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Production, Characterization and Application of Nano - Phase Change Materials: A Review

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Abstract

Phase Change Materials (PCMs) for heat storage and energy saving has been extensively used in many fields for heating and cooling processes, including building, solar energy, textiles, agriculture, and electronics. PCMs have been getting incredible attention for being low-cost materials and have potential materials for thermal energy storage (TES) with long cycle life. Though, the disadvantages such as flow, result in encapsulation in three scales of Macro, Micro and Nano capsules. Encapsulating PCM reduces the disadvantages and improves the efficiency of PCMs. Different methods for producing PCMs in the scale of nano and core-shell materials, have been developed and the capsules size in relation to parameters such as pH, stirring rate, material selection and preparation method have been investigated. In recent years, this subject has been extensively studied, seeking to find more efficient and safer PCMs. In this context, nanoscale PCMs have been produced and applied to the most diverse products and their performance evaluated. They simply modified and optimized production processes. The novelty of this study lies in the fact that merely a few articles have reviewed nano-encapsulating of PCMs, focusing on new developments on PCM nano-capsules. Moreover, few articles have compared nano and microcapsules of PCMs so far. The analysed papers suggest that the production methods influence the size of the obtained capsules. The purpose of this article is to make an updated review of the synthesis and application of nano-encapsulated PCMs.

Keywords: Nano-capsules, PCM, encapsulation, Thermal regulating.

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1. Introduction

Phase Change Materials (PCMs) are latent heat-storage materials which absorb heat when temperature increases, and the materials change from solid to liquid and desorb heat in the converse situation while changing from liquid to solid [1-3]. Phase change materials are widely utilized in various areas such as building walls such as perforated brick rooms for cooling storage [4], energy-efficient buildings [5], and vehicle cabin roof [6], solar energy utilization [7], enhancement [8], modelling and simulation [9], the effect of honeycomb core on the latent heat storage with PCM in solar air heater [10], drying applications in solar air heaters [11], solar collector system [12], textile such as coatings [13-16], composites [17,18], electrospun fibers [19] and many kinds of smart textile [15,19-21], agriculture [22,23], electronics [24,25].

The first research on this subject was conducted by Telkes and Raymond in 1949 and did not attract much attention [26]. Later in 1967, Messerly analysed the thermodynamic properties at the selected temperature from 0 to 300 k for the C5 to C15 n-paraffin; these thermodynamic properties included heat capacity, entropy, enthalpy-function, and Gibbs energy function [27]. Subsequently, in 1971, Hansen carried out a study in which he concluded that the incorporation of CO2 in hollow fibers can lead to heat-insulating ability when the CO2 solubility is diminished [28]. Vigo and Frost (1982, 1983, 1985) conducted studies in the field of PCMs by incorporating hydrated inorganic salt in hollow fibers, melding polyethylene glycol in polypropylene fibers, and coating PEG on the surface of fabrics [29-31]. At about the same time, Abhat used Differential Scanning Calorimetry techniques to investigate the importance of thermal cycling analysis in the long-term stability of the organic and inorganic storage materials, including paraffin, fatty acids, inorganic salt hydrates, and eutectic compounds [32].

Feldman, Shaprio, and Banu (1986) compared the melting point, freezing point and latent heat of melting and fusion of butyl, vinyl, ethoxylate linear alcohols, and isopropyl considering. They concluded that isopropyl can be utilized as a coolness storage material for desert regions [33]. In 1987, Vigo and Bruno studied wrinkle recovery, water absorbance and thermal storage of PEG- coated fabrics [34]. Bryant and Colvin (1994) utilized leak-resistant microcapsules which were filled with plastic crystals or phase change materials, and applied them to fabric to achieve specific thermal properties. Regarding microcapsules filled with PCMs or plastic crystals, they studied the enhancement of thermal properties at predetermined temperatures [35].

Coated fabrics and non-woven microencapsulated linear chain hydrocarbons were studied by Pause (1998) using an apparatus that simulates skin conditions [21]. Zhang et al. (2004) fabricated nanocapsules and microcapsules which contained n-octadecane with a melamine-formaldehyde shell through in-situ polymerization process. They concluded that with the increase of stirring rate, emulsifier content and cyclohexane content, the diameter of microcapsules decreased [36]. Meng and Hu (2008) investigated structure, crystalline morphology, phase change behaviours, dynamic mechanical properties, and melt-processing ability using thermoplastic polyurethane (PU) as a phase change material [37].

