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Review Article

Impact of Nano-Additives on the Thermal Performance of Nano-Enhanced Phase Change Material: A Review

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***Abstract -** Scientists from all around the world have been searching for other ways to address the energy crisis by implementing technology that runs on renewable energy. The main drawback of renewable energy sources, such as solar energy, is the complexity of energy storage. Research is being done to develop novel energy storage techniques. Phase Change Materials (PCMs), a type of latent heat storage material, are distinguished by their exceptionally high heat storage capacity. Nonetheless, the primary constraint on the realistic uses of PCMs is their limited thermal conductivity. Many techniques have been used, sacrificing a number of other aspects in the process of increasing their heat conductivity. Similar to every other sector, researchers started looking at the possibility of using nanoparticles to improve PCMs' thermal conductivity as soon as nanotechnology was developed. Many studies showed enhancement in thermal conductivity when PCMs are dispersed with nanoparticles. This proved that Nano Enhanced Phase Change Material (NEPCM) is a great thermal conductivity enhancer. A comprehensive literature study focusing on the preparation of NEPCMs, their thermophysical properties, the effect of nano-additives on these properties and their overall thermal performance are thoroughly discussed in this paper.*

***Keywords** - Efficient heat storage, Nanoparticles, Nano Enhanced Phase Change Material (NEPCM), Thermal Energy Storage (TES).*

1. Introduction

Phase Change Materials (PCMs) are considered highly effective for thermal energy storage due to their capability to absorb and release substantial amounts of heat in latent form during phase transitions between solid and liquid states, as illustrated in Figure 1. When exposed to higher temperatures, the material melts, storing energy as latent heat. As the temperature decreases, the stored heat is gradually released back into the environment, triggering the reverse process-solidification.

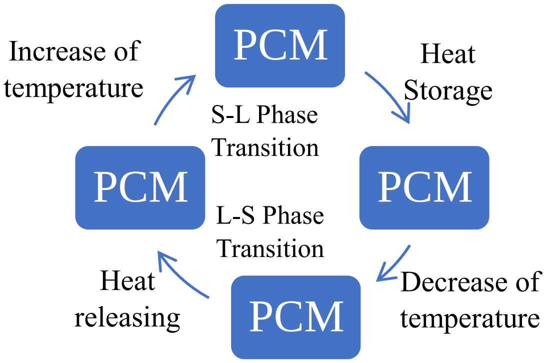

Fig. 1 Solid-liquid phase change process

These phase change processes have little volume changes and happen at constant temperatures. Due to this property, PCMs can be effectively utilized in thermal management systems by undergoing repeated cycles of melting and solidification. These materials can comprise various organic and inorganic substances, making them versatile for different applications. Water, anhydrous salts, and metallic salts are examples of inorganic PCMs, but paraffin waxes and fatty acids make up the majority of organic PCMs. Another type of PCM mixture created by combining two or more pure PCMs (often organic PCMs) that solidify at a minimum freezing point is called a eutectic mixture. In order to obtain PCMs with the necessary phase change temperatures, eutectic mixes are typically employed, which increases PCM availability for various temperature applications.

A thorough analysis of various PCMs in the range of 0°C - 250 °C was provided by Jose et al. [1]. Additionally, Amaral et al. [2] offered a detailed explanation of the various kinds of PCM material and their advantages and disadvantages. Slurries and phase change emulsions, such as water-in-oil and oil-in-water, are also utilized in various heat storage applications. The literature thoroughly analyses paraffin-based phase change emulsions, their preparations, thermophysical features, and heat transmission traits, explaining their potential uses in Heating, Ventilation, and Air Conditioning (HVAC) systems [3]. A phase change material, as previously indicated, goes through several cycles of melting and freezing, absorbing and losing heat from the stored latent energy in the form of heat. Using Differential Scanning Calorimetry (DSC), various PCM kinds are analyzed. The results of the DSC test verify the presence of an energy asymmetry in melting and freezing processes, meaning that they take place in different temperature ranges. This imbalance suggests that temperature impacts the PCM state as well as it was before [4].

The melting process is the objective of numerous in-depth studies, given the numerous variables affecting the heat transfer rates during the procedure. In short, heat conduction controls the starting of the process by changing the phase from solid to liquid, and as it does, natural convection takes over. At first, there are noticeably high heat transfer rates, but as time passes and the volume of liquid PCM grows, convection becomes more important, and melting rates get lowered. Buoyancy drives convection, and factors such as the thermophysical operational circumstances, PCM characteristics, and geometric arrangements of one significant element are the enclosures packed with PCM [5]. The impact of various enclosure forms and their geometrical characteristics, such as the phase proportion of the intra-molecular space, eccentricity, and spherical capsules' radius cavities, have been the subject of in-depth research [5, 6]. In essence, solidification is a process characterized by diffusion in the absence of natural convection currents [7] and only illustrates a heat conduction issue [8]. Trial and Numerical analyses show that solidification rates rise in proportion to regarding thermal conductivity.

