities of the treated fabrics were found to be 2.5-4.5 times enhanced to the reference fabrics for particular temperature intervals.

2.3.2. Building Applications

Phase change materials had been used in buildings to enhance the thermal comfort of lightweight buildings for energy savings [92] [93] [94] [95]. However, there were some limitations in using PCMs in building materials. Firstly, PCMs may interact with the building structure and change the properties of the building materials; secondly, leakage of PCMs could be a problem over the life time of the structure; thirdly, PCMs had poor heat transfer coefficients in the solid state. In order to overcome these problems, microencapsulated phase change materials (MEPCM) had been integrated into convectional building materials. This technology solved the above problems, and heat transfer rate raised significantly due to a much larger heat exchange surface was offered by microcapsules. A comprehensive review of MEPCM in building applications had been carried out by Tyagi et al [96]. Fig. 10 showed PCMs microcapsules integrated into plaster and Fig. 11 showed these microcapsules in gypsum plaster [97]. Since MEPCM technology was introduced, it attracted more attentions and there were many studies related to its application in buildings had been carried out by researchers. MEPCM was the most common application in building materials.

Su et al .[98] prepared a double-M/F shell MEPCM with the melting point of 24 ^{o}C and the heat of fusion of 225.5 kJ/kg for building application. They concluded that the double shell microcapsules were better than single shell ones in terms of avoiding penetration, and the average diameter of 5 μm were better than 1 μm. Mass ratio of

core and shell was 3:1 to ensure that the MEPCM had good thermal energy storage. The microcapsules did not crack at a pressure of 1.1 *10^5 Pa. Schossig et al. [97] carried out both simulation and experiments to investigate the application of MEPCM in building materials for a period of 5 years. The results showed that the simulation results were validated by the experiments and proved that microencapsulation made it possible to integrate PCM into convectional building materials. Lee et al. [99] integrated MEPCM into gypsum wallboards and olefin film for building materials. The latent heat of MEPCM samples is 210 kJ/kg (23 ^{o}C), 200 kJ/kg (24 ^{o}C) and 150 kJ/kg (28 ^{o}C), respectively. The melting points of these samples were all within the thermal comfort zone of the building. The results indicated that thermal conductivity of the gypsum wallboard without PCM was 0.144 W/m·K, but for the PCM gypsum wallboard was between 0.128 W/m·K and 0.163 W/m·K. With the thickness of PCM olefin film increases, the heat storage inside chamber increases. Cabeza et al. [100] conducted an experiments comparing two small house sized concrete cubicles with one integrated MEPCM and one without MEPCM for 6 months in Spain. The phase change material used with a melting point of 26 ^{o}C and the heat of fusion of 110 kJ/kg. The results demonstrated a real opportunity in energy savings for buildings with MEPCM in concrete walls. Castellón et al. [101] made the experiment further with adding a trombe wall in autumn for winter functioning based on their previous studies. The experiment was conducted for a year. They demonstrated that the temperature difference was up to 4 ^{o}C between two cubicles and peak temperatures in the PCM cubicle were shifted to 2 hours later. Kuznik and Virgone [102] investigated the thermal performances of a PCM copolymer composite wallboard (60 % microencapsulated paraffin) in a full scale test room. The experiments were conducted in three different climates: a summer day, a winter day, and a mid season day. The results indicated that for the three cases, the PCM wallboard reduced the air temperature up to 4.2 ^{o}C of the room compared with regular wallboards, and the PCM wallboards enhanced the natural convection in the room and then there was no thermal stratification contrary to the room without composite. Sarier and Onder [103] integrated MEPCM into polyurethane (PU) foams at different ratios for thermal insulation materials. They demonstrated that polyurethane composite foams could be used for energy savings. You et al. [104] indicated that qualified MicroPCMs/PU foams could not be fabricated when the content of MEPCM is higher than 12.59 wt.% (with enthalpy above 12 kJ/kg) and the addition of MEPCM had no significant

influence to the thermal stability of PU foam. You et al. [60] improved MicroPCMs/PU foams and the enthalpy was about 24 kJ/kg for the foam containing 26.8 wt.% MEPCM.

