

Characteristics and Potential Applications of Nano-enhanced Phase Change Materials: A Critical Review on Recent Developments

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Abstract

Owing to incessant proliferation of challenges pertaining to energy storage systems to attain optimum design and efficient performance, massive research is underway on the development of optimal storage medium (used to overcome the low thermal storage capacity of most of the thermal transport fluids). Phase change materials (PCMs) are of the high energy storage capacity and extensively used in various applications for thermal energy storage purposes. However, the poor thermal conductivity of PCMs limits their potential in different applications. Substantial research is being conducted on the dispersion of thermally conductive nanoparticles to tackle the low thermal conductivity of PCMs. This article reviews the recent numerical and experimental studies on the nano-enhanced PCMs (nano-PCMs) to analyse their effects of nanofillers on the thermophysical properties (latent heat and thermal conductivity) of the nano-PCMs. Comprehensive details of stability enhancement techniques such as dispersant addition, sonication, and surface treatment as well as concomitant challenges along with stability measurement techniques have also been presented in this paper. Furthermore, various applications, preparation, and characterization methods of nano-PCMs are also discussed. Lastly, this review article suggests the potential research directions of nano-enhanced PCMs for the storage of thermal energy.

Keywords: Nanofillers, phase change materials, latent heat, thermal conductivity, energy storage.

Nomenclature

LHTESS	Latent heat thermal energy storage system	Ø	Diameter
PEG	Polyethylene glycol	K	Thermal conductivity
NP	Nano particles	T _m	Melting temperature
EG	Expanded graphite	T _c	Crystallization temperature
PCM	Phase change material	L	Length
2D	Two dimensional	W	Width
PMMA	Poly (acrylamide-co acrylic acid) copolymer	T	Thickness
GO	Graphene oxide		
TD	Tetradecanol	TC	Thermal conductivity
ESH	Eutectic salt hydrate	PA	Palmitic acid
MWCNT	Multi wall carbon nanotubes	SA	Stearic acid
PAN	Polyacrylonitrile	EP	Expanded perlite
SiC	Silicon carbide	CuP	Copper powder
SDBS	Sodium dodecylbenzene	GNS	Graphene nanosheets
PCS	Phase change material slurry	CoO	Diamond oxide
CBNP	Carbon black nanoparticles	xGnP	Exfoliated Graphite Nanoplatelets
PW	Paraffin wax		
PV	Photovoltaic		
EP	Expanded perlite		
OD	Outer diameter		
Dt	Diatomite		
MA	Myristic acid		
SF	Silica fume		
OD	Outer Diameter		
PANI	Polyaniline		
S-MWCNTs	Small-Multi wall carbon nanotubes		
L-MWCNTs	Large-Multi wall carbon nanotubes		
CNFs	Carbon nano fibers		
GNP	Graphene nanoplatelets		
CNS	Carbon nano fillers		
CB	Carbon black		
PE	Pentaerythritol		
LA	Lauric acid		
PVP	Poly vinyl pyrrolidone		

1. Introduction

The planet is facing a lack of natural resources since the 1970's oil crisis [1]. The scientific community is deeply concerned about the rise in world energy use. Global energy demand is increasing steadily and increased utilization of fossil fuels results in higher greenhouse gas emissions, particularly carbon dioxide (CO₂), which leads to heavy environmental problems such as ozone depletion, climate change and global warming [2,3]. According to the International Energy Agency (IEA), Figures.1a and 1b shows the statistics of major energy-consuming sectors and their contribution to CO₂ emissions [4]. The primary reason for the increased energy consumption is the actual increase in the standard of living and convenience requirements for heating in cold areas and cooling in hot areas [5].

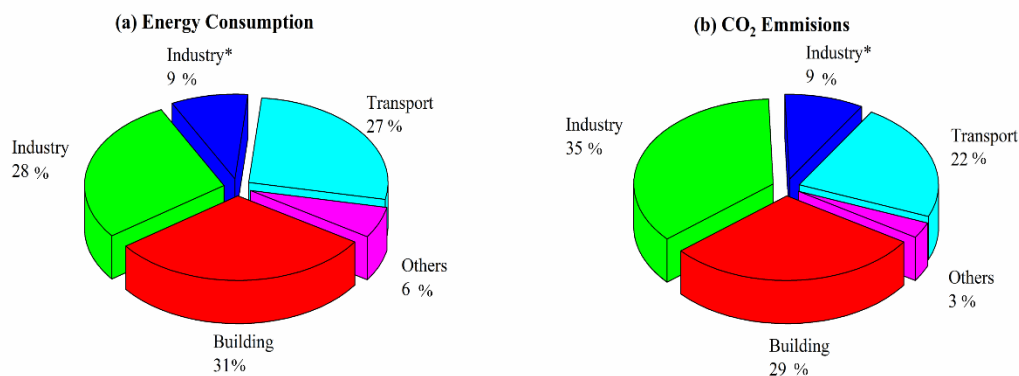


Figure 1 (a) Energy consumption sectors (b) Consequently, CO₂ emission [4]

Nature has several kinds of energy, including thermal energy, solar energy, wind energy, chemical energy, etc. Thermal energy is widely distributed between these types of geothermal energy, solar radiation, etc. Thermal energy is considered a low-grade type of energy and is generally treated as waste in industrial production [6]. On the other hand, during the daytime the solar radiation tends to provide ample solar energy. But significant quantities of energy are still wasted. If large quantities of thermal energy can be stored and discharged when supplied and demanded, the consumption of fossil fuels will be reduced, which plays an important role in overcoming the energy crisis and environmental pollution problems. Therefore, the storage of thermal energy has gained considerable attention and experienced rapid development [7].

Phase change material (PCM) has been investigated in the last two decades among the various thermal energy storage methods and a latent heat thermal energy storage system (LHTESS) using PCMs was the most suitable for their small variations in temperature and high energy storage densities [8]. Furthermore, LHTESS has more energy storage capacity compared to

sensible heat storage; that’s why it requires a relatively small storage volume, which reduces the amount of storage materials needed. Another benefit is that, due to the nature of the phase transformation process, the thermal energy stored can be recovered at an almost constant temperature. The use of PCM for thermal energy storage (TES) offers an excellent and realistic solution in many domestic and industrial sectors to increase the efficiency of storage and energy utilisation [9,10]. The deployment of PCM for energy storage eliminates the gap between supply and demand, increases energy delivery networks efficiency and reliability and plays an important general role in energy conservation [11,12]. Phase transition TES technologies have great fusion enthalpy and heat efficiency with the ability to absorb and release large quantities of thermal energy during a phase change process. The phase-changing thermal efficiency of PCMs, depends solely on the properties of PCMs. Phase change materials are divided into two main categories based on chemical composition: inorganic PCMs, and organic PCMs. Figure 2 shows the classification of PCM based on chemical structure, phase change temperature and phase change process.

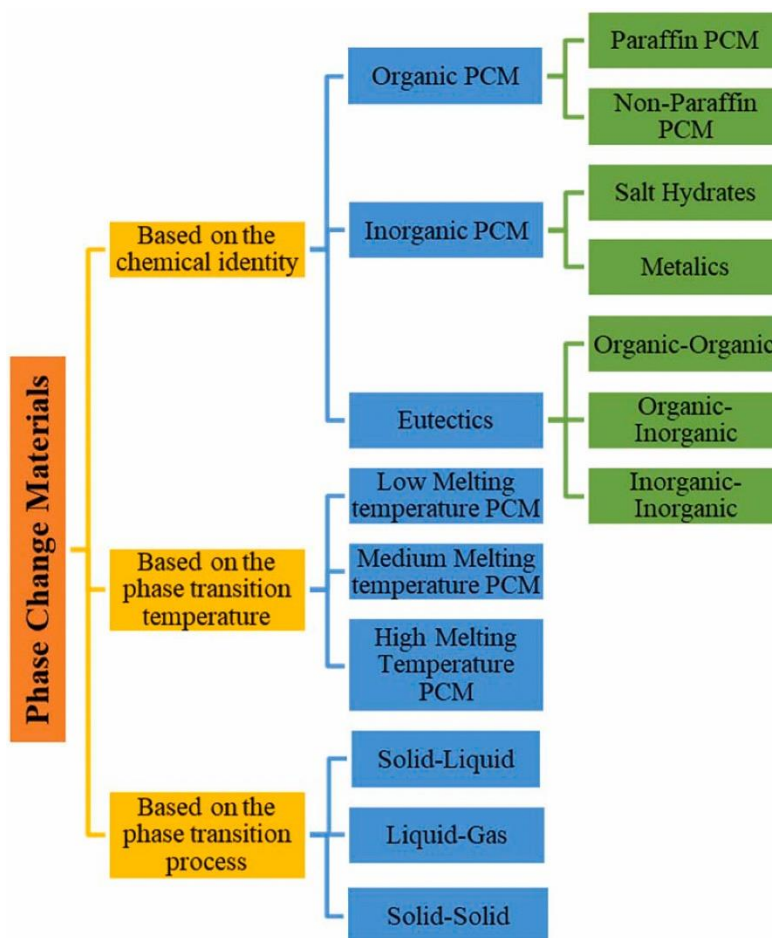


Figure 2 Phase change material classifications [13]

High energy storage capacity, higher stability, self-nucleation, no segregation, nontoxic, non-reactive, and non-corrosive are the strengths of PCMs and particularly organic PCMs, which include non-paraffins (n-alkenes) and paraffins (n-alkanes) materials [14]. Contrary to this, inorganic PCMs have high latent heat, flame retardance, and comparatively good TC. Nonetheless, inorganic PCMs have phase separation and subcooling, minimising their immediate discharge and utilisation of thermal energy for TES applications. For higher temperature applications inorganic PCMs are more suitable than organic PCMs, while for low-temperature applications organic PCMs exhibit better performance [15]. Anyhow, PCMs usually suffer from low thermal conductivity which hinders its heat transfer rate [16]. In addition, lower thermal conductivity (TC) and leakage of PCM through a phase change hinder the performance of the TES system. Due to the lower thermal conductivity of PCMs, they have less heat transfer rate and leakage of PCMs results in the reduction of energy storage capacity as its volume decreases during leakage. In recent years, the introduction of highly conductive nanoscale fillers into phase-change materials (PCMs) to enhance their thermal conductivity has attracted considerable attention [17,18]. The addition of nano additives such as CNTs, metal or metal oxide nanoparticles in one specific PCM enhances the thermal conductivity because nanoparticles have high TC and relatively low density [19,20].

In literature, many studies have been investigated to examine the PCM thermo physical properties with the addition of nanofillers. Furthermore, the different thermo physical properties (latent heat, thermal conductivity, and sub-cooling) of nano-PCMs have been investigated by different researchers. In this perspective, this paper presents a comprehensive literature review to illustrate the influence of the dispersion of various nanofillers on the thermal physical properties of PCM. Apart from the thermophysical properties of nano-PCM, preparation methods, challenges with nano-PCM, characterization and applications of nano-PCMs are also discussed in detail. Compared to other accessible reviews, exploiting this extensive and detailed coverage is what makes this review relevant and distinct. Most of the review articles on nano-enhanced PCM concentrate only on the selected area, and this has been explicitly illustrated in Table 1. The unique aspect of this review also focuses on the thermal stability of nano-PCMs and the different methods which help in the enhancement of thermal stability, which is missing in the review articles based on nano enhanced PCMs for thermal energy storage systems.

Table 1 Recently published review papers

Authors	Publication year	Review articles focus
Mohamed et al. [15]	2017	Inorganic PCM drawbacks and possible solutions to these disadvantages
Lin et al. [7]	2018	PCM thermal conductivity enhancement methods and applications of PCM.
Nizetic et al. [21]	2020	Applications of nano-PCMs and nano-fluids.
Jebasingh and Arasu [22]	2020	Effect of nanofillers on the thermo physical properties of low temperature range (20-37 °C) PCM.
Tariq et al. [23]	2020	Applications of nano enhanced phase change materials.
Kumar et al. [13]	2020	Summary of challenges and future prospective on nano-PCM based photovoltaic thermal systems

The present review has discussed the thermophysical properties of unitary and hybrid nano-enhanced PCMs with the description of the major reasons behind the variation in thermophysical properties (reduction or growth in thermal conductivity and energy storage capacity) of nano-PCM in consonance with nanoparticles category. The major challenge with these mono and hybrid nano-PCMs is that they are less stable. This paper has reported the different stability enhancement and measurement methods that can be very helpful for the researchers working in this area. In addition, authors also presented an overview of preparation, and characterization techniques and applications of nano-enhanced PCMs. Furthermore, an organised article on nano-PCMs would be very beneficial in helping researchers to move towards the effective use of nano-PCMs by overcoming the difficulties they encounter.

2. Thermophysical characteristics of nano phase transition materials

A brief discussion of the latest experimental and numerical studies published on nano-PCMs is provided in this section. Especially, this part is focused on the incorporation effect of nanoparticles on PCM thermal properties, specifically thermal conductivity, and energy storage capacity. All categories of nanofillers i.e., Graphene, CNTs, metals, metals oxides, metal carbides and nitrides and hybrid nanofillers are reported separately and a comparison between them has been presented in this segment. Therefore, for researchers who want to work on nano phase change materials these studies would be helpful.

According to the Scopus database and selected keywords, publications statistics for the last eight years, provided in Figure 3, shows that as technology progresses, the attention of scholars and intellectuals on the topic of nano-PCMs has steadily increased, because they have great potential for technological advances and, more importantly, they provide advantages that can

be linked to the implementation of nanomaterials for various purposes. Figure 4 shows the field of nano-enhanced PCMs applications found in the literature. Moreover, the countries with a higher number of studies on nano phase change materials are shown in Figure 5 and it can be seen that China has the greatest number of publications on nano-PCMs followed by the US and other countries.

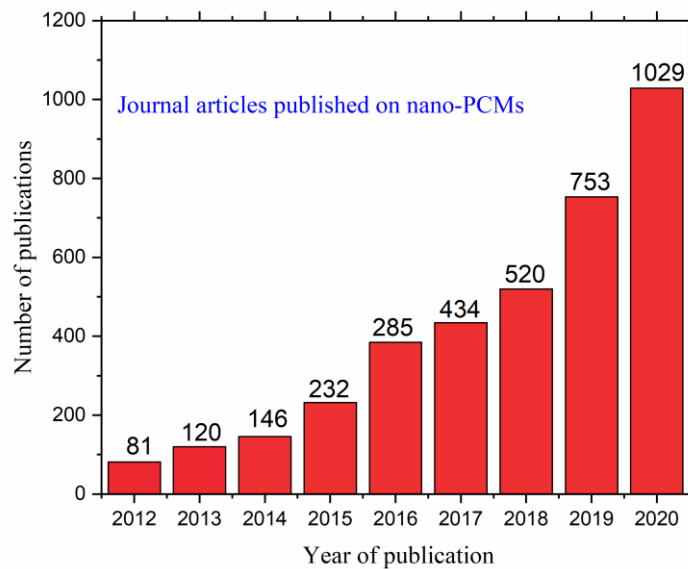


Figure 3 The trend of published articles in the recent years (statistics from the Scopus retrieved by the keyword of “PCM” and “nano phase change material”)

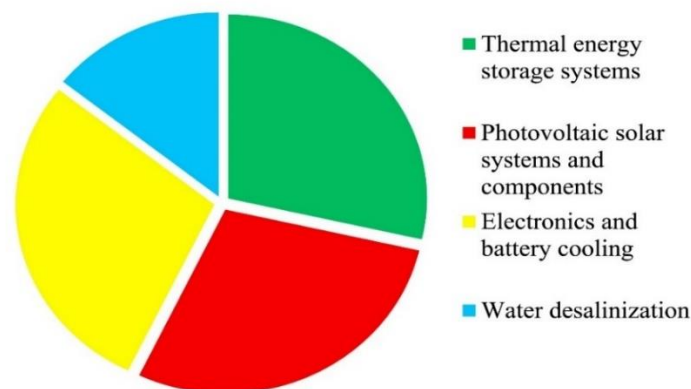


Figure 4 Applications of nano enhanced PCMs found in the literature [21]

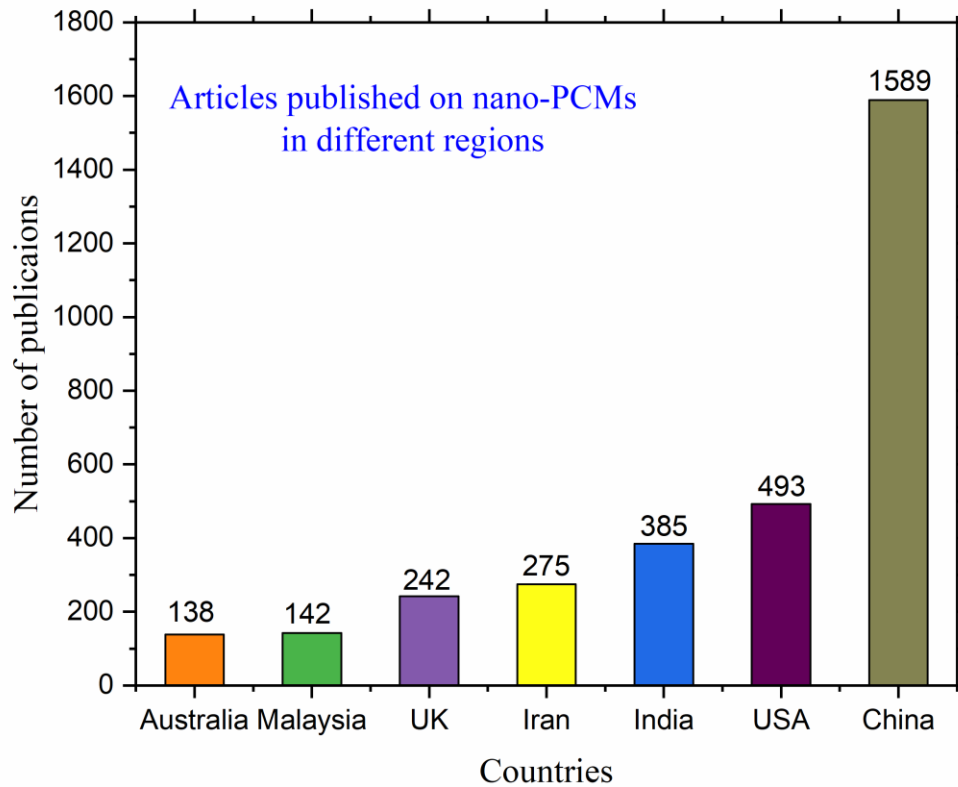


Figure 5 Publications on nano-PCMs in different countries (statistics from the Scopus retrieved by the keyword of “PCM” and “nano phase change material”)

2.1 Unitary nanoparticles based PCMs

There are various types of dispersants shown in Figure 6, such as metal, metal oxides, CNTs, etc. This section critically examines the impact of all of these nanoparticles on the thermophysical properties of PCM. Among all of these, carbon based nanofillers have high thermal conductivity (TC) and a list of the thermal conductivity of different particles is shown in Table 2.

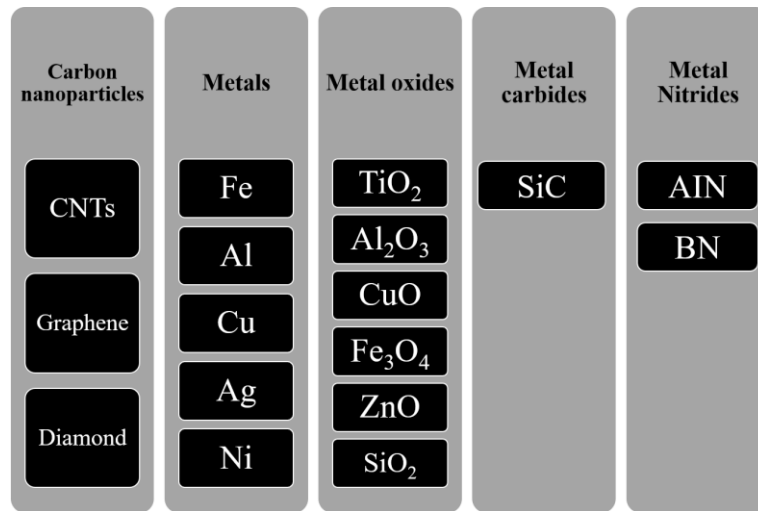


Figure 6 Graphical representation of the different type of nanoparticles

Table 2 Thermal conductivity of different particles

Nanoparticles	Thermal conductivity (W/m. K)
Titanium	21.9
Aluminum	237
Copper	401
Boron	27
TiO ₂	8.4
Al ₂ O ₃	36
CNTs	2000-6000
GNP	3500-5000
Diamond	2300
SiC	490

2.1.1 Graphene nanoparticle based PCMs

Graphene, “the mother of all graphitic forms of carbon”, has been widely used with PCMs because of its following advantages [24–26]:

- i. reduced need of heat transfer fluid.
- ii. reduced corrosion, clogging and erosion.
- iii. larger surface area to volume ratio–enhanced the heat transfer ability.
- iv. less Requirement of pumping power and energy saver.
- v. high thermal conductivity.
- vi. easily synthesized and more stable.

Researchers have conducted numerous studies to investigate the effects of thermal properties on PCM with graphene based nanofillers. For instance, Kim and Drzal [27] prepared paraffin ($T_m = 42\text{--}44^\circ\text{C}$) and xGNP based composite using melt and mixing method. They varied the concentration of xGNP by 1%, 2%, 3%, 5% and 7% to study their effects on the thermophysical characteristics of the PCM and they noted that a little rise in the thermal conductivity and latent heat was observed by increasing the volume fraction of xGNP. Similarly, Jeon et al. [28] prepared xGNP and paraffin ($T_m = 53\text{--}57^\circ\text{C}$) based composites by identical preparation method as utilized by Kim and Drzal for thermal energy storage applications in buildings. The size of xGNP particles was also similar, but the values of melting temperature of both paraffins were different. Both thermal conductivity and latent heat results of two different temperature paraffins were compared with the similar 3% xGNP concentration and DSC results showed that paraffin with higher melting temperature had higher values of thermal conductivity and latent heat in comparison to paraffin with lower melting temperature.

The graphene oxide particles were investigated experimentally to stabilise the shape of polyethylene glycol (PEG) PCM for TES [29]. It was noted that due to the hydrogen bonding interaction between graphene oxide (GO) and PEG, PEG formed a strong network with 4% GO and showed better stability and no leakage above its melting temperature. In addition, the composite PCM enthalpy decreases with an increase in the graphene oxide (GO) concentration. Furthermore, melting temperature remains almost identical at all concentrations of GO. However, the solidification temperature increases with particle concentrations, but decreases at a higher concentration of GO. In their other study [30], they used graphene and graphene oxide nanofiller for thermal conductivity enhancement and stabilization of PEG respectively. The results showed that the incorporation of GO and GNP was effectively supporting materials and conductive materials, respectively. Moreover, the latent heat was also enhanced slightly with the incorporation of hybrid nanofillers.