Sánchez et al. (2010) synthesized polystyrene microcapsules containing paraffin wax, and they incorporated them into textiles by coating techniques to impart thermal comfort to the fabrics. They concluded that the coated fabrics have an energy capacity of 7.6 J/g, and it exhibits high durability being suitably fastness to washing [38]. In 2010, Bayes obtained PCM Rubitherm microcapsules through two methods, one of which led to the obtaining of nanocapsules with an average diameter of 104 nm. The microcapsules resulting from both methods showed thermal energy storage capacity [39]. In a study carried out by Zhang (2012), nanocapsules containing PCM n-dodecanol and PMMA were synthesized, the former as core and the latter as shell, by miniemulsion polymerization. The mean diameter of these spherical nanocapsules was reported to be 150 nm, with a maximum value of 98.8 J/g for phase change latent heat, and 82.2% for encapsulation efficiency. They went further to mention that encapsulation of n-dodecanol is enhanced if hexadecane is added into the water phase [40].

Latibari (2013) synthesized PCM nanocapsules containing Palmitic Acid (PA) as core and SiO_2 as shell via the sol-gel method. Based on the results, encapsulated PA obtained a much higher thermal conductivity compared to pure PA. Moreover, the prepared nanocapsules have been reported as having good thermal reliability, acceptable thermal properties, uniform morphology, and chemical stability [41]. Sangphil (2014)

synthesized PCM nanocapsules based on paraffin core and poly-urea shell and prepared magnetic nanoparticle-embedded PCM nanocapsules which enhanced the thermal conductivity of PCM capsules [42].

Organic phase change material based on copolymer nanocomposites was nano-encapsulated through the mini-emulsion in-situ polymerization method, resulting in n-octadecane nanocapsules with an enthalpy of 107.9 J/g for melting and 104.9 J/g for crystallization. It was suggested that the obtained nanocapsules (n-octadecane/St-MMA) can be applied, namely in buildings, due to their potential for thermal energy storage [43]. Wang (2014) studied the effect of the production technology on the particle size distribution and thermal properties of stearic-eicosanoid acid/polymethylmethacrylate nanocapsules [44]. The spherical nanocapsules produced through UV initiated emulsion polymerization process were reported to have the

average diameter of 46 nm and excellent thermal properties and thermal reliability. The latent heat of these nanocapsules were determined as 126.4 J/g at 56.9°C and 128.3 J/g at 54.5°C; Repeated thermal cycles did not cause significant changes in their thermal and chemical properties [44]. Other studies have been carried out on the production and application of nanocapsules in recent years. Among them, are those referring to the application of nanocapsules as core and shell.]. Heat transfer behaviour of nanocapsules and solidification of PCMs investigated by Sheikholeslami (2018, 2019) with numerical simulation method emphasing on shape factor showed increase in heat transfer rate with enhancing shape factor [48-51]

2. Nanocapsules

2.1. Size

Sheikholeslami (2018) reported that shape factors and using nanoparticles enhance thermal behaviour in energy storage systems [48,52], and the size of the PCMs capsules is influenced by the method of production and increases the rate of heat transfer [49]. Table 1 shows nanocapsules with different types of core and shell, size, temperature range, and storage capacity. Based on the data presented, it can be noted that many materials were used to produce PCMs with a wide diameter range.

2.2. Production Method of NanoPCMs

The sol-gel is a low-cost chemical method for generating nanocapsules, namely SiO_2 and TiO_2 shell, which is based on hydrolysis or condensation reactions. Sol-gel techniques involve the development of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). Its greatest advantage over other techniques is that it uses low processing temperatures.

Yuan et al. (2019) developed sol-gel nanocapsules of lauric acid (LA)/SiO_2, and categorized the experiments into three groups according to the different volume ratios used. 1) ammonia-to-TEOS, (2) ethanol-to-TEOS, and (3) water-to-TEOS. Figure 1 shows the Fourier-Transform Infrared Spectroscopy (FTIR) spectra of LA, SiO_2 and the 11 samples analyzed. They found that increasing the ratio of ammonia-to-TEOS and ethanol-to-TEOS, and lowering the water-to-TEOS ratio, makes it possible to achieve nanocapsules of PCM with higher latent heat and better efficiency [75].