3. Microencapsulated phase change material slurry (MPCS)

When the MPCM is dispersed into the carrier fluid, e.g. water, a kind of suspension named as microencapsulated phase change material slurry (MPCS) is formed [13]. Shown in Fig. 12 are appearance of the MPCM slurry and SEM image of the MPCM particles [105]. During the fabrication process, an appropriate amount of surfactants are normally used for helping MPCM well disperse into the carrier fluid and increase the lifetime of MPCS. Water is normally used as the carrier fluid due to it has no obvious negative effect on fabricating MPCS and is cheap to get, although the carrier fluid should have high thermal conductivity and large specific heat capacity. In comparison of conventional phase change material slurries (PCS), better heat transfer performance can be achieved due to the relatively large surface area to volume of MPCM. Therefore, MPCS can be used as both thermal energy storage and heat transfer media.

3.1. Thermal and physical properties of MPCS

The thermal and physical properties of MPCS are crucial for the MPCS system design, and they are very different from those the MEPCM materials and carrier fluids. These mainly include the thermal conductivity, viscosity and specific heat. In the following paragraphs, this will be described and discussed in both experimental and theoretical studies by many previous researchers.

After Einstein [[106]cited [107]] published an analysis for the viscosity of dilute suspensions in 1905, one of the most challenging rheological problems has been the development of theoretical or empirical expressions for the viscosity of concentrated suspensions. A key early research activity of concentrated suspensions was carried out by Thomas [107] , he proposed a critical analysis on the extensive experimental data on the relative viscosity of suspensions of uniform spherical particles, with more concentrated suspensions, it was necessary to account for the hydrodynamic interaction of particles, particle rotation, collision between particles, mutual exclusion

of particles, doublet and higher order agglomerate formation, and ultimately mechanical interference between particles as packed bed concentrations are approached. This study provided evidence that concentrated suspensions were complex. Fig. 13 shows a spread of from about ± 20 % at = 0.20 to about ± 75 % at = 0.5 [107]. These data were obtained with both rotational and capillary viscometers and represent a range of particle diameters from 0.099 to 435 microns.

Phase change material slurry (PCS) has been investigated by many previous studies. The use of phase change material slurry in a district cooling system was carried out in order to increase the heat transfer performance of the system [108], [109]. Choi et al. [108] tried to use a small amount of emulsifier to fabricate PCS, and these caused remarkable effects on the production of fine PCM particles and successfully avoid the clogging of the piping system. They concluded that the critical value for the case of a 25/75 % mixture of hexadecane in water was found to be 680 ppm. Tetradecane and hexadecane binary mixtures with different concentration were used to make PCS, and thermal properties include freezing point, the heat of fusion, thermal stability and volume expansion during the phase change process were investigated and the results showed that these materials were attractive candidates as potential PCMs for cool storage in district cooling system [109].

The cold heat-release experiment of the emulsion, including the phase-change material (Tetradecane-latent heat 229 kJ/kg, melting point 278.9 K) as the dispersion medium, has been carried out by the hot air-emulsion direct contact heat exchange method [110]. The temperature effectiveness, the sensible heat release time and the latent heat release time were measured as experimental parameters. Roy and Sengupta [111] used n-Eicosane and stearic acid as phase change material for encapsulation of microcapsules for PCS, the microcapsules were manufactured with two different wall thickness (15 % and 30 % of the total microcapsule volume); the results showed that the microcapsules with thinner walls were unable to withstand repeated thermal cycling past the melting point. However, the microcapsules with thicker walls were found to be both structurally as well as thermally stable. Therefore, it can be concluded that microcapsules with thicker walls can be used in practical heat transfer media. Table 2 showed microcapsule sizing results before and after thermal cycling [111]. Inaba [112] reviewed some previous researchers on thermal energy

transportation using thermal fluid, which is a mixture of heat transfer medium like water and other material with or without phase change , he concluded that utilization of some functionally thermal fluids offered attractive opportunities for advance thermal energy transportation and heat exchanger systems.