Various PEG and GNP based composites were also developed in which they varied the concentration of GNP from 0.5% to 2% with an interval of 0.5% [31]. Nano-PCMs were prepared by solution blending method which is different from the physical blending method used by Qi et al. [29] in their both studies. The DSC analysis showed that the nano-PCMs prepared by this method depicted higher values of latent heat and thermal conductivity that was increased by 146% with only 2% of GNP. In addition, pure PEG and PEG/GNP composites were tested to investigate the photothermal performance and results revealed that PEG/GNP composites exhibit better heat storage performance than pure PCMs.

The influence of GNPs on the crystallization kinetics of pentaglycerine (PG) ($T_m = 81^\circ\text{C}$) was investigated [32]. Both PCM and GNP were mixed for one hour at 400 rpm by a planetary ball mill. Activation energy which is a crucial factor in describing the complexity in the kinetics of crystallization was studied by a multiple scanning method. The results have indicated that the GNP content increases the activation energy throughout the analysis and the macroscopic thermal conductivity enhancement has a greater impact on the phase transition of PCMs compared with the microscopic activation energy. Thus, improving the thermal conductivity enables the crystallization of the PG/GNPs composites, which helps to increase the crystallization rate. Cui et al. [33] dispersed GNPs into the $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ inorganic PCM ($T_m = 78^\circ\text{C}$) to study the supercooling, TC and heat storage performance of composite PCM. It has been reported that adding graphene nanoplatelets effectively reduces the supercooling degree and heat release time of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. In addition, Zhang et al. and Cui et al. investigated GNPs with organic and inorganic PCMs respectively although their melting temperatures were almost identical. In the comparison of their results, DSC results showed that pure organic PCM exhibited greater energy storage value than virgin inorganic PCM. On the other hand, inorganic nanocomposite PCMs demonstrated higher thermal conductivity value than organic nanocomposite when they are compared at similar concentrations of nano particles.

Graphene nano platelets with bee wax ($T_m = 62^\circ\text{C}$) composite PCM were developed by sonication and ultra-sonication method for the improvement in the thermophysical characteristics of PCM [34]. The mass concentrations of GNP for the preparation of nano-PCMs were 0.05, 0.15 and 0.3 %. The results showed significant improvement in the latent heat (22.32%) when the mass concentration of graphene nano platelets was increased. The reason behind the increase in the latent heat was explained by Brownian motion and nanoparticles clustering mechanism [35]. The graphene nanoplatelet random motion increased the likelihood of agglomeration within the base fluid of the beeswax. In addition, the Van der Waals forces attracted each other between the graphene nanoplatelets and produced particle clusters [35]. Nevertheless, lower nanoplatelet concentrations allowed thermal storage to be more efficient per unit volume. The PCM with almost similar melting temperature ($T_m = 66^\circ\text{C}$) as used by Amin et al. was investigated with graphene particles (1, 2, 3 and 4%) in the study conducted by Yavari et al. [36]. The method used for the preparation of nano-PCMs was also similar to the Amin et al. [34]. The results showed a decrease in the latent heat was noted with the rise in the particle concentration and at 4% of graphene the maximum reduction in the latent heat was 15.4%. They gave the reason behind the reduction in the latent heat that by the

addition of graphene some PCM volume is replaced by graphene sheets which are not subject to the phase transition. A similar reason for the reduction of latent heat of PCM by the addition of nanoparticles was given in the reference [37]. Furthermore, the results also showed that nano composite with a lower concentration of nanoparticles showed improvement in the latent heat value in contrast to the nano composites with the higher concentration [13, 32].

An experimental investigation on xGNP and graphene-based PCM composites was conducted to investigate the thermal performance and stability of PCM by solution mixing method [38]. Due to the larger surface area of graphene than that of xGNP, 2% graphene showed better stability because PCM absorbed completely in graphene. However, xGNP showed noticeable enhancement in the thermal conductivity compared to the graphene particles. Putra et al. [37] experimentally studied the Graphene/RT-22 ($T_m = 22\text{--}24^\circ\text{C}$) based nano-PCM for the cold storage application. The width and thickness of graphene nanoparticles were less than $2\mu\text{m}$ and 2 nm, respectively. The result showed that with the addition of nanoparticles latent heat decreases, while the thermal conductivity of particles increases by 89.6% with the increase in the concentration of graphene nanoparticles.

Silver based graphene nanosheets (GNS) were developed and integrated with PEG PCM [39]. The multi-folded layered structure provides Ag-GNS a large surface area to support PEG for achieving the shape stability. Moreover, the results showed that the freezing and melting temperatures remained almost unchanged and latent heat was decreased when a concentration of Ag-GNS particles was increased. However, the developed Ag-GNS/PEG composites showed high thermal energy storage properties and efficient photothermal conversion. The hybrid nanofillers (Ag-GNS) increased the composite photothermal conversion efficiency (88.7–92.0%) and materials thermal conductivity (49.5–95.3%). Like Zhang et al., Yang et al. [40] tested PEG PCM with boron nitride and GNP composite by solution mixing method. The synergistic effect between GNP and BN results in the improvement in TC and stability of PCM even at a small concentration of GNP (1%). What is more, the DSC results showed no significant change in their melting and solidification temperatures of the composite. Similarly, Zhou et al. [41] conducted an investigation on PEG PCM but in this study PCM was impregnated into the cellulose nanocrystal (CNC) hydrogel by a novel solvent exchange method. At the 97% mass concentration of PEG, PEG/CNC exhibited good latent heat value 151.8 J/g which was slightly lower than pure PEG 155 J/g. In addition, the PEG/CNC composite slowed down the crystallization rate indicating the extremely high specific area of the CNC nanofiber network and the heavy hydrogen bonding between CNC and PEG. In the

meantime, the crystalline phase change temperature of PEG decreased from 40.1°C pure PEG to 33.5°C of PEG/CNC hybrid PCM. From these studies [39–41] in which PEG was used as PCM, [41] showed good thermal performance in comparison to other studies. This may be because of the strong bonding between PCM and nanofiller which results in higher thermal efficiency. Furthermore, the size of nanoparticles may also be a factor because nanoparticles used in the study [41] were smaller than other ones and large size particles usually results agglomeration.

2.1.2 CNTs nanoparticles based PCMs

Carbon nanotubes (CNTs) are commonly used as dispersants because of their high thermal conductivity. Therefore, in recent years the use of novel carbon allotropes has continued to increase. CNTs are lightweight materials and have greater surface area and small particle size, that the small size improves the intermolecular attractiveness among the molecules in nano-PCM. Recent studies on the effect of CNTs on PCM thermal characteristics are critically explored in the following paragraphs.

The effects of applying different carbon nanofillers (CNs) over the energy storage capacity and TC of nanocomposite PCMs based on paraffin were examined [42]. The tested CNs included long and short MWCNTs, carbon nano fibers, and GNPs. Nanocomposite PCM samples with CNs mass concentrations of (1–5) wt. % were prepared for each form of CNs with an increase of 1 wt.%. The results reported that the existence of carbon nanofillers improved nanocomposite TC, but the improvement depended on both the shape and size of the carbon nanofillers. Because of their 2D planar structure, which resulted in decreased filler/PCM thermal interface resistance, an increase of up to 164 % in the TC value was achieved at the concentration of 5 wt.% of GNPs. The small-multi wall carbon nanotubes (S-MWCNTs) showed the best dispersion among the three wire-shaped fillers and consequently the most pronounced enhancement. The existence of CNs, however, contributed to the diminution of latent heat ability with the increasing concentration of all CNTs. The PCM/CNF composite offered the highest latent heat potential at constant loading, which could be due to the size and shape of the particle (the larger shape and the size of the filler improves the heat conductive connections). Like CNFs as discussed earlier in [42], it was found that similar results in their experimental and numerical study in which they examined the effect of particles size on the latent heat diminution of MWCNTs based paraffin composite [35]. All volume fractions MWCNTs with larger diameters in the PCM resulted in good latent heat compared to CNTs with smaller diameters. Correspondingly, its numerical results reported that even though

microscale particle adding improves performance the of thermal storage, nanoscale particles will degrade storage performance compared to pure paraffin.

The processing methods have also been explored. Zhang et al. [43] prepared nano-PCM emulsion using sonication method in which n-octadecane, octadecanol and MWCNT were used as PCM, nucleating agent and nanoparticles, respectively. The results showed that with 10% nano-PCM emulsion thermal conductivity was increased linearly by the addition of MWCNTs, but with a little decrease in the latent heat. However, at 20% nano-PCM emulsion, the composite with 0.1% MWCNT and 0.5% octadecanol doubled the values of latent heat as compared to 10% nano-PCM emulsion. Meng et al. [44] prepared an eutectic mixture of three fatty acids the melting temperature of this eutectic mixture was nearly similar to the PCM used by Zhang et al. and the nanomaterial in both of these studies were also identical. Moreover, the infiltration method was used to prepare MWCNTs and fatty acids-based nano-PCM. They figured that latent heat values of mixed PCMs were lower than their individual values and by incorporation of different concentrations of MWCNTs (10%, 20%, 30%, 40%, 50%) latent heat of melting and solidification further decreased. Furthermore, this composite nano-PCM showed higher heat storage capacity than the nano emulsion-based composite used by Zhang et al. However, nano emulsion-based composite decreased the supercooling up to greater extent.

A study of a comparison between pristine and modified MWCNTs based nano enhanced PCM for thermal energy storage usages was reported [45]. The organo-silane-modified CNT based PCM demonstrated better stability dispersion compared to the pristine CNTs based PCM. What is more, with the incorporation of pristine CNTs electrical surface resistivity decreases. At lower concentration (0.1 %) of pristine CNTs they showed little increase in latent heat values. This could be because the larger surface area, greater dispersion capability of CNTs and great intermolecular interaction between the molecules had resulted in an increases in the latent heat [46]. On the other hand, silanised CNTs were found to be nonconductive because the functional groups attached to the surfaces significantly modified the surface properties of the Si-MWCNTs.

The other approaches of particle treatments have been studied. Qian et al. [47] have tried to develop the PEG and diatomite coated MWCNTs based stable composite PCM which showed good stability at PCM concentration of 60%, but with a significant decrease in the latent heat. In another study, [48] they compared two different carbon based nanofillers (GNPs and

SWCNTs) with PEG as PCM. The small volume concentrations of 4% GNPs and 8% SWCNT were added into the PEG to form shape-stable composites. It was found that GNPs/PEG and SWCNTs/PEG held 96% and 92% heat storage density of pristine PCM and enhanced thermal conductivity by 1096% and 950% respectively as compared with the virgin PCM.

The concentration effects of CNTs and CNFs on the thermal conductivities of CNT and CNF based PCMs have been studied [49]. It was observed that the thermal conductivity increased with an increase in the content of (S-MWCNTs and L-MWCNTs) CNTs or CNFs. But CNFs exhibited higher thermal conductivity values compared to CNTs. Because CNTs easily entangle and form clusters which limits their efficiency in the PCM matrix. Moreover, CNFs having a higher diameter and have weak Van der Waals forces between the fibers results in the uniform dispersion of the PCMs matrix. That is why CNFs performed better than CNTs for thermal conductivity enhancement. Likewise, similar behaviour was observed [49] when CNFs and CNTs were compared. It was found that thermal conductivity increased with the addition of CNFs and CNTs, but CNFs showed higher thermal conductivity than CNTs for all concentrations. On the other side, when Fan et al. [42] compared S-MWCNTs and L-MWCNTs (CNTs) with CNFs they found CNTs showed higher thermal conductivity than CNFs. This might be because of the difference in their sizes, as in both studies the sizes of nanofillers were different and this needs further investigation to identify the effect of the size of nanoparticles on thermal conductivity. However, PCM/CNFs composite offered the highest latent heat potential at constant loading. This could be due to the size and shape of the filler (the larger size and the shape of the form improves the heat conductive connections).

There are a few more reports of CNF effects on thermal properties of phase change materials. Like, Elgafy and Lafdi [50] compared experimental and numerical results of the paraffin based raw CNFs and surface treated CNFs composites. A good relationship between both experimental and analytical models was observed. By increasing the concentration of CNFs, the output power from the composites increased. Furthermore, surface treated 4% CNFs indicated better performance compared with untreated 4% CNFs based composite. Darzi et al. [51] combined electrospinning and electro spraying concurrently to develop PCMs based nanofibers. The spraying of graphene and carbon fibre powder significantly reduced the melting temperature of PCMs, whilst a decrease in the latent heat by large amount.

2.1.3 Metal and metal oxides nanoparticles based PCMs

Nanoparticles based on metals are produced through metals to nano size materials by constructive or destructive processes. The metal nanoparticles have unusual characteristics, for example small size around 10-100 nm and cylindrical and spherical structures. On the other hand, metal oxide type nanofillers are produced to change the characteristics of their corresponding metal nanomaterials. In contrast with their metal counterparts, these nanoparticles have excellent properties.

The effects of TiO₂ nanoparticles on the thermal properties of paraffin wax PCM have been studied. Wang et al. [52] tested TiO₂ nanoparticles (20nm) with paraffin wax to enhance the thermophysical characteristics of PCM. The increase in thermal conductivity and latent heat was spotted by the inclusion of 0.7% TiO₂, while latent heat started decreasing when TiO₂ concentration exceeded 0.7%. In another study [53] Teng and Yu also used paraffin as PCM and tested with different concentrations of TiO₂ nano additives. The nanoparticles size and nano-PCM preparation method were similar to the study performed by Wang et al. Moreover, they also found an increase in the latent heat of melting with the addition of up to 2% of TiO₂ in the paraffin. However, the thermal conductivity of nano-PCM composite increased linearly with TiO₂ nano fillers but TiO₂ base nano-PCM was found to be more thermally and chemically stable.

A two-step method was employed to prepare TiO₂/paraffin composites for the improvement of thermal properties of energy storage materials [54]. TiO₂/paraffin composites with and without stearyl lactylate sodium (SSL) as a surfactant were tested for thermal characteristics and stability. Several volume concentrations of TiO₂ (0.5%, 0.7%, 1%, 2%, 3% and 4%) were investigated and the results showed that paraffin samples with 1 wt.% and 3 wt.% of TiO₂ had the highest latent heat values of 165.1 and 167 J/g for without and with SSL respectively. Haghghi et al. [55] investigated SDS surfactant with TiO₂ and paraffin based nanofillers to study the thermal performance of nano-PCM, except surfactant remaining materials (PCM and nanoparticles) was almost identical to the material used by Sami and Etesami [54]. The results showed that SDS-based TiO₂/paraffin composites exhibited highest (179.8846 J/g) enthalpies compared with the pristine PCM having an enthalpy of 142.3565 J/g. By comparing these two studies [54] and [55], it was observed that latent heat value was increased compared to pristine PCM, however SDS surfactant based nano-PCM showed higher energy storage value as compared to the SSL surfactant based nano-PCM composite. Haghghi et al. [55] also performed a comparative analysis by employing different nanofillers (i.e. CuO, TiO₂, Al₂O₃

and graphene) with paraffin and the latent heat values of these composites are shown in Figure 7. It was found that at 2 wt.% TiO₂/paraffin composite revealed high heat storage capacity than other composites, while graphene/paraffin composite depicts higher thermal conductivity because of the higher thermal conductivity value of graphene. Correspondingly, when examining the energy storage capacity of various nanofillers (Al₂O₃, TiO₂, SiO₂, and ZnO) Teng and Yu [53] uncovered that the TiO₂/paraffin combination exhibited high heat storage capacity at all concentrations in comparison to other nanofillers.

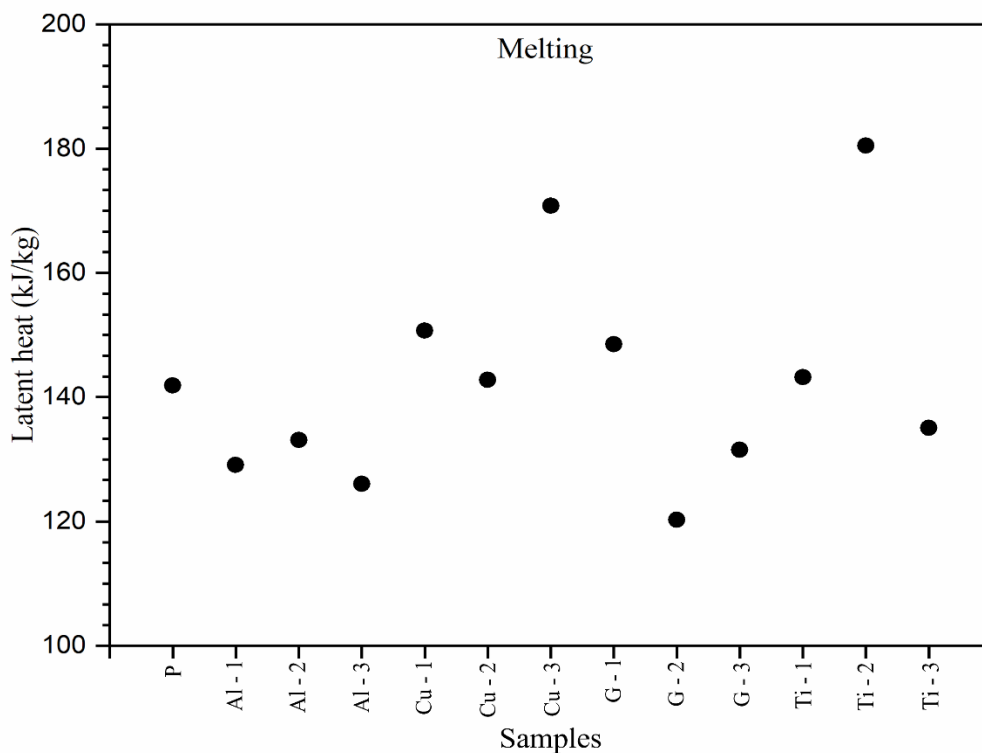


Figure 7 Latent heat comparison between paraffin based different composites [55]

The two step method has also been employed to prepare nano enhanced PCM in which stearic acid ($T_m = 57 - 59$ °C) was used as PCM and TiO₂ as nanoparticles [56]. The results showed an inverse relationship between latent heat and TC as shown in Figure 8. It was explained that it was due to the interaction between the nanoparticles and PCM. Moreover, both decline in latent heat and increase in TC of the PCM strongly depend on the type (i.e., grapheme, CNTs, metal, and metal oxide nanoparticles), shape, size, and volume fraction of the nanoparticles. Similarly, a slight decrease in the latent heat of fusion was noticed with an upsurge in the particle concentration in another experimental study investigated by Sharma et al. [57]. This may be because of changes in physicochemical characteristics caused by the TiO₂ nanoparticles

dispersal. Both palmitic acid PCM and TiO₂ (0.5%, 1%, 3% and 5%) nanoparticles were employed to develop nano-PCM for solar thermal energy storage energy application [57]. The nano composite has shown that the TiO₂ nanoparticles do not affect PCM chemical structure but do improve the chemical stability.

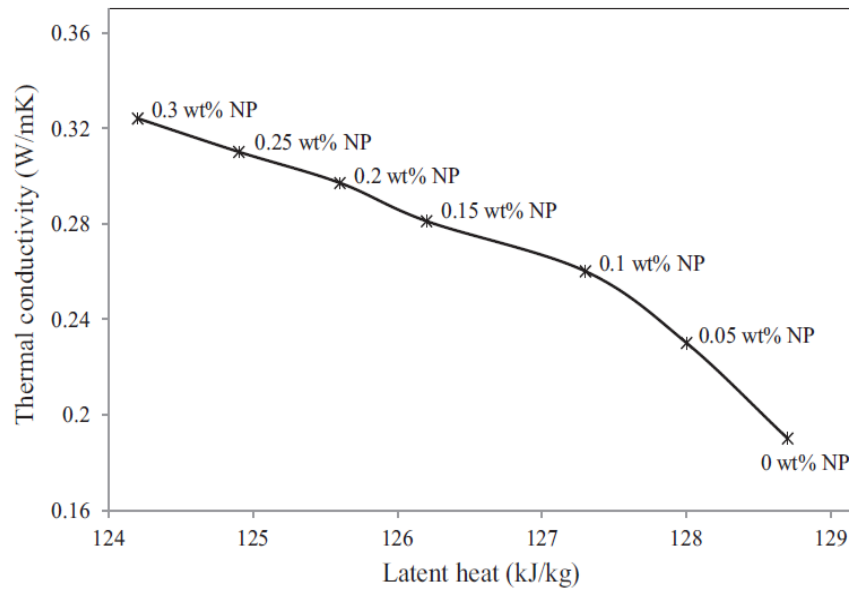


Figure 8 Nanoparticle effects on the thermal conductivity and latent heat of composite PCMs [56]

An effect of the size of TiO₂ nanoparticles on the eutectic salt hydrate inorganic PCM was reported [58]. The results revealed that the smaller size of TiO₂ nanoparticles (25nm) had greater stability with PCM than particles with greater size (100nm). Moreover, it was noticed that surface adsorption capacity was improved with a reduction in the size of nanoparticles, which increased the nucleation and growth rate of nano-PCM while producing improved crystalline content.

Many studies were carried out on PCMs with Al₂O₃ particles. Mohamed et al. [59] developed α -Al₂O₃ (1.4–2 nm) nanoparticle paraffin wax based PCM in which an upsurge in thermal conductivity and latent heat was observed with the increase in nanoparticles concentration, while Babapoor and Karimi [60] found the decrease in the latent heat value for Al₂O₃ (20nm) based paraffin composite even at the same concentration of nano alumina used by Mohamed et al. This may be because of different particle size utilised by Mohamed et al. and Babapoor and Karimi. Furthermore, different metal oxide nanoparticles having particle size of 11 and 20 nm (SiO₂, Al₂O₃, ZnO, and Fe₂O₃) were compared with paraffin. The results showed that 8%

SiO₂ (11nm)/paraffin composite indicated better stability compared to other composites. However, Al₂O₃/PCM composite demonstrated highest thermal conductivity value and overall and it performed better than other composites.