Latibari et al. (2013) studied the production of nanocapsules of PCM using the sol-gel method at different pH alkaline conditions (11 to 12). They obtained nanocapsules with 183.7 nm and 722.5 nm at pH = 11 and pH = 12, respectively. The results suggested that increasing pH leads to an increase in size. They prepared nanocapsules with PA (palmitic acid) core and SiO_2 shell by adding sol solution to the PA emulsion under stirring at 500 rpm for 4 hours 57. In another study, Shi et al. (2015) employed the sol-gel method in the production of different forms of nanocapsules by changing the TEOS/MMA ratio used. They reported spherical and homogeneous forms when they used a ratio of 1: 3.5 and 1: 5.75, and heterogeneous and abnormal capsules when they used a ratio of 1:12.5 [61].

Latibari (2015) produced nanocapsules at pH 10, with a minimum diameter of 583.4 nm and a maximum diameter of 946.4 nm, with a variation of 30.36% and 64.76% respectively in the mass ratio. Their durability was also tested during 2500 melting/solidification cycles [68]. Yuan (2018) also employs the sol-gel method to synthesize the stearic acid (SA)/silicon nanocapsules. The first phase of the preparation was SA o/w emulsion in an aqueous solution containing sodium dodecyl sulfate (SDS) as a surfactant, which then forms a soluble

silica sol. Ammonium hydroxide is used as a catalyst and in the final step, the silica sol solution was added dropwise in the o/w emulsion, as illustrated in Figure 2 [55].

In-situ polymerization is a method applied to the surface of core materials following chemical modification or monomer / prepared polymer absorption. Cross-linkers form a network-based shell that encapsulate the core to form nanogels via polymerization method.

In-situ polymerization techniques are suitable methods to produce nanocapsules of PCM. This approach implies that the cross-linkers are involved to form a shell that encapsulates the core material. Swelling and viscosity should be controlled as they affect the properties of nanogels. In this article, we review some examples of nanocapsulation via *in-situ* polymerization processes.

Table 1. Nanocapsules with various size and composition

Core	Shell	Size	Temp.	Storage capacity(J/g)	Ref.
***n*-Tetradecane**	urea and formaldehyde	about 100 nm	9.01	134.16	[53]
Paraffin	Polyurea	400-600 nm	56.54	101.1	[42]
Lauric acid	SiO_2	340 nm	39.8	165.6	[54]
Stearic acid	SiO_2	62, 158, 259 and 464 nm	60.4	169.4	[55]
Paraffin	SiO_2	250–400 nm 550–700 nm	49.74	156	[56]
Stearic acid	TiO_2	317.6, 583.4-946.4 nm	54.35	50–109	[57]
***n*-dodecanol**	polymethyl methacrylate	150 nm	18.2	98.8	[40]
Stearic acid	polymethyl methacrylate	98 nm	56.33	155.6	[58]
Paraffin	SiO_2	200–700 nm	56–58	13	[59]
Stearic acid	SiO_2	20–80 nm	68–70	46	[59]
Eicosane	urea-formaldehyde	150 nm	29	109.37	[60]
Paraffin	PMMA and SiO_2	120 nm	26.8	71	[61]
***n*-Octadecane**	St (styrene) – MMA (methylmethacrylate)	63 -129 nm	29.5	107.9	[43]
Rubitherm® RT 27*	Sterilized Gelatine/Arabic Gum	104 nm	25–28	184	[39]
***n*-Octadecane**	Silver	274 nm	28.51	120.60	[62]
Palmitic acid	SiO_2	183.7, 466.4 and 722.5 nm	61.06	168.16	[41]
Oleic acid-Polyethylene glycol eutectic	SiO_2/SnO_2	530 and 610 nm	3.11	58.79	[63]
***n*-Octadecane**	Silica	169–563 nm	27.35	109.5	[64]
***n*-Alkanes (C*n*H2*n*+2)**	poly(styrene-co-ethylacrylate)	50–200 nm	3.97	182.68	[65]
Butyl palmitate	polystyrene-*co*-methyl methacrylate	0–150 nm	21.1	116.6	[66]
***n*-Octadecane**	polystyrene	124 nm	About 31	124.4	[67]
***n*-Octadecane**	organosilica	200–693 nm	27.92	107.5	[68]
***n*-Nonadecane**	poly (methyl methacrylate)	1–1000 nm	31.23	139.20	[45]
***n*-Octadecane**	SiO_2	4.2 nm	-	-	[69]
***n*-Tetradecane**	Polystyrene	120 nm	4.04	98.71	[70]
***n*-Tetracosane and n-octadecane**	Polystyrene	0.01–115 μm	25.96	156.39	[46]
***n*-Dotriacontane**	polystyrene	168.2 nm	70.9	174.8	[71]