Lu and Bai [113] developed a thermodynamic derivative method to calculate the specific heat at a constant pressure in the latent functional fluid with microencapsulated phase change materials, they concluded that on the basis of the theorem of thermodynamics and two-phase flows, the relation between the specific heat of the mixture and every phase, and the latent heat, the volume fraction, the mass fraction of every phase, and other thermo-physical parameters was theoretically analysed by this method. Yang et al. [114] studied thermal physical property of MPCS using tetradecane as phase change material and poly vinyl acetate (PVAc), polystyrene (PS), polymethyl methacrylate (PMMA) and polyethyl methacrylate (PEMA) as shell materials. Thermo-physical properties, such as the heat of fusion, viscosity, diameter and its distribution of microcapsule and emulsion were investigated and the relationship between the concentration of tetradecane and physical properties have been discussed in detail. See table 3 and 4 for detail [114]. Microencapsulated paraffin in phase change slurries can be used as heat transfer fluids [115], a test system was built to investigate thermal cycling of different MPCS while MPCS was pumped through heat exchanger, including the stability of microcapsules, thermal behaviour of MPCS.

Microencapsulated phase change material with a double-layered shell was prepared using melamine resin as the shell material and *n*-Docosane as the core material for enhancing fluid flow heat transfer [35]. Some important parameters like the size of the MEPCM, the core mass fraction in the MEPCM, and the thermal properties of the prepared MEPCM have been measured and analysed. The results showed that to obtain a MEPCM particle size of 10 μm, the corresponding emulsification-stirring rate was 6000 rmp; to get a better microencapsulation efficiency of the core material in the preparation experiment, the core mass fraction in a single MEPCM particle was lower than 70 %; DSC thermal analysis showed that the prepared MEPCM with a core mass fraction of 60 % had a high thermal storage capability of 150 kJ/kg. The thermal stability of the MEPCM behaved well over the temperature range of 0 °C to

180 °C. Thermal and physical performance of microencapsulated phase change material slurry was studied by Alvarado et al. [116], they used *n*-tetradecane as phase change material. Differential scanning calorimetry (DSC) was used to determine the thermal properties; durability of MPCM was measured by continuous pumping, see table 5 [116]; a Brook-field viscometer was used to measure the viscosity of the MPCS, see Fig. 14 [116].

3.2. Flow and heat transfer characteristics of MPCS

3.2.1. Natural convection heat transfer

Datta et al. [117]studied natural convection heat transfer in a cubical enclosure heated from below with MPCS. MPCS was made of Eicosane and a mineral oil. The data showed that up to 80 % heat transfer enhancements could be obtained with concentrations as low as 1 %. However, for increasing in the concentration above 5 %, the heat transfer steadily decreased below that of the pure fluid case due to particle clumping resulting in larger difference between the diffusive and convective time scales. "Rayleigh number", "Stefan number" and the volumetric particle concentration were dominating parameters. Inaba et al. [118] presented a numerical study in natural convection heat transfer enhancement of MPCS in enclosures on considering that fluids have a continuous variation in density and enthalpy with temperature. The results showed that the heat transfer enhancement was closely related to the specific heat capacities at the temperatures of bottom heating and top cooling plates, the maximum enhancement in heat transfer could be up to 30 % compare to those fluids without PCM. The results also indicated that "Rayleigh number", "Prandtl number" and aspect ratio could be the main parameters for evaluating a natural convection in enclosures for most of Newtonian and non-Newtonian fluids. Inaba et al. [119] also carried out an experimental study in natural convection heat transfer characteristics of PCM slurry in rectangular enclosures. The PCM mass concentration of the MPCS was varied from a maximum 30 mass % to a diluted minimum 5 mass %, and the experiments have been done in a solid phase, two phases (coexistence of solid and liquid) and a liquid phase. The results showed that the "Nusselt number" increased slightly with the PCM mass concentration for the slurry in solid phase. In the phase change temperature range, the "Nusselt number" increased with an increase in PCM mass concentration of the slurry at low "Rayleigh

numbers", while it decreased with increasing PCM mass concentration of the slurry at high Rayleigh numbers. There was not much difference in natural heat transfer characteristics of the PCM slurry with low PCM concentrations (<10 mass %), however, the difference was getting greater with increasing the PCM concentration, especially for the enclosure at a lower aspect ratio (width/height of the rectangular enclosure). Based on the previous studies, Inaba et al. [120] made the experimental study further and concluded that evaluation for natural convection became much more complicated, and can't be completely relied on the "Rayleigh number", the "Prandtl number, the "Nusselt number" should also be taken into account and a modified "Stefan number" was introduced as well.

