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## **REVIEW**

# An Updated Review on Low-Temperature Nanocomposites with a Special Focus on Thermal Management in Buildings

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## ABSTRACT

Buildings contribute to 33% of total global energy consumption, which corresponds to 38% of greenhouse gas emissions. Enhancing building's energy efficiency remains predominant in mitigating global warming. Advancements in thermal energy storage (TES) techniques using phase change material (PCM) have gained much attention among researchers, primarily to minimize energy consumption and to promote the use of renewable energy sources. PCM technology stays as the most promising technology for developing high-performance and energy-efficient buildings. The major drawback of PCM is its poor thermal conductivity which limits its potential use which could be resolved by dispersing conductive nanofillers. The acquired database on synthesis routes, properties, and performance of nano-dispersed phase change materials (NDPCMs) with various techniques presented in the paper should deliver useful information in the production of NDPCMs with desirable characteristics mainly for building construction applications. An outline of contemporary developments and use of NDPCMs as TES medium is delivered. Finally, a brief discussion on challenges and the outlook was also made. In-depth research is needed to explore the fundamental mechanisms behind the enhanced thermal conductivity of NDPCM with nanofillers dispersion and also a thorough investigation on how these mechanisms drive improvement in building performance.

## **KEYWORDS**

Thermal conductivity; latent heat; building applications; energy savings

## Abbreviations

Three Dimensional
Aluminium Oxide
Building Attached Photovolatic
Building Integrated Photovolatic
Capric Acid



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$Cs_xWO_3$	Cesium Tungsten Bronze
CuO	Copper (II) Oxide
CuS	Copper (II) Sulfide
ESS	Energy Storage Systems
GHG	Green House Gas
GNP	Graphene Nanoplatelets
GO	Graphene Oxide
h-BN	Hexagonal Boron Nitride
HNT	Halloysite Nanotube
HPAC	Highly Porous Activated Carbon
HVAC	Heating, Ventilation, and Air Conditioning
LA	Lauric Acid
LH	Latent Heat
MA	Myristic Acid
MPCM	Microencapsulated Phase Change Material
MWCNTs	Multi-Walled Carbon Nanotubes
NDPCMs	Nano-Dispersed Phase Change Materials
PAHXs	PCM-to-Air Heat Exchangers
PCM	Phase Change Material
PV	Photovoltaic
rGO	Reduced Graphene Oxide
SA	Stearic Acid
SiO <sub>2</sub>	Silicon Dioxide
SWCNTs	Single-Walled Carbon Nanotubes
TC	Thermal Conductivity
TES	Thermal Energy Storage
TiO <sub>2</sub>	Titanium Dioxide
xGnP	Exfoliated Graphite Nanoplatelets

## **1** Introduction

Buildings account for one-third of global energy consumption and remain a key contributor to the carbon footprint. Heating Ventilation & Air Conditioning (HVAC) systems hold a massive 50% share in building energy consumption [1]. Air conditioners hold a significant role in mitigating human vulnerability to adapt to changing climate because of uncertain climatic events such as heatwaves. It is expected that by the year 2100, the percentage of buildings that have air-conditioning units installed will be closer to 99.9%, from its present 2% position [2]. The UN member states are obliged to curtail the fossil fuel by 20% to attain reduction in greenhouse gas emission as per the Paris Agreement made in 2015 [3]. Increased energy consumption of buildings and associated GHG emissions makes energyefficient building materials and energy storage technologies the predominant requisite of the hour [4]. The European Union, in its energy road map for 2050 proposed that 66% of energy must be availed from zero carbon sources [3]. According to Eurostat data in 2015, a staggering 39% of the total energy consumption was dedicated to building-related structures (a detailed pattern is shown in Fig. 1) [5]. In addition to peak load aversion, energy storage systems (ESS) mostly improve mobility, reliability, and even financial merit. ESS can effectively support both energy security and reduction in global warming thereby offering an invaluable service to the world [6]. Normalizing the energy demand curve (transferring the energy demand from peak hours and reducing the total peak demand) is a potential solution. Innovative techniques like the usage of thermal energy storage may deliver thermal inertia and avert peak energy demands [7].



Figure 1: Energy consumption pattern in residential building sector [8]

Energy conversion systems rely heavily on thermal energy storage (TES) as it remains one of the vital systems for storing and retrieving energy. A reduction in fossil fuel usage and energy conservation could be attained with latent heat energy storage technology based on TES [9]. A paradigm shift towards green energy sources is of paramount importance as nonrenewable fuels attributes to 75% of greenhouse gas emissions [3]. Sensible heat storage and latent heat storage comes under TES [9,10]. TES permits a logical use of stored heat energy and delivers significant advantages like; cutting the running costs, swapping the peak load, reducing running costs, and even lowering GHG emissions [10]. TES system could be integrated with HVAC applications to deliver a shift in the thermal load from higher to lower conditions [11]. Phase change materials (phase transition shown in Fig. 2) inherent high energy storage density. Thermal conductivity, energy storage density, and melting temperature characterize the thermal performance of a PCM (classification of PCM is given in Fig. 3) [12]. It is highly advisable to have a PCM with swift melting and solidification rates for the proper functioning of a PCM-based thermal energy storage system. However, the thermal conductivity of commonly used PCMs remains comparatively low (paraffin-0.205 W/m.K [13]) which is the primary drawback that hampers their utilization [14].



Figure 2: Phase transition of PCM in hot climate [5]

The inherent mass of the structure remains a major stakeholder in Thermal energy storage associated with it. Contemporary buildings maintain a heavier mass in comparison with current highrise buildings, which thereby results in higher temperature fluctuations for indoor air temperature [7]. The Phase Change Materials (PCMs) integrated with structures could be used for improving the heat storage density of buildings [15]. The phase transition temperature of the PCM primarily helps in the building's thermal management. PCMs could be deployed either as active systems (HVAC systems) or passive systems (heat dissipation methods) [1] and a lot of parameters (cost, availability, energy price) depends on their implementation [7]. Passive design delivered maximal energy efficiency as it relies on an abundant, clean, and reliable energy source, the Sun [16].

To outrun the problem of poor thermal conductivity in PCMs various thermal energy transport enhancement techniques have been attempted. Dispersion of fins, heat pipes, foams, micro, macro, and even nanoencapsulation, application of multiple PCMs, and adding high thermally conductive materials. Among these dispersing, highly conductive nano-sized materials in PCMs significantly enhances its thermal conductivity ( $\lambda$  value) and improves the capability of energy exchange. They had attained immense research interest [14,17]. The dispersion of nano additives into PCMs could boost their thermal energy transport on account of the huge surface area-volume ratio of additives and can even alter melting and solidification rates [13,18]. This emergent composite is termed nano-enhanced phase change material/nanocomposites/NDPCMs in this article. In 2005, Elgafy et al. [19] made the first attempt to disperse nanomaterials in PCMs for enhancing TES. The amount of nano additives added must be well enough to generate a conductive thermal network [10]. Aluminum oxide, copper, copper oxide, silver, SWCNTs, MWCNTs, graphene, graphene oxide, exfoliated graphene, silicon carbide, zinc oxide, titanium oxide, titanium carbide are the most extensively used nano additives for thermal applications [13,20].