Low heat conductivity, phase separation problems, and supercooling are the main drawbacks of typical PCMs. By incorporating a nucleation agent that can start the nucleation process during solidification, the problem of supercooling can be partially resolved [9]. Phase separation, which is frequently experienced by inorganic salts, can also be avoided by employing certain additions. The aforementioned disadvantages primarily apply to inorganic PCM use; as a result, organic PCMs are proven for heat energy storage systems. However, since low thermal conductivity in organic PCMs influences heat transfer rates and causes sluggish charging and discharging in energy storage devices, this issue requires further attention [3]. It might also have an impact on thermal management systems' capacity to keep a steady temperature. Thus, in addition to the phase change temperature, the ideal thermophysical characteristics of a Phase Change Material (PCM) for a given application should include high thermal conductivity and large latent heat capacity, high density, minimal volume changes, supercooling, and phase segregation. Other considerations include inert chemical composition, affordability, and simplicity of availability.

1.1. Techniques to Enhance Thermal Conductivity

When creating a thermal storage system with waxes and fatty acids, the lower thermal conductivity of organic PCMs is a concern in their application. The original study recommended using expanded surfaces like metallic fins to enhance the distribution of heat effectively and fast. As far as the overall weight is concerned, the enhancement in the thermal conductivity of the system is being done by reducing the quantity of base material. Utilizing high-temperature nanostructured foams as Thermal Conductivity Enhancers (TCEs) emerged as a substitute [9]. Out of the two enhancing approaches, extremely porous nanostructured foams were shown to be a preferable option due to their continuous structure, which encourages a faster flow of heat and preserves the phase change energy-holding ability of the PCM injected into it. The three techniques for increasing thermal conductivity using highly conducting nanoparticles as an addition, finned structures, and foams saturated with PCM were compared by Sahoo et al. [10]. It was discovered that the ideal number of fins, which varies depending on different fin characteristics and PCM kinds, can effectively manage the heat sink's base temperature. The investigation found that pore density and porosity were related to metal foam efficiency. An effective porosity selection must counter the effect of reduced PCM convection inside the metal foams. The assessments also revealed that PCMs distributed with nanoparticles performed better than metallic foams at low power loads and heat flux, with the main benefit being no change in PCM volume. Micro fins attached to heat sinks filled with nano-enhanced PCMs were shown to increase a solar module's efficiency by up to 18.5% when compared to traditional cooling systems in a study by Sharma et al. [11]. When compared to micro fins and PCM, it was discovered that PCMs containing nanoparticles were more effective on an individual basis. A carbon foam impregnated with CNT-dispersed PCM for use in the thermal control of electronic devices was the subject of another study that used a combined thermal conductivity enhancement approach [12]. The scientists ascribe the observed significant effect on the thermal sensitivity of the low-conducting carbon foam infiltrated with the nano-enhanced PCM to the greater heat transfer rates caused by the entrapped CNT fillers. To date, there is a fairly little body of literature that examines the synergistic effects of various methods for improving thermal conductivity.

2. Nano-Enhanced Phase Change Materials

Using multiple PCM systems, expanded surfaces like fins, and porous structures and nanoparticles as heat conductivity enhancers are just a few of the strategies that have been the subject of several studies and investigations aimed at increasing the thermal performance of PCMs. A novel class of PCMs known as Nano-Enhanced Phase Change Materials (NEPCMs) was created as a result of the discovery that using nanoparticles can improve a PCM-based system's heat transfer capabilities.

2.1. Preparation of Nano-Enhanced Phase Change Materials

Nanoparticles in PCM play an important role in improving its thermal conductivity. As mentioned earlier, thermal conductivity is also the main and serious concern for PCM. Organic NEPCMs are generated using a method akin to nanofluids, often involving two steps in the production process. To distribute the surfactants and nanoparticles, an emulsification procedure or melt-blend method is used in necessary proportions in the PCM, which is heated much over its melting point. Sonication in the bath after mechanical stirring guarantees proper dispersion during the liquid phase of the PCM. The length of time these procedures take depends on the number of surfactants, the concentrations of nano-additives, and both. Additionally, NEPCMs are made using the one-step approach, which is an in-situ technique.

For instance, by adding silver neo-decanoate to a solution containing eicosane and oleoyl sarcosine, a dispersion of silver nanoparticles in eicosane was created [13]. It was discovered that the solvent was functioning as the reducing agent in this process. Additionally, the impact of various solidification methods on the creation of NEPCM was examined in the study. Samples prepared using three different methods of solidification- oven, ambient temperature, and ice-water bath- were subjected to thermal conductivity measurements. Samples that were solidified in the oven had the maximum thermal conductivity.