R80**	styrene–butyl acrylate	52-112 nm	1–7	5–25	[72]
Paraffin	SiO_2	100 nm	27.53	112.8	[73]
Paraffin	SiO_2/expanded graphite	100 nm	27.72	104.4	[73]
Paraffin	melamine-urea-formaldehyde	340 to 455 nm	27.0	79.8	[74]

* DNS-86, Industrial grade, Qingxin Hanerchem Chemical Technology Limited Company. ** Agar-agar/Arabic gum, Gelatine/Arabic gum, Sterilized Gelatine/Arabic gum .*** Poly (ethylene glycol) mono octyl phenyl ether

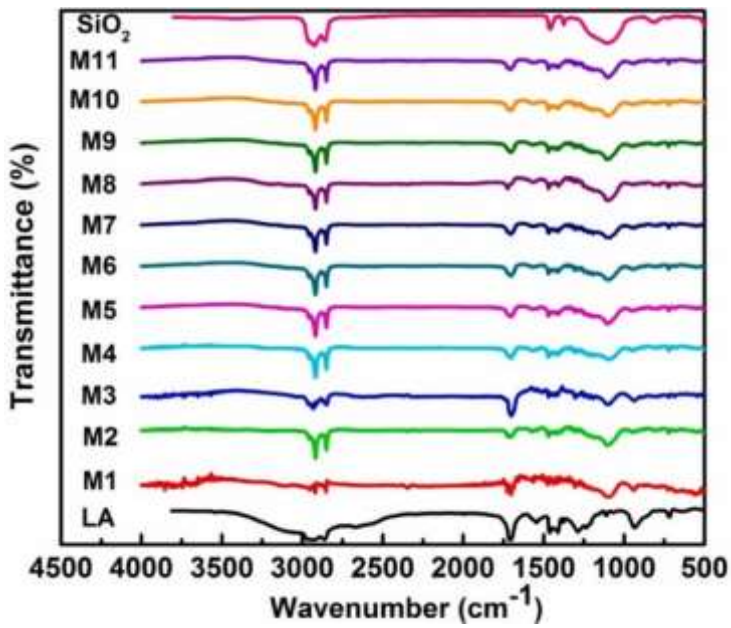

Fig. 1. FT-IR spectra of the LA, SiO_2, and as-prepared NEPCMs: M1–M1175.

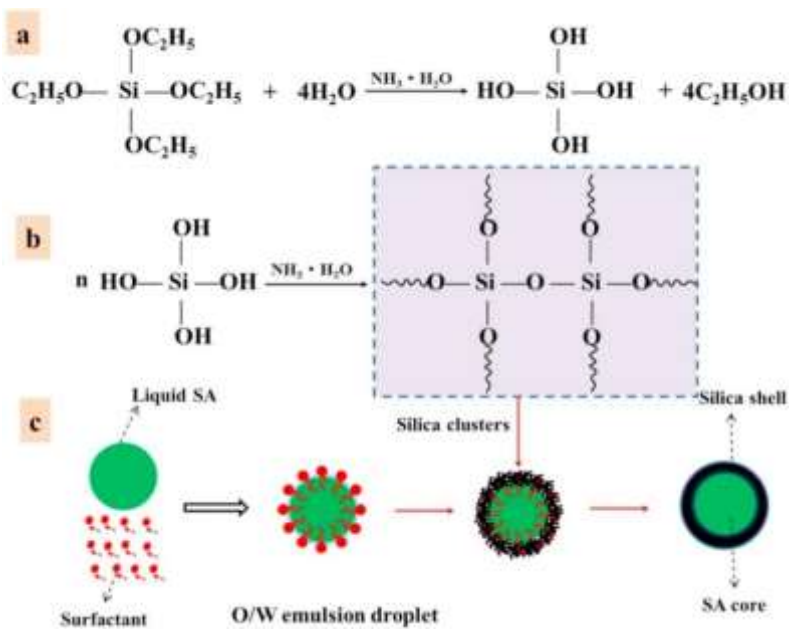

Fig. 2. Schematic formation of the SA/SiO_2 nanocapsules by sol-gel process: (a) hydrolysis of TEOS with

ammonia used as the catalyst, (b) condensation of the hydrolysis product, and (c) silica clusters coated in the SA emulsion droplets to form the nanocapsules [55].