Figure 3: Classification of PCM [21]

Ma et al. [22] made the lone attempt to review the building applications of NDPCMs. An outline of contemporary development and application of NDPCMs, when used as TES media, was provided. Following are prior review attempts on PCM usage on the building. Raquel et al. [23] made a comprehensive review to explore the relation between phase change materials, energy deficiency, and energy efficacy. Applications of PCM in glazed zones, ceiling areas, walls, and floors of the buildings were detailed and mentioned about PCM selection criteria. Kumar et al. [24] primarily analyzed

micro-encapsulated PCM-based research works and observed an improvement in thermal efficiency with MPCM. Real-time testing with mortar, brick, cement, wallboard, gypsum, and MPCM-based simulation works were reviewed. Li et al. [25] condensed the research articles discussing the optical and thermal efficiency of PCM-based glazing units. Experimental and simulation works with glazing units containing PCM were analyzed. Challenges and upcoming works in the area were also presented. Dardir et al. [26] summarized the publications made mainly on free cooling in buildings using PCM incorporated air heat exchangers. Merits and demerits of PCM containing air heat exchangers (PAHXs) for the desert climate were discussed in detail. The effect of phase change temperature, inlet temperature, and air flow rates on PAHXs free cooling in buildings were also explained. Berardi et al. [27] attempted to review the usage of PCM in concrete for building applications. Microencapsulation and macro encapsulation methods for avoiding PCM leakage were also explained in the concrete-PCM perspective. Jimenez et al. [28] reviewed studies related to numerical thermal modeling of conventional solar chimneys and solar chimneys with phase change materials (PCM). The tools for analysis were Computational fluid dynamics (CFD) and Global energy balance (GEB), of which CFD was found to be a powerful tool to investigate numerous aspects concerning the heat transfer mechanisms in a solar chimney. Rathore et al. [29] made a comprehensive review on energy-efficient microencapsulated PCM for buildings and Materials for encapsulation. The potential of PCM in indoor thermal management of buildings was also analyzed. Shah et al. [30] condensed research works on NDPCMs that could be employed in building applications. Kasaeian et al. [31] summarized and critically analyzed research articles on integrating PCMS and NDPCMs onto buildings.

This review article is trying to focus on research works that had reported variations in thermophysical properties of PCM when dispersed with nanoparticles. Numerous research papers were published on PCMs and NDPCMs. Among these published ones, only a handful of them were focusing on low temperature PCMs. Moreover, a few of them have highlighted low temperature thermal energy storage applications of NDPCM. This review paper tries to highlight the research works where NDPCMs have delivered a competitive edge over PCMs in thermal management of buildings. It also provides a deep insight into the thermophysical characteristics of NDPCMs. A detailed discussion on the impact of nanoparticle dispersion on thermal conductivity and latent heat along with its reasons for variations are also briefed. As per authors knowledge the different methods adopted for thermal management in buildings using nano composite phase change materials are summarized for the first time. A comprehensive and in-depth coverage on thermophysical properties of low temperature NDPCMs makes this article substantial and different when compared with other available reviews in the same domain.

This review paper attempts to summarize the relevant research articles published where the usage of NDPCMs had made a profound impact on the thermal management of buildings. The generic problems and key issues related to the use of this new class of materials in buildings for improved indoor thermal performance and enhanced energy efficiency are discussed. The review article is structured in the following pattern. A brief overview of energy usage patterns in buildings and methods to mitigate them are provided in Section 1. A synopsis on different synthesis routes for low temperature is given in Section 2 with a detailed focus on two-step method. Section 3 provides a discussion of reasons for variations in thermal conductivity and latent heat. Thermal management applications of NDPCMs are systematically condensed in Section 4. Section 5 delivers the challenges, and a conclusion is given at the end.

#### 2 Synthesis Routes for Nano-Dispersed Phase Change Materials

The synthesis of nanocomposites does not include the mere incorporation of nanofillers into a matrix. For obtaining consistent dispersion, appropriate mixing and stabilization approaches are necessary. NDPCMs can be synthesized either by one-step or two-step methods. In one-step method, nanomaterial production and dispersion occur simultaneously in the base PCM, and in the two-step method the nanofillers are synthesized first, and then added into the base. The two-step method remains further economical, and it is widely preferred in NDPCM synthesis [14,32].

### 2.1 One-Step Synthesis

Nano additives were synthesized and dispersed simultaneously in one-step method. Drying, storage, transportation, and mixing of nanoparticles in PCM are not adopted in this method. It can reduce the particle agglomeration issue [32]. This synthesis pattern is preferred for small-scale production as it is costly in comparison with two-step method. Xu et al. [33] adopted one-step method (shown in the Fig. 4), to synthesize CuS decorated MWCNT dispersed in Paraffin. Calculated amounts of CuO, sublimation sulfur, oleic acid, paraffin, and MWCNT were added to a three-distillation flask of 50-ml capacity. The flask was stirred continuously for 3.5 h at 180°C, and the resultant was a NDPCM of Cus-MWCNT/paraffin. Several researchers [34,35] had followed similar synthesis routes.

## 2.2 Two-Step Synthesis

First nano additives are collected in dry powder form using various mechanical and chemical methods (chemical reduction, sol-gel, and ball milling) in two-step method. The nano additives are then added to the base matrix for getting a consistent dispersion (ultrasonic bath magnetic stirring and high shear mixing). The main advantage of this method is that it can synthesis NDPCMs on a large scale. Particle agglomeration stays as a major setback with this method [32].



Figure 4: One-step synthesis

#### 2.2.1 Surfactant

The consistency of nanocomposite relies on the nature of nanofillers and base PCM. Nanofillers can be hydrophobic/hydrophilic and base matrix could be polar/non-polar. Hydrophilic nanofillers (oxides) can be easily dispersed into polar base fluids (water) and hydrophobic nanofillers (MWCNTs) can be dispersed in non-polar base fluids (oils) with no surfactant. However, when hydrophobic nanoparticles had to be dispersed into polar base fluids and hydrophilic in non-polar base fluids, then surfactants are needed to stabilize the nanocomposite (in liquid state) [36,37]. Surfactants stay as a bridge between nanofillers and PCMs and create continuity between both [38]. Surfactants contain hydrophilic and lipophilic groups. They modify the surface properties of the particles and prevents

cluster formation [39]. Fig. 5 shows the classification of surfactants. Surfactants generate a barrier and minimize surface tension between liquid PCM and dispersed nano additives. The repulsive forces and zeta potential generated due to surfactant stabilize the composite in the liquid state [36]. Surfactants are divided into anionic, cationic, non-ionic, and amphoteric [40]. At high temperatures, surfactants might exhibit altered properties or even generate foam [41]. They might cause a decline in thermal conductivity values with the thermal resistance created among nanofillers and PCM [42]. The different synthesis methods of low-temperature NDPCMs using surfactants are discussed in Table 1.



Figure 5: Classification of surfactants

РСМ	Nanoparticles	Surfactant	Synthesis method employed	Reference
Paraffin	MWCNT	SDBS	Ultrasonication	[43]
Paraffin	MWCNT	Gum Arabic	Ultrasonication	[44]
LA+SA	TiO <sub>2</sub>	SDBS	Ultrasonication	[45]
LA+SA	ZnO	SDBS	Ultrasonication	[45]
LA+SA	CuO	SDBS	Ultrasonication	[45]
Paraffin	$TiO_2$	SDBS	Ultrasonication	[46]
$CaCl_2 \cdot 6H_2O$	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	CTAB <sup>1</sup>	Ultrasonication	[47]
$CaCl_2 \cdot 6H_2O$	$Cs_xWo_3$	CTAB <sup>1</sup>	Ultrasonication	[48]

Table 1: Overview of two step nanocomposite synthesis using surfactants

Note: <sup>1</sup>Strontium chloride hexahydrate was used as a nucleating agent.

