Chapter 3
A Brief Review on Nano Phase Change Material-Based Polymer Encapsulation for Thermal Energy Storage Systems

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Abstract In recent years, considerable attention has been given to phase change materials (PCMs) that is suggested as a possible medium for thermal energy storage. PCM encapsulation technology is an efficient method of enhancing thermal conductivity and solving problems of corrosion and leakage during a charging process. Moreover, nanoencapsulation of phase change materials with polymer has several benefits as a thermal energy storage media, such as small-scale, high heat transfer efficiency and large specific surface area. However, the lower thermal conductivity (TC) of PCMs hinders the thermal efficiency of the polymer based nano-capsules. This review covers the effect of polymer encapsulation on PCMs while concentrating on providing solutions related to improving the thermal efficiency of system.

Keywords Nano-phase change materials · Polymer encapsulation · Thermal energy storage · Nanotechnology · Heat transfer enhancement

3.1 Introduction

The main factors pushing the world towards the use of renewable energy sources are the continuous increase in carbon emissions and the increase in fuel costs. Direct solar radiations are considered among the most potential source of energy in many parts of the globe. The researcher's community around the globe is looking for renewable and novel energy sources. The storage of energy in suitable forms, which can be converted traditionally into the required form, is a challenge to the technologists of today. Energy storage not only eliminates the difference between demand and supply, but also increases system efficiency and reliability and performs a significant role in energy conservation [1]. The different energy storage techniques are given in Fig. 3.1.

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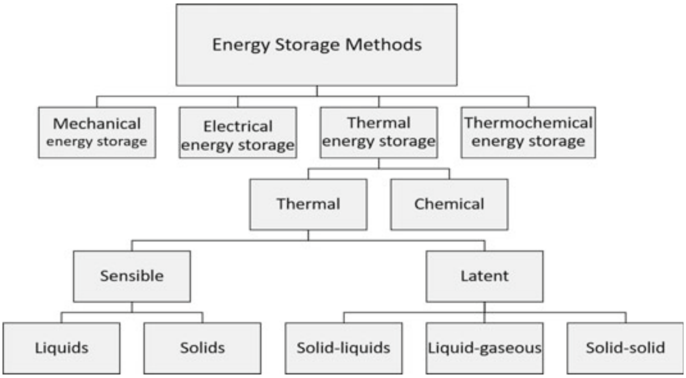

Fig. 3.1 Energy storing techniques [2]

Thermal energy storage (TES) contributes to a significant part in the efficient usage of thermal energy and has utilization in various fields, for instance, in buildings cooling/heating systems, solar collectors, electricity and industrial thermal energy storage [3]. Amongst many thermal energy storage methods, latent heat thermal energy storage is a highly desirable method and has the property of storing heat at a uniform temperature which is the phase change temperature.

Latent heat thermal energy storage (LHTES) which are phase change materials can be classified mainly into two categories i.e. organic and inorganic PCMs. The organic PCMs have higher stability, high energy storage capacity, no segregation, un-toxic, un-corrosive, and un-reactive [4]. Contrary to this, Inorganic PCMs have comparatively higher thermal conductivity, higher density volumetric energy storage, and flame retardance [5]. The organic PCMs have potential advantage as thermal energy storage materials in many applications, such as desalination [6], thermal management of electronic devices [7] passive heating of buildings [8, 9] and other thermal integrated systems. However, PCMs experience less thermal conductivity which is usually (0.2 W $m^{-1}K^{-1}$) and leakage during the phase transition [10]. The enhancement of thermal conductivity not only increase heat storage and release capacity, but it also improves the performance of the system. There are several methods for the improvement of PCM thermal conductivity, such as by utilizing nanoparticles, encapsulation of PCMs, expanded graphite, fins, heat pipe, and by metallic foams [11].

At present, polymer-based encapsulation of the PCMs attracted the researchers because polymers are flexible which allows the expanded PCM volume during the phase change results in ease of melting while maintaining the stability and shape of the prepared nano-capsules. In addition, encapsulation provides large surface area, high heat transfer rate, prevents leakage and encapsulation also reduces the reactivity of PCMs with external environment. In this study, we will discuss the latest studies on encapsulation of PCMs and its future aspects.

3.2 Polymer Encapsulation-Based Phase Change Materials

Encapsulation is the procedure of enclosing PCMs within coating materials to develop a type of composite PCMs [12]. The major reason to use polymers as core material is that they are mechanically stable, lightweight, inexpensive, and compatible with PCMs [13]. Moreover, the encapsulation technology can be separated into macro encapsulation, micro-encapsulation, and nano-encapsulation, depending on the size. Different forms of physical properties, such as, capillary behaviour, adhesion forces, and surface chemistry, are more efficient at the nanoscale encapsulation. Nano-encapsulation technique has proved to be extra useful than micro and macro-encapsulation for that purpose [14, 15].