Fang (2009) reported that for preparing nanocapsules, pre-polymer solution was added dropwise to o/w emulsion. The o/w emulsion was previously prepared by adding SDS to distilled water with resorcinol and sodium chloride, stirred and heated to 60°C. Then, tetradecane was added and the mixture was emulsified at 60°C for 30 minutes under stirring at 1500 rpm. Fang went further to mention that by adjusting the stirring rate to 200 rpm, and the pH of the mixture to 3–4 with 40% formic acid solution, and controlling the temperature at 60°C, the reaction was continued for 4 hours. Afterwards, nanocapsules were formed, filtered, and washed with distilled water for three times, finally they were dried in a vacuum oven for 2 hours [53].

Table 2. Methods of synthesis of PCMs nanocapsules

Core	Shell	Method	Additive material	Emulsifier	Ref.
***n*-Tetradecane**	Urea and Formaldehyde	*In-situ* Polymerization	-	Sodium dodecyl sulfate	[53]
Paraffin	Polyurea	Interfacial polycondensation	Magnetic Fe_3O_4 nanoparticle	-	[42]
Lauric acid	SiO_2	Sol-gel	-	Sodium dodecyl sulfate	[54]
Stearic acid	SiO_2	Sol-gel	-	Sodium dodecyl sulfate	[55]
Paraffin	SiO_2	Sol-gel	-	-	[56]
Stearic acid	TiO_2	Sol-gel	-	Absolute ethanol	[57]
***n*-Dodecanol**	Polymethyl methacrylate	Mini emulsion polymerization	-	DNS-86* and co-emulsifier hexadecane	[40]
Stearic acid	Polymethyl methacrylate	*Via* a reverse iodine transfer polymerization	CNC (carbon nanocapsules)	-	[58]
Paraffin, Stearic acid	SiO_2	*In-situ* emulsion interfacial hydrolysis and polycondensation technique		Cetyltrimethyl ammonium bromide	[59]
Eicosane	Urea-formaldehyde	Mini-emulsion polymerization	-	-	[60]
Paraffin	PMMA and SiO_2	Sol–gel and self-assembly methods.	-	Sodium dodecyl benzene sulfonate	[61]
***n*-Octadecane**	St (styrene) – MMA (methylmethacrylate)	Mini-emulsion *in-situ* polymerization	-	-	[43]
Rubitherm® RT 27*	Sterilized Gelatine/Arabic Gum	G/AG Method SG/AG Method AA/AG Method**	-	-	[39]
***n*-Octadecane**	Silver	Interfacial co-hydrolysis and condensation of TEOS and MTMS in mini emulsion	-	-	[62]
Palmitic acid	SiO_2	Sol-gel method	-	-	[41]
Oleic acid-polyethylene glycol eutectic	SiO_2/SnO_2	*In-situ*	-	acetyl trimethyl ammonium bromide	[63]
***n*-octadecane**	Silica	Interfacial hydrolysis and polycondensation in miniemulsion	-	Cetyl trimethyl ammonium bromide	[64]
***n*-Alkanes (CnH2n+2)**	poly(styrene-co-ethylacrylate)	Emulsion copolymerization	-	-	[65]
Butyl palmitate	Polystyrene-co-methyl methacrylate	Suspension-like free radical polymerization process with use of hybridized suspension agent	-	-	[66]
***n*-Octadecane**	Polystyrene	Ultrasonic-assistant mini-emulsion *in-situ* polymerization,	-	-	[67]
***n*-Octadecane**	Organosilica	Interfacial co-hydrolysis and co-polycondensation of functional silane precursors in mini emulsion	-	Cetyltrimethylammonium bromide	[68]
***n*-Nonadecane**	Poly (methyl methacrylate)	Emulsion polymerization reaction	-	-	[45]
***n*-Tetradecane**	Polystyrene	Mini-emulsion i*n-situ* polymerization	-	Sodium dodecyl sulfate	[70]