The various two-step methods widely adopted for synthesizing low-temperature nanocomposites are briefed below. Karaipekli et al. [49] initially transferred expanded pearlite to a flask integrated with a vacuum system. N-eicosane was gradually added to the flask in the presence of air for half an hour to facilitate infiltration of n-eicosane. The composite was then allowed to cool for a day to solidify the n-eicosane entirely within expanded perlite pores. The mass fractions of n-eicosane were varied from 30%–70% until a leakage-free sample was obtained. A composite obtained with 60% of eicosane was found to be form stable. A calculated quantity of CNT was dispersed in acetone using ultrasonication during the second step. To the previously prepared form stable PCM, CNT/acetone was added and stirred continuously for 180 min with a magnetic stirrer. Finally, using oven (60°C for 360 min) acetone was removed. The same synthesis method was also used in the following study [50]. Li et al. [51] dissolved anhydrous calcium chloride in pristine water with a molar ratio of 1:6. Strontium chloride hexahydrate (2 wt%.) was added as a nucleating agent. The mixture was put to a temperature

of 50°C and stirred (magnetic stirrer at 300 rpm) for 15 min. To promote crystallization, the mixture was cooled down to 40°C. For adsorption of CaCl<sub>2</sub>.6H<sub>2</sub>O onto porous SiO<sub>2</sub> nanoparticles, the former was melted down entirely at 50°C, and SiO<sub>2</sub> nanoparticles were gradually added to the PCM matrix. To ensure uniform dispersion of nanoparticles in PCM, the mixture was again put to magnetic stirring for half an hour at 300 rpm. Finally, the mixture was cooled down to obtain the Form stable NDPCM. Li et al. [52] mixed CNT(nitric acid-treated)/ethanol suspensions in stearic acid/ethanol (shown in Fig. 6). The mass of CNTs was varied from 50%, 33%, and 25%, then subjected to ultrasonic treatment for half an hour. Then the mixture was stirred for 4 h under 70°C in a water bath. Finally, the mixture was made ethanol-free by vacuum drying at 80°C for 24 h. Researchers [53,54] had also followed a similar synthesis method. Kazemi et al. [44] melted pure paraffin thoroughly, and MWCNT with parameters OD < 8 (nm), length 30 (nm) were added to PCM. The suspension was put to an ultrasonic bath for 30 minutes to prevent agglomeration. Gum Arabic (surfactant) was added to ensure proper dispersion of nano additives. The mixture was then sonicated to 1.5 h which yields the NDPCM. This is the most widely preferred two-step synthesis route [48,55]. Su et al. [56] prepared a eutectic mixture of octadecane and stearic acid based on the lowest eutectic point theory. The optimum ratio for the eutectic of SA:ODE was estimated as 2:98 at a phase transition temperature of 25°C. The mixture was heated up to 70°C followed by intense stirring for 5 min until the entire mixture was melted. The mixtures were cooled down to promote crystallization at room temperature. Estimated quantities of hBN were added to the liquid eutectic mixtures and stirred vigorously for 10 min at 70°C for uniform dispersion of nanoparticles into the eutectic mixture. A similar route was adopted in this study [57].



Figure 6: NDPCM synthesis by Direct Impregnation method [52]

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matrix. To ensure uniform dispersion of nanoparticles in PCM, the mixture was again put to magnetic stirring for half an hour at 300 rpm. Finally, the mixture was cooled down to obtain the Form stable NDPCM. Li et al. [52] mixed CNT(nitric acid-treated)/ethanol suspensions in stearic acid/ethanol (shown in Fig. 6). The mass of CNTs was varied from 50%, 33%, and 25%, then subjected to ultrasonic treatment for half an hour. Then the mixture was stirred for 4 h under 70°C in a water bath. Finally, the mixture was made ethanol-free by vacuum drying at 80°C for 24 h. Researchers [53,54] had also followed a similar synthesis method. Kazemi et al. [44] melted pure paraffin thoroughly, and MWCNT with parameters OD < 8 (nm), length 30 (nm) were added to PCM. The suspension was put to an ultrasonic bath for 30 min to prevent agglomeration. Gum Arabic (surfactant) was added to ensure proper dispersion of nano additives. The mixture was then sonicated to 1.5 h which yields the NDPCM. This is the most widely preferred two-step synthesis route [48,55]. Su et al. [56] prepared a eutectic mixture of octadecane and stearic acid based on the lowest eutectic point theory. The optimum ratio for the eutectic of SA:ODE was estimated as 2:98 at a phase transition temperature of 25°C. The mixture was heated up to 70°C followed by intense stirring for 5 min until the entire mixture was melted. The mixtures were cooled down to promote crystallization at room temperature. Estimated quantities of hBN were added to the liquid eutectic mixtures and stirred vigorously for 10 min at 70°C for uniform dispersion of nanoparticles into the eutectic mixture. A similar route was adopted in this study [57].

Researchers are also going on in the direction of employing functionalized nanoparticles to enhance dispersion stability. Sonication is the most widely preferred two-step synthesis route. Generally, for form stable NDPCMs vacuum impregnation is widely preferred as it delivers maximum adsorption.

#### **3** Thermophysical Characterization

The characteristics (shape, size, loading concentration) of nano additives alter the thermophysical properties of dispersing PCM matrix. Hence the evaluation and determination of thermophysical properties is a crucial factor [14,22]. The major thermophysical properties of low-temperature nanocomposite phase change materials are summarized in Table 2.

РСМ	Additives	Fill%	$T_{\text{NDPCM}}$	$\mathbf{K}_{\mathrm{NDPCM}}$	Change in K	$H_{\text{NDPCM}}$	Fc	Reference
Paraffin	MWCNT <sup>o</sup>	0.5	24.1	0.203	49.2	180.1	86.19	[44]
Paraffin	Graphene <sup>o</sup>	0.3	24.84	1.44	860	155.98	102.48	[58]
Paraffin	Graphene <sup>o</sup>	3	28.12	0.303	146.34	216.1	96.86	[59]
Stearic Acid	CNT <sup>o</sup>	20.5	29	_		111.8	99.80	[52]
Paraffin	<b>GNP</b> <sup>o</sup>	1.0	28.97	0.378	89	248.69	98.61	[43]
Paraffin	<b>MWCNT</b> <sup>o</sup>	1.0	28.96	0.355	77.5	248.22	98.43	[43]
Hexadecane	xGnPo	5	18.65	1.61	74	217.33	98.43	[60]
Octadecane	xGnP <sup>o</sup>	5	28.91	0.99	101	240.92	104.81	[60]
Paraffin/ExP	CNT <sup>o</sup>	1	36.47	0.32	113.3	157.43	57.63	[49]
CA-OA	HPAC <sup>o</sup>	0.1	13.1	0.45	125	52.7	87.92	[61]
Paraffin	GO <sup>o</sup>	1.0	36.08	0.957	181	240.83	95.07	[62]
Paraffin	rGO <sup>o</sup>	1.0	36.26	0.935	175	245.16	96.78	[62]

Table 2: Summary on thermophysical properties of low-temperature NDPCMs

(Continued)