The ice-bath solidification, on the other hand, produced the lowest values; this is thought to be because of the gas bubbles that were trapped inside the samples as a result of abrupt temperature changes. When Nabil et al. [14] investigated the thermal conductivity of CuO nanoparticle-based NEPCM, they found similar results. In investigations using Multi-Walled Carbon Nanotubes (MWCNTs) that had been treated and dispersed in palmitic acid, Wang et al. [15] conducted studies and discovered that the pre-treatments significantly affected the thermal conductivity of the nanocomposites by altering the surface of the enhancers. Comparing MWCNTs treated with mechanochemical reactions to other techniques such as acid oxidation, ball milling, grafting, etc., it was discovered that the latter exhibited reduced thermal conductivity.

Although surfactants are not used in all NEPCMs with low additive concentrations, most studies included calculated amounts to guarantee uniform nano-additive dispersion. Surfactants create a shield around paraffin particles to stop coalescence by lowering the interfacial tension between the molecules. Shao et al. [3] provided a summary of surfactants, their kinds, and their mechanisms in relation to the phase change emulsion production process. Surfactants can generally be classified as polymer-based, ionic, non-ionic, or amphoteric. A non-ionic surfactant was employed in the majority of investigations utilizing metal/metal oxide nanoparticles as additions in order to enhance the dispersion. According to Nourani et al.'s experimental investigation [16], adding sodium stearoyl lactylate, a non-ionic surfactant, may enhance the composite's dispersion stability and promote strong thermal reliability for up to 120 melting/freezing cycles. To increase a GNP / paraffin wax composite's dispersion and stability, a polymeric dispersant was employed [8]. Hitesol BC-10 produced the most stable suspension, according to sedimentation studies that examined the impact of five distinct dispersants on the stability of the nanocomposite with copper additions.

The authors proposed that the dispersant's steric hindrance mechanism may have caused this [17]. It was discovered that 1% oleic acid worked well as a dispersion while creating paraffin-nano magnetite composite [18]. Sharma et al. [19] employed sodium dodecylbenzene sulfonate, or SDBS, to guarantee that TiO_2 nanoparticles were uniformly dispersed in palmitic acid. However, when cetyltrimethylammonium bromide or CTAB, was employed instead of SDBS, a different study employing the same base PCM and MWCNTs as nano-enhancers discovered that the thermal conductivity of the nanocomposite increased [20]. This showed that using CTAB guaranteed a more even dispersion of MWCNTs in palmitic acid. To enhance the dispersion of n-HBN nanoparticles in n-octadecane, 2 mass % stearic acid was added [21]. With a melting point of between 54 and 56 degrees Celsius, stearic acid and fatty acid are itself PCM. Together, these two compounds created a eutectic.

Nano-Encapsulated Phase Change Material (NEPCM) preparation methods typically involve techniques such as emulsion polymerization, sol-gel synthesis, and microencapsulation. These methods enhance thermal stability, prevent leakage, and improve thermal conductivity. The selection of the encapsulation technique depends on the desired particle size, shell material, and application requirements. Advanced methods like electrospinning and in-situ polymerization are also explored for improved performance.

2.2. Applications of Nano-Enhanced Phase Change Materials

Nano-Enhanced Phase Change Materials (NEPCMs) have a wide range of contemporary technological applications in addition to conventional engineering uses. The primary reason behind the limited adoption of NEPCM systems is the comparatively high expense of nanoparticles and an uncertain cost-benefit ratio [22]. However, NEPCM content is likely to find application in broader use in the upcoming years, particularly concerning energy applications for storage. In general, classification is somewhat challenging. NEPCMs are an excellent option for thermal energy storage, passive cooling, heat transfer fluids, waste heat recovery, and other applications due to their capacity to absorb comparatively large amounts of heat at roughly constant temperatures. In the work, an extensive classification approach was used to classify NEPCMs based on their most common use.

3. NEPCM's Thermophysical Characteristics

Similar to nanofluids, the technique of distributing nanoparticles in a base PCM to increase their thermal conductivity and enhance a PCM's heat transfer capability has been documented in numerous research. Numerous studies have been conducted on this kind of composite PCM, which consists of metallic, metal oxide, and carbon-based nanoparticles distributed throughout organic and inorganic PCMs. Depending on the application, paraffin wax in various grades is the most popular type of PCM. It is clear from the literature that the system's thermal performance is increased without an appreciable rise in unit size. Although the majority of the time, there is an increase in thermal conductivity, the high loading of nanoparticles in the system has resulted in detrimental effects on other parameters such as dispersion stability, latent heat, viscosity, and specific heat [23]. Thus, it can be said that a NEPCM's performance depends on striking a balance between several thermophysical factors. With a few exceptions, the majority of studies, including nano-additives, ignored their impact on heat storage capacity while guaranteeing improved thermal conductivity. In a system containing Al_2O_3 nanoparticles dispersed in paraffin wax, Ho and Gao [23] investigated the thermophysical characteristics such as thermal conductivity, dynamic viscosity, and latent heat of fusion. There has been a noticeable decrease in the latent heat of fusion and an increase in the dynamic viscosity, even though it was discovered that the thermal conductivity was rising at various temperatures as the loading levels increased. The scientists, therefore, questioned a NEPCM's overall effectiveness as a thermal storage device. Similar studies were carried out in various PCMs using various copper, iron, zinc oxide nanoparticles, etc. Latent heat often decreased as additive concentration increased in the majority of these circumstances. Given that the nanoparticles themselves do not undergo phase transition, this effect is expected. When the quantities of additive loading were relatively low, there were ambiguous trends seen in the latent heat capacity of the NEPCMs, particularly with carbon-based nano-additives.