***n*-Tetracosane and n-Octadecane**	Polystyrene	Emulsion polymerization method	-	-	[46]
***n*-Dotriacontane**	Polystyrene	Mini-emulsion polymerization		Sodium dodecyl sulfate OP-10***	[71]
RT80**	Styrene–butyl acrylate	miniemulsion polymerization	-	-	[72]
Paraffin	SiO_2	Sol–gel	Expanded graphite		[73]
Paraffin	melamine-urea-formaldehyde	*In-situ* polymerization	-	-	[74]

He (2008) also prepared mixture "A" by adding {St (10 g), BA (0.2 g), AIBN (0.1 g) and DDM (0.08 g)} to melted n-octadecane (10 g) and mixture "B" obtained by dispersing composite surfactant (SDS/OP-10 = 1/1) in water (120 g) and a combination of them produced a third mixture, which, after sonification, was placed in four flasks equipped with a stirrer and a condenser for five hours and under nitrogen exposure at 60°C of bath temperature to make latex [67].

Table 2 summarizes the conditions in terms of composition of the different methods used in the nanoPCMs production.

2.3. Application of PCMs

Regarding the use of PCMs in the form of capsules, nano or micro particles, numerous articles have been published describing several potential applications or the results of their application in different fields [76-86]. PCM nanoparticles as an additive without encapsulation are used for cases where the releasing or washing stability is not an important issue [25, 90, 97-104]. Macro, micro, or nanoencapsulation of PCM can prevent its release by melting and might lead to an increase in efficiency, durability, and improve thermal conductivity and energy storage properties of the material [87-100].

In this review, the obtained information is divided into two categories. The first one deals with potential suggestions of investigators for the suitable usage of PCM nanocapsules and the other one incorporates the results of applying nanocapsules in different specimens.

2.3.1 Suggested Potential Usage

Sangphil et al. (2014) described PCM nanocapsules produced with paraffin core and polyurethane shells with magnetic nanoparticles Fe3O4 characterized by the adequate temperature of melting and high thermal energy storage to be used in clothing, building, electronics, and biomedical applications [42]. Zhu et al. (2015) produced nanocapsules through a mini-emulsion method, with *n*-octadecane core and shell of organosilica. These PCMs with 200-693 nm have the potential to be used as Latent Functionally Thermal Fluid (LFTF) and polymer/PCM composite materials [68]. Li et al (2014) have produced nanocapsules through a one-pot polymerization method with Hexadecanol core and polystyrene as a shell with a size of about 120 nm. They analyzed PCMs thermal properties by Differential Scanning Calorimetry (DSC) and Thermogravimetry. Their results showed that the synthesized nanocapsules were suitable for the energy industry due to their thermal durability and mechanical properties [101].

According to the research conducted by Latibari et al. the nanocapsules are suitable for energy storage [40,56,57,61,102-104]. Khadiran et al. (2015) nanocapsulated *n*-nonadecane using vinyl copolymer as shell 106, and the results of many experiments showed that nanocapsulated PCMs have good thermal storage properties to be used in buildings, textiles and other areas [40,56,57,61,102-104].

Yuan et al. (2019) have produced different sizes of lauric acid/ eicosane nanocapsules *via* sol-gel method with 165.6 J/g latent heat. After 1200 times repeating the cycle of the melting/cooling, less than a 10% decrease in efficiency was observed. According to them, these nanocapsules can be used in solar energy [75]. He (2018) also synthesized nanocapsules of stearic acid core and silicon dioxide shell with similar properties. These capsules presented little reduction of efficiency after 3,000 cycles repetition of the melting/cooling. Based on this behavior, they were proposed to be used in energy storage of solar thermal systems [106].

The other nanocapsules that could be used in buildings due to their chemical stability and good thermal

reliability were investigated by Tumira[43]. Composed by styrene/MMA (methylmethacrylate), these nonocapsules presented a melting point of 29.5°C and an enthalpy of 107.9 J/g. PCM nanocapsules with *n*-octadecane core and silica shell coated with silver with high thermal conductivity are suitable for cooling systems [62].

Latibari et al. (2013) synthesized nanocapsules with palmitic acid core, and SiO_2 shell via sol-gel method. Three nanocapsule sizes were obtained, 183.7, 466.4 and 722.5 nm, by changing the pH conditions [41]. They presented acceptable thermal properties, good thermal, and chemical stability, uniform morphology and thermal conductivity. These characteristics allow them to be suitable for use in energy storage of slurry systems.