Two recent experimental studied have been conducted by Diaconu et al. [121] and Diaconu et al. [122] to investigate the natural convection heat transfer in a MPCS. A novel microencapsulated PCM slurry at high concentration (45 % w/w) was used. The experiments were carried out in a vertical helically coiled tube. They first tested water in order to obtain natural convection heat transfer correlations and then a comparison was made with the results obtained from MPCS. The results indicated that inside the phase change interval the value of the heat transfer coefficient for the MPCS were significantly higher than water, which could go up to five times depending on temperature conditions, as shown in Fig. 15, for h_{mpcs} *vs* h_{water} correlation [122] .

3.2.2. Forced convection heat transfer

Forced convection heat transfer enhancement in MPCS through a circular tube attracted quite a lot of attentions because of its fundamental importance. Investigations have been carried out in both theoretical analysis and experimental analysis since early 1990, and these previous studies would be summarized and discussed in the following paragraphs.

Charunyakorn et al. [123] developed the governing equations for forced convection heat transfer of MPCS, heat generation, the enhancement of thermal conductivity due to the particle interactions were considered. In addition, dimensionless parameters like the bulk "Stefan number" (which is the ratio of sensible heat capacity of the suspension to its latent heat capacity), the particle concentration, a modified "Peclet number", the particle-to-tube radius ratio and the conductivity ratio were all taken into

account. The results showed that the bulk "Stefan number" and the concentration were the most important dominant parameters, and the variation of the particle size was not critical to the thermal performance of the MPCS. An experiment study by Goel et al. [124] was conducted and it was using a suspension of *n*-eicosane microcapsules to evaluate the laminar forced convection heat transfer of MPCS. The results showed that the primary parameters in the study were the bulk "Stefan number" and the volumetric concentration, which were similar to the study of Charunyakorn et al. [123]. However, they indicated that the volumetric concentration did not have a significant effect directly on the heat transfer but has an indirect effect. The experiment results also found out that the use of phase change material suspensions could reduce the rise in wall temperature by up to 50 % as compared to a single phase fluid for the same non-dimensional parameters and an increase in particle diameter by a factor of 2.5 was found to further reduce wall temperature rise by 15 %. Zhang and Faghri [125] developed a numerical model of laminar forced convection heat transfer of a MPCS in a circular tube with constant heat flux, and they found that after considering the effect of the microcapsule's crust and initial sub-cooling, the difference between their numerical results and the experimental results were reduced from 45 % in Goel (et al., 1994)'s study to 34 % [124]. The results also showed that the effect of MPCM on the forced convective heat transfer in a tube could be significantly reduced by increasing the width of phase change temperature range. They urged to determine the width of phase change temperature range by further experiment work.

Eunsoo et al. [126] carried out experiments to investigate the increase in the convective heat transfer coefficient as well as the increase in the thermal capacity of phase change slurry. They found out that the advantages of a three-region melting model, which was proposed to estimate the bulk mean temperature of a mixture fine PCM particles and water, and to analyse experimental data for a two phase liquid-solid mixture. Roy and Avanic [127] conducted an experiment to investigate laminar convection heat transfer in circular duct with a phase change material slurry (*n*-octadecane in water), the results showed that the heat transfer characteristics for phase change material emulsions were similar to those of microencapsulated phase change material suspensions, thus confirming that the microcapsule crust did not affect the heat transfer process significantly, see Fig. 16 [[115] cited [127]]. The results also

showed that the overall heat transfer characteristics did not change significantly even at higher concentrations and the experiments also proved that the "Reynolds number" was not an independent parameter for the heat transfer process as predicted previously. Brown et al. [128] investigated MPCS as heat transfer media in gas-fluidized beds. The results showed that microcapsules with shells of gelatin and cores of octadecane proved most satisfactory in this study. Heat transfer enhancements of 30 % were found although enhancement of at least 85 % was expected based on the effective specific heat of the microcapsules due to the thermal resistance from shell and core materials. They also indicated that smaller microcapsules of phase change material might demonstrate better enhancements. Yamagishi et al. [129] conducted a quite detailed experiments of the MPCS with octadecane as the core materials. The size of MEPCM particles were 2-10 microns. Pressure drop and local connective heat transfer coefficient of the slurry in a circular tube with uniform heat flux were measured. The particle volume fractions in the MPCS were varied up to 0.3. The results showed that when particle volume fractions increased the slurry flow structure changed from turbulent to laminar, and the pressure-drop reduction of the slurry flow relative to a single phase water flow was under the same flow rate conditions. In the case of turbulent flow, the local heat transfer coefficient increased when MEPCM melted; in case of laminar flow, the heat transfer performance was found to degrade compared with that of turbulent flow.