When employing this method, it's critical to optimize the loading level of the nano-additives because an excessive concentration may cause the NEPCM's latent heat capacity to decrease. This suggests that different loading levels should be considered when characterizing NEPCMs. Thermal analysis and differential calorimetry are typically employed for its thermophysical characterization. In the majority of the research, a Differential Scanning Calorimeter (DSC) is used to assess the latent heat capacity, an inherent feature of the material. Typically, transient methods like the Transient Hot Wire (THW) method and the Transient Planar Source (TPS) method are used to measure thermal conductivity.

DSC provides data on a range of thermal characteristics, including specific heat, latent heat capacity, and the beginning and peak phase transition temperatures (melting and solidification). Li et al.'s detailed explanation of the DSC measuring method for these parameters may be found [24]. In summary, the heat flux DSC employed for this purpose uses thermal fluctuations to compare the heat flow to the sample and the reference. When these thermal changes are transformed into heat flux signals, the temperature-heat flow curves measure all the phase change-related parameters. The latent heat of fusion and solidification can be found by examining the area beneath the melting and freezing peaks. The thermal investigation of the phase change processes of several PCMs was carried out in the study by Li et al. [24], which also covered the impact of heating/cooling rates on the observed peaks. Samples discovered to be out of thermal equilibrium required a greater heating rate. When calculating the latent heat capacity of nanocomposites, some research even proposed heating the sample at a rate as low as 0.5 °C/min to bring it to a quasi-equilibrium condition. This was done using the theory of mixtures. Comparability between the computed and measured values was demonstrated by Wang et al. [25]. According to Su et al.'s [21] approximation of the latent heat of a composite PCM based on the base PCM mass percentage, the latent heat of pure PCM will always be higher than the latent heat of the composite PCM.

Thermal diffusivity, specific heat, and density were multiplied to determine the room-temperature thermal conductivity of the nanocomposite, according to Elgafy et al. [26]. A DSC device was used to assess heat capacity, and the laser flash method was used to evaluate thermal diffusivity. A number of research [15, 25] employed the transient hot-wire approach, which measures thermal conductivity by utilizing a platinum wire that doubles as a heater and sensor unit. The most popular technique for determining the thermal conductivity value is to employ a hot disc thermal constant analyzer, which operates on the transient plane source concept [20]. This approach was described in detail by Ghossein et al. [13]. Using the Nano flash apparatus, Parameswaran et al. [27] measured the thermal conductivity of the PCM composite that was scattered with silver nanoparticles in 2013. An infrared detector was used to quantify the temperature change that occurred after heating samples within a crucible with a brief light pulse. The thermal conductivity values of the samples were determined by their density, and these temperature fluctuations were associated with specific heat and thermal diffusivity. Since the nanocomposite will be out of equilibrium, measuring thermal conductivity close to the melting point might not produce reliable findings [28].

Using an experimental setup, Sahan et al. [18] measured the thermal characteristics of a paraffin-nano-magnetite composite using a Diffusivity and Conductivity (DICO) measurement equipment. Samples were sandwiched between two parallel copper and brass plates, one of which was regularly heated and the other of which was left at room temperature. The literature provided a detailed explanation of the sample preparation procedure and the experimental setup. However, in contrast to other approaches, it was discovered that the results' uncertainty levels were substantial. Teng et al.

[29] elaborated on another experimental setting that used the steady-state measuring technique without needing pricey, complex equipment. Yinping et al. [30] presented the T-history method, a straightforward and efficient way to examine all the thermophysical characteristics of phase transition materials. Because of the increased sample size, the method was found to be superior to other traditional calorimetric methods and thermal analysis techniques, like DSC and DTA. Nevertheless, no comprehensive research reports have employed this method to describe NEPCMs.

Thermophysical characteristics of numerous PCMs distributed with various nano-additives have been documented in the literature using the aforementioned techniques. It was discovered that NEPCMs with various kinds of these additives showed distinct trends in their thermophysical characteristics. Based on the literature, the following sections attempt to address these trends and concentrate on how nano-additives affect thermal behavior and overall heat transfer performance in solid-liquid organic phase change materials.