Table 2 (continued)								
РСМ	Additives	Fill%	$T_{\text{NDPCM}}$	$K_{\text{NDPCM}}$	Change in K	$H_{\text{NDPCM}}$	Fc	Reference
Paraffin	GNP <sup>o</sup>	1.0	36.76	0.966	184	243.85	96.26	[62]
Paraffin	<b>MWCNT</b> <sup>o</sup>	1.0	36.38	0.921	171	246.28	97.22	[62]
Eicosane	MLG <sup>o</sup>	45	36.24	1.11	282.76	136.6	98.21	[50]
Capric Acid	CuO <sup>I</sup>	3.0	32	0.235	44	159	106.44	[63]
Octadecane	TiO <sub>2</sub> <sup>I</sup>	3.0	28	0.394	1.74	_	_	[64]
LA+SA	TiO <sub>2</sub> <sup>I</sup>	1.0	34.38	0.27	50	173.22	98.86	[45]
LA+SA	ZnO <sup>I</sup>	1.0	34.47	0.29	61	173.64	99.10	[45]
LA+SA	CuO <sup>I</sup>	1.0	34.56	0.32	77.78	173.86	99.23	[45]
Paraffin	CuO <sup>I</sup>	1.0	28.90	0.318	59	249.27	98.85	[43]
Paraffin	$Al_2O_3^{I}$	1.0	28.94	0.332	66	247.03	97.96	[43]
Paraffin	TiO <sub>2</sub> <sup>I</sup>	2	36.5	0.341	70.5	227.74	90.82	[46]
Nonadecane	Rut-TiO <sub>2</sub> <sup>I</sup>	2	25	0.19	37.6	114.2	94.28	[53]
$CaCl_2 \cdot 6H_2O$	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> <sup>I</sup>	2	28	1.373	303	157	89	[47]
PEG2000	Ag <sup>I</sup>	35	34.06	0.552	84	121.7	100	[35]
$CaCl_2 \cdot 6H_2O$	$Cs_{x}WO_{3}$ <sup>I</sup>	1.0	28.75	0.51	$30\%_{fall}$	129.5	84.19	[48]
$CaCl_2 \cdot 6H_2O$	SiO <sub>2</sub> -50nm <sup>1</sup>	30	25.6	0.148	_	136.3	97.40	[51]
Capric Acid	SiO <sub>2</sub> <sup>I</sup>	1.5	31.2	0.529	78.72	160	112.35	[55]
CA:MA	SiO <sub>2</sub> <sup>I</sup>	1.5	22.1	0.4	142	158	108.38	[55]
CA-PA-SA	SiO <sub>2</sub> <sup>I</sup>	25	17.6	0.082	$76\%_{fall}$	99.43	95.17	[57]
heptadecane	SiO <sub>2</sub> <sup>I</sup>	54.6	25.6	0.284	70.58	123.8	-	[54]
SA-ODE	$h-BN^{I}$	15	29.86	0.327	9.73	189.07	99.44	[56]
Paraffin	GNP/MWCNT <sup>H</sup>	1.0	28.94	0.430	115	245.18	97.22	[43]
Paraffin	$Al_2O_3 + CuO^H$	1.0	28.93	0.328	64	248.51	98.54	[43]
Paraffin	GO+MWCNT <sup>H</sup>	1.0	36.11	0.961	182	237.42	93.84	[62]
Paraffin	rGO+MWCNT <sup>H</sup>	1.0	36.57	0.965	184	235.35	92.91	[62]
Paraffin	GNP+MWCNT	1.0	36.17	0.970	185	230.82	91.11	[62]
PEG1000	HNT65@Ag 3 <sup>H</sup>	3	33.6	0.9	207	71.3	97.44	[65]

Note: <sup>O</sup>Organic, <sup>I</sup>Inorganic, <sup>H</sup>Hybrid.

## 3.1 Impact of Nanoparticle Dispersion on Thermal Conductivity

Nanotechnology along with its attained advancements had enabled particles synthesis even at a nanoscale (10<sup>-9</sup>). These nanoparticles mainly comprise of metallic, metallic oxide, carbon nanotube (SWCNT, MWCNT), graphene, graphite, and even hybrid ones [14]. The classification of nanoparticles is given in Fig. 7. Nanoparticles possess some signature properties in contrast to solids due to their exorbitant surface area-volume ratio [66]. The dispersion of nanofillers with extremely high thermal conductivity (monolayer graphene 5300 W/m.K [67]) is anticipated to enhance the thermal energy transport in PCM. The amount of nanofillers dispersed must be good enough to generate thermally conducting pathways [68]. The formed thermally conducting paths facilitate the heat transfer process within the composite and this was seconded by Zhang et al. [69]. Dispersing highly conductive nanofillers does not guarantee a nanocomposite with superior conductivity. Factors like the homogenous distribution of conductive fillers in the PCM should be taken into consideration. Particle

accumulation causes improved Van der Waal forces among nanofillers and this force eventually attracts the nanofillers and they remain clustered [70].



Figure 7: Classification of nanoparticles

#### 3.1.1 Organic Nanoparticles

Ashiq et al. [59] synthesized NG/paraffin composites with 146% improvement in thermal conductivity and they provided thermal comfort for more than 4 h and 2 h at ambient temperatures of 35°C and 40°C. Arshad et al. [43] reported a downward drift in the  $\lambda$  value of paraffin and nanocomposites along with rising temperatures. The phase transition turns the organized microstructured pure paraffin (solid-phase) into a disorganized microstructured (liquid-phase) paraffin. The thermal transport in solids is mainly attributed due to lattice vibration when the molecules vibrate inside their lattice structure. Even at a lower temperature the particle inside a crystal vibrates near the equilibrium position. So, the PCM lattice could be considered as a coupled mass and spring system. When the crystal is subjected to heat the vibrations will deviate from equilibrium position. The generated high energy phonons diffuse, and it forms the temperature gradient. Thus, in the presence of a temperature gradient heat will drift from hot end to cold end [71,72]. The free-electron motion and lattice vibration are prominent in solids than liquids. Hence solids normally have a greater  $\lambda$  value than liquids. Arshad et al. [62] dispersed different carbon nanoparticles in paraffin to form nanocomposite and obtained thermal conductivity increment in the range of 180%. Numerous factors account for this increment and are concentration, interfacial thermal resistance high aspect ratio, clustering, Brownian motion, purity, and intermolecular interaction [73]. A longer phase transition time may result in bigger microscale grains formation; which shortens thermal resistance between layers leading to an increment in  $\lambda$ value [74]. According to Zhang et al. [50], the addition of multi-layer graphene (MLG) accounts for the 282% increment in  $\lambda$  value in the composite. Due to the planar morphology of graphene nanosheets, the thermal interface resistance got reduced in n-eicosane/graphene PCM composites, which introduces an increment in heat transfer of samples during heating and cooling [75,76]. The improved thermal conductivity accounts for a reduction of 45.7% and 67.1% in thermal storage and release times of C20/MLG45 when compared with pure PCM.

#### 3.1.2 Inorganic Nanoparticles

Li et al. [51] used nano-silica of different pore sizes to synthesize form stable composites. The  $\lambda$  value of form stable PCM got reduced with a reduction in pore diameter despite an increase in nanoparticles loading rate. It could be due to phonon-phonon scattering at the interface of

nanoparticles and composites. This produces thermal resistance in non-metallic materials and gets intense along with a large specific area [77].