Two types of organic PCMs (RT-20 and RT-25) with carbon black (CB) and Al₂O₃ nanoparticles were studied and tested [61]. The results showed that an addition of only 1% of carbon black and Al₂O₃ particles resulted in the enhancement of latent heat value for all composites, except for RT25/CB composite. Furthermore, the nano-PCMs based on Al₂O₃ were considered unstable and a certain deposition of nanoparticles was identified. However, the nano-PCMs based on CB were highly stable and showed higher thermal conductivity than Al₂O₃ based nano composite[61]. Coated Al₂O₃ nanoparticles with ionic surfactant were also investigated to improve the stability of based nano-PCM [62]. It was found that emulsion density fit excellently with the prediction based on the theory of mixtures. Further, a decrease in the latent heat was observed in the nano-PCMs as compared with pure PCM. In theory (equation (1)), the latent fusion heat of composite materials is supposed to decrease linearly with the addition of particles [35].

$$h_{sl,nPCM} = \frac{\rho_{pcm,s} h_{sl,bPCM} (1 - \phi_p)}{\rho_{nPCM}} \quad (1)$$

where, $\rho_{pcm,s}$ represents the PCM density in the solid phase, ρ_{nPCM} is the theoretical density of nano-PCM, and $h_{sl,bPCM}$ is the solid-liquid latent heat of the base fluid.

Similarly, inorganic salt hydrates PCM and nano- α -Al₂O₃ have also been investigated with surfactants [63]. It was reported that the latent heat was decreased from 280 J/g to and 256.9 J/g for with and without nano- α -Al₂O₃ particles, correspondingly. The results also showed that the impregnation of 4.5% of nano- α -Al₂O₃ particles decreased the supercooling degree from 7.8°C to 1.6°C and their melting temperature was also reduced from 33.7°C to 31.6°C. Moreover, it was observed that nano- α -Al₂O₃ particles had a small influence on phase transition behaviour. As the nano- α -Al₂O₃ mixing ratio increased from 3.0 to 4.5 wt. %, the latent heat of modified ESH decreased further slightly.

The numerical studies have also been performed by various researchers on the based nano-PCM to investigate their thermal characteristics. Akhmetov et al. [64] numerically scrutinized the impact of doping of Al₂O₃ nanofillers on paraffin wax. The simulation results showed that the incorporation of Al₂O₃ improved the heat transfer of PCMs, but no significant change was observed in latent heat and specific heat capacity. Furthermore, composite PCMs reduces the

melting and solidification time compared to pristine PCMs, these reductions in charging and discharging time led to greater charging and discharging efficiency of the system. Bayat et al. [65] numerically investigated the two different nanoparticles (CuO and Al₂O₃) with paraffin as PCM to observe a melting process of PCM. They found that by adding a small percentage of nanoparticles (2 %) thermal performance was enhanced. Arasu et al. [66] in their numerical investigation also found that lower volumetric alumina content in paraffin wax had lower cost and high energy storage capability compared to higher concentrations. Furthermore, raising the percentage of nanoparticles not only stops the thermal enhancement but also decreases it and Al₂O₃ nanoparticles showed better performance than CuO at the same concentration. Despite the higher thermal conductivity of CuO, due to the high viscosity, heat transfer decreased [65]. Chen et al. [67] used PCM slurry with three different nanoparticles (i.e. Cu, TiO₂ and Al₂O₃) to enhance the performance of solar thermal energy storage systems. The results demonstrated that TiO₂ with 0.1% concentration in PCM showed better stability and thermal performance compared to Al₂O₃ nanoparticles. Similar to the study [67] it was reported in a current study that Cu nanoparticles exhibited poor stability they precipitated completely at the bottom after 72 hours.

In an empirical investigation on the melting of nano enhanced PCM (i.e. Al₂O₃/paraffin) in a squared enclosure heated horizontally and vertically, it was reported that with an increase in the volumetric concentration of alumina the melting rate of PCM was decreased [66]. This was because of the increased viscosity at higher concentrations of alumina which hindered the natural convection. Furthermore, vertical wall heating depicts a better melting rate and energy stored than horizontal wall heating in a square enclosure due to the increased natural convection effect. In the subsequent study [68], a numerical investigation on PCM embedded nano-Al₂O₃ (2%, 5% and 10%) was also performed and the results were compared with those from pure PCM in a concentric double pipe heat exchanger. In comparison to simple paraffin wax, nano-Al₂O₃ based paraffin wax greatly enhanced the charging and discharging performance. Table 3 demonstrates the influence of nanofillers on the charging and discharging rate of PCM.

PCMs with metal nanoparticles have also been studied. Ma et al. [69] investigated metal nanoparticles and expanded graphite (EG) as a supporting material based nano-PCM. It was observed that 11% EG and 1.9% Cu nanoparticles with paraffin were an optimal composition for nano-PCM at which no leakage was found during the phase change of PCM. Moreover, with this composite PCM thermal conductivity was enhanced by nine times, while a little decrease in the latent heat value was noted. Cui et al. [70] also examined Cu nanoparticles but

they used an inorganic PCM. In their study, they synthesised nano enhanced PCM to study the effect of supercooling. It was concluded that 0.5% of Cu nanoparticles in the salt hydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) PCM showed a minimum supercooling effect on the composite system.

What is more, that the inclusion of Cu nanofillers improves the heat storage efficiency by storing heat in a short time as compared to virgin PCM. Subsequently, Gupta et al. [80] examined magnesium nitrate hexahydrate (MNH) an inorganic PCM with two different metallic nanoparticles (Cu and Fe) for the solar thermal energy systems. The results have shown that 0.5% of Cu and Fe nanoparticles enhance the melting and solidification rate of nano-PCMs by (5.6% and 7.8%) and (30% and 35%) respectively compared to pristine PCM. Moreover, like the study [70] Gupta et al. also examined 0.5% Cu nanoparticles which displayed higher thermal conductivity compared to 0.5% of Fe nanofillers.

Due to their high thermal conductivity copper oxide was also used as a nanofiller with PCMs for the improvement in the thermal properties of PCMs. CuO nanoparticles with the RT-42 PCM were studied for the enhancement of thermal performance of Building-Integrated Concentrated Photovoltaics (BICPV) and were compared with the different configurations [81]. Only 0.5% of nano enhanced PCM showed an increase in the thermal conductivity and depicted better heat transfer performance than pure PCM. In another study [82] a comparative analysis between two different nano enhanced PCMs (i.e. PANI/paraffin wax (PWP) and CuO/paraffin wax (PWC)) was performed. It was found that 1% PANI/PCM and 0.1% CuO/PCM based nano enhanced composites increased the latent heat of nanocomposite by 8.20% and 7.81% respectively. The latent heat improvement maybe because of the strong interaction between the paraffin wax and the PANI nanofillers. Further, the large surface area of PANI nanofillers might also be the reason, which leads to the greater intermolecular interaction between the PCM and nanoparticles. Therefore, for the nanocomposite to shift its phase from solid to liquid, more energy needs to be supplied. The nano-PCM showed visual signs of agglomeration and deposition of nano-CuO composite due to the difference in their densities. In future work, other forms of TCE of nanoparticles with a density of the similar order as the base PCM could be used to overcome agglomeration problem.

Table 3 Influence on the charging and discharging time with nanoparticles incorporation

Reference	Nano-enhanced PCM		Charging/discharging effect
	PCM	Nanofiller	
Ebrahimi and Dadvand [71]	Paraffin wax	Al ₂ O ₃	By the addition of the 2wt.% of Al ₂ O ₃ nanoparticles the melting time was reduced at all heating modes.
Singh et al. [72]	Sugar alcohol (d-mannitol)	GNP	The melting time was reduced by 11%, 39% and 55% with the 1, 3 and 5 wt.% of GNP nanoparticles in the PCM.
Ebadi et al. [73]	Coconut oil	CuO	With only 0.0218 wt.% of CuO nanofillers the overall melting time was reduced by 15%.
Farzanehnia et al. [74]	Paraffin wax	MWCNTs	Compared to pristine PCM, applying MWCNTs to PW decreased the discharging period by 6 %. In addition, the PCM and nano PCM presence reduced the temperature rise and improved the electronic components working time.
Abdulateef et al. [75]	RT-82	Al ₂ O ₃	In paraffin, the existence of nanoparticles enhances the overall performance, particularly in the discharging phase.
Khan and Ahmad Khan [76]	Paraffin	GnP, Al ₂ O ₃ and aluminium nitride (AlN)	Introducing AlN, Al ₂ O ₃ and GNP to pristine PW raises the melting rate by 36.47%, 28.01% and 44.57%, and the solidification rate by 34.95%, 14.63% and 41 %, respectively.
Kalaiselvam et al. [77]	Eutectic PCM	Al and Al ₂ O ₃	In comparison with pure PCM, the addition of Al and Al ₂ O ₃ nanofillers decreased the discharging process by 4.97 % and 12.97 %, respectively.
Ma et al. [78]	RT-24	Cu	At a specific time, Cu/RT-24 based nano PCM charged and discharged 8.3 and 25.2 times more energy respectively, as compared to the neat PCM.
Xiao et al. [79]	Binary nitrate	EG	The dispersion of 20% EG into the PCM decreased charging and discharging time by 26.9% and 68.8%, correspondingly.

Nano magnetite (Fe_3O_4) based PCM needs to be prepared by sol-gel method and dispersed these particles in the paraffin PCM for energy storage purposes [83]. In this study, the particles having different concentration (1%, 5%, 10% and 15%) was added to melted PCM then this mixture was stirred for two hours with an ultrasonic water bath to get a homogenous mixture. In the DSC analysis, it was discovered that latent heat of the nano composite PCM was increased by 20% by the addition of 10% of Fe_3O_4 and with almost negligible change in melting temperature. Later, in the other study [84] a higher concentration of Fe_3O_4 (10% and 20%) was employed. For 10% and 20% Fe_3O_4 the thermal conductivity was enhanced by 48% and 67% respectively. Besides, when latent heat value was compared with that from their previous study for 10 % of Fe_3O_4 [83] both studies showed an increase in the latent heat compared to virgin PCM, but their previous study showed higher latent heat than the current study [83]. This may be because of little difference in the preparation method of nano-PCM from the same team, however, this needs a further investigation for future work to identify the reason.

Silicon nanoparticles based PCM has also been explored to observe their thermal characteristics. From the literature silicon-based nanoparticles were found to be stable. Although thermal conductivity increased with the addition of Si based particles, latent heat was found to be decreased with these particles. Recently, Ranjbar et al. [85] have reported excellent thermal stability, good phase change behavior, and enhanced thermal conductivity for n-heptadecane by the loading of SiO_2 nanoparticles. The melting and solidification enthalpies for nanocomposites were 123.8 and 120.9 J/g respectively. Furthermore, gypsum was added into the nanocomposites to observe its performance for building performance and they found that nanocomposites integrated gypsum maintains the room temperature at a comfortable range. Babapoor and Karimi [60] also found good stability of SiO_2 based nano-PCM when they compared it with other nanoparticles. They dispersed different metal oxide nanoparticles (SiO_2 , Al_2O_3 , ZnO , and Fe_2O_3) in paraffin PCM and it was noted that 8% SiO_2 /paraffin composite showed better stability compared to other composites.

In some studies, authors investigated a combined effect of silicon-based nanoparticles with other supporting materials. For example, Zhang et al. [86] experimentally studied the effect of silica nano particles and EG on n-Eicosane phase change material. It was noted that silica nano particles prevent leakage during melting due to their strong adsorption capability and the leakage test showed that the maximum adsorption mass fraction of n-eicosane in CPCM occurred at 70% wt.%. Moreover, the addition of 3% EG into n-Eicosane/silica nano-PCM increases the thermal conductivity and latent heat of nano-PCM, but a decrease in the latent

heat was also observed when EG concentration exceeds by 3%. Tony and Mansour [87] investigated paraffin with silica treated ZnO nanofillers and compared the results with untreated ZnO. The results illustrated that treated ZnO/PCM showed better stability than untreated ZnO due to the synergistic effect between PW and SiO₂. This may be explained by the presence of the coated layer of SiO₂ on ZnO enabling a good dispersion throughout the host paraffin wax. This provides more sites for inorganic nanoparticle materials, which enhances the probability of absorbing heat leading to an increase in the latent heat of fusion of paraffin wax.

2.1.4 Metal carbides and metal nitrides nanoparticles based PCMs

Different forms of nano boron nitrides (BN) have been studied for better performance of composite PCMs. Fang et al. [88] integrated hexagonal boron nitride nanosheets (h-BN 100nm) with PEG for the preparation of nanocomposites. As a result of improved thermal conductivity by the incorporation of h-BN, the melting and crystallization rates were also reported to be accelerated by up to 25%. Moreover, 10% of h-BN improved the TC of composite by 60% and reduced the latent heat by 12%. Huang et al. [89] prepared anisotropic reduced graphene oxide/boron nitride (rGO/BN) composite aerogel to form CPCM. The addition of BN enhances anisotropic aerogel rigidity to lessen its contraction during the thermal cycle, and also increases its thermal conductivity. The axial thermal conductivity was 1.68 W/m K, which was 504 % greater than that of pure paraffin, while the mass ratio of GO to BN was 1:20. At the identical BN concentration, latent heat was decreased at a higher rate for rGO/BN composite than h-BN/PEG composite in the previous study [88]. This is because of rGO does not contribute towards the latent although rGO contributes towards the enhancement in the thermal conductivity.

It has been reported that an introduction of metallic carbides (MXene) to PCM may have significant effects on PCM properties. Aslfattahi et al. [90] integrated metallic carbides (MXene) with paraffin PCM for the development of energy storage materials. They investigated nanocomposite at different concentrations of MXene (0.1, 0.2 and 0.3%) and found an increase in the thermal conductivity and specific heat capacity of nanocomposites by 29.5% and 43% for 0.2 and 0.3 wt. % of MXene particles. In comparison to pure PCM, the latent heat of nanocomposite decreased with the addition of particles, however, a larger concentration of particles showed greater latent heat compared to particles with lower concentration. In the other study, Krishna et al. [91] used (Ti₃C₂) MXene nanofiller with palmitic acid as PCM (T_m=60-62°C) for solar thermal power plants. In this study, thermal

conductivity enhancement at 0.1% of MXene was greater than that in their previous study because the DSC results showed that no shift in melting temperatures for MXene/PA composites was noted. However, with 0.1% MXene concentration an increase of 4.36% in the palmitic acid enthalpy was observed probably because of strong interactions between PA and MXene.

A variety of nanofillers were investigated to examine the performance of the nano-PCM composite. Typically, Rao et al. [92] prepared nano aluminum nitride (AlN) and paraffin based nano PCM for energy storage purposes. The DSC results indicated that with 3% of AlN latent heat of the nano PCM was decreased from 171.13 J/g to 165.32 J/g. However, AlN/paraffin composite PCMs exhibited good structural and thermal stability. Selvaraj et al. [93] used beryllium oxide nanomaterials (0.5%, 1%, 1.5% and 2%) with deionized water and PEG PCMs. It was found that latent heat efficiency and thermal diffusivity of 2% BeO nano-enhanced PCM was improved by up to 23% and 30%, respectively, compared with those of the base material (PEG). Wu et al. [94] prepared two dimensional montmorillonite nanosheets (2DMts) using the ultrasonic method. A phase-change energy storage composite material (2DMt/SA) was prepared using a self-assembly technique, with 2DMts as the host and energy storage molecule stearic acid (SA) as the guest. The composite 2DMt/SA had a high latent heat storage potential (192.4 J/g), almost similar to that of the pristine PCM. Moreover, the thermal stability of 2DMt/SA was significantly improved as compared with SA PCM.

2.1.5 Overview of the effects of single type of nanoparticles in PCM thermal properties

Overall, the dispersion of different nanofillers in the PCM matrix could result in an increase in the thermal conductivity and a decrease in the latent heat value. In comparison to other nanoparticles, carbon-based particles have showed good thermal stability which results in the greater enhancement of thermal conductivity and moderate decrement in the energy storage capacity of PCM because carbon based nanofillers are highly conductive and their greater surface area contributes towards the greater intermolecular interaction with PCM molecules.

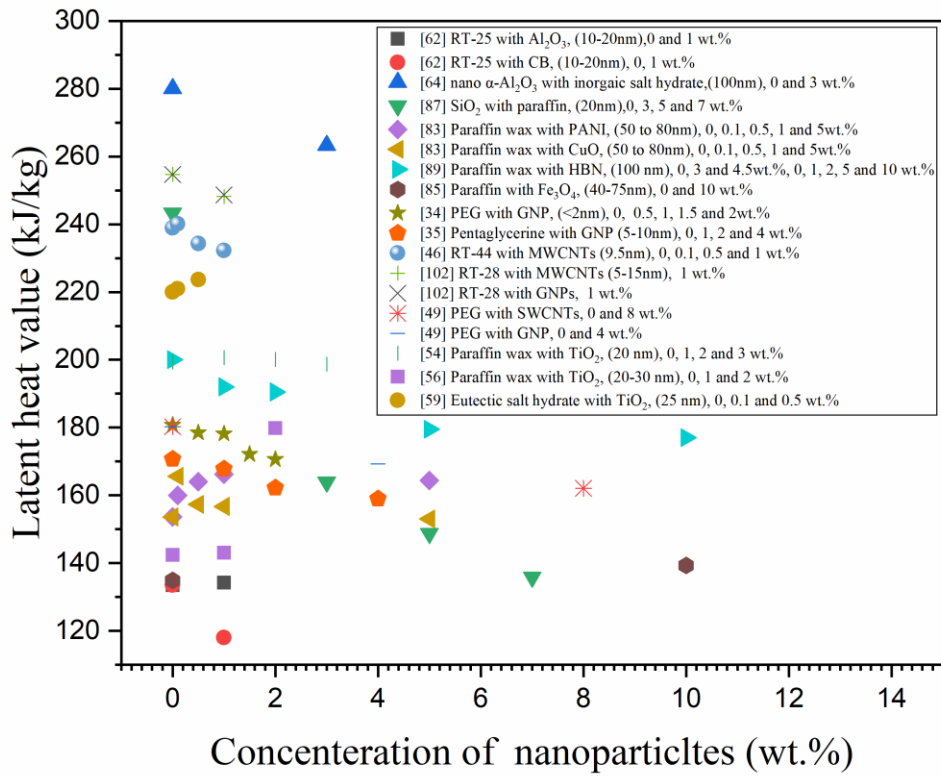


Figure 9 Effects of nanoparticle concentration on latent heat

Important parameters of nano-PCMs from useful studies have been summarised in Table 5. Figure 9 and Figure 10 show the latent heat and thermal conductivity comparison of some important studies, when different nanoparticles were used with PCMs.

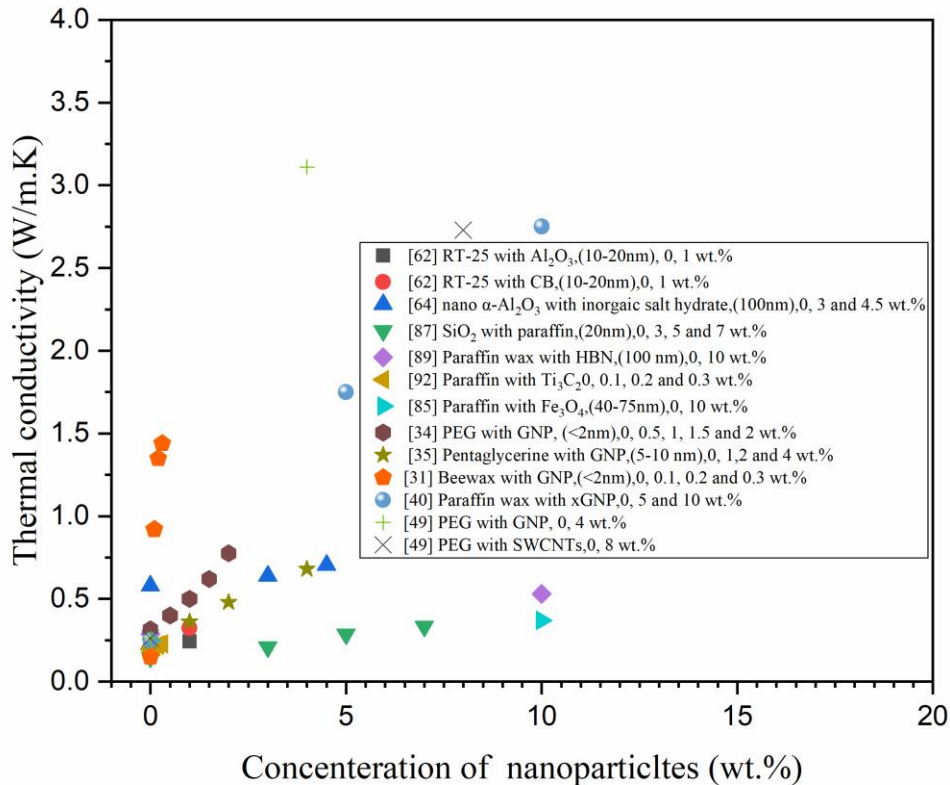


Figure 10 Effects of nanoparticle concentration on thermal conductivity

The latent heat and thermal conductivity data from different studies is collected to compare the results of latent heat and TC when the PCM is pristine and when different types of nanofillers were dispersed into it. Although the difference in the various parameters (thickness, size, and PCM) make the comparison between references complicated, the best composite by keeping an eye on all aspects could be identified. As shown in Figure 9, almost in all studies latent heat value reduces with a rise in the nanoparticles concentration as compared with pristine PCM. Several justifications for the decrease in the latent heat have been reported by different scholars, as given below.

- This might be due to the increased thermal conductivity on PCM based composites, which accelerates the evaporation of pure PCM [95].
- The weak intermolecular forces between PCM and nanoparticles [95].
- The non-melting enthalpies of nanoparticles, that would reduce the composites melting enthalpy [95].

- The realignment of the PCM molecules in the existence of severely charged nanoparticles is difficult, which is also a significant explanation for the reduction of the composites latent heat [96].
- Latent heat may also decrease due to the reduction of mass fraction of PCM in PCM based nano composites [37].
- The leakage of PCM during phase change also contributes to the reduction of latent heat [97].
- Since the distributed filler inhibits the local molecular bonding condition and impedes the PCM melting cycle [98].

However, polyaniline (PANI) and CuO based paraffin wax composites showed little enhancement in energy storage capacity compared with the virgin PCM this may be because of the large surface area of nanoparticles and strongest intermolecular interactions between PCM and nanofillers. On the other hand, SiO₂/paraffin combination showed highest decrement in the latent in contrast to the pure paraffin wax. Furthermore, among all the nano composites CNTs and TiO₂ based PCM composites showed excellent stability for the thermal energy storage capacity. PCM incorporated with TiO₂ nanoparticles either showed an increase in the latent heat or demonstrated little decline in the value compared to the pure PCM.