4. Nano-Additives' Impact on The Thermal Performance of NEPCM

For the practical applications, it is imperative to choose the best nano-additive. Making the wrong decision could lead to thick interface layers, raising the interface thermal resistance and impairing heat transfer efficiency. Since the layers are not involved in the phase change processes, it might also have a detrimental effect on the phase change [29]. Carbon-based and metal-based are two main categories into which common nano-additives can be divided. Metal oxides, semiconductor oxides, and nitrides are examples of ceramic and metal nanoparticles that are included in the category of metal-based nanofillers. These days, carbon-based nano-fillers are used in most systems because of their high aspect ratios and superior application possibilities. In order to examine the impact of nanoparticle dispersions in PCMs on their thermophysical characteristics, such as thermal conductivity, latent heat capacity, viscosity, etc., Kibria et al. [31] examined the experimental research. The review made it abundantly evident that an ideal nanoparticle loading level is needed to achieve a balance between rising thermal conductivity and fluctuating latent heat values with rising additive loading levels. Numerous more reviews of theoretical and experimental work that improved NEPCM heat transfer performance were also published, with an emphasis on the improvement of thermal conductivity [32, 33].

4.1. Thermal Conductivity Enhancer: Metal-Based Nanoparticles

Ho and Gao [23] examined the thermophysical properties of a system containing alumina nanoparticles scattered across paraffin and n-octadecane (M.P. 28.5 ºC), including thermal conductivity, dynamic viscosity, and latent heat of fusion. While thermal conductivity increases with temperature, it was found that the latent heat of fusion decreased by roughly 7% at a loading level of 5 mass% and the dynamic viscosity increased by almost 20% at a loading level of 5 mass%. The natural convection-driven melting cycle may be adversely affected by an increase in viscosity. As a result, the authors had concerns over the NEPCM's overall effectiveness as a thermal storage device. Wang et al. [34] reported similar outcomes using a different grade of paraffin wax (M.P 52–54 ºC) as the base PCM. This suggested that paraffin waxes' melting and freezing properties are not significantly influenced by their melting point. The experimental results of Ho and Gao [23] were validated by Arasu et al. [35] through numerical research on the melting of paraffin wax dispersed with alumina nanoparticles. The numerical investigation was based on a physical model of a square enclosure filled with NEPCM heated from the bottom walls and sidewalls. The study's findings, which included the observation that the melting rate of paraffin-based NEPCM decreased with increasing additive content, demonstrated the critical function that higher dynamic viscosity plays in this process. The same authors [36] and Arici et al. [37] carried out comparable numerical investigations on a concentric pipe and a partially heated square enclosure (both sides and bottom walls) filled with NEPCMs, respectively. The findings showed that energy storage capacity is increased compared to pure PCM at lower concentrations of alumina additions, along with increased heat transfer rates during melting and solidification. Additionally, it is discovered that the augmentation is more noticeable when the square enclosure is heated from the bottom. The impact of nano-additives based on aluminium on the latent heat and thermal conductivity of different PCMs is summarized in Table 1.

A comparative analysis of PCMs dispersed with various metal oxide nanoparticles revealed that paraffin dispersed with 4% alumina nanoparticles had the greatest improvement in thermal conductivity and onset solidification temperature [38]. This also led to the greatest reduction in the NEPCM's liquid phase heat capacity (almost 50%) [39]. Together with other pure metal nanoparticles, Owolabi et al. [40] conducted an experimental investigation to determine how aluminium nanoparticles affected the thermophysical characteristics of paraffin wax. Because pure metal nanoparticles have a higher thermal conductivity value than their oxide counterparts, the solid-state thermal conductivity improvement was found to be more than 20% for all mass fractions.

It has been discovered that thermal conductivity and, consequently, heat transfer rates are significantly impacted even by the addition of micro-sized Al nanoparticles [41]. When 2 mass% Al powder was introduced to paraffin wax inside a spherical, it was discovered that the melting time was reduced by 39%. An intriguing finding from the study was that, in contrast to the uniform dispersion of additives, the deposition of nanoparticles in the spherical enclosure led to a faster melting rate and a lower solidification rate. This disparity results from the fact that natural convection does not occur uniformly in the case of a sphere. The increased presence of nanoparticles at the bottom owing to sedimentation makes the melting process more uniform throughout the enclosure, even if it has no effect at the bottom of the sphere. A study on paraffin-based composite PCM with Cu, Al, and C/Cu as nano-additives was carried out in 2010 by Wu et al. [17]. The optimal heat transfer capability of copper nanoparticles as a heating-cooling rate test confirmed additions. The two reasons given by the authors for this phenomenon are the transient hot-wire method's confirmation of the increased thermal conductivity and the potential for nano-additives to behave as nucleating agents to improve phase change processes. Cui et al. [43] found that adding 0.5 mass% nano-copper decreased sodium acetate trihydrate, an inorganic PCM, from supercooling to 0.5 ºC, serving as both a nucleating agent and an enhancer of thermal conductivity.