Roy and Avanic [130] developed a model to study forced convection heat transfer of PCS in circular ducts. They found that the specific heat function was not critical as long as the latent heat is incorporated correctly within the melting temperature range. The bulk "Stefan number", the degree of sub-cooling, and the dimensionless melting temperature ranger were dominant parameters and the effect if the specific heat ratio was very small. Hu and Zhang [131] presented a novel model for forced convective heat transfer enhancement of MPCS through a circular tube with constant heat flux . They found that the conventional "Nusselt number" correlations for internal flow of single phase fluids were not suitable for the heat transfer enhancement with MPCS. In addition, their numerical analysis were reasonably agreed with experimental data reported in Goel et al [124], "Stefan Number" and volumetric concentration of MPCS were the most important parameters influencing the heat transfer enhancement of MPCS. Zhang et al. [132] also carried out a theoretical analysis of convective heat

transfer enhancement of MPCS in a circular tube with constant heat flux, a improved "Nusselt number" was proposed to describe internal flow; the heat transfer could be enhanced by phase change; the effective thermal conductivity of the slurry influence the heat transfer enhancement by changing the slurry temperature distribution; the heat transfer enhancement in the thermally fully developed region was much greater than in the thermal entry region. Bai and Lu [133] proposed a new numerical model of laminar forced convection heat transfer in MPCS by combing the finite difference method (FDM) with the dual reciprocity boundary element method (DRBEM). The model could describe the physical process of the problem, including the heat transfer process between the working fluid and the microcapsules and the enhanced heat transfer process between the mixed fluid and the wall in the tube. The results showed that microencapsulated PCM suspensions could effectively control the wall temperature of the tube. Improvements on enhanced heat transfer capability of the latent functionally thermal fluid can be further achieved by properly augmenting the microcapsule's radius, enhancing the volume fraction of the microcapsules, and either decreasing the Stefan number or increasing the Reynolds number. The numerical results were similar to the experimental data by Goel [124]. Ho et al. [134] considered effects of wall conduction in heat transfer of MPCS in circular tubes, and they used a numerical analysis via finite-volume approach. The results showed that the conduction heat transfer propagating the tube wall resulted in significant preheating of the slurry in the non-directly heated region upstream of the heated region, where melting of the particle might occur and therefore the contribution of the latent heat transfer to convection heat dissipation over the heated region was markedly decreased. Heat transfer enhancement were influenced by various sets of the relevant dimensionless parameters, including the particle volume concentration, the modified "Stefan number", the "Peclet number" of MPCS, the wall thickness ratio, and the wall to fluid thermal conductivity ratio.

The heat transfer enhancement of the plural MPCS has been investigated experimentally under the flow conditions of both laminar and turbulent flow in a circular tube with constant wall heat flux [135]. The heat transfer coefficient of MPCS was increased by both effects of latent heat in phase change process and convection around particles with different diameters. The results also showed that the average heat transfer coefficient of MPCS was about 2-2.8 times greater than that of a single

phase of water. Wang et al. [136] proposed a turbulent heat transfer model to analyse the turbulent heat transfer enhancement of MPCS, and this model was based on the effective specific heat model. This study was a further research on Roy and Avanic [130], which they found the bulk "Stefan number", the non-dimensional melt temperature range and the degree of sub-cooling were the three parameters of importance. The results showed that the "Stefan number" was the most important parameter. The turbulent heat transfer enhancement degree increased with decreasing "Ste" and dimensionless initial sub-cooling degree & dimensionless phase change temperature range.