According to Motahar et al. [64], the thermal conductivity of both PCM and the nanocomposite (octadecane/TiO<sub>2</sub>) counts on temperature and it becomes intense at a temperature range of 25°C– 30°C where the crystalline structure of PCM is unsteady. The  $\lambda$  value varied from 0.375 W/m.K-0.394 W/m.K and 0.144 W/m.K–0.150 W/m.K when the sample temperatures were 5°C and 55°C. The  $\lambda$  value was 0.852 W/m.K near the melting point. Arshad et al. [43] accounted for this abrupt rise. A similar phenomenon was previously reported by Wang et al. [78] with palmitic acid/CNT composite. Higher thermal conductivity of the composite close to phase transition temperature is highly desirable in thermal energy storage applications using PCMs. Xie et al. [48] reported a 30% reduction in thermal conductivity with calcium chloride hexahydrate/cesium tungsten bronze nanocomposite. Strontium chloride hexahydrate was used as the nucleating agent. The probable causes for reduced thermal conductivity could be the interface resistance among components hinder the rise in conductivity with low nanoparticle concentration and the elevated viscosity caused by surfactant dampens the heat transfer with 1.5 wt.% SiO<sub>2</sub> CA-MA. Martin et al. [55] had an outstanding 142% rise in thermal conductivity. The thermal conductivity varies linearly along with nanoparticles content (0–1.5 wt.%) This could be detailed by phenomena like phonon interaction, clustering of nanoparticles (proved by SEM results) Brownian motion, and surface morphology effects which all could be the reasons for this enhancement [79,75].

## 3.1.3 Hybrid Nanoparticles

Arshad et al. [43] analyzed the  $\lambda$  value of paraffin/CuO and paraffin/Al<sub>2</sub>O<sub>3</sub>+CuO and the composites showed a slight variation in trends mainly because of the density, size, dispersion stability, and morphology of nanofillers and their intrinsic  $\lambda$  value. CuO holds a higher thermal conductivity than Al<sub>2</sub>O<sub>3</sub>, paraffin/CuO also had a higher  $\lambda$  value than paraffin/Al<sub>2</sub>O<sub>3</sub>+CuO. Moreover, the Al<sub>2</sub>O<sub>3</sub> nanoparticles had a reduced size and density compared to CuO nanofillers, which possess a better degree of homogenization and rate of dispersion in pure PCM. This accounts for the improved dispersion stability of hybrid nanofillers (Al<sub>2</sub>O<sub>3</sub>+CuO) dispersed in paraffin. Moreover, the thermal boundary resistance among the nanofillers and matrix molecules plays a prominent role in inconsistency [76]. Carbon-based hybrid nanocomposites possess a higher capability to store and release thermal energy when correlated with metallic oxide-based hybrid nanocomposites, primarily due to higher improvement in  $\lambda$  value. Two major factors contribute towards the enhanced thermal energy transport rate of NDPCMs. First, the high  $\lambda$  value of nanofillers, and second, the motion of the nanofillers inside nanocomposites in liquid-phase, that attributes to a quasi-convection phenomenon [80]. Moreover, the interfacial thermal resistance got reduced with 3-D nanostructure as compared to 2-D nanostructure (metallic oxide-based nanocomposites) between pure PCM and nanoparticles. This also assists in improving the thermal conductance rate. Arshad et al. [62] found that the heat transfer improved effectively in all directions of the PCM as the 3D matrix of hybrid nanocomposites forms a 3D path for both lattice resonance transport and phonon transmission [43,81]. The crystal lattice resonance remains the primary heat conduction mechanism in non-metallic PCMs. Consequently, phonons are the dominant thermal transport carriers in the PCM [72]. Furthermore, the thermal boundary resistance (between nanoparticles and PCM) gets reduced in hybrid NDPCMs which enhances thermal energy transport, resulting in an improvement in thermal conductivity. Song et al. [65] explained a 200% increment in thermal conductivity (two-step process). Silver nanoparticles also contributed to conductivity enhancement. Numerous thermal conductive pathways were provided by

1D HNT hybrid hierarchical nanostructure which improves the thermal transport. The composite also showed antibacterial activity.

## 3.1.4 Discussion on Thermal Conductivity

The  $\lambda$  value of nanocomposites can be enhanced with nanofiller dispersion, as the surface-tovolume ratio rises with a decline in nanofiller size, which would eventually raise the thermal energy transport in composites. Thus, a high thermal conductivity results in a reduced solidification and melting time in composites. Carbon-based nanomaterials are commonly preferred for the improvement of  $\lambda$  value. They also deliver photothermal and electrothermal capabilities. The need to enhance the  $\lambda$  value of PCMs is apparent due to their poor energy charging/discharging rates. For improving these parameters nanofillers of high  $\lambda$  value can be dispersed. The higher  $\lambda$  value in the fluid state is due to thermal dispersion and profound turbulence, initiated by nanofiller motions. Fig. 8 summarizes the significant factors that influence the  $\lambda$  value of nanocomposites.



Figure 8: Significant factors influencing the thermal conductivity of nanocomposites

## 3.2 Impact of Nanoparticle Dispersion on Latent Heat

The predominant property of PCMs is their comparatively higher latent heat capacity and this privilege of PCMs could be availed when it undergoes a phase transition process. However, the degraded  $\lambda$  value restrains entire PCMs from participating in the phase transition process. Dispersing nano additives alters the thermal conductivity [73]. The impact of nanofillers on the latent heat of nanocomposites had to be well analyzed. Researchers had reported different conclusions in this regard. Few researchers had reported a positive effect, i.e., nanofiller dispersion enhances the latent heat. Most researchers had reported negative effects, i.e., the nanofiller dispersion depletes the volume of PCM and subsequently minimizes the latent heat. Few researchers had found that a reduced volume fraction had a positive impact on nanofillers melting enthalpy and vice versa.

### 3.2.1 Organic Nanoparticles

Putra et al. [58] used theories like interfacial liquid layering, particle clustering, and Brownian motion to justify the decline in melting enthalpy and specific heat capacity of the nanocomposites. The interfacial liquid layering theory explains that the dispersion of nano additives could affect the molecular structure of base fluid. A solid layer was created by base fluid molecules. The stretching of molecular bonds in nearby molecules causes the solid layer to get exposed to low energy to separate molecular bonds in melting and freezing. The Brownian motion explains that the rapid movement of nano additives in the base fluid weakens the bonding in base fluid, so it takes less energy to melt and freeze [14]. The theory of particle clustering was related to the decline in melting enthalpy and specific heat capacity of the composite and the clustering strengthens the thermal conductivity. However, nanographene particles attract paraffin to form particle groups that could minimize the energy for melting and freezing because of weak molecular bonds [74]. Thermophysical properties were stable even after 1000 cycles. Jeon et al. [60] synthesized nano-composites with hexadecane xGnP. The Latent heat of hexadecane decreased slightly with xGnP loading. This is because of the good dispersion of xGnP in hexadecane with a high surface area and nanoparticle size. With Hussain et al. [61] the latent heat of nanocomposites got declined around 5% and was due to the physio-chemical changes in nanocomposites. The stability of the composite was evaluated even after 200 cycles and the latent heat remained constant. Dispersion of the highly porous activated carbon (HPAC) suppresses the subcooling effect in eutectic PCM and improves the  $\lambda$  value. Activated carbon carriers immense surface energy due to sheet-like structure. The non-settling property of HPAC had linearly minimized the degree of sub-cooling in every proportion. The change in melting and freezing time establishes that the nanofillers dispersed into eutectic PCM served as nucleating agents and even improved the thermal conductivity. All samples synthesized by Arshad et al. [62] exhibited a bimodal crystallization behavior during the solidification process. The initial smaller peak represents the crystallization temperature and the second one denotes the transition of lattice structure from triclinic to hexagonal [82]. The dualphase transformation phenomenon was caused by the presence of a metastable rotator phase before finishing the whole crystallization and a result of heterogeneous nucleation during the cooling [43,83]. The changes in peak melting and crystallization temperatures was due to crystallization confinement of mono and hybrid nanoparticle's surface layers in the nanocomposite. The interfacial surface layers cause the formation of an imperfect PCM and result in a minor variation in peak melting and crystallization temperatures. These factors can enhance the degree of supercooling. The heterogeneous nucleation may be favored as the nanofiller dispersion was at the cost of a fall in crystallization point [83]. A higher degree of super-cooling may deliver a hysteresis response to thermal energy transfer, and it makes the PCM unsuitable for thermal management applications.