Table 1. Provides an overview of the research on PCMs distributed using nano-additives based on aluminium

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Paraffin Wax (20 ºC)	Al_2O_3	1	-8	Data NA	11	Colla et al. [42]
Paraffin Wax (25 ºC)	Al_2O_3	1	-7	Data NA	1	Colla et al. [42]
n-octadecane (26.5 ºC)	Al_2O_3	5	Data NA	7.4	-7	Ho & Gao [23]
		10		17	-13	
Paraffin Wax (46-48 ºC)	Al_2O_3	2	4.8	53.8	-9.02	Arasu et al. [33]
		5	14.3	30.8	-19.5	
		10	33.33	23.1	-33.9	
Paraffin Wax (48-55 ºC)	Al_2O_3	0.5	22.3	Data NA	Data NA	Owolabi et al. [40]
		1	23			
		1.5	24.2			
Paraffin Wax (52-54 ºC)	Al_2O_3	1	17	6	-4.3	Wang et al. [34]
		2	20	11	-4.15	
		5	25	18	-5.7	
Paraffin Wax (53-57 ºC)	Al_2O_3	2	43	Data NA	0.95	Babapoor et al. [39]
		4	120		-3.3	
		6	140		-4.76	
		8	142		-14.3	
Paraffin Wax (54-58 ºC)	Al_2O_3	2.5	15.23	2.7	-2.01	Nourani et al. [16]
		5	19.8	5.4	-2.64	
		7.5	24.36	9.5	-7.27	
		10	31.47	12.8	-10.76	
Paraffin Wax (60 ºC)	Al_2O_3	1	No direct data available		-0.75	Teng et al. [29]
		2			-2.4	
		3			-7.63	

The unidirectional freezing process of cyclohexane mixed with CuO nanoparticles at mass fractions of 1, 2, and 4 mass% was investigated by Fan et al. [44]. While the differences in solid-phase thermal conductivity did not follow any specific trend, the liquid-phase thermal conductivity increased as the loading level of additives increased. Up to 2 mass% of nanoparticles were found to accelerate the freezing process; however, above that point, a non-monotonic enhancement in the rate was noted, which the scientists linked to a corresponding observation in the solid phase thermal conductivity.

A study by Nabil et al. [14] that examined the impact of dispersing CuO nanoparticles on the thermal conductivity of eicosane at various loading levels (0–10 mass%) revealed a similar result. Thermal conductivity was shown to increase monotonically in all samples with additions up to 2 mass %. The melting of noctadecane distributed with CuO nanoparticles (0, 1, 3, 5 mass%) contained in a horizontal cylindrical capsule subjected to a constant heat flow was studied experimentally and numerically by Nabeel et al. [45]. It was discovered that the changes in the solid-liquid interface throughout the melting process corresponded to the isotherms that the numerical analysis simulated. The rise in melting rates is a feature of NEPCM with low loading levels, as demonstrated by both experimental and numerical experiments. The increase in viscosity and agglomeration problems significantly impede the melting rate despite increased thermal conductivity.

Table 2. An overview of the research on PCMs distributed with Cu-based nano-additives

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Cyclohexane (4-7 °C)	CuO	1	2.79	0.49	Data NA	Fan et al. [41]
		2	6.55	1.06		
		4	10.04	1.45		
Ecosane (37 °C)	CuO	1	1.4	Data NA	Data NA	Nabi et al. [14]
		2	6.18			
		3.5	4.32			
		5	2.74			
		6.5	2.57			
		8	6.86			
		10	8.42			
Paraffin Wax (58-60 °C)	Cu	0.5	No direct data available		-4.37	Wu et al. [17]
		1			-11.17	
		2			-11.65	
Paraffin Wax (48-55 °C)	Cu	0.5	20.2	Data NA	Data NA	Owolabi et al. [40]
		1	20.4			
		1.5	20.6			

The heat transmission coefficient increased by 78% throughout the freezing process at a 10 mass % loading level, according to Jesumathy et al. [46] studies in a concentric double pipe heat storage system filled with paraffin wax distributed with CuO nanoparticles. Their usefulness as an effective thermal storage system was validated by a reduction in charging and discharging times and an increase in thermal conductivity with loading levels.

The suitability of paraffin-nano magnetite (Fe_3O_4) composites at mass fractions of 10 % and 20 % was evaluated for thermal energy storage systems [18]. The system's thermal conductivity increased by 48 % and 60 %, respectively. It's interesting to note that the latent heat capacity increased by 3.3 % and 8.8 % (for 10 and 20 mass %, respectively) even at these comparatively high mass fractions of additions. Oxide nanoparticles that increase PCMs' capacity to store heat have not been extensively studied in the literature despite the fact that several carbon-based nano additives have demonstrated comparable patterns. The authors used Shaikh et al.'s intermolecular attraction theory to support these findings [46]. According to a comparative analysis of four oxide nanoparticles, paraffin containing 8 % Fe_2O_3 nanoparticles showed the most increase in thermal diffusivity [37].