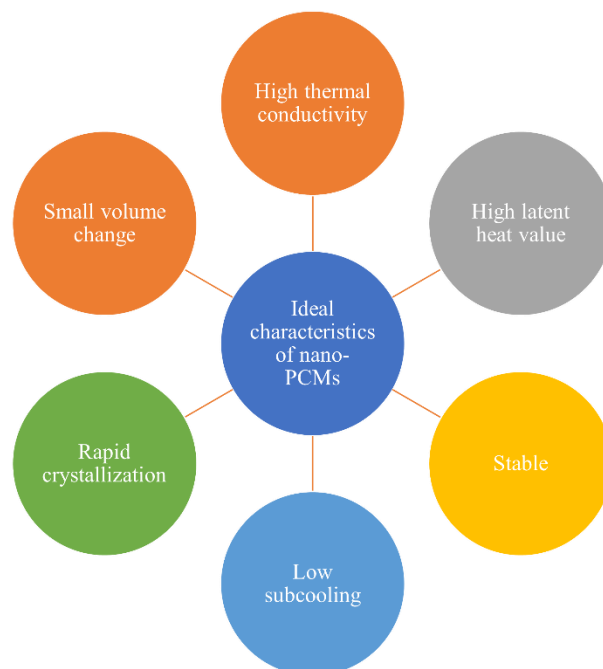


Figure 11 Ideal characteristics of nano-PCMs

Figure 10 shows the relationship between particles concentration and thermal conductivity and it appears that they have a direct relation between them. As the weight percentage of the nanoparticles increases, the thermal conductivity value surges. It can be suggested that the nanofillers with high thermal conductivity values have shown greater enhancement when they are impregnated with PCM. For instance, a small concentration of GNP particles has shown magnificent improvement in the TC due to their high TC values. Moreover, Figure 11 shows some ideal characteristics of nano-enhanced PCMs identified from the literature.

2.2 Hybrid nanoparticles based PCMs

The studies have been reported by different investigators in which they examined the thermo physical properties of more than one nanoparticle (hybrid nanoparticles) with different PCMs. Qi et al. [30] used graphene and graphene oxide nanofiller for thermal conductivity enhancement and stabilization of PEG respectively. The nanocomposite samples were prepared by physical blending method with 2 wt. % of GO and 0.5 wt. %, 1 wt. %, 2 wt. % and 4 wt. % of GNPs. The results showed that the incorporation of GO and GNP was shown to be effective supporting materials and conductive materials, respectively. Moreover, the latent heat was also enhanced slightly with the incorporation of hybrid nanofillers. In the other study [99], again they investigated hybrid graphene nanoplatelets (GNP) and graphene oxide (GO) with PEG but used a different preparation method (Vacuum impregnation). Further, in this study the content of nanoparticles was lesser than in their previous study [30]. The comparison results of the two experiments showed that the low nanofiller content displayed more latent heat than the higher particulate content. For thermal conductivity, it was the opposite that a high concentration of particles led to higher thermal conductivity compared. Because graphene-based particles have greater thermal conductivity so a higher concentration of graphene nanoparticles in the PCM further boosts their TC value. However, further investigation is needed by using both methods for similar particle concentration to identify the efficient method.

A few of studies was found on hybrid nanoparticles in which researchers combined different nanoparticles to improve the thermal properties of PCM. Zhang et al. [100] used GO/SiO₂ hybrid aerogel as the matrix supported for the preparation of composite PCMs for insulation. The hybrid aerogel was synthesised with the addition of 0.5 wt.% of GO in silica gel with a high surface area (948 m²/g) and low thermal conductivity (0.0277 W/m k). The latent heat and thermal conductivity of the composite PCM reached maximum values of 145.6 J/g and 0.0808

(W/m K) respectively when the mass percentage of graphene oxide was 0.5 %. Moreover, the GO/SiO₂ hybrid aerogel-supported composite PCM was found to be beneficial for conversion from light to heat. Arshad et al. [101] experimentally investigated carbon and metal oxides based single and hybrid nanoparticles for the thermal management of electronic devices. The experimental results showed a little decrease in the latent heat capacity of hybrid nanoparticles based PCM as compared with pristine PCM. However, hybrid metal oxides (Al₂O₃/CuO) based nano-PCM showed a higher latent heat value than that of carbon-based hybrid nanoparticles (GNPs/MWCNTs), while for thermal conductivity (GNPs/MWCNTs) hybrid composite exhibited better performance than hybrid metal oxides. So, further research may be needed on the metal oxide and carbon-based hybrid nanofillers to investigate their performance. Manirathnam et al. [102] conducted an energy analysis for a solar water heater and compared the results with three cases, PCM, nano-PCM and without both. The nano-PCM was prepared by using the two-step method in which paraffin wax was combined with SiC and CuO (1 wt.%) nanoparticles. The results showed that the values of energy efficiency were 33.8%, 38.3% and 41.7% for all three cases i.e., without PCM, with PCM and with nano-PCM, respectively. Parameshwaran et al. [103] developed hybrid nanofillers (Cu and TiO₂) and dispersed these fillers into the PCM for enhancement in the thermal properties of composite PCMs. They found that Cu nanoparticles were adsorbed on the TiO₂, which helped to achieve better heat transfer across pure PCM layers. The addition of these fillers into PCM also minimised the supercooling effect and enhanced the latent heat values contrast to pure PCM. Moreover, nano enhanced PCM remained thermally stable up to 100.4 °C.

A comparison between hybrid nano-PCM and mono nano-PCM regarding the latent heat and thermal conductivity is shown in Figures 12 and 13, respectively. Both figures show the enhancement or deterioration in the percentage of latent heat and thermal conductivity when nanoparticles were incorporated into the PCM.

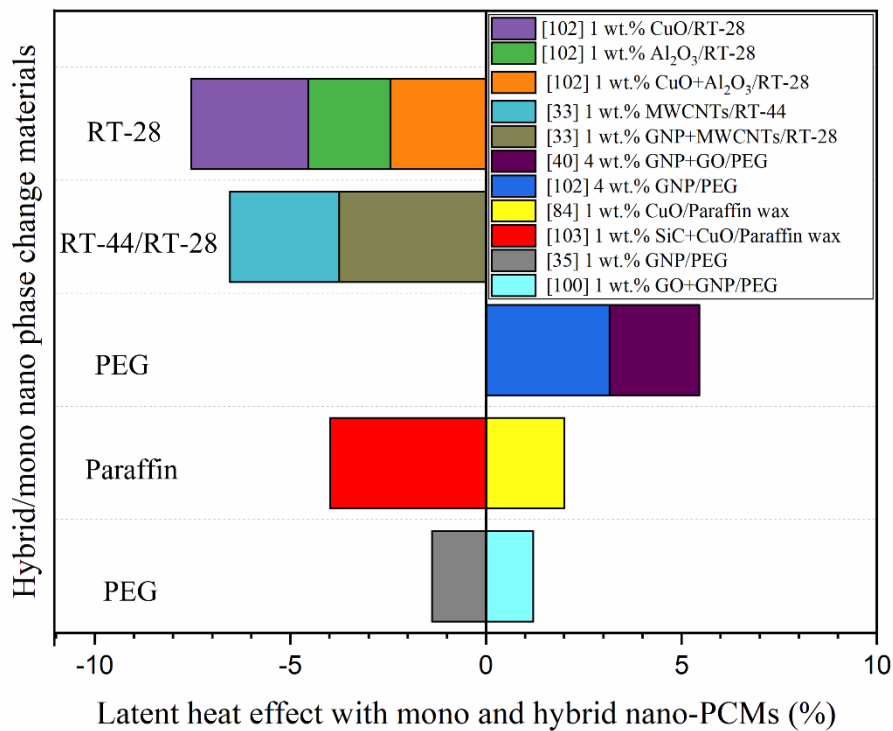


Figure 12 Hybrid and mono nanofiller effects on PCM latent heat

As shown in Figure 12, the increment or decrement in a percentage of latent heat has been taken with reference to the latent heat of pure PCM. Figure 12 demonstrates that latent heat percentage declines with the addition of either mono or hybrid particles and the possible reasons for this decline in energy storage capacity have been discussed in the previous section. Among all composites, PCM dispersed with SiC/CuO nanoparticles shows a greater decrease in the latent heat. GO/GNP based PEG PCM composite shows little increase in the energy storage capacity due to the strong physical interactions between GO and PEG in PEG/GNP/GO composite, which has also prevented the leakage of PCM during phase change. In addition, CuO/paraffin composite also reveal an intensification in the latent heat, and it might be attributable to the large surface area of CuO nanofillers this leads to an intermolecular contact between the PCM and CuO, while due to the poor physical interaction between SiC and paraffin the decrement in the latent heat has been reported. Although in most cases latent heat diminishes with impregnation of mono or hybrid nanofillers, mono nanoparticles have shown more decline than hybrid nano-PCM composites.

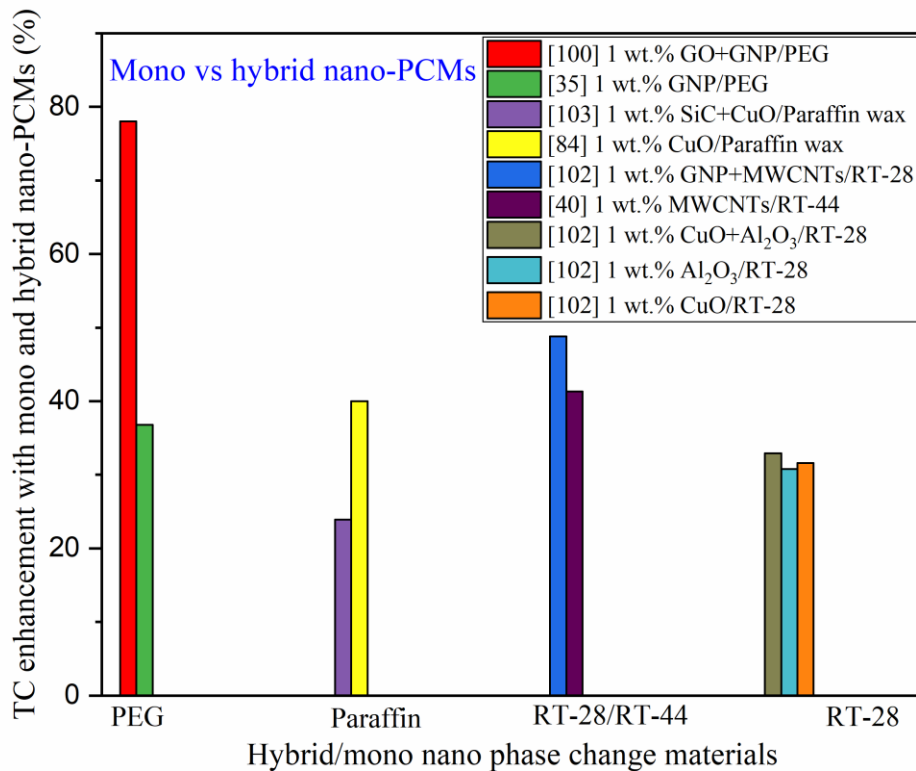


Figure 13 Hybrid and mono nanofiller effects on PCM thermal conductivity

Similarly, a thermal conductivity comparison of mono and hybrid particles shown in Figure 13 has been conducted to get an idea about the potential nanofillers. From Figure 13 it can be seen that the hybrid nanofillers based PCM composites have shown a higher increase in thermal conductivity than mono nanofillers, but due to the poor interaction and thermal resistance between SiC and paraffin wax it has shown a decrease in thermal conductivity, while CuO/paraffin has depicted excellent TC. What is more, due to the higher TC value of GNPs it demonstrated a great enhancement in TC than other nanoparticles. Table 4 has summarised the thermal properties of different studies on hybrid nanofiller based PCM composites.

Table 4 Thermal properties of nano-PCMs

References	PCM		Nanoparticles		Thermal conductivity (W/m. K)		Latent heat of melting (kJ/kg)		Latent heat of crystallization (kJ/kg)		Nanoparticles		
	PCM	T _m (°C)	T _c (°C)	Material	Wt. (%)	Pure	Nano-PCM	Pure	Nano-PCM	Pure	Nano-PCM	Shape	Size
[37]	RT-22	22	-	GNP	0.05	0.15	0.46	163.31	161.43	169.02	68.68		
			-		0.1		0.92		160.95		165.56	Rolled thin	w 2µm thick 2 nm
			-		0.15		1.1		155.47		164.53		
[31]	PEG	55.8		GNP	2	0.316	0.776	180.7	170.6	161.3	151.3	-	T < 2 nm, W < 2nm
[104]	RT-64	61		GNP	3	0.295	0.605	230.4	225.38	-	-	-	130 nm
					5		0.830		210.18				
					7		1.040		194.53				
[105]	n-octadecane	28	-	xGNP	3	0.28	0.98	256.5	245.8	-	-	-	-
[28]	Hexadecane	18-20		xGNP	3	0.66	0.992	232.41	217.33	-	-	-	T < 10 nm
	Octadecane	26-30				0.49	0.873	241.97	240.92				
	Paraffin wax	53-57				0.35	0.454	142.72	140.99				
[106]	Salt hydrate	30	-	GO	2	0.68	1.05	220	200.3	147	160	Hexagonal	thick 1.318nm
[42]	Paraffin wax	59	-	S-MWCNTs	5	0.263	0.324	207	178.2	-	-	-	Size 500nm 815 nm
				L-MWCNTs	5		0.309		177.3				3050nm
				CNFs	5		0.305		185				150200 nm
				GNP	5		0.7		186.5				420 nm

Continued...

References	PCM		Nanoparticles		Thermal conductivity (W/m. K)		Latent heat of melting (kJ/kg)		Latent heat of crystallization (kJ/kg)		Nanoparticles		
	PCM	T _m (°C)	T _c (°C)	Material	Wt. (%)	Pure	Nano-PCM	Pure	Nano-PCM	Pure	Nano-PCM	Shape	Size
[53]	Paraffin	60	54	TiO ₂	1	-	-	199.4	200.6	194.5	193.9	-	20-30nm
					3	-	-		198.7		193.6	-	
[84]	Paraffin wax	42	-	Fe ₂ O ₃	10	0.25	0.37	134.9	139.3	-	-	-	40-75nm
[59]	Paraffin wax	30	-	α Al ₂ O ₃	2	-	-	159.46	210.99	26.143	34.591	-	1.4-2nm
[62]	Paraffin wax	26.5		Al ₂ O ₃	5	0.13	-	243.1	225.6	-	-	-	-
					10				212.3				
[70]	Inorganic SH	59		Cu	0.5	0.921	1.155	242.4	234.5	-	-	-	10-30 nm
[82]	Paraffin wax	58	-	PANI	0.1	0.203	0.203	153.6	160.03				
					1		0.298		166.2				
					5		0.247		164.43				
				CuO	0.1	0.203	0.246	153.6	165.62	-	-	-	50-80 nm
					1		0.332		156.76				
					5		0.268		153.04				

Table 5 Thermal properties of hybrid nano-PCMs

References	PCM		Nanoparticles		Thermal conductivity (W/m. K)		Latent heat of melting (kJ/kg)		Latent heat of crystallization (kJ/kg)			Nanoparticles	
	PCM	T _m (°C)	T _c (°C)	Material	Wt. (%)	Pure	Nano-PCM	Pure	Nano-PCM	Pure	Nano-PCM	Shape	Size
[29]	PEG	60	-	GO/GNP	2/0.5 2/1 2/2 2/4			170.5	174.6 174.7 175.9 178.1	0.29	- - - 1.72	- - - -	-
[102]	Paraffin wax	60	-	SiC/CuO	0.5/0.5	0.172	0.226	166.7	160.3	-	-	-	15 nm
[101]	RT-28	28	-	CuO/Al ₂ O ₃	0.75/0.25	0.22	0.328	254.73	248.51	-	-	-	CuO <50 nm, Al ₂ O ₃ 13 nm
				GNP/MWCNTs			0.430		245.18	-	-	-	MWCNTs 5- 15nm
[100]	n-octadecanol	61	-	GO/SiO ₂	0.05/0.05 0.5/0.5 2/2	-	-	237.8	136.2 145.6 129.6	-	-	-	15 nm

2.3 Summary

Overall, the inclusion of all nanomaterials into a PCMs results in an increase in thermal conductivity and a decline in latent heat. The carbon-based nanofillers showed greater enhancement in the thermal conductivity than other particles because of their high conductivity values. In addition, carbon-based nanoparticles have good stability because of their lower density and large surface areas. Moreover, carbon-based nanoparticles have good stability because of their lower density and large surface area. However, CNTs do not disperse into the PCM properly, which leads to agglomeration because of their hydrophobic nature. This issue can be overcome by the surface treatment of CNTs. On the other side, metal oxide particles, such as, TiO₂ particles showed little decline in the latent heat because of their greater intermolecular interactions with the PCM, but they depict only small increase in the thermal conductivity, as metal and metal oxide particles have low thermal conductivities. That is why carbon-based particles are usually preferable by researchers since a significant improvement in thermal conductivity with carbon-based fillers is appropriate for a small reduction in the energy storage capacity of PCMs. But one main disadvantage of the carbon-based particles is that they are expensive compared with the metal and metal oxide particles. Hybrid nanoparticles (i.e., carbon and metal or metal oxide particles) with a small proportion of carbon particles and a large concentration of metal or metal oxide particles can minimise the overall cost of particles, while also improving the thermophysical characteristics of the nano-PCM.

3. Preparation methods for nano-PCMs

Two main techniques are commonly followed for the preparation of nano phase change materials to conduct an experimental investigation and are termed as single-step method and two-step method. Figure 14 shows the preparation methods for nano enhanced PCM composites. Simultaneous dispersion of individual nanoparticles or the dispersion of nanocomposites in the base fluid is the approaches listed in the literature for the preparation of nano-PCM. This section has presented a brief overview of nano phase change material preparation techniques.

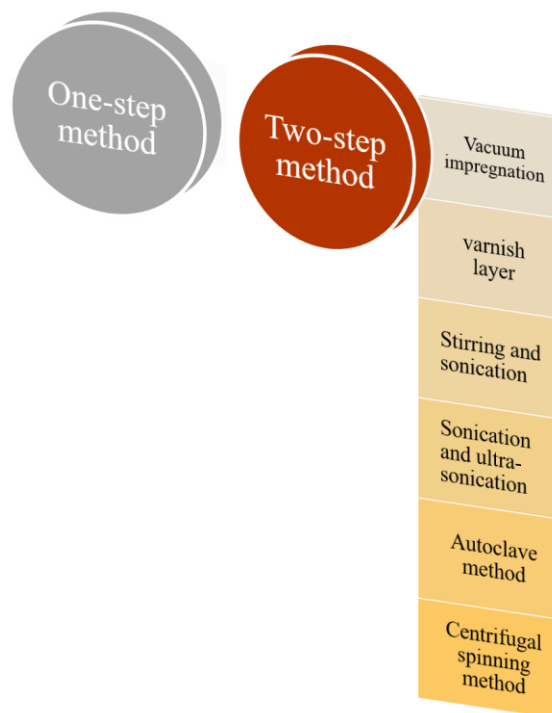


Figure 14 Preparation methods for nano enhanced PCMs

3.1 One-step method

As shown in Figure 15, nanoparticles are synthesised and dispersed at the same time in one-step process, in simple words, all the processes are carried out in a single phase, that is the reason why this method is called the one step method. In order to achieve better stability and to avoid the formation of clusters this approach is considered the most successful. Moreover, the transporting, storage, drying, and mixing of nanofillers in the PCM does not require in this process, thus optimizing the dispersion of nanoparticles in the corresponding PCM and decreasing the conundrum of particle accumulation.[107]. This technique is only utilized on a limited scale since it is more expensive than the two-step method.

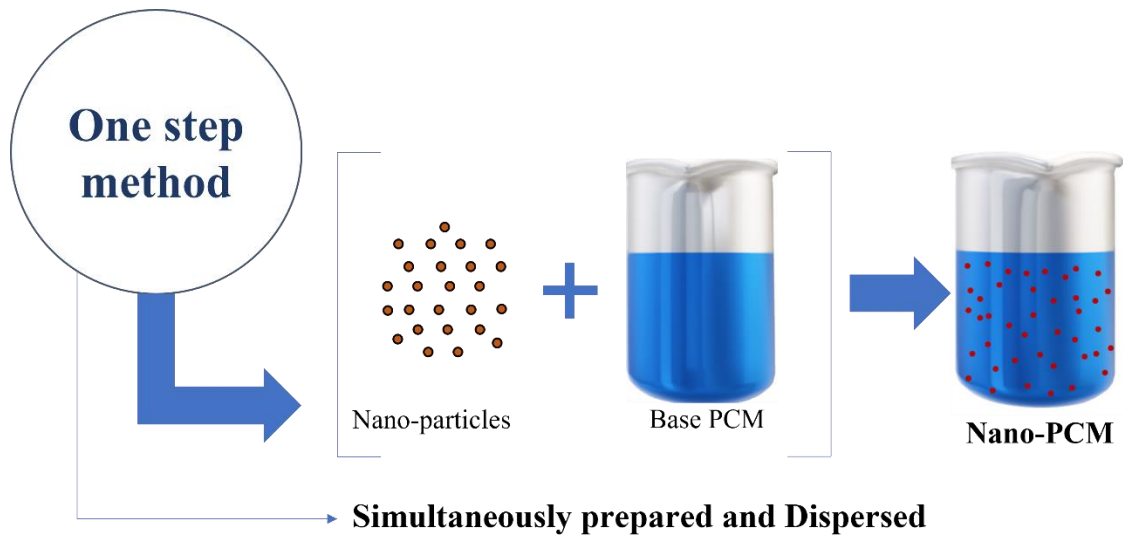


Figure 15 One step method for a PCM preparation [23]

Typically, Mohamed et al. [59] blended urea and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into purified water and microwaved this mixture for 3-5 minutes. The petroleum wax was then applied to this solution and the mixture was sonicated for half an hour to obtain the petroleum wax/alpha-nano alumina composite. By direct synthesis technique, Teng and Yu [53] prepared nano-PCM in which TiO_2 , Al_2O_3 , ZnO and SiO_2 nanoparticles were mixed with paraffin wax with 1.0 wt.%, 2.0 wt.%, and 3.0 wt.% concentration, and the concoction were stirred for 0.66 hours to attain smooth dispersion.

3.2 Two-step method

In two step technique, nanofillers are primarily collected in dry powder form utilizing various mechanical and chemical methods such as, ball milling, chemical reduction, and sol-gel methods. The nanofiller powder obtained is then combined with the base PCM and for homogeneous particle dispersion. Distinct methods were used including ultrasonication and magnetic stirring. The two-step schematic diagram is shown in Figure 16. The greatest advantage of this method is the processing of nanocomposites on a commercial scale; however, this technique has the problem of agglomeration of particles and thus enhances the use of a single-phase preparation process [107,108]. To prevent filler agglomeration, surfactants are used by forming a barricade and reducing the surface tension among the PCM and the suspended fillers. Furthermore, surfactants help to stabilise the nanofluid by generating zeta potential and repulsive forces [109].