## 3.2.2 Inorganic Nanoparticles

With nano-silica/CaCl<sub>2</sub>·6H<sub>2</sub>O nano-composite, Li et al. [51] had a 31% decline in latent heat. The relative error among experimental and calculated latent heat tend to follow a linear pattern along with the pore diameter of nano-SiO<sub>2</sub>. The potential reason behind this phenomenon could be; the restricting effect of SiO<sub>2</sub> tends to get weak, as pore diameter rises [84]. Arshad et al. [46] accounted for a decline in latent heat during melting and solidification process. The TiO<sub>2</sub> nano additives take over the paraffin molecules resulting in a reduction in melting enthalpy of NDPCM. As the interaction between TiO<sub>2</sub> and paraffin gets stronger, the higher will be the latent heat capacity of NDPCM. Using advanced wet impregnation technique, Saxena et al. [53] synthesized nonadecane/rutile TiO<sub>2</sub> nano-composites. Along with nanoparticle dispersion, a reduction of phase transition temperature was noted which, was due to enhanced thermal conductivity (37%). A 7.6% fall in latent heat capacity for NDPCMs was

attributed due to the addition of nanofillers which were solid and does not undergo a phase transition in the melting range of PCM. Li et al. [47] added  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles and SrCl<sub>2</sub>·6H<sub>2</sub>O (nucleating agent) in CaCl<sub>2</sub>·6H<sub>2</sub>O to form nanocomposites. Latent heat got declined by 12.7%. The dispersion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanofillers caused a fall in the degree of supercooling, and a maximum enhancement in thermal conductivity. The degree of supercooling of CaCl<sub>2</sub>·6H<sub>2</sub>O/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocomposite lies in the range of 0°C–2°C, which indicates that surplus latent heat was liberated from the nanocomposites.

#### 3.2.3 Hybrid Nanoparticles

Arshad et al. [43] reported a decrease in melting enthalpy for nanocomposites and was due to the increment in  $\lambda$  *value*. The degree of supercooling was almost constant around 2°C. The enhanced phase duration for latent heat and uniform natural convective heat transfer of paraffin/GNPs+MWCNTs evades overheating and has huge capability in thermal management of microelectronics.

### 3.2.4 Discussion on Latent Heat

In general, nanofiller dispersion in salt hydrates minimizes the stored enthalpy whereas with organic PCMs this decrease remains relatively low. Thus, the energy storage performance of the salt hydrate remains untouched as the latent heat values remain over 100 kJ/kg. The ratio of effective PCM in a nanocomposite that can successfully store heat by completing solidification is provided by the term crystallization factor Fc. When a part of PCMs got confined in the porous structure of the matrix, (disorder PCMs) and cannot complete the crystallization, it leads to a decrease in Fc value [85]. A lower shift in crystallinity values of the composite means that the incorporated PCM can still work efficiently even though the content of nanofillers in the composite was raised to a higher level. Furthermore, thermal properties got enhanced, as the thermal conductivity got improved and the subcooling degree was reduced or eliminated.

#### 4 Thermal Management in Buildings with Nano Composite Phase Change Materials

As per International Energy Agency reports, the global energy consumption trends are expecting a rise of 44% for 1.5 decades from 2016 [86]. Buildings incur almost 30%–40% of energy usage in the European Union which accounts for 30% of greenhouse gas emissions. In buildings, 60% of the energy is designated for HVAC systems [30,87]. The ultimate necessity of low energy consumption paved the way for new methods of temperature management in buildings [87]. To store and release excess thermal energy PCMs could be deployed. High performance together with the energy-efficient building was made possible with PCMs. They primarily store energy as latent heat and possess quite compatible energy storage density [88]. However, the conventional PCMs possess a low heat transfer rate and it can be improved by dispersing thermally conductive nanoparticles [89].

Carneiro et al. [90] evaluated the heat transfer performance of a building wall model under the influence of  $TiO_2$  coated plastering mortar. When compared with the standard wall model the  $TiO_2$  coated mortar degrades the steady-state thermal behavior of the wall by 10% (for conduction thermal resistance) and 13% (for thermal transmission coefficient). Moreover, the exterior wall with  $TiO_2$  nanofillers on the façade enhances the water evaporation rate by 136%. A 136% increment in the water evaporation rate was observed with  $TiO_2$  nanofiller coated exterior façade

Parameshwaran et al. [91] synthesized a hybrid nanocomposite (Ethyl trans-cinnamate/silvertitania). The composite exhibited improved thermophysical properties. The NDPCM exhibited enhanced thermal stability than pure PCM. When compared with pure PCM freezing and melting duration of NDPCM got reduced by 23.9% and 8.5%. Energy efficiency and savings were obtained with freezing rate reduction. The viscosity got enhanced to 3.89% with a rise in hybrid nanoparticle loading This suggests that there exists a relative dependency between thermal properties and viscosity of the NDPCM.

## 4.1 Active Thermal Management

According to Lechner active cooling methods are termed as "mechanical equipment to satisfy the needs (of cooling within a building) not provided by nature" [92]. Active methods mainly rely on electric power and heat as energy sources [92]. The heat energy could be the exhaust heat derived from other processes if available [93] or even from district heating systems. Moreover, renewable energy systems could be deployed to run the active devices [94]. Nonetheless, apart from fans, all active methods have significant energy demand [95]. Active thermal management applications for cooling in buildings are categorized as: free cooling, active solar façade, ventilated Trombe wall, thermally activated building structures with PCM (PCM-TABS), evaporative and radiative systems, geo cooling, and ice storage [5]. Said et al. [96] introduced a novel technique to improve the productivity of an AC unit by integrating a PCM heat exchanger with the condenser of the AC unit. Nano additives (Al<sub>2</sub>O<sub>3</sub>, CuO, and Cu) were dispersed into PCM. The cold ambient air at night was used to charge. The cold energy storage inside the NDPCM was charged by using cold ambient air at night. The hot air at daytime was cooled down by passing it through the NDPCM heat exchanger before it flows to the AC condenser. The AC unit delivered a maximum power saving of about 7.41% (NDPCM-Cu nanoparticles 5%) for an inlet temperature of 45°C. The best conditions for this method could be achieved with optimization studies. Parameshwaran et al. [97] used a MATLAB simulation environment to study the effect of silver nanoparticles dispersed in water on a variable air volume air conditioning system. For year-round operation, LHTES air conditioner with silver nanoparticles delivered an energy saving of 36%-58% on-peak and 24%-51% average per day. An improvement in the overall thermal performance of the system was noted. SVAV-AC gave energy saving of 7.5%-18.6% onpeak and 7.9%-17.8% average per day. In total, the combined air conditioning system was found to be beneficial in attaining good thermal comfort, acceptable indoor air quality, and energy redistribution needs of the building. Parameshwaran et al. [98] used simulations to investigate the performance of silver-titania/Dimethyl-adipate HiTES (hybrid nanocomposites based CTES) system integrated on a building HVAC system for year-round weather conditions. Thermal conductivity enhancement lies in the range (7.3%-58.4%). The complete freezing time of the hybrid nanocomposites got reduced by 15%. A 46.3% decline in chiller cooling capacity (under part load) and 39.6% (on-peak load) was noted. The novel system gained 27.3% and 32.5% reduction on-peak energy savings potential in summer and winter respectively. Reported an yearly energy savings of 12.2% in summer and 10.2% in winter.