Rezvanpour et al. (2018) have used *n*-eicosane and PMMA nanocapsules, due to their thermal stability below 100°C 108, in textile applications, photovoltaic panels, and in the buildings, Author's name(2014) suggested that PCM produced with *n*-nonadecane and poly methylmethacrylate shell are suitable for thermal conductivity, solar thermal control of the building, and thermal protection of batteries. Nanocapsules produced from polystyrene-tetradecane have a melting point of -3.43°C. Therefore, they were proposed for cooling systems [45].

2.3.2. Usage of PCMs

Heming et al. (2009) applied nanocapsules with a melting point of 37.1 and 33.1°C and enthalpy reported respectively (57.2 J/g) and (57.8 J/g) by pad-dry-cure process on cotton fabrics. Their size was approximately150 nm. The resulted materials showed excellent thermal performance [108].

Ho et al. (2014) utilized encapsulated PCM in a water-based suspension in a natural circulation loop. Nanocapsules with eicosane core and urea-formaldehyde shells with 150 nm have been added to pure water. The results clearly shown that heat transfer has improved [60]. Zhu et al. (2018) have developed nanocapsules for textile applications. However, despite the positive effect on the thermal behavior, the air permeability, capillary, and softness of the materials were affected by the capsule application [109]. Sun et al. (2017) applied PCM nanocapsules to cotton fabric by pad-dry-cure method to achieve more comfort in cold weather. They also used polypropylene monofilaments and calculated the difference in thermal behavior between the fibers with nanocapsules and microcapsules. The results showed greater durability when the nanocapsules were used [110].

Iqbal et al. (2018) developed nanocapsules with a size of about 500 nm using Glauber's salt as a phase change material. They added these PCMs to cotton cloth by pad-dry-cure. They compared this application with another with microcapsules and the results showed that cotton with nanocapsules had better results and greater fastness to washing [112]. Mohammadi et al encapsulated butyl palmitate in polystyrene-co-methyl methacrylate and applied it in a gypsum wall. They achieved good results in terms of thermal storage [66].

3. Conclusion

Phase Change Materials (PCMs) as latent heat-storage materials absorb, store and release heat when temperature increases/decreases, so they can be used as sustainable energy -saving material. In recent years, phase change materials have been gaining tremendous attention for being affordable and capable of storing a large quantity of thermal energy with a large range of temperature distinction for long cycle life. However, the disadvantages such as flow during the phase transition, washing resistance, super-cooling, low thermal conductivity, result in encapsulation. Encapsulating PCM is a way to eliminate the disadvantages and improve the efficiency of PCMs in the case of thermal and physical properties. Due to the increased useful surface of PCMs, reduced reactivity, improved thermal conductivity and heat transfer rate, nanocapsulated PCMs have received great attention. PCM nanocapsules might be used in several contexts such as textile, electronics, building walls and roofs, agriculture, and solar energy with the goal of saving energy. As a confinement method, SiO_2 and TiO_2 are the most commonly used materials as the shell for PCMs encapsulation, and additive materials such as Fe_3O_4 nanoparticle, graphite, and CNC (carbon nanocapsules) are used to achieve conductivity as an extra property of PCMs capsules.

In this review, we have provided a list of methods for producing PCMs with so many nano-size and core-shell materials. Due to the importance of the capsule's size, many parameters such as pH, stirring rate, material selection, and preparation method have been investigated to engage the optimum size and distribution. Research shows that by reducing the size of the capsules, their efficiencies and durability will be higher. The potential of their application has been reviewed in this article. They were proposed to be used in energy storage of solar

thermal systems, buildings, and textiles as the most common usage.

Storage capacity (J/g) of produced nano-PCMs is influenced by core material, shell material, and the size of capsules. Based on the reviewed articles, the sol-gel method is a widespread approach to produce nanoconfined materials, and regarding raw materials, the cost may be different. Controlling the material and process is the most important factor in this method.

By improving the nanocapsulated PCMs in size, thermal energy storage, thermal conductivity and distribution, in the future the usage of this material as a great energy -saving method in several contexts of industrial scale will be increased.

Suggestions for further research

It is suggested that in addition to synthesizing phase change materials and nanocapsules with varying melting temperature and latent heat, other additives are also used to obtain new properties and improve the performance of nanocapsules. As a new idea of PCMs application, it can be suggested that a combination of dyes and nanocapsules of PCMs is appropriate where color and energy savings are important.

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