By two-step method, prominent researchers prepared various nano-PCMs under distinct stirring and sonication times. Sharma et al. [81] developed nano-PCM by mixing CuO with a

mass fraction of 0.5% in RT-24 PCM at 60°C and then the blend was ultrasonicated for 1440 minutes in an ultrasonicator apparatus. Latibari et al. [110] investigated SiO₂ nanofiller with palmitic acid as PCM and SDS dispersant using the two-step method. Firstly, dispersant was dissolved into the distilled water and then PCM was incorporated, and the mixture was stirred at 1000 RPMs for two hours. The solution was added to the palmitic acid emulsion drop by drop, and the mixture was stirred for four hours at 500 rpm. The emulsion was then cooled to room temperature and rinsed with centrifuged and distilled water. The white powder produced by the process was collected and dried for 10 hours before being washed with toluene to extract any unencapsulated palmitic acid. The solvent was centrifuged once more, and the white powder was collected and dried for an entire day.

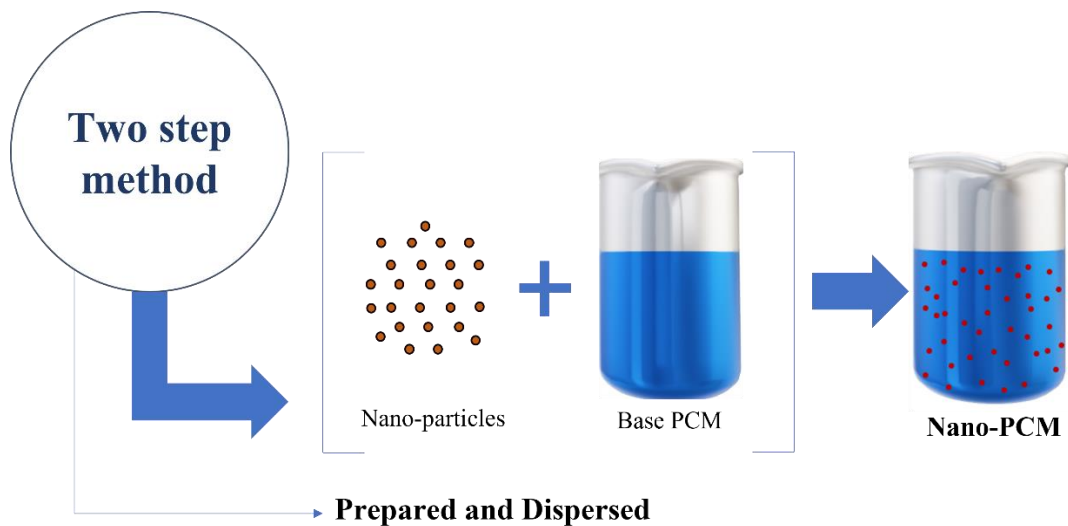


Figure 16 Two-step method for a PCM preparation [23]

3.2.1 Vacuum impregnation method

Figure 17 shows a vacuum impregnation process. Typically, Sari et al. [111] prepared the expanded graphite (EG) and fatty acid (PCM) composite using the vacuum impregnation method. There are three stages. Firstly, porous expanded graphite was placed into the flask which was connected with water trap apparatus for the removal of air from porous EG, for a 30-minute evacuation process continued at vacuum. After the removal of air from EG, the valve between the PCM container and flask was opened to permit melted PCM into the container to cover up all porous EG. Lastly, the vacuum procedure was completed, and the air was permitted into the container which forces the melted PCM to penetrate completely into the pores of EG. The EG/fatty acid was instantaneously heated through the infiltration procedure at a steady temperature beyond the melting point of PCM to check the leakage from the pores.

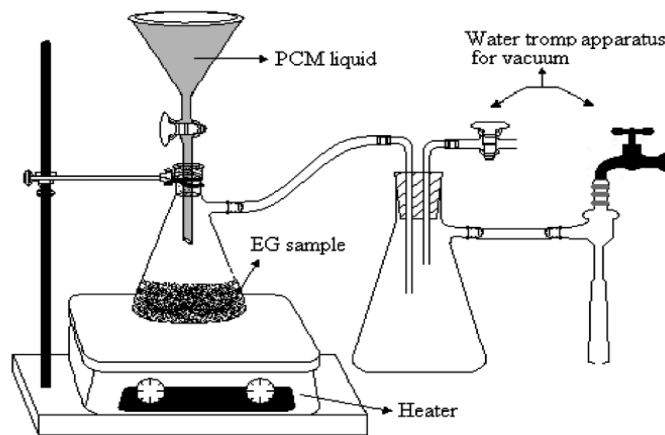


Figure 17 Vacuum impregnation process [111]

3.2.2 Varnish layer method

Varnish is a hard, transparent, protective film that is mainly employed in wood finishing but can also be implemented to other materials. The varnish layer method is used to prevent PCM leakage during solid-liquid phase change by film formulation utilising varnish [112]. Wi et al. [105] used the varnish layer technique for the preparation of PCM/xGNP composites. In this method, n-octadecane melted PCM was directly mixed with xGNP. Then this mixture was impregnated into the hollow to form a cylindrical sheet, and the cylindrical sheet was enclosed with varnish to prevent the seepage of PCM during melting. Finally, the composite was allowed to be dried for two complete days at 50% relative humidity and a constant temperature of 25°C. The cylinder-shaped hollow was formed by blending 1:0.45 water and plaster, creating a cuboid using a cylindrical mould.

3.2.3 Stirring and sonication

In the stirring and sonication method mixtures are first stirred using magnetic stirrer for certain time and rotational speeds, and then the stirred mixture is subjected to sonication at a particular frequency to get uniform dispersal of nanofillers in the base PCM. Jeon et al. [28] followed a stirring and sonication method for the preparation of PCM/xGNP composite. In this method, PCM was melted beyond its melting point and in the next step liquid PCM was mixed with xGNP using a stirrer for 20 minutes at the stirring speed of 1000 rpm. Then this mixture was sonicated in a sonicator for 20 minutes and left for cooling.

3.2.4 Sonication and ultra-sonication

Figure 18 shows the schematic of this process. Typically, Putra et al. [37] prepared their nano-PCM using sonication and ultra-sonication method. In this method, the graphene and melted PCM were mixed with a stirrer and left for sonication at the frequency of 40 Hz. Then the

obtained nano-PCM was subjected to ultra-sonication in the ultra-sonicator bath at 45°C for three hours till the full dispersion of graphene with RT-22.

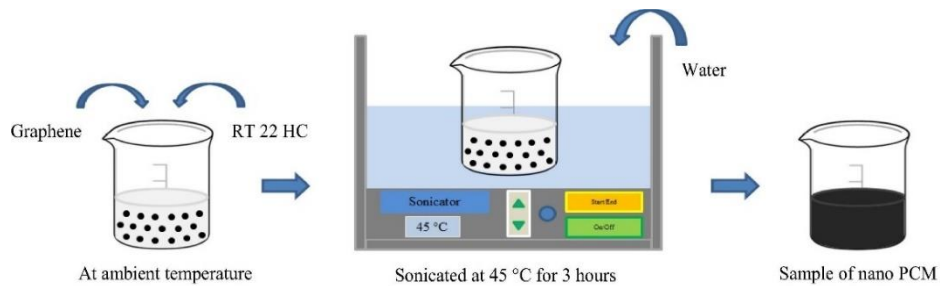


Figure 18 Schematic of sonication and ultra-sonication method [37]

3.2.5 Autoclave method

Autoclave processing is among the oldest and most commonly used methods of processing high-performance composite materials. Zeng et al. [113] prepared nano-PCM using the autoclave method, which to enhance the absorptivity of PCM. In their approach, PCM (TD) was mixed with ethanol. After mixing, PCM was melted and infiltrated directly into the EG then TD/EG composite was heated up to 70°C to evaporate the ethanol from the composite.

3.2.6 Centrifugal spinning method

Centrifugal spinning is a better and effective way to quickly produce nanofibers. It uses centrifugal force rather than high voltage to generate nano-PCM. Figure 19 shows the schematic and actual illustration of centrifugal spinning method. Chen et al. [114] prepared shape-stable nano-PCM using the centrifugal spinning method. Firstly, PAN/PEG/SiC were mixed in the N-dimethylformamide solvent. Then for the homogenous dispersion of PAN, PEG and SiC in the N-dimethylformamide solution, the mixture was stirred in a magnetic stirrer at 25°C for 24 hours. After stirring the prepared solution was allowed into the spinning vessel and PCMs fibres were obtained by ejecting the solution at 4300rpm.

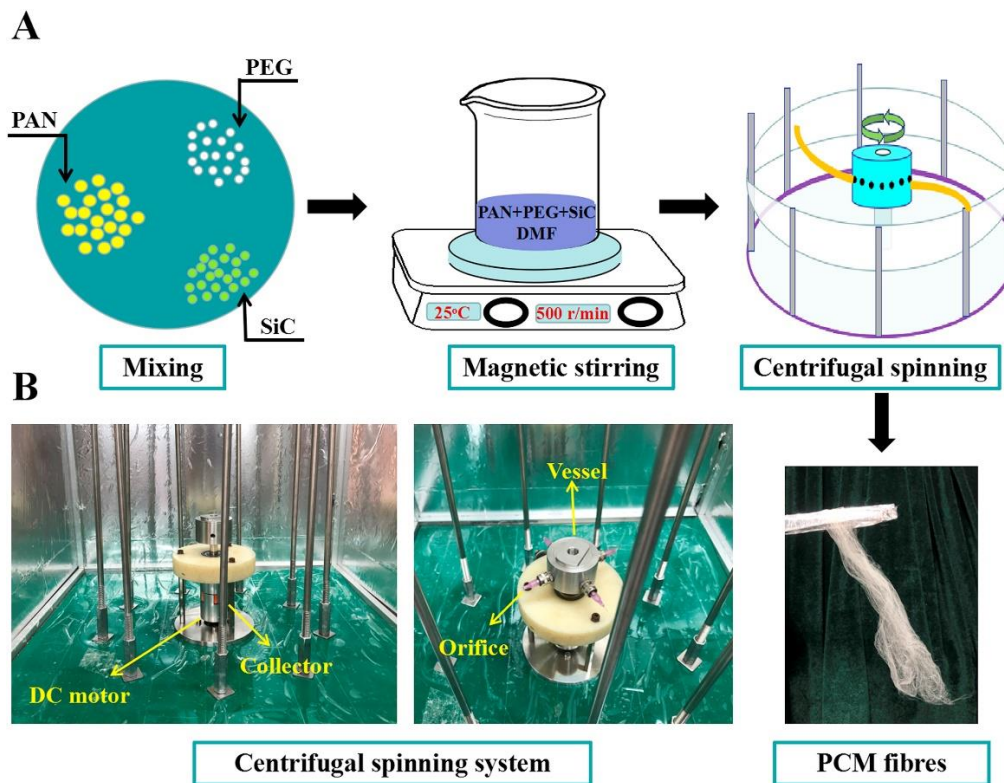


Figure 19 Centrifugal spinning method [114]

3.3 Summary of nano-PCM preparation methods

Even though the one-step method improves the stability duration and provides better dispersion of nanoparticles, its disadvantages, such as high costs, complex process, and the limitation of small-scale production of nano-PCMs limit its application. In addition, one step nano-PCM preparation technique can help to achieve long-term stability, but it still awaits the attention of the investigators to make it a more cost-effective and smart process by eliminating the production quantity constraint. On the other hand, the two-step technique is the most employed method for the preparation of nano phase change materials at a larger scale, but this method suffers from stability issues. To deal with the stability issue investigators used different techniques these techniques are discussed in the next section.

4. Stability measurement and improvement methods

The three key problems associated with the implementation of nanoparticles that typically occur are agglomeration, sedimentation, and long-term stability. The stability measurement and enhancement methods reported by different researchers are discussed below.

4.1 Stability measurement methods

In the literature, different methods were utilised for the measurement of thermal stability of nano enhanced phase change materials which includes zeta potential measurement, electron

microscopy, 3ω method, dynamic light scattering (DLS) and centrifugation method. Among these stability measurement techniques, DLS and electron microscopy (SEM and TEM) are discussed in the characterization analysis (section 5). In addition, brief description of the other methods is given below.

4.1.1 Zeta potential

The potential difference between the stable layer of the base fluid trapped with suspended fillers and the suspension is zeta potential. The schematic illustration of zeta potential is shown in Figure 20. The greater value of the zeta potential indicates that the sample being evaluated is more stable whereas the values are considered unstable below ± 25 mV. Further, fluid samples with a zeta potential value greater than ± 60 mV are known to be highly stable [115].

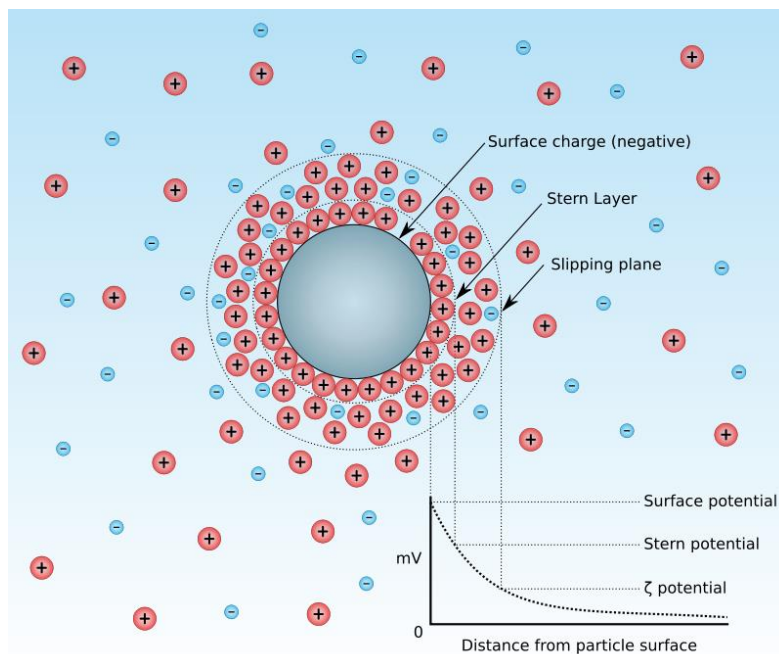


Figure 20 Schematic view of zeta potential [115]

4.1.2 3ω method

In this technique, the stability of nanofluids is examined by considering thermal conductivity. 3ω is a thermal conductivity gauging technique, the improvement in the TC depicts that the particles were well suspended in the base fluid. Though, thermal conductivity begins to decrease when clusters are formed. For example, Oh et al. [116] used this methodology to evaluate the stability of Al_2O_3 based nanofluid, as 3ω method accesses either the homogeneous mixture is obtained with the incorporation of nanofillers.

4.1.3 Centrifugation

The centrifugation technique is used to assess the sedimentation time of the properly dispersed particles. The centrifugation mechanism accelerates the sedimentation of the particles by forcing the suspension outwards with the effect of the centrifugation force. Techniques such as centrifugation offer a qualitative study of the dispersion behaviour of nanofluids. For example, in the study [117], the researcher employed this method for stability measurement. Compared to the other stability measurement techniques this method takes more time in stability measurement.

4.2 Stability improvement

The biggest problem is the stability of nano particle enhanced PCMs, which not only disturbs the efficiency of the system but also swaps the tremendous results into disturbing ones. The justification for the increased thermal conductivity of nanofluids is the proper dispersion of nanoparticles in base fluids. As the particles form clusters, they begin to settle at the base of the in-service unit, which increases the thermal resistance. As phase change does not occur in the thermal resistance layer in the experimental temperature range, this interface layer does not contribute to the phase-change heat, but it can reduce the unit volume of the thermal storage. In addition, the thicker thermal resistance layer also decreases the efficiency of the nano-PCMs heat conduction. The reason for starting with stability is that it is the issue that invites the researchers to consider the various particles and their combinations, the testing of multiple PCMs, the use of magnetic stirrers and ultrasonic mixers, and their effects on thermo-physical properties. Therefore, it is the stability that has created many problems or, in other words, a great challenge for researchers. The various strategies for enhancing the stability of nano-PCMs are shown in Figure 21 and detailed discussion will be followed.

4.2.1 Surfactants Addition

In these studies, [43,54–57,60,67,70,98,118–121] dispersants have been used to make the nano particle/tube enhanced PCMs more stable. The dispersants are organic molecules that prevents cluster formation and modifies the nanoparticles surface properties[122]. Dispersants are categorized into four categories and each type either carries negative, positive or no charge heads as shown in Figure 22. The types of dispersants chosen for various nanoparticles vary because of the different characteristics of the different nanoparticles in suspension. If the type of dispersants is not correct, the dispersants will not be adsorbed stably on the surfaces of nanoparticles, and the particle coating will be incomplete, thereby weakening the nanoparticles' dispersive effects [67].

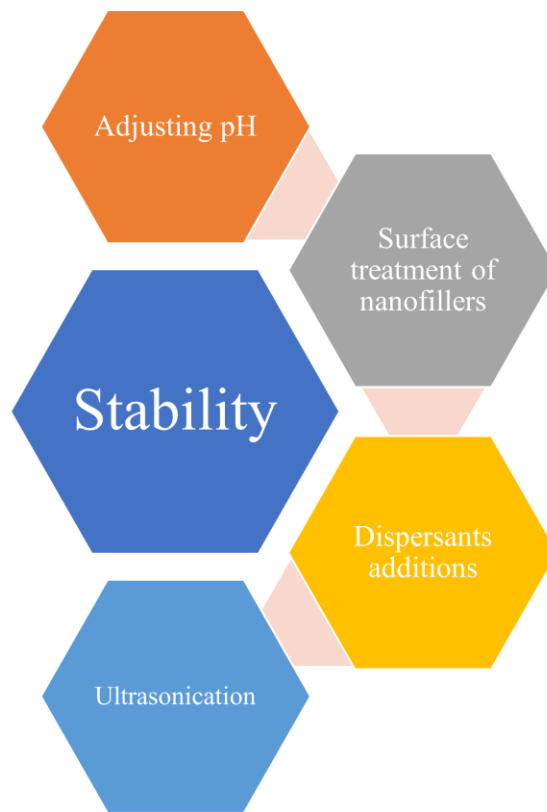


Figure 21 Nano-PCM Stability improvement techniques

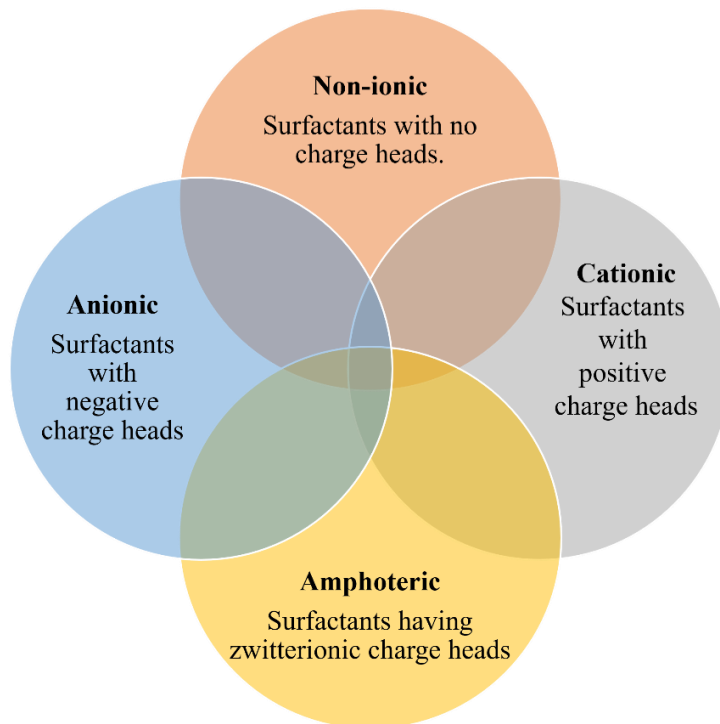


Figure 22 Classification of surfactants based on the composition of the head

Chen et al. [67] used dispersants (i.e. GA and SDBS) in their preparation of TiO₂ based nano-PCM and observed the stability of nano-PC. SDBS showed better stability than GA even after six months. Tao et al. [119] investigated the effects of two different surfactants (SDS and SDBS) on nano-PCMs (i.e. carbonate salt/MWCNTs). They concluded that without surfactants nano-PCMs nanomaterials would aggregate which weakened the thermal performance of nano enhanced PCMs and especially when nanoparticles had large surface areas (SWCNTs, graphene). The nano-PCM dispersion could be improved with the addition of surfactants. However, these surfactants decompose at higher temperatures that result in a reduction of thermal performance. So that is the reason that an optimum concentration of surfactants is important. It is worth to note that SDS decomposes less mass (18%) compared with SDBS (89%). Table 6 shows the incorporation effects of different surfactants on the thermophysical characteristics of nano-PCM.

Table 6 Surfactants used with different nano-PCM composites

Reference	Surfactant	PCM	Nanoparticles	Surfactant %
[67]	SDBS, arab gum (GA)	Alkyl hydrocarbon PCS	TiO ₂	0.1
[121]	SDBS	Paraffin wax	GO	0.3
[43]	Sodium dodecyl sulphate (SDS)	n-octadecane	MWCNT	2
[54]	SSL	Paraffin	TiO ₂	1
[123]	SSL	Paraffin	Al ₂ O ₃	1
[70]	Sodium dodecyl sulfonate	Salt hydrate (CH ₃ COONa.3H ₂ O)	Cu	0.25
[54]	SSL	Paraffin	TiO ₂	1

Zeng et al. [124] used cetyltrimethylammonium bromide (CTAB) for the better dispersion of MWCNTs in the tetradecanol PCM. Similarly, Wu et al. [94] used CTAB as supporting material with 2DMt/SA composite and it was observed that CTAB based nano-PCM showed higher stability compared to pure nano-PCM. Asadi et al. [125] investigated the effect of three different surfactant forms (SDS, CTAB, Oleic acid) on the stability of water-based nanofluid Mg(OH)₂. The supplementation of CTAB surfactant has shown a great impact on stability according to the results. Figure 23 shows the samples which were prepared after 30 days with different surfactants and it can be seen that without dispersant particles settled down at the bottom of the surface, among all surfactants CTAB based nanofluid showed better stability. Wu et al. [126] examined five different surfactants (GA, Span-80, cetyl trimethyl ammonium

bromide (CTAB), Hitenol BC-10 and SDBS) with various nanoparticles based PCM. The Cu/paraffin composite PCM with Hitenol BC-10 shows strong dispersed properties after 12 hours, due to large steric hindrance.