## 4.2 Passive Thermal Management

Passive thermal management mention technologies/design features devised to reduce building temperature with zero or even with minimal energy consumption [99] to improve the structure's energy efficiency [100]. The amount of energy consumption is small in comparison to active methods [99,100]. Moreover, renewable energy sources power them [100]. The use of PCM for passive thermal management comprises of integrating them in: free cooling, passive solar façade, building envelope components (floors, ceilings, walls, windows, shutters, and blinds) Trombe wall, solar chimney [5].

## 4.2.1 Building Impregnated Systems

Ashok et al. [101] used shape stable bio NDPCM to analyze the thermal energy penetration performance of NDPCM integrated buildings. The green buildings improve thermal comfort inside

the building and conserve energy. A novel NDPCM integrated composite was introduced to a hollow solid concrete block. An experimental building of size 1 m<sup>3</sup> was constructed to analyze the thermal effects of NDPCM (paraffin/Graphene) integration. Chitosan Shell was used as a shell to prevent leakage. The building integrated with NDPCM showed a maximum reduction of 5.3°C in room temperature when compared with building without NDPCM. The indoor temperature of the NDPCM integrated building increased by 1.8°C when the outdoor ambient temperature dropped below 23.6°C. The NDPCM integration delivered an improved thermal comfort in buildings for all seasons. Thus, NDPCM integration in buildings provides passive cooling of buildings along with energy savings. Ranjbar et al. [54] used the impregnation technique to synthesize heptadecane/SiO<sub>2</sub> nanocomposite. The thermal performance of nanocomposite mixed with gypsum was analyzed by examining the effect on the indoor temperatures of the test room. The nanocomposite had excellent thermal cycling reliability and thermal conductivity. When the mass % of nanocomposite in the gypsum board was increased, the rate of temperature rise got reduced. In the test room, indoor temperature fluctuation curves declined from 41.2°C to 40.2°C, 37.4°C, and 35.5°C when the top gypsum board had 0, 1, 4, and 8 wt.%, of nanocomposites. These results showed that the A5 nanocomposite-gypsum composite had an excellent thermal performance. They could be deployed for TES and building thermal management. Sarrafha et al. [102] used the finite difference method to measure the effectiveness of nano encapsulated NDPCM (octadecane/MWCNT) integration in building walls. During the summer, autumn, and winter days, a 50.1%, 18.5%, and 39.7% increment in latent heat activation with NDPCM integration was observed. Moreover, a rise in the aspect ratio of MWCNT's had a noticeable incremental effect on thermal conductivity, up to a certain limit for NDPCM loading rate. Li et al. [51] analyzed the thermal management potential of CaCl<sub>2</sub>·6H<sub>2</sub>O dispersed in silica for a laboratory-scale test chamber. When compared with pure PCM, NS<sub>1</sub> needed the longest hysteresis time (about 7 min) before peak temperature was observed. During the cooling, the temperature curve of nanocomposites had a smooth decline. The form stable NDPCMs were able to reduce the indoor peak temperature greatly during the melting process and extended the duration of heat preservation during the cooling. FSNDPCMs could maintain suitable indoor temperatures when the external temperature is lower than the required internal temperature during winter. Hence the heating load could be drastically minimized. From these results it is evident that NS<sub>1</sub> had relatively good thermal properties, making them efficient thermal management materials. Xie et al. [48] successfully reduced the room temperature using a NDPCM (CaCl<sub>2</sub>·6H<sub>2</sub>O/Cs<sub>x</sub>WO<sub>3</sub>) kept between doubled layered windowpane of the test chamber. The loading rate of nanoparticles was varied from 0.25%-1.0% with an increment of 0.25%. The non-freezing liquid layer [103] (between PCM and nano-particles) accounts for the difference between calculated and experimental values of latent heat There was a slight deviation in melting point with nanocomposites which can be neglected. The degree of supercooling was slightly reduced for nanocomposite which is primarily because nanoparticles acted as nucleating agents and facilitate heterogeneous nucleation and thereby increases the crystallization rate [104]. Too much loading of nanoparticles hinders crystal growth, and this is visible from the results. The thermal reliability was established by thermal cycler testing. After 100 cycles the latent heat was reduced by 4.1% and melting temperature by 1.75% which establishes the thermal reliability of the nanocomposite The thermal conductivity got degraded from 0.732 W/m.K (pure) to 0.584 W/m.K (NDPCM). The degradation could be due to interface resistance between components (for low loading of nanoparticles). The elevated viscosity of CTAB also lowers the heat transfer rate. The glass window with NDPCMs delivered a 90%NIR radiation shielding. The indoor temperature was maintained between 22°C-28°C for a longer duration. Temperature fluctuations were minimized and exhibited thermal inertia. Li et al. [105] conducted both simulation and experimental studies to analyze the indoor performance of a double glazed window pane filled with NDPCM. The key

findings were, (1) indoor temperature depends on nanoparticle size and concentration. (2) The impact is more significant in winter. (3) The energy consumption could be minimized to 1.5% in summer, 2% in autumn, and 4% in winter (based on NP volume fraction & size). The energy consumption rises with the volume fraction of nanoparticles and a fall in energy consumption was noted with large particle diameter. The lowest energy consumption was recorded with a nanoparticle concentration of 1% as well as a particle diameter of 100 nm with all seasons. The simulated results were found to agree with measured values. The temperature difference between the interior surface of glazed windows and the indoor environment was mainly in the range of 1°C-4°C for summer, 5°C-10°C for autumn, and 14°C–16°C for winter seasons. Venkitraj et al. [106] studied the performance of a building model integrated with macro-packed NDPCM (Neo Pentyl Glycol/0.1% CuO). The thermal conductivity got enhanced by 12.7% along with a reduction in charging and discharging time. An 11% decline in latent heat was observed with 100 thermal cyclings of the nanocomposite. The NDPCM integration was able to deliver a reduction of 3.5°C in room temperature. Li et al. [52] observed that the maximum temperature gained by SA/CNT composite was almost 133% higher when compared with pure stearic acid. The exposure duration in the solar simulator was 1250 s. The NDPCM got cooled down to 20°C by 2500 s. However, the final temperature of SA was 125% higher. This enhancement was due to enhanced photon capture and molecular heating by optical absorption of CNTs. The composite had high thermal management abilities, especially for buildings. Sayyar et al. [107] incorporated NDPCM (capric acid/palmitic acid- graphite nanosheets) into gypsum wallboard using a sandwich structure. Under simulated day and night conditions the thermal performance of gypsum wallboards incorporated with NDPCM was evaluated. The energy efficiency of NDPCM integrated tests cells (representing a scaled building). was estimated using a numerical model. The use of NDPCM in wallboards enabled (i) reduced fluctuations in interior temperature and (ii) shifted (delayed) the time for peak temperature attainment. With NDPCMs the energy demand for cooling was 544 J and for heating was 332 J. Energy demands for cooling (2224 J) and heating(1967 J) were comparatively high in the absence of NDPCM. A 79% reduction in indoor temperature and improvement in energy savings was noted. The indoor temperature was maintained within the comfort zone. Biswas et al. [108] used both numerical simulation and experiments to evaluate the performance of a prototype of shape stable NDPCM enhanced wallboard. The efficiency gained by the system was found to rise with a rise in temperature (19°C–23°C). The integration showed a reduction in cooling electricity consumption.