Zhao and Shi [137] carried out an experimental investigations of flow resistance and convection heat transfer for MPCS in a coiled double circular tube heat exchanger. This experiment was design for predicting performances of a cold storage system. The results indicated that the emulsion had a typical non-Newtonian characteristic, and its viscosity was higher than water when the emulsion concentration was higher. The exponential function between the additional pressure loss coefficient ψ and the modified Dean number *De*', as well as the functional relationship between the Nusselt number Nu_e and the modified Dean number *De*', as shown in Fig. 17 and 18 for details [137]. The pressure drop of the emulsion in a coiled circular tube was quite a lot higher than water when the emulsion concentration was reasonably higher. The emulsion Nusselt number Nu_e in the coiled tube was notably higher than water and the amount by which it was raised increases with emulsion concentration. For a given higher total concentration, the convection heat transfer in the solid dispersed phase was higher than that in the liquid dispersed phase. As latent heat storage material, the emulsion had 50–160 % larger cold storage capacity than the sensible heat storage capacity of water. Base on their previous experimental investigation, Zhao et al. [138] carried out a parametric analysis of enhanced heat transfer for laminar flow of MPCS in a circular tube with constant wall temperature. Two enhancement ratios, the traditional enhancement ratio and a modified enhancement ratio, were used to quantify the enhanced heat transfer characteristics of the microencapsulated phase change suspension for six major parameters. The six parameters were the bulk "Stephan number", the volumetric concentration of the solid-phase, the particle-to-tube radius ratio, the dimensionless initial sub-cooling, the dimensionless phase change temperature range, and the bulk "Reynolds number". The simulations showed

that the bulk Stephan number and the volumetric concentration were the most important parameters influencing the heat transfer enhancement of the microencapsulated suspension. These all agreed well with previous numerical studies by Charunyakorn et al. [123], Hu and Zhang [131], Zhang el al. [132], Wang et al. [136], Ho et al. [134], and also agree well with some previous experimental research by Geol et al. [124], Roy and Avanic [127].

A series of experimental investigations have been carried out to study the flow and convective heat transfer behaviours of MPCS by using microencapsulated 1-bromohexadecane ($C_{16}H_{33}Br$) as phase change material [139], [140], [141], [142]. Wang et al. [139] developed a new laminar correlation equation from appropriate dimensionless group used in the convectional laminar convective correlations that could satisfactorily predict the local heat transfer data within the error of $\pm$ 15 %. Wang et al. [140] proposed two new heat transfer correlations for predicting the heat transfer behaviours of MPCS (Table 6 showed Physical Properties of MPCM Slurry and its Components [140]), one used for the slurry under laminar condition ($0<Re<2000$) and another used for the slurry under slightly turbulent condition ($2200<Re<3500$); they also developed a new heat transfer correlation using dimensionless groups for both laminar and turbulent flow, which predicted the average heat transfer data within an error of $\pm$ 10 %. Chen et al. [141] used a new expression of "Stefan number", according to the physical definition of Stefan number. The heat transfer enhancement ratio was larger as the mass fraction of MPCM was higher. Zeng et al. [142] carried out both numerical an experimental investigation to study the convective heat transfer of MPCS, three kinds of fluid–pure water, micro-particle slurry and MPCMS were numerically investigated by an enthalpy model. The numerical analysis was agreed well with the present experimental data. The result showed that in the phase change heat transfer region the "Stefan number" and the Mr number (dimensionless phase change temperature range) were the most important parameters influencing the "Nusselt number" fluctuation profile and the dimensionless wall temperature. Re_b (Reynolds number of slurry), d_p (particle diameter) and c (volumetric concentration of slurry) also influence the "Nusselt number" profile and the dimensionless wall temperature, but they were independent of phase change process.

3.3. Application of MPCS in thermal systems

The applications of MPCS to the thermal systems are mainly in the thermal energy storage and transportation system, and in the thermal controlling aspects. The most common example is the secondary loop for refrigeration and air conditioning.

Mulligan et al. [143]applied MPCS for heat transfer in spacecraft and thermal systems. The results showed that MPCS reduced system temperatures and to increase effective specific heats and heat transfer coefficients. Coolant flow rate and temperature, heat exchanger design factors, and the MPCS flow rate were important factors in thermal performance of such a loop system.