Figure 23 Impact of surfactants on stability of nanofluid $Mg(OH)_2$ /water (after 30 days) [125]

Table 7 shows the surfactant used with different nanoparticles. It appears that sodium stearoyl lactylate (SSL) surfactant is attractive to paraffin matrix PCMs [54,123] to improve the stability of nano-enhanced Paraffin PCMs. Sami and Etesami [54] also investigated the effect of the sodium stearoyl lactylate (SSL) surfactant on the stability of paraffin/ TiO_2 composites. They found that the addition of SSL induced delays in instability and enhanced sample properties. The nanocomposite's thermal conductivity with SSL, after thermal cycles, was more than that of the nanocomposite without SSL. Liu et al. [63] used mixed surfactants (MS) for the preparation of ESH/ $\alpha-Al_2O_3$ nano composite, where MS consists of hydroxyethyl cellulose (HEC) and sodium alginate (SA) in mass at a rate of 1:1. To achieve a more uniform solution, HEC plays the role of stabiliser, and SA acts as an emulsifier. In addition, SA as anionic surfactant and HEC as a non-ionic surfactant were mixed to produce a synergistic effect of the non-ideal mixed surfactant system, which had a better performance in the EHS high-concentration salt solution.

Table 7 Effects of surfactants on thermophysical properties of nano-PCMs

Reference	Nano-PCM/Surfactants		Findings
	Nano-PCM	Surfactants	
Harikrishnan et al. [127] (2017)	Myristic acid Silicon dioxide (0.2 to 1.0 wt.%)	SDBS	<ul style="list-style-type: none"> • TC increases with the increase in the concentration of the nanofillers. • 1.0 % of SiO₂ nanoparticles enhanced the TC by 87.27% and slightly decreased the latent heat of melting by -1.09%, which is almost negligible.
Rufuss et al. [128] (2018)	Paraffin CuO, TiO ₂ , GO (0.3 wt.%),	SDBS	<ul style="list-style-type: none"> • TC improves with the inclusion of nanomaterials. Pristine PCM (0.26 W/m.K), CuO (0.335 W/m.K), GO (0.523 W/m.K) and TiO₂ (0.325 W/m.K). • The increase or decrease of energy storage capacity varies with nanoparticles. Pristine palmitic acid (102 kJ/kg), CuO (168 kJ/kg), TiO₂ (118 kJ/kg) and graphene oxide (64.7 kJ/kg) respectively.
Zeng et al. [124] (2009)	Palmitic acid with long and short MWCNTs (0- 5 wt.%),	CTAB and SDBS	<ul style="list-style-type: none"> • CTAB composites showed greater TC than SDBS samples. Further, CTAB samples also have higher thermal conductivity relative to surfactant-free composites at low nanoparticle concentrations. • At small concentration of pure MWCNT latent heat decreases, then slightly improves and decreases with more increases in concentration value. The phase transition enthalpy of pristine MWCNT enhanced PCM was influenced by surfactants.
Parameshwaran et al. [129] (2013)	Organic ester Ag (0.1, to 5.0 wt.%)	PVP	<ul style="list-style-type: none"> • The TC of PCM with the incorporation of silver nanoparticles increases linearly. At 5.0 wt.% of Ag nanofillers TC value was increased from 0.257 to 0.765 W/m.K). • Incorporation of 5 wt.% nanomaterials decreased the latent heat of solidification and melting by 7.3 % and 8.2 %, receptively.
Lin et al. [98] (2018)	PW, stearic acid, octadecanol, rGO fillers (0.5 to 10 wt.%),	SDBS	<ul style="list-style-type: none"> • PCM TC enhances with the increase in particle concentration. • With the incorporation of fillers, PCM latent heat of fusion declines.

Continued...

Reference	Nano-PCM/Surfactants		Findings
	Nano-PCM	Surfactants	
Bahiraee et al. [130] (2017)	Paraffin wax CNF, graphene, and graphite (2.5 to 10 wt.%)	PVP	<ul style="list-style-type: none"> The TC of composites increases with the inclusion of nanofillers in the solid state. This situation is not, however, valid in a liquid state. Thermal conductivity is not dependent on temperature in both solid and liquid states. At low particles concentrations the addition of nanoparticles found advantageous. However, the latent heat of fusion deteriorates at a higher particle volume in comparison to that of pristine paraffin wax.
Zhang et al. [43] (2020)	n-octadecane MWCNT (0.1, 0.25, 0.5 and 1.0%)	SDS	<ul style="list-style-type: none"> It was noted that with SDS surfactants MWCNTs displayed excellent dispersion and stability even after three months. TC increased linearly with fillers concentration, but with a little decrease in the latent heat.
Kabeel et al. [121] (2020)	Paraffin wax GO (0.3 wt.%),	SDBS	<ul style="list-style-type: none"> Comparison to PCM without nanomaterials as an additive element, the TC of Nano-PCM was enhanced by 52%.

4.2.2 Surface treatment of nano particles/tubes

The surface treatment of CNFs/CNTs with acid, oxidation and alkali could minimise the impurities on the surface and result in better stability with PCMs. The shape alteration of nanoparticles was usually observed in CNTs. In this method, nitric and sulphuric acids are used to wash the surfaces of CNTs [122]. Meng et al. [44] prepared shape stable PCM by using the combination of three inorganic fatty acids as a PCM (Palmitic acid, Lauric acid and Capric acid). CNTs were used not just as thermal conductivity enhancers but as well as supporting material. The MWCNTs were treated with acid and the morphologies of untreated and treated MWCNTs can be seen in Figure 24. Through Figures 24 (a) & (b), it is shown that the morphologies of pristine MCNTs and modified MCNTs are very different. The presence of certain particles adherences on the surfaces of the pristine CNTs leading to CNT's size enlargement. This means the pure CNT's multi-porous structure had consumed those impurities which leads to the agglomeration phenomenon. Fortunately, its size became smaller when CNTs were processed and dispersed which showed the reduced impurity content. In addition, CNTs may be used as suitable supporting materials for PCM shape stabilisation due to the multi-porous structure and greater physical absorption ability in PCM. The pore structure and better adsorption characteristics of the CNTs make the fatty acids firmly attached to the CNTs channel and reduce the liquid of internal fatty acids to guarantee fatty acid stability. Likewise, Harish et al. [131] treated GNP with nitric acid before dispersion in to PCM, modified GNP showed high thermal boundary conductance compared to other nano fillers (CNTs) reported in the literature [132,133]. Furthermore, exfoliated GNP based PCM composite exhibit almost no change in the latent heat and melting temperature compared to pristine PCM. Elgafy and Lafdi [50] also treated CNTs with acid which results in better stability and reduction in cooling time of PCM.

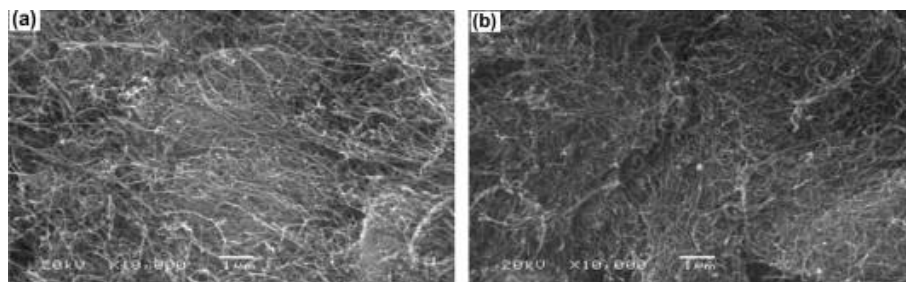


Figure 24 (a) untreated MWCNTs, and (b) treated MWCNTs [44]

Wang et al. [134] applied a mechano-chemical treatment to customize CF surfaces to increase CF's dispersibility. The results depicted that treated CF based PCM composite showed better enhancement in thermal conductivity and latent heat values in comparison with untreated CF/PCM composite. Because treated CFs have strong interactions with PCM than untreated CFs. Consequently, treated CF/PCM absorbed more heat during melting compared with untreated CF/PCM with identical mass. Avid et al. [45] treated MWCNTs by a silanization process and it was found that silane modified MWCNTs exhibited better stability than pristine MWCNTs. It is suggested that surface treatment of nano particles/tubes plays a key role in stability of nano enhanced PCMs. Table 8 shows the effect of surface modification of nanofillers on the thermal properties of nano-PCM especially on TC and latent heat. It appears that acid treated particles showed enhancement in both TC and latent heat. Further, small size particles exhibit greater thermal properties due to their better dispersion in the PCM matrix.

4.2.3 Ultrasonication treatment of nano PCM solution

Ultrasonication is a process by which the suspended nanoparticles are disturbed by using high-frequency waves. Researchers used this technique most frequently because of its ease. The other advantage of this technique over others is that it does not affect on nanoparticles surface properties. The instruments used in the ultrasonication procedure are the ultrasonic vibrator, ultrasonic bath and homogenizer, nevertheless magnetic stirrer also allows the process to increase stability. The stability of the different nano-PCMs prepared using a two-step method has been summarised in Figure 25. In most cases, after using dispersion methods such as ultrasonication and/or magnetic stirring the thermal cycles do not exceed 1000. The maximum thermal cycles achieved with nano-PCM was 5000 utilising TiO₂ nanoparticles.

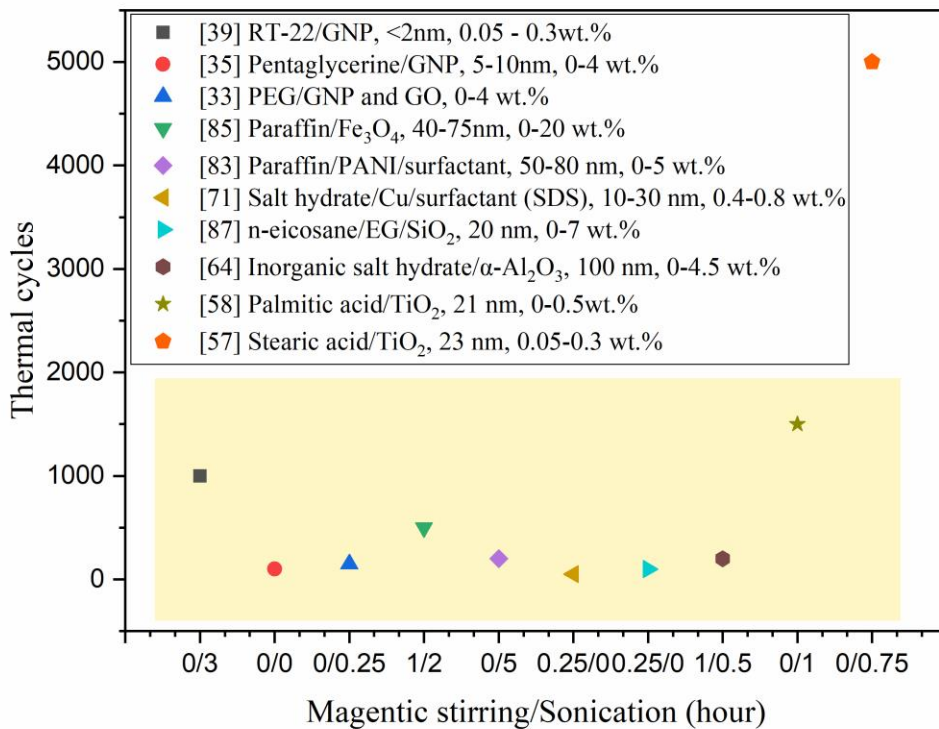


Figure 25 Nano-PCMs thermal cycle stability with different magnetic stirring and sonication time

He et al. [31] dispersed GNPs in the ethanol and ultrasonicated for one hour to obtain homogeneous suspension, and then these GNPs were impregnated into the PEG PCM. Manirathnam et al. [102] ultrasonicated SiC and CuO nanoparticles and paraffin wax based PCM at 36 kHz for two hours to obtain the homogenous solution. Similarly, Arshad et al. [101] performed ultrasonication at 40 kHz for one hour and at temperature of 50°C during the preparation of different hybrid nano-PCMs. Afrand et al. [135] performed seven hours of ultrasonication and two hours of magnetic stirring for the ethylene-glycol based hybrid nanofluid to obtain the stabilized nanofluid. Asadi et al. [125] disclosed that sonication was significant on the stability, but up to a certain limit after that antithesis effect had been exerted. Moreover, they investigated the stability of Mg(OH)₂ nanofluid over different sonication periods of time (i.e. 10, 30, 50, 80, and 160 minutes) and better stability of nanofluid was observed at sonication duration of 30 minutes. Besides, there are many studies in which either ultrasonication duration, frequency or temperature was missed. Due to lack of information, it is difficult to compare the results from these studies. For instance, Salyan and Suresh [136] investigated the effect of various concentrations (0.1%, 0.2% and 0.5%) of CuO nanoparticles

Table 8 Thermophysical characteristics of nano-PCMs with surface treatment of nanoparticles

References	PCM		Nanofillers			Thermal conductivity		Latent heat		Morphology	
	PCM	T _m (°C)	Modification	Material	Wt. (%)	Pure	Nano-PCM	Pure	Nano-PCM	Shape	Size
[27]	Paraffin	51	Sulfuric acid	xGnP	1	0.28	0.35	128.8	134	-	< 10nm
					3		0.55		132.4		
					5		0.7		131.5		
[28]	Hexadecane	18-20	Sulfuric acid	xGnP	3	0.66	0.992	232.41	217.33	-	
	Octadecane	26-30				0.49	0.873	241.97	240.92		< 10 nm
	Paraffin	53-57				0.35	0.454	142.72	140.99		
[44]	Fatty acids	16.8	Nitric acid	MWCNTs	10	0.15	0.40	140.5	122.3	-	8–15nm
					20		0.63		101.6		
					30		0.64		87.1		
					40		0.65		76.4		
					50		0.66		57.3		
[45]	Paraffin	44	Saline treated	MWCNTs	0.1	0.15	0.232	238.9	236.3	-	9.5 nm
					0.5		0.241		236		
					1		0.261		239		
[95]	Paraffin	40	Microwave	xGnP	0.2	0.29	0.31	135.65	141.61	-	-
					0.5		0.32		163.28		
					1		0.34		169.02		
					2		0.41		143.83		

on the D-Mannitol. A low-energy ball mill was used for 2.5 hours at 250 rpm to properly disperse the nanoparticles in the PCM. Subsequently, at a frequency of 40 kHz, an ultrasonic vibrator was used, but not specifying the time duration and temperature. Motahar et al. [137] performed an experimental analysis on n-octadecane PCM solidification enhanced with titanium oxide (TiO₂) nanoparticles with mass fractions of 1%, 2% and 4%. The blend was first mechanically stirred and then used in an ultrasonic bath for 15 minutes, 40°C. The mixing conditions in the study were not specified. It appears that ultrasonication treatment of nano PCM solution is an efficient way to improve the stability of nano enhanced PCMs.

4.2.4 Particle size

Stokes presented an expression as shown in equation (2) according to which the speed of particles sedimentation (V) depends upon the viscosity of the base fluid μ_{bf} , size of nanoparticles (r), the gradient between the suspended nanoparticles and the base fluid ($\rho_{np} - \rho_{bf}$).

$$V = \frac{2r^2}{9\mu} (\rho_{np} - \rho_{bf}) \quad (2)$$

From the above equation it is clear that the velocity of particle sedimentation reduces with a reduction of the particle size. The Brownian motion theory about nanoparticles states that when the particle size is reduced to the critical particle size determined from Eq. (2), the sedimentation shall then be zero [138]. Liu et al. [58] inspected an effect of the size of TiO₂ nanoparticles on the eutectic salt hydrate inorganic PCM. The results revealed that the smaller size of TiO₂ nanoparticles (25nm) had greater stability with PCM than particles with greater size (100nm). Esfe et al. [139] stated that the fluid's thermal conductivity was improved when particle size decreased as a result of better dispersion of nanoparticles in a base fluid as shown in Figure 26. From the aforementioned studies, it can be concluded that the smaller size nanofillers depicts better stability than the large size particles.

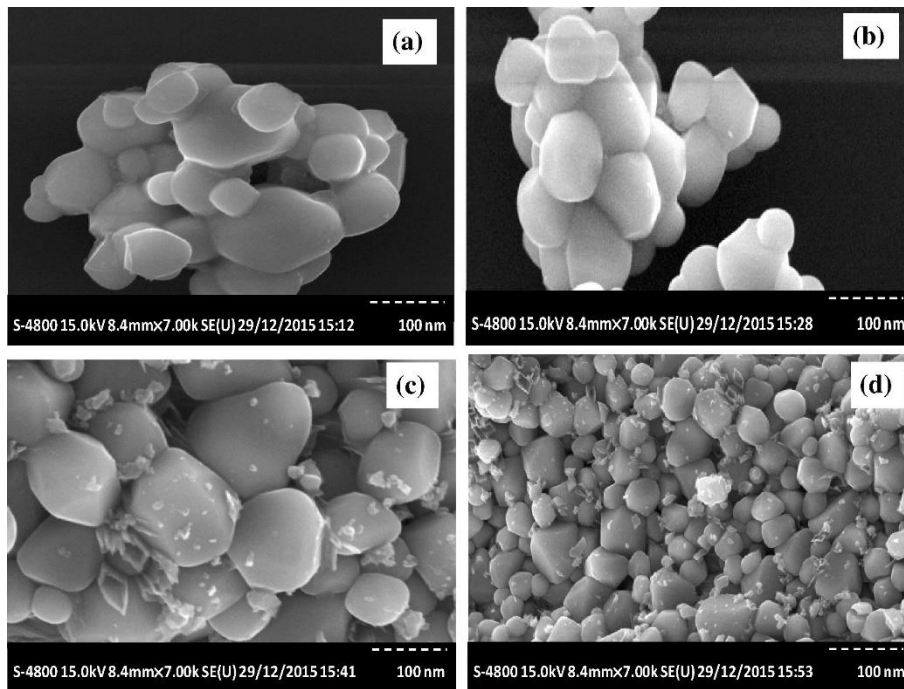


Figure 26 SEM images of TiO₂ nanoparticles: (a) 15, (b) 30, (c) 45, (d) 60 min after execution of sonication [140]

4.2.5 pH maintaining method

The similar pH value of the nanofluid and the pH of the base fluid (PCM) will result in stable suspension. Second, to get a sustainable suspension, the nanofluid's pH should be far from the isoelectric point [141,142]. The Al₂O₃-Cu hybrid nanofluid exhibited well-dispersed nanoparticles with a pH value of 5.5 according to Suresh et al. [141]. Xian-Ju et al. [142] proposed optimum pH values of 8 and 9.5 for alumina (0.1 wt. %) and copper (0.2 wt. %) water-based nanofluids, respectively. Qing et al. [143] analysed the impact of pH on transformer oil stability SiO₂-graphene hybrid nanofluid and observed that pH samples 9 and 12 exhibited low stability of compared with pH fluids 10 and 11. Toghraie et al. [144] examined the effect of pH on TiO₂ nanofluid stability when preparing MWCNT-TiO₂/EG-W hybrid nanofluid. The samples were prepared using specific pH values of 3, 6, 9 and 12. After 48 hours, the samples were analysed and revealed that the pH-value 9 fluid supported the particles better dispersed than others. Askari et al. [145] tested the stability of the nanofluid iron oxide and Graphene at various pH values (3, 5, 7, 8, and 10). The tests were analysed after 10 min, two weeks, and one month after sonication and showed that the sample with pH values of 8 and 10 was stable even after one month as shown in Figure 27. Qing et al. [146] tested SiO₂-graphene stability at four different pH values, ranging from 9 to 12. The results showed that the sample became more stable at a pH value of 11, while at a pH value of 12 the stability was disrupted. It is observed that the optimal pH value is important factor for the better stability of

the nanofluid, and the studies showed that preparation of the nanofluid with the pH value identical to the pH value of base fluid results in good stability.

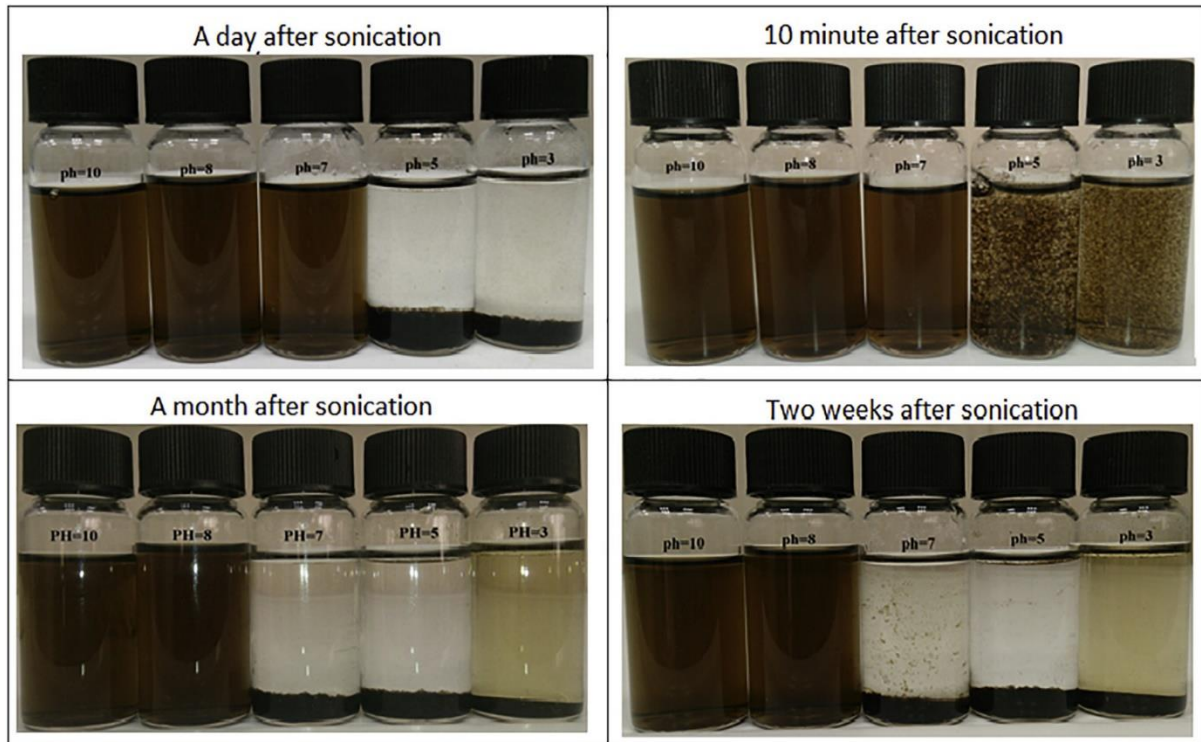


Figure 27 pH-value effects on stability of Fe₃O₄/graphene nanofluid [145]

4.3 Summary

Our stability study has found that the stability of nano-PCM can be influenced by variables such as surfactant addition, surface treatment, ultrasonication, particle shape and size, pH value, stirring time and particle concentration. Researchers need to concentrate on the above-mentioned considerations for their future studies in order to achieve better dispersion of nanoparticles in PCMs. The stability study ends by stating that the use of nanofluids in real life applications is not feasible without achieving long-term stability. However, the following points are concluded from the aforementioned stability improvement methods.