Table 3. An overview of the research on PCMs distributed with nano-additives based on iron (Fe)

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Paraffin Wax (46-48 ºC)	Fe_3O_4	10	48	Data NA	3.26	Sahan et al. [18]
		20	60		8.83	
Paraffin Wax (53-57 ºC)	Fe_2O_3	2	64	Data NA	-43.21	Babapoor et al. [39]
		4	85		-48.14	
		6	135		-55.55	
		8	145		-70.37	
Paraffin Wax (48-55 ºC)	Fe	0.5	39.5	Data NA	Data NA	Owolabi et al. [40]

Table 4. An overview of the research on PCMs distributed with nano-additives based on zinc (Zn)

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Paraffin Wax (60 ºC)	ZnO	1	No direct data available		-6.02	Teng et al. [29]
		2			-7.37	
		3			-13.8	
Paraffin Wax (53-57 ºC)	ZnO	2	30	Data NA	-19.5	Babapoor et al. [39]
		4	85		-21.5	
		6	100		-23.5	
		8	110		-34.5	
Paraffin Wax (46-48 ºC)	ZnO	10	Data NA	Data NA	-7	Sahan et al. [47]
Paraffin Wax	Zn	0.5	46.4	Data NA	Data NA	Owolabi et al. [40]
		1	57.1			
		1.5	61.5			

When 0.5 and 1.5 mass percent of zinc nanoparticles were added, the base PCM's thermal conductivity increased by 46.4 % and 61.5 %, respectively. With the inclusion of copper nanoparticles, which have higher bulk thermal conductivity values, the improvement was only about 20 %. The enhancement's anomalies suggested that each nano-filler's ideal weight fraction for maximizing thermal conductivity enhancement needed to be examined. Studies on four oxide nanoparticles (SiO_2, ZnO, Fe_2O_3, and Al_2O_3) at mass fractions of 2, 4, 6, and 8 mass percent were carried out by Babapoor and Karimi [39] and Babapoor et al. [38]. They investigated how these nano-additives affected a variety of metrics, including specific heat, phase transition temperatures, latent heat capacity, and thermal conductivity and diffusivity. It was found that ZnO nanoparticles dissolved in paraffin do not exhibit an increase in the specific heats of the liquid and solid phases, which is a highly sought-after property for an effective thermal storage system.

Table 5. Literature overview on PCMs distributed with nano-additives based on titanium

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Paraffin Wax (60 °C)	TiO_2	1	No direct data available		0.6	Teng et al. [29]
		2			0.35	
		3			-0.35	
Paraffin Wax (48-50 °C)	TiO_2	0.5	1.5	2	5.6	Wang et al. [48]
		0.7	1	4	14.3	
		1	4	0.7	5.6	
		3	8	6	-3.5	
		5	6.5	6.5	-5.95	
		7	10	17	-9.5	
Palmitic acid (60-62 °C)	TiO_2	0.5	16	Data NA	-2.08	Sharma et al. [19]
		1	21		-4.95	
		3	42		-13.6	
		5	79		-15.67	

Only a 7 % reduction in latent heat capacity was noted in a recent study by Sahan and Paksoy [47] that examined the thermal characteristics of ZnO nanopowder in a tubular construction at a mass fraction of 10 % in paraffin.

This discovery allowed the scientists to propose using nano-additives in PCM-based solar applications, even at a comparatively high concentration of these substances.

Titania nanoparticles significantly impact the thermal conductivity and heat storage capacity of the paraffin PCM, according to a comparative analysis of several oxide nanoparticles [29].

Interestingly, TiO_2 nanoparticles somewhat increased the latent heat capacity at 1 mass percent. TiO_2 nanoparticle loading levels ranging from 0.3 to 7 mass percent produced comparable outcomes [48]. Latent heat was found to rise below the 1 mass percent loading level, with the greatest enhancement occurring at 0.7 mass percent. Sharma et al. [19] examined the thermal characteristics and heat storage capacity for usage in a solar thermal energy storage system using titania nanoparticles as enhancers and palmitic acid as the base PCM. At a 5 mass percent loading of nanoparticles, it was discovered that thermal conductivity was increased by 80 % while the latent heat capacity was reduced by a relatively little amount (around 15 %).