The important parameters to evaluate the thermal performance of encapsulated PCMs are core and shell materials, latent heat, melting temperature of PCMs (T_m), encapsulation method and encapsulation efficiency (EE), as listed in Table 3.1.

The data given in Table 3.1 showed that in situ polymerisation techniques exhibit better thermal performance by providing more encapsulation efficiency and thermophysical stability compared to the other encapsulation methods.

Shi et al. [21] examined an interfacial polymerization technique for the development of paraffin-polymethyl methacrylate (PCM-PMMA) nano-capsules. At melting and solidification enthalpy of 64.93 J/g and 66.45 J/g respectively (PCM-PMMA) nano-capsules found stable and reliable. Furthermore, thermal gravimetric analysis (TGA) results showed the decent thermal stability with PCM content of 52.95%. Tumirah et al. [18] experimentally investigated the physical, thermal and chemical properties of the St (styrene)-MMA (methyl methacrylate) copolymer shell with n-octadecane as a core using miniemulsion in situ polymerization. After 360 cycles of heating/cooling, the nano-capsules had reasonable thermal efficiency in terms of chemical stability and thermal properties. The DSC results showed the solidification and melting temperatures of PCMs inside the nano-capsules were 24.6°C and 29.5°C

Table 3.1 Summary of nano-PCMs prepared utilizing various methods

References	Core/PCM	Shell	Latent heat (J/g)	T_m (°C)	EE%	Encapsulation method
[16]	n-octadecane	PMMA/SiO_2	178.9	–	10	Sol-gel method
[17]	n-octadecane	PBMA, PBA	96–112	29.1–31.6	47.7–55.6	Suspension-like polymerisation
[18]	n-octadecane	PS-PMMA	107.9	29.5	–	Miniemulsion in situ polymerisation
[19]	n-Dodecanol	Melamine formaldehyde	187.5	21.5	93.1	In situ polymerisation
[20]	n-Nonadecane	PMMA	139.20	31.23	60.3	Emulsion polymerisation

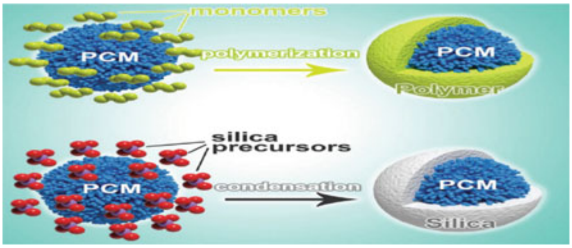

Fig. 3.2 Synthetic explanation of encapsulated PCM [24]-reproduced by permission of The Royal Society of Chemistry

respectively, which indicates they have a high ability to be utilized for the purpose of thermal energy storage. Fuensanta et al. [22] studied miniemulsion polymerisation (chemical method) in which (RT-80) PCM with melting temperature 80°C was utilized as core material and styrene-butyl acrylate copolymer as shell material. The nano-capsules showed thermal stability even after 200 heating/cooling cycles. In addition, Differential Scanning Calorimetry (DSC) analysis confirmed the thermal energy storage capacity of RT80/styrene-butyl acrylate nano-capsules by obtaining the melting and solidification enthalpies in the range of 10 to 20 J/g. Chen et al. [23] utilized miniemulsion polymerization method to synthesized styrene-butyl acrylate (SBA) copolymer as shell and n-dodecanol as core. The thermal performance, particle size and morphology were measured by DSC, particle size distribution (PSD) and transmission electron microscope (TEM) respectively. The results revealed that the encapsulation efficiency (EE) had touched 98.4% and phase transition enthalpy and phase transition temperature were 10932 J/g and 18.4°C, respectively. Sari et al. [20] prepared micro/nano capsules by emulsion polymerization method using paraffin eutectic mixtures (PEMs) as core material and PMMA as shell materials. The TGA results indicated that the encapsulated PEMs remained durable until 160°C. In addition, after exposure to 5000 thermal cycles, they had good chemical and thermal stability. A synthetic explanation of encapsulated PCM is shown in Fig. 3.2.

The encapsulation performance is still relatively low and faces the lack of industrial application requirements. What is more, the one reason for its low encapsulation performance is the very low thermal conductivity of PCM which hinders the heat transfer rate. Many studies have been investigated in which only PCM is used as the core material, but rare work is done on improving the thermal conductivity of core material. The addition of nanoparticles in PCMs increases the TC of PCMs because they possess high TC materials. We discussed the effects of nanoparticles on the PCMs in the next section.