- The stability of nano-PCMs can be improved by the addition of surfactants, but they decompose at higher temperatures when they are added in a large amount which results in the reduction of thermal performance. That is the reason that a concentration of the surfactant in the nano-PCMs is an important factor.
- The surface treated nanoparticles with acids showed good dispersion in PCMs as compared with the pristine nanoparticles.

- Ultrasonication of the nano-PCM enhances the stability of particles, however in some studies mixing parameters are missing. The stability of nano-PCM can be further analysed by varying the different parameters, such as an ultrasonication frequency, temperature and time.
- It was found that smaller size with larger surface area particles show better stability because the small size particles increased the Brownian motion which leads to greater particles to particles interaction.
- The pH value adjustment provides better stability results because the ideal pH value increased the electrostatic repulsive forces that decreased the agglomeration effect of particles and improved the nanofluid stability time. Many research have been done on the impact of pH on nanofluids pH, but a gap is open for researchers to work in the case of mono nano-PCMs and hybrid nano-PCMs.
- The stability of the nano-PCMs depends on the different factors as discussed above but as shown in the Figure 25, TiO₂ based nano-PCMs remain stable for higher thermal cycles than carbon nanomaterials based nano-PCMs.

5. Characteristics evaluation strategies of nano-PCMs

The characterisation of nano-PCMs depends on physical, thermal, and chemical characteristics. In order to meet renewable energy demands, the development of nano enhanced PCMs is only beneficial and effective when they meet industrial and consumer requirements. The characteristics of nano-PCMs are evaluated using different quantitative and qualitative techniques. Table 9 shows a list of different characterisation strategies carried out by scholars.

5.1 Common approaches in chemical analysis

5.1.1 Fourier transformation infrared spectroscopy (FT-IR)

The Fourier Transformed Infrared Spectroscopy method measures the chemical structures of organic and inorganic compounds. In addition, in the set of specific absorption bands, FT-IR also confirms the detection of various impurities in a pure compound. FT-IR is the technique of infrared spectroscopy chosen to transfer IR radiation through the sample. The sample receives certain IR radiation and some of it passes through the sample. In the FT-IR system, the infrared spectrum is first achieved by using an interferometer to collect an interferogram of a sample. Moreover, the Fourier transform (FT) is implemented on the interferogram through which the resulting spectrum is derived. The FT-IR spectrometer collects and digitises the interferogram that performs the FT function, and then displays the spectrum. The FT-IR peaks

were presented by different researchers to reflect the chemical composition of nano-PCMs. For instance, Zhang et al. [147] showed the FT-IR spectrum of the paraffin (PA), expanded perlite (EP), and composite form stable PCMs at different concentrations of CNTs. It can be seen in Figure 28 that no new dominant peak was observed with the incorporation of nanoparticles, indicating no chemical interaction between form stable composite nano-PCMs (FS-CPCMs). Chen et al. [114] conducted FT-IR investigation on the PAN/PEG/SiC and showed that the main characteristic adsorption peak was in agreement with all the individual peaks and no new peak was observed and. Furthermore, peaks did not shift their positions which implies no chemical interaction between the PCM and nanomaterials.

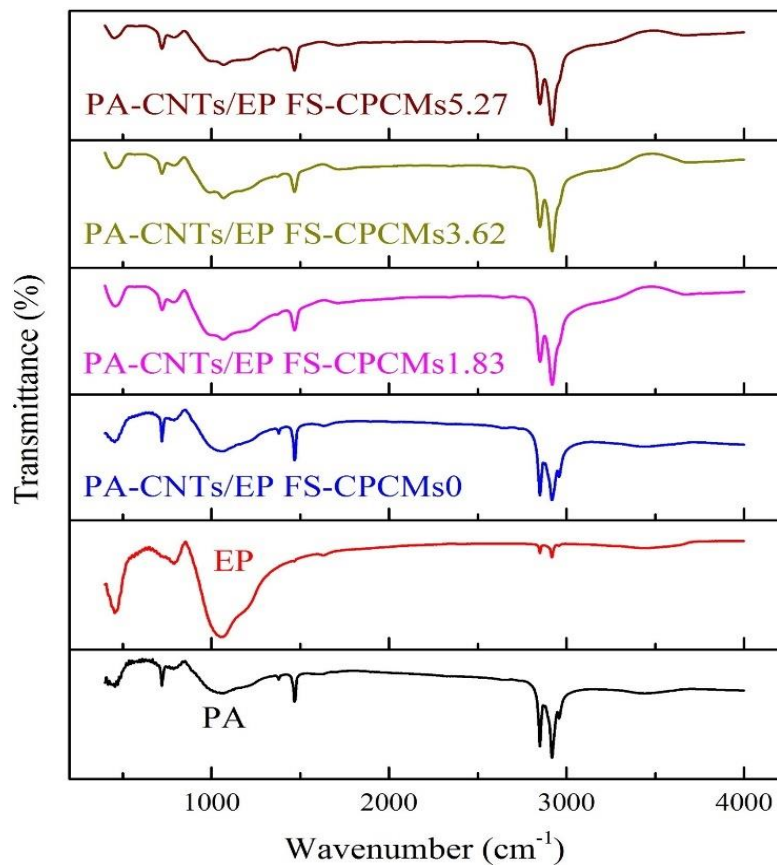


Figure 28 FT-IR Spectrum of different combinations of pristine PCM/EG and nano-PCM [147]

Table 9 Characterization techniques utilized by various researchers for the nano-PCMs characteristic evaluation

Characteristics evaluation methods	References
Fourier transformation infrared spectroscopy	[30,32,37,39,44,45,47,48,51,52,55–58,63,80,82,86,89–91,94,97–99,101,103,106,113,126,134,147–168]
X-ray diffractometer	[32,34,39,51,52,56,58,59,80,86,89,90,94,98,101,103,106,113,120,148,151–153,157,159,162,165,169,170]
Scanning electron microscopy	[27,28,32,34,37,39,42,44,45,47–49,51–58,60,63,69,80,82,84,86,88–90,94,97–99,101,103,104,106,113,118,120,124,134,147–149,151–153,155–167,170–179]
Differential scanning calorimeter	[27,28,30,32,34,36,37,39,42–48,51–60,62,63,67,69,70,82,84,86,89–91,94,97–99,101,103–106,111,113,118,120,124,126,134,147–155,157,159–165,167,170–174,176–178,180]
Thermogravimetric analysis	[27,37,44,47,48,51,54,57,82,86,90,91,94,97,101,103,113,120,147–149,151–153,158–160,162,165,167,170,176,181]
Thermal conductivity	[27,28,30,32,34,36,37,39,42,43,45,47–49,52,54–57,59–63,67,69,80,82,86,88–91,94,98,101,103–106,113,118,120,121,124,134,147,148,150,151,153–167,170–174,176–178,182]
Dynamic light scattering (DLS)	[43,49,98,162,183]

5.1.2 X-ray diffractometer (XRD)

The XRD method is used to gauge the material structure, crystalloid segment, size and crystallite atomic composition and crystal orientation. XRD can measure the various factors such as stain and crystallinity. In addition, it also characterizes the crystalline and amorphous material. Presented XRD results by Chen et al. [114] showed XRD patterns of PAN/PEG/SiC composites and from patterns it revealed that the main curve contains all individual peaks and no new peak was noticed, which showed that no chemical reaction took place during phase change of PCMs, validating outstanding chemical compatibility of PCM fibres. Furthermore, XRD diffraction analysis shown in Figure 29 indicates the diffraction curves of CNTs, MA, SF, MA/SF and MA/SF/CNTs composites. Even though little intensities of peak slightly differ in contrast to their pure curves, no new peak was noted in the main composite curve. This implies that the addition of CNTs did not influence the crystal of MA/SF composite structure, and no chemical reaction between the components [152].

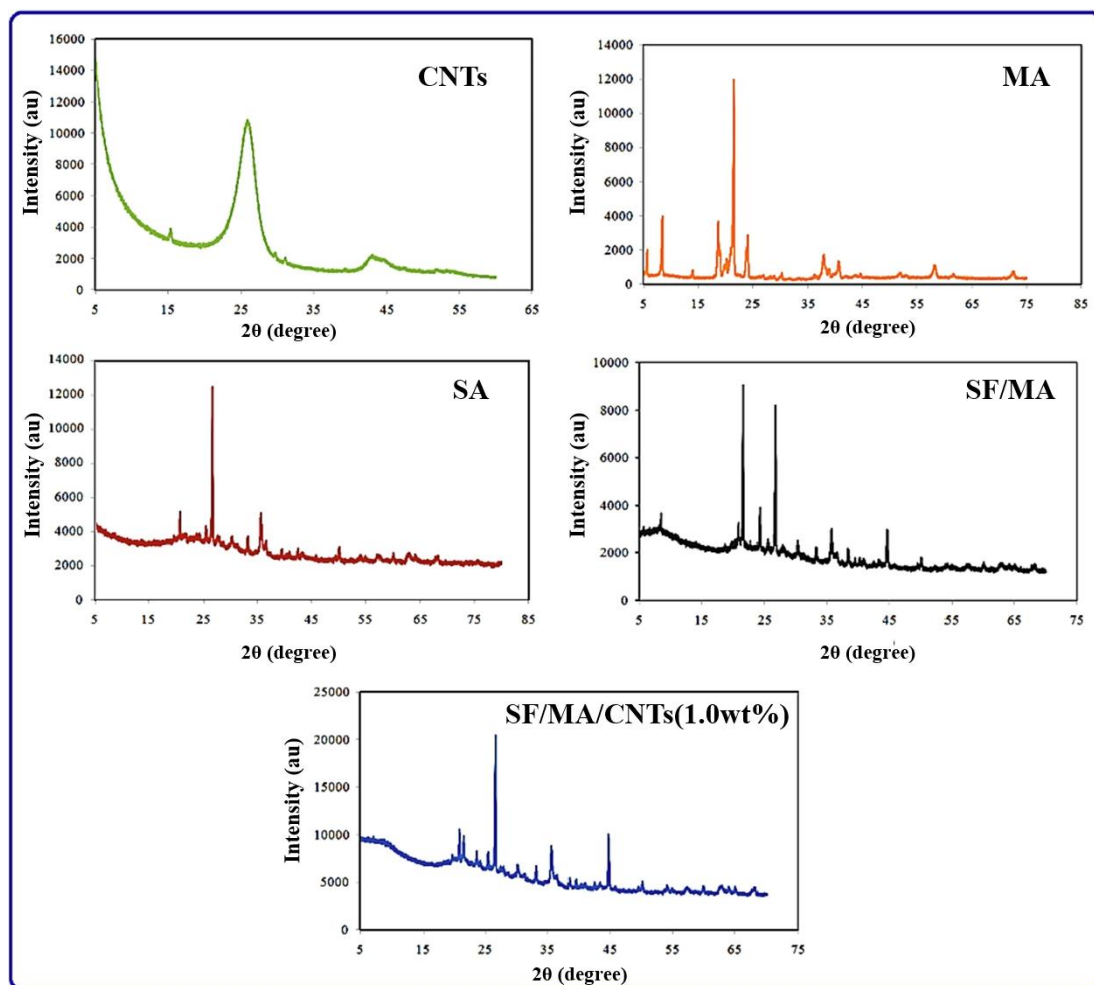


Figure 29 XRD analysis curves of pure CNTs, MA PCM, SF, SF/MA, and composite SF/MA with 0.1% CNTs [152]

5.1.3 Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray (EDX) spectroscopy is an analytical method often used to analyse a sample's chemical characterization, elemental composition, or surface elemental examination. During the bombardment of a high-energy beam of charged particles like electrons or a beam of X-rays centered on the sample, the EDX method measures the X-rays generated from the specimen. Generally, in combination with scanning electron microscopy (SEM), the EDS process is carried out. Many researchers [184–186], utilized EDX technique to determine the elemental composition of the nano-PCM samples. For example, Arshad et al. [101] performed EDX analysis to show the distribution of the copper and aluminum oxide nanoparticles in the hybrid nano-PCM of RT-28/CuO+AL₂O₃.

5.2 Typical methods in physical analysis

5.2.1 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) technique is used to determine the shape and the size of particles utilising an electron microscope. Zeng et al. [113] conducted a SEM analysis to observe the morphology of TD/EG composites. The SEM images depicted that TD was absorbed completely in the worm-like structure of EP and the graphite layer became thick compared with pure TD. In the study [28], SEM morphology appeared ordered and homogeneous dispersion in xGNP based PCM. Zhang et al. [86] investigated the SEM images of SiO₂/EG/n-Eicosane composite in which even and the layered structure was observed with the 7% EG concentration as shown in Figure 30.

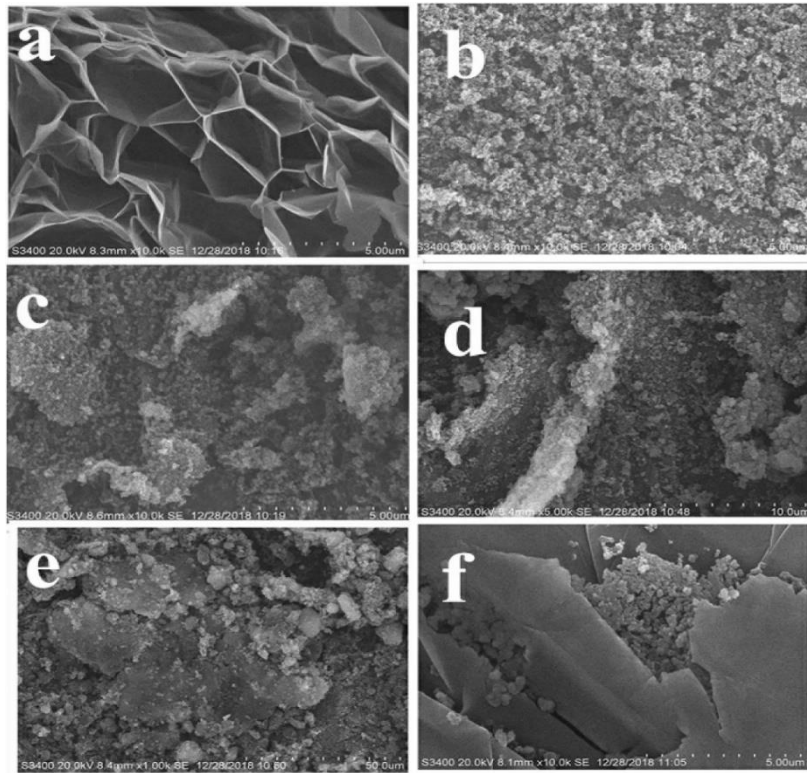


Figure 30 SEM images of (a) EG (b) SiO₂ nano particles (c) n-Eicosane/SiO₂ (d) 3% EG/SiO₂/ n-Eicosane (e) 5% EG/SiO₂/ n-Eicosane (f) 7% EG/SiO₂/ n-Eicosane [74]

5.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy is a technique of microscopy, in which a beam of electrons is transmitted to form an image through a specimen. Furthermore, TEM is used to observe a higher resolution than SEM, based on the transmitted electrons, for instance, a nano scale nearer to the atomic arrangement. Liu et al. [58] investigated the size difference of two different size nanoparticles using TEM. TEM images clearly showed the smaller and larger size particles. Similarly, He et al. [118] conducted a TEM analysis to measure the size of TiO₂ nanoparticles. It is noted that electron microscopy techniques i.e. SEM and TEM are very useful methods to determine the morphology of the nano-enhanced PCMs.

5.2.3 Brunauer-Emmett teller (BET)

BET analysis is used to calculate the specific surface area, porosity, and volume of the pores. This analysis helps to identify the adsorption of nanofillers into the PCM. Kim et al. [149] performed a BET analysis to access whether the PCM was properly introduced into the material or not. The decrease in the surface area and pore volume of the PCM/EG composite showed the proper adsorption of PCM into the expanded graphite. In another study [47], it was observed that an infiltration of PCM into the diatomite (Dt) coated SWCNT porous structures results in

a decrease in the BRT area, pore volume and pore diameter, stipulating the complete adsorption of PCM.

5.2.4 Dynamic light scattering (DLS)

The dynamic light scattering (DLS) method is used with a particle size analyser to measure the particle size distribution and particle dispersion index (PDI) of nano-PCMs. In order to observe the particle size distribution and dispersion of nanoparticles, Zhang et al. [43] conducted DLS analyses and it was noted that MWCNTs displayed excellent dispersion and stability even after three months. Similarly, Yu et al. [49] compared the nominal mean diameters obtained by the TEM images and DLS technique, and the results showed good agreement between the TEM and DLS values of diameters.

5.3 Thermal analysis

5.3.1 Differential scanning calorimeter (DSC)

DSC is used to calculate thermo-analytical characteristics such as cooling initiation and maximum temperature, melting initiation and maximum temperature, cooling and melting latent heat, heat power, and supercooling degree [187]. The amount of energy consumed or released during heating or cooling is determined during a DSC study, offering quantitative and qualitative statistics through changes in the exothermic (heat rejection) and endothermic (heat absorption) phases. The change in heat flux is reported about to time in the DSC analysis; but, the heating rate and specimen mass are truly significant since temperature-heat flow responses will be provided by the varying heat rate and specimen mass [188,189].

5.3.2 Thermal conductivity analysis (TC)

TC is the main and essential characteristic of various thermal systems for evaluation of their heat transfer performance. Until now, different instruments have been used to measure thermal conductivity. Putra et al. [37] calculated TC of graphene/RT-22 nano-PCM by using the thermal Conductivity meter at the controlled temperature of 28°C and tests were repeated three time to get higher accuracy. The studies [34,43,86] also used a thermal conductivity meter for measuring the thermal conductivity of PCM and it was reported that thermal conductivity increases with the increase in the percentage of nanoparticles in the PCM.

Liu et al. [106] compared experimental thermal conductivity with the theoretical S type growth model expressed in Equation (3), both experimental and theoretical curves showed good respectability to each other.

$$Y = 1.1342 - \frac{0.4348}{1 + \left(\frac{x}{1.1364}\right)^{3.4853}} \quad (3)$$

Where Y is the thermal conductivity and x is the content of nanoparticles.

5.3.3 Thermogravimetric analysis (TGA)

The thermogravimetry or TGA technique calculates the volume and rate of changes in material weight as a function of the temperature after melting and solidification under regulated environmental conditions [190]. Zhang et al. [86] performed TGA analysis in which one-step decomposition was observed and it was maximum in the case of pure PCM, while below 200°C almost no weight decomposition was observed for all composites. From Figure 31 (a), both PEG and PEG/Dt/MWCNT curves were closer to each other in the lower temperature zone, demonstrating strong thermal stability before 250°C. There is however, an apparent deterioration stage for PCM and composite at an arrange of temperature between 250 to 400°C, linking to a full evaporation and decomposition of the organic alcohol compounds. Hardly 1.7% of the residue for PEG is achieved at 600°C, whereas the PCM composite has 40.9% more residue. The DTG thermographs shown in Figure 31 (b) displays a small peak, which correlates to the temperature at the PEG's drastic weight reduction. It is reasonable to conclude that the enclosed PEG must first break through the diatomite pores during the heating process and then evaporate away. From the result, it is obvious that the SWCNs/PEG/Dt were more stable as well as displayed greater heat resistance than the pristine PCM [47].

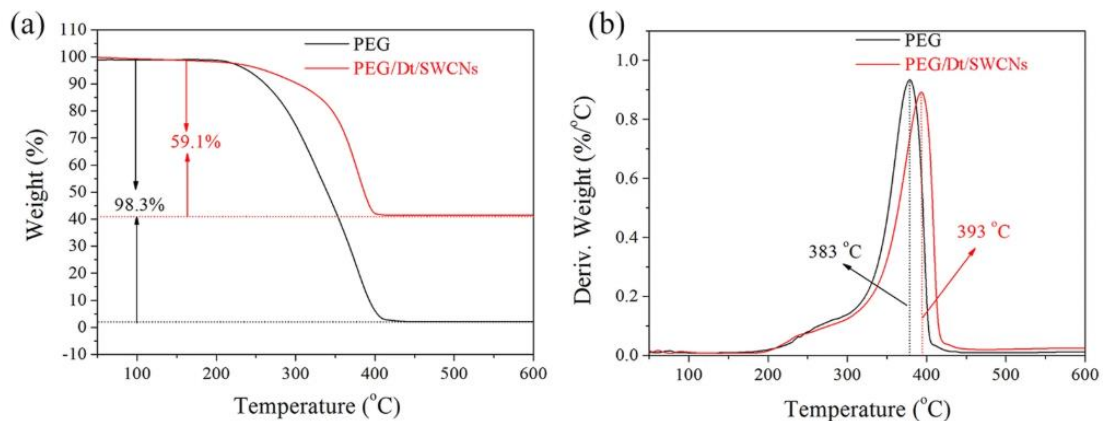


Figure 31 (a) TGA curves and (b) DTG thermographs of PEG and PEG/Dt/SWCNT [47]

5.4 Overview

The physical, chemical, and thermal properties of nano-PCMs were measured using several characterisation approaches. In this section, several characterises evaluation techniques have been discussed. XRD, FT-IR, and EDX were employed to examine the crystal structure,

functional groups, and elemental composition of nano-PCMs, respectively. For physical study of nano-PCMs, such as surface morphology, surface area, and particle size measurement, researchers used SEM, TEM, BET, and DLS. However, compared to SEM, TEM measures surface morphology at a higher resolution because electrons in TEM penetrate through the sample, whilst electrons in SEM pass over the sample's surface. In addition, DSC, TGA, and TC analysis were carried out to determine the thermal properties of the nano-PCM samples, such as latent heat, volume change, and thermal conductivity.

6. Applications of nano-PCMs

The new renewable energy sources, such as wind energy & solar energy, have been created and used to protect the environment and conserve energy. Nevertheless, these renewable energy resources are fluctuating and intermittent. PCMs can fill the gap between energy demand and supply, and thereby address the limitations of renewable energy. In phase change materials, energy is stored as latent heat which can be used for industrial and domestic purposes beyond peak hours. Because of the higher energy storage capability of PCMs they could be employed in buildings, electronics management, solar, refrigeration, excess heat recovery, textiles, food preservation, underfloor heating systems, etc.