### 4.2.2 Building Integrated Systems

Photovoltaic (PV) systems used on buildings can be classified into two Building attached PVs (BAPVs) and Building Integrated PV(BIPV) [109]. BAPVs are simply attached to the buildings and do not have any structural functions. Conversely, BIPVs are PV modules, which can be integrated into building envelopes (roofs/façade) by swapping traditional construction materials [110]. Therefore, BIPVs have a significant impact on building functionality and could be recognized as an indispensable part of the building energy system. The electrical efficiency of BIPV declines with a rise in working temperature. The operating temperature must be maintained at standard test conditions to outrun this drawback. PCMs were found to be most appropriate and perfect for cooling PV cells when compared with other technologies as they possess good energy storage density, zero operating and maintenance cost, and zero external power required to operate the system [111]. The integration of the PCM with the PV panel delivers additional thermal comfort along with power savings [112]. The operating temperature of BIPV can be maintained steady and an improved efficiency was attained with PCM usage. However, the heat transfer rate of conventional PCMs were low and can be enhanced by dispersing thermally conductive nanomaterials [89].

Nada et al. [113] installed three PV panel configurations, a normal PV panel, a PV panel with PCM, and a PV panel with NDPCM(paraffin/Al<sub>2</sub>O<sub>3</sub>) mounted on a building wall. The results showed that in stand-alone PV, PV with PCM, and PV with NDPCM, the panel temperatures got minimized by 1.8°C and 10.6°C, respectively. Their efficiency was improved by 5.7% and 13.2% when compared with PV panels. Sharma et al. [114] attempted to deliver passive thermal management in Building-Integrated Concentrated Photovoltaics using micro fins, PCM, and NDPCMs (paraffin/CuO). A 12.5°C reduction in temperature at the center of the systems was noted using micro-fins with NDPCM as compared to the micro-fins and PCMs had a reduction of 10.7°C. The NDPCM with the un-finned surface had a temperature reduction of 11.2°C whereas with the un-finned PCM the reduction was 9.6°C. Ma et al. [22] dispersed a 10% volume fraction of Cu nanoparticles in paraffin. A lumped enthalpy model was used for PCM modeling. Mathematical models were used in estimating the thermal conductivity (Maxwell model) and latent heat of NDPCM. The building system simulation of the building system was done using TRNSYS. The amount of heat absorbed showed an 8.3% increment with NDPCMs (23.85 kWh) when compared with pure PCM (22.03 kWh). Similarly, the heat discharged was also higher with NDPCMs. NDPCMs (10.66 kWh) discharged 25.1% more heat when compared with PCMs (8.52 kwh). The tests were performed in winter for a duration of three days. Kant et al. [89] used computational fluid dynamics to analyze the impact of various nanofillers on the working temperature of a BIPV. Octadecane dispersed in Al<sub>2</sub>O<sub>3</sub>, Cu, CuO, and TiO<sub>2</sub> were used as nanocomposites. The result established that the dispersion of nanofillers in an optimum quantity greatly minimized the working temperature of BIPV for a prolonged time. The maximal temperature fall was noted with Cu and the minimal with TiO<sub>2</sub>. The panel temperature was kept below 40°C for 1 h with 5% Cu nanoparticles. NDPCM minimized the working temperature of the PV panel when compared with pure PCM. A maximal operating temperature difference of 1.65°C, 1.19°C, and 1.15°C was noted for 3 days at around 12.50 PM.

#### **5** Outlooks and Challenges

Most studies implied that the thermal conductivity of NDPCM stays comparatively higher than the base material [115]. A high-grade thermal conductivity can compensate for negative effects like sub-cooling. The most common synthesis route is sonication in which the power used, and duration remains different in almost all cases. A uniform protocol for synthesis must be devised. The latent heat behavior of NDPCM must be well studied. Most of the studies indicated that nanoparticle dispersion degrades the latent heat and vice versa. In-depth, studies must be done to address the inconsistency in the findings. The reliability of thermophysical properties must be done with required cycling tests. The optimum nanofiller concentration which can deliver both maximum thermal conductivity and minimal degradation of latent heat must be identified. Thermal cycling may affect nanoparticles dispersion where the crystallization structure of NDPCM could be altered and may eventually affect entire thermophysical properties. The leakage of NDPCMs during phase transfer was averted with form stable NDPCMs. The supporting skeleton used lowers the thermal conductivity. Particle agglomeration in NDPCM relies on repulsive and Van der Waals forces. During heating, Van der Waals forces (attractive force) in nanofillers becomes weak and the repulsive force becomes stronger. Consequently, it reduces the agglomeration tendency of nanofillers. The repulsive force varies linearly along with the temperature. During cooling, the nanofillers tend to agglomerate and sediment, which could be averted by shortening the solidification time. Under a short solidification time, nanofillers are restrained from moving close to each other or even falling due to gravitational force. Further study on this aspect should be done. Moreover, researchers should also focus on the safety aspect of NDPCM towards human health and the environment since the fillers being used are at the nano level. Also, a Techno-economic analysis, life cycle analysis (LCA), and life cycle cost analysis (LCCA) must be done to justify the application of nanocomposites. The simulation and porotype studies conducted in applications must be integrated to a larger level to prove their viability.

# 6 Conclusions

During the selection of PCM/NDPCM researchers should consider factors like  $\lambda$  value, enthalpy, phase transition temperature, thermal diffusivity, volume change, stability, density, vapor pressure, crystallization duration effect of sub-cooling, cost, safety. An adequate amount of nanofillers dispersion is needed to enhance the overall thermal conductivity of the composite. The thermal conductivity of NDPCM normally rises with the rise in nanoparticle concentration. However, it is noted that the temperature effect on the  $\lambda$  value of NDPCM is similar to the characteristic of pure PCM towards temperature variations. Surfactant dispersed in nanocomposites ensures uniform distribution of nanofillers. The interaction between PCM molecules and nanofillers is restricted to physical. There exists inconsistency in the enthalpy of NDPCM. Carbon-based nanoparticles have delivered a maximum increment in conductivity. Hybrid nanoparticles with their synergistic effect also provided maximum thermal conductivity enhancement. Most researchers revealed that nanofillers degrade latent heat but the increment in latent heat was also reported. This could be attributed to the amount of nano additives dispersed in PCM. Nanofiller dispersion reduces sub-cooling and phase change duration. An inconsistent trend in phase change temperature variation after nanofillers dispersion is widely observed in the literature. The addition of nanofillers in liquid PCM improves its viscosity behavior. Thermophysical properties of Ne PCM get slightly degraded with repeated thermal cycles. Even though the building integration of NDPCMs had derived energy savings, statistical analysis and further research must be done to implement it in real-life conditions.

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