3.3 Nanoparticles Based Phase Change Materials (Nano-PCMs)

By increasing the thermal conductivity of PCMs, heat storing and release capacity surges, which results in the improvement of thermal performance of the system.

In addition, thermal conductivity of the PCMs can be improved by the usage of nanoparticles possessing high thermal conductivity.

Qu et al. [25] studied the impact of two distinct nanoparticles (i.e. Expanded Graphite-Multi-walled Carbon Nano-tube (EG-MWCNT) and Expanded Graphite-Carbon Nano-fiber (EG-CNF)) on the phase change material (Paraffin) at five different mass ratios, and it was found that maximum thermal conductivity increased by the incorporation of EG-MWCNT and EG-CNF was 60% and 21.5% respectively. Rufuss et al. [26] investigated three different nanoparticles (copper oxide (CuO), titanium dioxide (TiO2) and graphene oxide (GO)) with paraffin. The results exhibited that the TC of paraffin was enhanced by 101.2%, 28.8% and 25% by the adding 0.3 wt% of graphene oxide, copper oxide and titanium dioxide nanoparticles, respectively. Sharma et al. [27] experimentally inspected the performance of PCMs and nano-PCMs integrated micro-fins for the Building-Integrated Concentrated Photovoltaics technology. Paraffin wax was used as PCM and Cupric oxide (CuO) as nanoparticles with 0.5% by mass. Results exhibited that the average temperature was decreased by 12.5 °C using micro-fins with nano-PCMs and 10.7 °C using micro-fins with PCMs as comparison to utilizing micro-fins only. Nourani et al. [28] experimentally inspected the effect of Aluminium oxide nanoparticles (Al_2O_3) on paraffin using different concentrations of (Al_2O_3) nanoparticles. The results revealed that the thermal conductivity improvement ratios for liquid and solid states were 13% and 31% respectively for a sample containing 10 wt% of Al_2O_3. Li [29] prepared nano-graphite (NG) and paraffin based composite PCMs. The thermal effects of nano-PCMs were examined using SEM and DSC. The results depict that the thermal conductivity of PCMs increases with the increase in the percentage of nanoparticles. Moreover, addition of 10% of (NG) nanoparticles raised the thermal conductivity to 0.9362 W/m K.

From the literature stated above it is clear that addition of nanoparticles to PCMs improves the thermal conductivity of the PCMs because both metallic and carbon-based nanoparticles have high TC. Moreover, carbon-based nanoparticles, such as carbon nanotubes, carbon fiber and graphene possess better stability, low density, and good dispersion in phase change materials compared to metallic nanoparticles.

3.4 Discussion and Future Work

Polymer-based encapsulated PCMs are widely used in many industrial applications, such as in thermal management, buildings, and medical industry because they have potential to store thermal energy with higher efficiency than other energy storage methods. But still more attention is needed for the further development of the thermal performance of encapsulated PCMs, as suggested below.

- Until now, work was focused on simple PCMs based polymer encapsulation, so future studies need to be conducted on nano-PCMs based polymer encapsulation for the enhancement in the thermal performance of polymer-based nano-capsules.

- In addition, the stability of nano-capsules can be improved by using nano-PCMs as core materials which help in a reduction of encapsulation cost.
- Previously, usually organic PCMs were used as core materials for the micro/nano encapsulation. Hence, there is the need to investigate inorganic PCMs as core materials because they have high latent heat of fusion during phase transition.
- Further studies on improvement of encapsulation efficiency, better thermal performance and better stability need to be conducted.
- Hybrid nanoparticles-based polymer nanocomposite materials also need attention for the development of potential energy storage materials.
- It has been stated that the encapsulation of PCMs results in the reduction of melting temperature latent heat compared to pure PCMs. PCMs aim to use in TES systems as energy storage materials without loss of heat transfer and fluid flow efficiency. This is therefore a major challenge for encapsulated PCMs to raise or sustain the latent fusion heat with different melting and solidification temperatures. Future studies are therefore required to concentrate on encapsulation of PCMs in this direction.

3.5 Conclusion

This paper mainly focused on encapsulation of PCM work success over recent years. Further, addition of nanoparticles in PCMs for the enhancement in the thermal efficiency of polymer-based nano-capsules are also studied. From this study the following findings are summarised.

- PCM encapsulation with a polymer as shell material is easy and does not require any complication, and the introduction of simple polymerisation techniques it can be achieved.
- The problems of leakage, subcooling, and segregation had been somewhat solved after encapsulation of PCMs.
- Addition of high thermal conductive nanoparticles in-to PCMs the thermal performance of encapsulation can be improved.
- In combination with various subsystems such as heat sinks, heat pipes, micro-minichannels, heat exchangers, panels, wallboards, and slabs, encapsulation of PCMs is the most suitable for thermal management and TES applications.

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