6.1 Buildings

As an energy storage material, the available or extra energy could be stored in the PCM during a charging cycle. The retained energy can then be recovered and distributed to the end-user through the discharging cycle. As a result, stored energy helps to reduce the peak demand on the national electricity grid and to use power during off-peak time. The use of thermal energy storage (TES) systems will help the consumer by a reduction in energy rates, technologically advanced load factor, enhancing space temperature regulation plus slower capital expenditure in modern generation equipment [191]. PCMs are widely used in construction in numerous ways of such as cement mortar, concrete mixing, sandwich panels, gypsum plaster, wall panels, and blocks to fulfil the energy utilization of buildings for cooling, warming, ventilation and air conditioning and lighting [192]. But very few studies are available in which nano enhanced phase change materials were used as energy storage materials in buildings for heating and cooling purpose PCMs. Table 10 summarizes the application of nano-PCM in buildings. Parameshwaran and Kalaiselvam [193] used silver nanoparticles with PCM for air conditioning purposes in buildings. PCM incorporated with nanofillers showed enhancement in the heat transfer process during charging and discharging cycles. Furthermore, the results depicted that the developed air conditioning system with nano-PCM showed 24-51% and 58%, per day and

an on-peak energy saving potential, correspondingly for a yearly operation comparison to the traditional air conditioning unit. Similarly, Ke et al. [194] investigated fatty acids eutectics/silver nanoparticle composite for thermal energy storage applications. The developed composite showed low phase change temperatures, high phase change enthalpies and good thermal stability, which indicates that the composite has the potential to be used in buildings for energy storage purposes. Hussain et al. [195] developed activated carbon and eutectic PCM based nano-PCM for cold storage applications. The synthesized material showed excellent enhancement in the heat transfer with little thermal expandability and could be used for low thermal energy storage applications in buildings. Sayyar et al. [196] incorporated graphene nanosheet based PCM into the gypsum wallboard and its thermal performance was evaluated. The use of nano-PCM in the wallboard delayed the time at which peak temperature was reached and reduced the interior temperature fluctuations. The findings of the numerical studies showed that substantial improvements in the energy efficacy of buildings can be achieved by integrating nano-PCM with building materials. Moreover, the findings suggested that by applying nano-PCM a reduction of 79% in energy consumption to maintain the internal temperature within the thermal comfort range was observed. Zhang et al. [197] dispersed modified MWCNTs with the organic n-hexadecane PCM. The significant effect of MWCNT particles on the reduction of n-hexadecane supercooling allows a compelling way to increase system energy efficiency in building heating and cooling applications. Jeon et al. [28] impregnated xGnP particles with three different PCMs having distinct melting temperatures. They found that xGnP based nano-PCMs maintained the latent heat and the melting temperature of the PCM and developed composite can be classified as energy-saving materials for domestic buildings utilizing the radiant heating method. Ma et al. [78] integrated solar photovoltaic thermal (PVT) collectors and nano-PCM with a ceiling ventilation system to examine the effect of copper nanoparticles in the PCM. Comparison with the use of pure PCM, 25.1 % more heat was discharged, and 8.3 % more heat was charged from nano-PCM during the three winter test days. Sharma et al. [81] reported passive cooling approach for the BICPV by integrating micro-fins, PCM and nano-PCM. They also carried out this work with the goal

Table 10 Summary of literature on energy preservation by integration of nano-PCMs in buildings

Reference	Nano-PCM		Findings
	Nanofiller	PCM	
Xie et al. [198]	Cesium tungsten bronze	Salt hydrate	Nano-PCM was incorporated into a double-walled glass to preserve solar energy and minimize heat transfer. The findings showed that the amount of heat transfer from an atmosphere reduced with the dispersion of nano-PCM.
Zhao et al. [199]	Bentonite	n-octadecane + n-eicosane	Authors utilized two distinct nano-PCMs in bentonite to conserve thermal energy that can be sufficient to adjust indoor temperatures in both summers and winters. The analysis indicates that the developed nano-PCM could be used to control indoor temperature.
Li et al. [200]	Al ₂ O ₃	Paraffin wax	To boost the thermal efficiency, nano-PCM was filled in double glazed windows. The numerical and experimental findings showed that the minimal energy consumption was achieved with a 1 % Al ₂ O ₃ nanoparticles and at a 100 nm nanoparticle diameter.
Sayyar et al. [196]	xGnP	Palmitic and capric acid	The eutectic fatty acid/graphite nanofiller based composite was integrated with a panel wall to improve the thermal performance. It was observed that the room with the nano-PCM wall could minimize the heat transfer by 79%.
Venkitaraj et al. [201]	CuO 0.1 wt.%	Neopentyl glycol	The experimental study was conducted to develop nano-enhanced PCM for the cooling purposes of buildings. The results indicate that the nano-PCM reduced the melting and solidification rate with 0.1 wt.% nanoparticles. Further, the decline in the room temperature by 3°C was observed.

Continued...

Biswas et al. [202]	EG	n-heptadecane, paraffin	The investigation was conducted to examine the cooling and heating effect by the integration of nano-PCM in the building wall. The wall comprising nanoparticles was found to reduce the maximum temperature and reduce the interior heat transfer, allowing air-conditioning devices to work more effectively in order to cool the interior.
Parameshwaran and Kalaiselvam [193]	Ag 1wt.%	Paraffin	The experimental examination was conducted to enhance the thermal efficiency of the air-conditioning system. The outcomes showed that, due to the enhancement of TC and heat transfer rate, nano-PCM enhance heat transfer mechanisms and improves the charging and discharging by about 10 %.
Huang et al. [203]	MWCNT 0.0625 to 0.5 wt.%	Ethylene glycol	The nano-PCM was developed for the cold energy storage applications. It was noted that the MWCNT enhanced the TC up to great extent without effecting the latent heat.

of implementing the advantages of this method in order to improve the efficacy of BICPV. The experimental findings revealed that when micro fins were integrated with PCM, the temperature at the centre of the system decreased by 10.7°C and 12.5°C when nano-PCM was integrated micro fins. Correspondingly, a temperature drops of 9.6°C and 11.2°C was found when PCMs and nano-PCM were used for unfinished surfaces relative to natural convection. In addition, the effective TC has been increased by 0.35%. Therefore, these findings have shown that a combination of these passive technologies can be considered for the thermal improvement of BICPV. As the building sector is the largest energy consuming sector and the integration of nano-PCMs with buildings were found to be very useful in terms of reduction in overall energy consumption, but no significant attention is utilized in this area. Moreover, that stability of nano-PCMs also needs an attention of the researchers because poor stability of nano-PCM limits its application in building sector. Therefore, there is needed to critically explore the further aspects of the application nano-PCMs in buildings.

6.2 Electronics thermal management

PCMs have been used for the thermal control of electronic components. To boost the thermal efficiency, many researchers have integrated nanofillers with the pristine PCM since they have superior thermal characteristics so in electronic devices, they can be used as coolants. Tariq et al. [204] narrated graphene nanoparticles with two different organic PCMs for the thermal controlling of electronic components. The results reported that with only 0.008% of graphene nanoparticle RT-44/GNPs composite reduced the base temperature of the heat sink by 25% and 16% with RT-64HC/GNPs combination. Figure 32 shows the schematic of their experimental setup. In another study, Fan et al. [173] examined GNP and CNTs/PCM based heat sinks using different heat loads. Results demonstrated that GNP/PCM composite based heat sink exhibited better performance than CNTs. However, CNTs were shown to be beneficial for the enhanced heat transfer of the TES-based heat sink. Kumar et al. [205] carried out an experimental investigation to verify the thermal efficiency of nano-PCM heat sinks together with heat pipes for electronic cooling purposes. It was noted that heat storage capacity was improved by the addition of nano-PCM due to which a decline in sensible temperature increase occurred, further preserving the central temperature of the heat sink at ambient temperature for a prolonged period. Bahiraei et al. [130] inspected the thermal control of electronics using paraffin-based carbon nanostructures. Prepared nano-PCM samples were perceived to regulate the system temperature adequately by using 18% of the system's latent heat capacity compared to pure paraffin. Moreover, the results also showed that with 7.5% and 10% graphite-based nano-PCM

improved the thermal efficiency of latent heat management systems. Having analysed the phenomenon of thermal characteristics of RT65 PCM and CNTs Alshaer et al. [206] found that along with the introduction of even a small quantity of CNTs, TC was substantially improved compared with numerical models. Further, there was also a remarkable improvement in the latent heat of the composite relative to the pure PCM (RT65). Another study, done by Alimohammadi et al. [207] presented an impact of nano-PCM on the electronic chipset cooling by considering both natural and forced convection conditions. For the distinct values of the heat flux, six different heat sink configurations were carried out. In both forced and free convection, these cooling-combinations were investigated i.e., simple heat sink, heat sink with PCM, and heat sink with nano-PCM. Further, only 1% of Fe_3O_4 nanoparticles was used with $\text{Mn}(\text{NO}_3)_2$ PCM. Results depicted that the nano-PCM and PCM heat sinks, reduced the temperature of the electronic chipset to 10.5°C and 14°C for both forced and free convection as compared with an empty heat sink. Wang et al. [208] examined paraffin based nano SiO_2 composite for the thermal management of electronic devices. Three paraffin/ SiO_2 composites were prepared with 60%, 70% and 75% of PCM in nano- SiO_2 . The results indicated that with 75% PCM and 25% nano- SiO_2 nanoparticles based nano-PCM showed enhancement in the thermal performance of electronic components was around 21.8%. Colla et al. [209] discovered the effects of different concentrations (0.5 wt.% to 1 wt.%) of Al_2O_3 in the RT-55 and RT-44 organic PCMs with melting temperature of 55°C and 45°C respectively. The results showed that the nano-PCM were able to delay the melting process relative to the reference temperature. As a result, these findings of thermal characteristics indicated that nano-PCM could be used in electronics for passive cooling and energy storage purposes. The aforementioned studies show that for electronic components nano-PCM performed better than pristine PCM because of the presence of high conductive particles. Further, type of nanofiller play a significant role in the stability of nano-PCM and it is found that carbon based nanofillers showed good thermal stability than other nanoparticles.

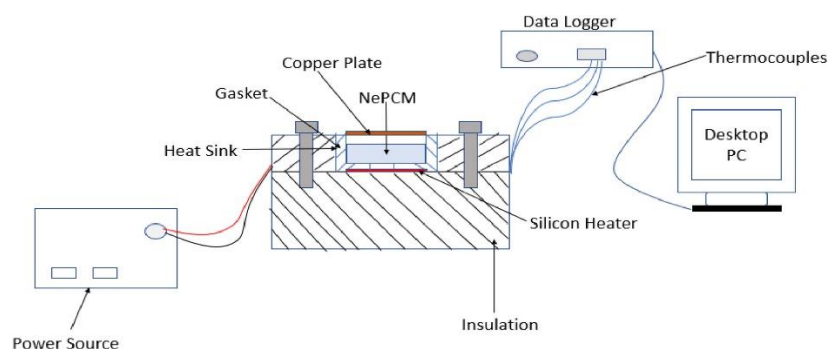


Figure 32 Schematic of the experimental setup used by Tariq et al. [204]

6.3 Textile

PCMs have been used in textiles for safety or durable finishing of cotton or wool, softeners of the skin and durable fragrances [210]. Furthermore, textiles must be designed and processed in such a manner that they have the potential to control dynamic heat besides the skin [211]. Such thermo-modulated textiles require the usage of PCMs which provide thermal comfort to the human body by maintaining the body hot or cold depending on the immediate climate. A great deal of attention has been paid to the evolution of usable textiles with PCMs, which can retain and emit excess heat during their phase transition.

The pre-treated polyamide and polyester fabrics with silver nanofillers showed improvement in the anti-fungal efficiency [212]. Due to the anti-bacterial properties of silver nano-crystals Potiyaraj et al. [213] synthesised silver nano-crystals on silk fibers. The resulting silk fibres can be utilised as an antibacterial agent and photo-catalyst in water splitting applications. Hebeish et al. [214] processed silver nanofillers utilising hydroxypropyl starch for the preparation of highly efficient anti-bacterial textiles. The solution of silver nanofillers was applied with and without binders to cotton fabrics. The authors found that after 20 washing cycles, the binder maintained its anti-bacterial properties and that silver nanoparticles stayed static on the surface of the fabric material. Li et al. [215] examined the resilience of nano-ZnO antibacterial properties for the functionalization of cotton fabric to sweat.

The fabrics treated with Ag/TiO₂ showed a color change, hence Dastjerdi et al. [216] conducted an investigation to resolve this problem. Both nanoparticles were treated with different concentrations of the cross-linked polysiloxane. The findings showed that treatment with polysiloxane could help to increase the bioactivity of TiO₂ together with its photo-catalytic function. The production of smart textiles with good thermal stability and added durability is currently a hot research subject.

6.4 Medical

The antiseptic usefulness of PCMs is a substantial and evolving area for the advancement of hybrid functionality materials. Silver-based nanocomposites are widely utilised materials with PCMs due to their inherent antibacterial activity in medical uses. Tobaldi et al. [217] prepared Ag-modified TiO₂ nanoparticles using the sol-gel method to analyse the photocatalytic and antibacterial properties of both ultraviolet and visible light displays. Under ultraviolet light, Ag nanoparticles demonstrated strong antibacterial activity against *Escherichia coli* (Gram-negative bacteria) relative to methicillin-resistant *Staphylococcus aureus* (Gram-positive bacteria). Hirst et al. [218] shown the high-tech applications of self-assembled supramolecular

nanostructured phase change materials whilst progressing to regenerative medicine electronic devices. Previous molecular gels have been used for low cost operations, but then several changes have been made to nanoscale assembly processes. Besides that, in the future, this technique would have to cope with a better understanding of the connections that would promote nanomanufacturing between molecular building blocks. For enhancement beyond the skin-depth limit, a metallic nano slit was used by Seo et al. [219]. They proposed that a wide range of applications will be provided for nanostructures for these operations to improve skin-depth treatments, in concentrating systems and as an enabling mechanism for applications in sub-nano-optics. Further, nano-PCMs can also be used with certain vaccines/medicines to keep them at their desired temperature.

6.5 Overview of nano-PCM applications

Due to the global increase in energy demand, nano-PCMs are used in buildings by different incorporation methods. In addition, because of their better thermal conductivity and high latent heat of the nano-PCM researchers have employed nano-PCM composites in many other applications such as smart textiles, thermal cooling of electronics and the medical industry. Apart from these applications, nano-PCMs have also been used for PV panels cooling, food packaging and cold storage applications. A detailed review on the applications of nano enhanced phase change materials has recently been reported by Tariq et al. [23]. The important elements that researchers should need consider are the choice of PCM and the concentration of nanoparticles. PCM phase transition temperature should be in the range of application temperature and an appropriate concentration is also essential because higher concentration leads to higher viscosity, which hinders the natural convection. Furthermore, the proper selection of PCM and nanofillers lead to the long-term thermal stability which is an important factor and results in greater performance of nano-PCMs in all applications. That's why it is important to select an appropriate material and different stability improvement methods can also be employed for better efficiency of nano-PCMs. Figure 33 shows some of the applications of the nano-enhanced phase change materials.

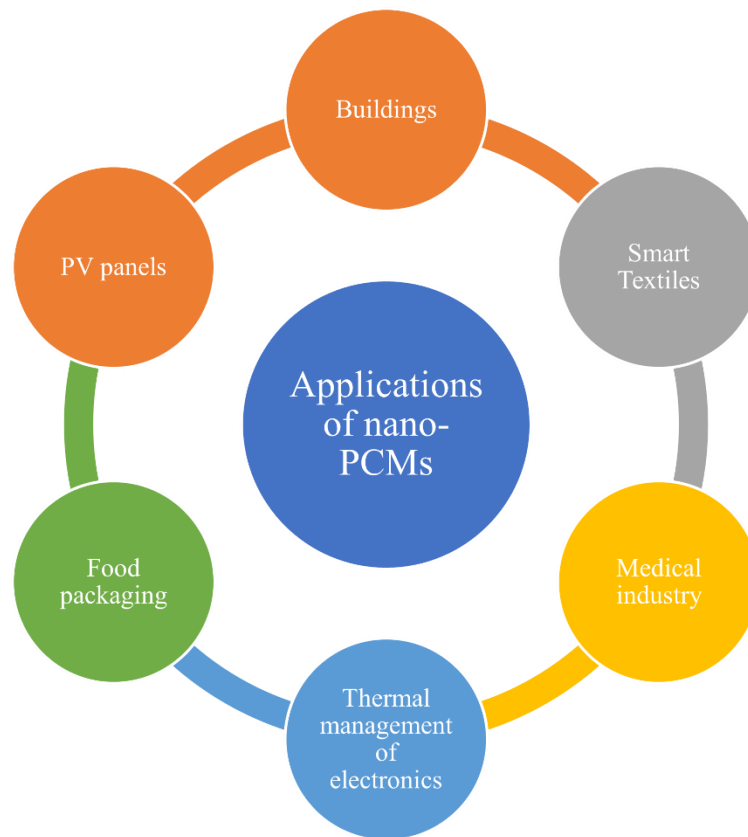


Figure 33 Applications of nano enhanced PCMs

7. Summary and future work

The efficiency of a thermal energy storage system is largely influenced by the PCM's thermal characteristics. The important findings from this study are summarised below:

- From Figures 9 and 10, it can be seen that the incorporation of nanofillers enhances the thermal conductivity of the PCM even though it has good or negative impacts on the thermal energy storage capacity of the nano-PCM. Furthermore, carbon-based nanoparticles depict better performance than metal oxide and metal nanomaterials.
- The summary on the effect of thermal conductivity and latent heat of mono and hybrid nano-PCMs is recorded in Tables 4 and 5, respectively.
- The two-step method is the most cost-effective method for the preparation of nano-PCMs on a larger scale, but this method has agglomeration issues. That is why more investigations are needed to address this problem, or another efficient method needs to be developed.

- Stability of nano-PCMs mainly depends on the size, shape, concentration, and type of the nanoparticles. But it can be improved by surface treatment, ultrasonication and surfactant addition.
- The characterization analysis of the nano-PCMs can be done by using various methods listed in Table 9.
- Nano-PCMs have various applications in different industries, such as, building, medical, and textile industry. However, the selection of the appropriate PCM is an important factor since the phase transition point of the PCM should be in the application temperature range.

The nano enhanced phase change material composites have a great potential to be employed in thermal energy storage applications. Especially, in the renewable energy system where sometimes the supply of the energy is inconsistent and the nano-PCMs can store energy from the renewable energy sources where the supply is turbulent. What is more, nano-PCMs can also be used in medical, electronics etc. as discussed in the above section. Even though several scientists are presently focusing on the preparation and characterization of nano enhanced PCMs, there is still a need for more development for their better performance in practical applications. Following are the ideas for impending research:

- So far, many studies have been reported on the mono nanomaterial based PCM composites to investigate the effect of mono nanofillers on the overall thermophysical properties of nano-PCMs. However, some researchers investigated the effect of hybrid nanofillers on the thermal performance of nano-PCMs, but there is still a lack of rigorous investigation on the synergistic impact of hybrid nanofillers. A hybrid arrangement of nanoparticles is still a field to be further explored to find a mechanism for reducing interfacial thermal resistance.
- Occasionally, after several thermal heating and cooling cycles the nanoparticles lead to agglomeration, to resolve this problem 3D carbon aerogels can be used in future investigations, as the porous structure and admirable thermal conductivity of carbon aerogels can also support the stability of the form and the heat transfer efficacy of PCMs.
- The addition of surfactant in the nano-PCMs improves the static and dynamic stability, but with little decrease in the thermal conductivity and latent heat, so proper investigations are needed to study the proper amount of dispersant in the nano-PCM.

- Although surface treatment of nanofillers with strong acids increases the stability of nano-PCMs, only a few researches have been undertaken on it. Therefore, there is a need to investigate the effects of surface modification of particles on the stability and thermal properties of nano-PCMs.
- Further studies are also needed on the optimum concentration of nanofillers in one specific PCM, which would have less impact on the latent heat value of the PCM and have high thermal conductivity.
- Until now, researcher mainly focused on the comparison of different nanoparticles on the performance of PCMs. The effect of size and shape on the PCMs still need attention.
- Since salt hydrates (inorganic PCMs) have high thermal conductivity and latent heat value during phase transition, they have more potential in the heating, and cooling of thermal energy storage applications. However, they showed high super-cooling. Work has so far concentrated on the use of organic PCMs and inorganic PCMs (molten salts and salt hydrates) based nanocomposite also need more attention to use as base materials with nanofillers.
- The two-step method is a popular method of preparing nano enhanced PCMs. A more effective and agglomeration free method is required to enhance the nanoparticle dispersion into the PCMs.
- The nano-PCMs can also be encapsulated as the encapsulation minimizes the nano-PCMs interaction with the environment and prevents a potential leakage of the nano-PCMs during the phase transition period. In addition, the thermal conductivity and heat transfer rate of the PCMs can also be improved by encapsulation.

8. Conclusions

A comprehensive literature review on thermal properties, thermal stability, preparation, stability, characterization, and applications of nano enhanced PCMs was conducted in this article, which is expected to be very effective and useful for researchers.

Effects of the dispersion of various nanoparticles such as carbon-based, metals, metal oxides, metal carbides and nitrides and hybrid materials in the PCM matrix have been analysed in this review article with the technical explanation behind the impact. Moreover, this paper will facilitate the readers in the selection of suitable nanofiller for the thermal enhancement of TES systems. However, in the relation to the literature reviewed, the following key conclusions were drawn on nano-enhanced PCMs.

- Overall, the incorporation of nanofillers has shown a small decline in latent heat and a substantial improvement in the thermal conductivity values. However, a significant improvement in thermal conductivity is appropriate for a small reduction in the energy storage capacity of PCMs.
- Hybrid nanoparticles have exhibited remarkable improvement in the thermal conductivity and minor reduction in latent heat as compared with mono nanoparticle based PCMs. As at the same time, the single material does not possess superior thermal and rheological properties.
- The choice of the appropriate PCM and optimum concentration of nanofillers play a critical part in the stability of nano-PCMs. Further, a higher concentration of nanoparticles results in the cluster formation which affects the stability of the nano-PCM. Different methods, such as surfactant addition, particle coating, pH adjustment, etc. can be used to improve the stability of nano-PCMs.
- Small size particles have exhibited higher thermal conductivity values due to their better dispersion with the base fluid.
- Due to their high thermal conductivity, greater surface areas and good intermolecular interactions with PCMs, carbon-based nanoparticles have demonstrated better performance than other nanoparticles.
- The acid treated carbon-based nanoparticles have depicted better thermal properties than un-treated particles since modified carbon nanoparticles have strong interactions with PCMs and less interface thermal resistance.
- The nano-PCMs have potential to be utilized in different applications such as buildings, textiles, food packaging, medical industry, etc.
- To evaluate the chemical and thermophysical properties of the nano-enhanced PCMs the chemical, physical, and thermal characterization techniques could be utilized.

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