Griffiths and Eames [144] used MPCS with melting temperature around18 °C in a test chamber containing a chilled ceiling. The results showed that a concentration of 40 % MPCS could be used as the heat transfer fluid in a chilled ceiling application from over four months continuous testing. The slower fluid rate and smaller volume flows should be concerned in the experiment. Wang et al. [105] proposed a low energy air conditioning strategy using a combination of evaporative cooling technologies and MPCS into cooled ceiling system. The MPCM particles consisted of $C_{16}H_{34}$ (with melting temperature of 18.1 °C) as the core material and amino plastics as the shell material. The results showed that the new system offered energy saving potential up to 80% under northern Chinese climate and up 10 % under southern Chinese climate. Wang and Niu [145] took the study further and proposed a new design of air conditioning system which was a combination of cooled ceiling and a MPCM slurry storage tank under Hong Kong climate condition. The hexadecane ($C_{16}H_{34}$) which has a melting temperature of 18.0 °C and latent heat of 224 kJ/kg with thin film shells was chosen as PCM in this study. A mathematical model of the combined system was prepared. The results indicated that a small MPCM slurry storage tank was able to shift the part of cooling load from the daytime to nigh-time and proposed combined system was an energy saving and economy favourable air conditioning system. This system could be used to assess the performance of the MPCM slurry storage system under different climate conditions and help size the storage tank. Diaconu et al. [122] used a commercial PCM (product of CIBA Chemicals—UK) with mass fraction 45 % as a heat transfer media for air conditioning application. The results showed that such

a system was an alternative to high temperature energy storage ensuring the cooling demand during intervals when energy supply was not available.

Choi and Cho [146] investigated the effect of a commercial paraffin with melting temperature of 43.6 °C on heat transfer enhancement in a multichip application. The results showed that the paraffin slurry with a mass fraction of 5 % showed the most efficient cooling performance when the heat transfer and the pressure drop in the test section was considered simultaneously. Hao and Tao [147] carried out a numerical simulation of the laminar heat transfer enhancement of MPCS in a micro-channel with constant heat flux. They proved that the introduction of PCM particles strongly enhanced the heat transfer in the melting region and also indicated that an optimal design would match the micro-channel geometric parameters, which were MPCS volume fraction, and "Reynolds number" with the desired heat flux. However, the current model could not predict any contribution of MPCS on the heat transfer enhancement in the solid and liquid regions and only in solid-liquid regions. Sabbah et al. [148] made the research further, they developed a 3D, one phase, laminar flow model of a rectangular channel using MPCS. The results showed a significant increase in the heat transfer coefficient under certain conditions for heat flux rates of 100 W/cm^2 and 500 W/cm^2 that was mainly dependant on the channel inlet and outlet temperatures and the selected MEPCM melting temperature. The use of low concentration of MPCS gave better cooling than water at high flow rates. These were agreed well with numerical study by Rao et al. [149]. Rao et al. [149] conducted a comparative experimental study to investigated the convective heat transfer of MPCS flowing through rectangular copper mini-channels. The core material was *n*-octadecane, which had a melting temperature of about 28 °C. They found that the cooling performance of the MPCS strongly depended on the mass flow rate and the MPCS mass concentration. The 5 % slurry always showed a better cooling performance, which were same as Choi and Cho's study [146]. They also concluded that the slurry with higher mass concentration was more effective only at low mass flow rate; in contrast, at higher mass flow rates they showed a less effective cooling performance than water.

4. Conclusions

This review paper is focused on the microencapsulated phase change material. The review is divided into four parts: fabrication and characterization of MEPCM, applications of MEPCM to the textile and building, fundamental properties of MPCS, and application of MPCS to the thermal energy storage system. Available fabrication methods on microencapsulated phase change material (MEPCM) had been introduced, together with MEPCM's characterization. Applications of MEPCM in the textile and building were presented; the results concluded that MEPCM had good potential for thermal energy storage purposes and it could be used for solar space heating as well. Nevertheless, the potential utilization of MEPCM in various thermal control applications is limited to some extent by their cost, which still needs more intensive research. Fundamental properties of MPCS are described from both theoretical and experimental studies in terms of its thermal & physical properties and flow & heat transfer characteristics, and it considered different simulation techniques and experiment set up for MPCS. Finally, the application of MPCS to the thermal energy storage system is also presented and the results are quite promising for its' future utilization in practice. Instability and agglomeration of MPCS still needs further investigations such as how to enhance the contents of materials and reduce particle sizes from micro to nano in the fabrication process.

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