Table 6. An overview of the literature on PCMs distributed with nano-additives based on silicon

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Paraffin Wax (60 °C)	SiO_2	1	No direct data available		-6.92	Teng et al. [29]
		2			-9.52	
		3			-12.2	
Paraffin Wax (56-58 °C)	Si_3N_4	1	10.42	Data NA	3.42	Yang et al. [49]
		2	13.61		-0.29	
		3	13.74		-9.13	

		4	15.96		-13.64	
		5	21.81		-23.71	
		10	34.76		-39.1	
Paraffin Wax (53-57 °C)	SiO_2 (11 nm)	2	40	Data NA	-8.64	Babapoor et al. [39]
		4	75		-18.5	
		6	110		-23	
		8	110		-25.92	
Paraffin Wax (53-57 °C)	SiO_2 (20 nm)	2	5	Data NA	-1.23	Babapoor et al. [39]
		4	70		-11.11	
		6	95		-23.46	
		8	120		-33.33	

Numerous comparative research examined the impact of nano-silica distributed within PCMs. Comparing them to other oxide nanoparticles. However, they did not have a noteworthy impact on the PCMs [38, 39]. Yang et al. [49] investigated the impact of nano-Si_3N_4 at various mass fractions in paraffin. They found that at 1 mass percent, the latent heat increased by 3.42 %, in addition to the thermal conductivity increasing by about 10 %. The following is how the fundamental thermodynamic equations can be used to describe this phenomenon: A PCM system's entropy rises when nano-additives are introduced because the mixture often becomes chaotic. Internal energy and, consequently, enthalpy rise as a result. The internal energy and, thus, the enthalpy drop as the concentration of nano-additives rises because the volume growth outweighs the entropy increase. The study also examined a formula for determining the composite PCM's latent heat and discovered that the findings closely match the actual values.

Because of their well-known ability to improve heat transfer performance, silver nanoparticles as additives in nanofluids are the subject of extensive research. The thermophysical characteristics of PCMs containing silver-based nanoparticles are listed in Table 7. Using 1-tetradecanol (TD) as the basis PCM, Zeng et al. [50] created a nanocomposite in 2007 and examined its thermal characteristics. Instead of using the most popular two-step synthesis, the composite was made using an in-situ technique. The Ag and TD ratios used in the experiment ranged from 1:64 to 8:1. The homogeneous dispersion of silver nanoparticles in PCM was verified by microscopic characterization. As anticipated, when the loading level rose, thermal conductivity rose while latent heat capacity sharply decreased. In 2010, the authors used silver nanowires for the same research [51]. In order to create the nanocomposite, silver nanowires had to be synthesized separately and then combined using a two-step process. The maximum weight percentage of nano additive decreased the latent heat by over 65% and increased thermal conductivity by over 35%.

Table 7. A review of PCMs, including Ag-based nano-additives

PCM	Nano-additive	Loading level (Mass %)	Thermal Conductivity Enhancement (%)		Latent Heat Enhancement (%)	Author
			Solid	Liquid		
Tetradecanol (38 °C)	Ag	1.54	No direct data available		-4.12	Zeng et al. [48]
		3.03			-10.87	
		5.88			-10.87	
		11.11			-20.96	
		20			-24.38	
		33.33			-33.14	
		50			-46.6	
		66.67			-64.49	
		88.9			-85.27	
		9.09	31.25	Data NA	-20.45	Zeng et al. [49]

Tetradecanol (38 ^{o}C)	Ag Nanowires	23.08	50		-28.18	
		37.58	81.25		-36.36	
		46.08	156.25		-50	
		62.73	356.25		-65.91	
Ethyl Cinnamte	Ag	0.1	10.51	Data NA	-1.75	Parmeswaran et al. [27]
		0.5	28.4		-2.73	
		1	75.1		-3.9	
		2	133.46		-6.12	
		5	197.66		-7.3	
Ecosane (37 ^{o}C)	Ag	1	16.67	Data NA	-4.98	Ghossein et al. [13]
		2	17.86		-13.7	
		3.5	16.5		-20.33	
		5	11.9		-26.56	
		6.5	10.71		-39	
		8	19.05		-44.4	
		10	21.43		-67.63	

When silver nanowires were used as additives, their high aspect ratio compared to nanoparticles resulted in a comparably high improvement in heat conductivity. In a different investigation by Parameswaran et al. [27], silver nanoparticles were utilized to create a NEPCM using an organic ester and ethyl cinnamonate as the base. The DSC data demonstrated that NEPCMs experience less supercooling than base PCMs, suggesting that the inclusion of silver nanoparticles as thermal enhancers aided in heterogeneous nucleation throughout the freezing process.

The impact of this nucleation on the NEPCM's heat storage and release rates was also thoroughly covered in the study. The authors attempted to develop an empirical relationship between the various thermophysical properties of a PCM based on the latent heat enthalpies and thermal conductivity data from various research. Latent heat, thermal conductivity, phase change equilibrium temperature, and the composite's dynamic viscosity are all related in this expression. This association suggested that increased viscosity is the cause of the decrease in latent heat with increasing nano-additive concentrations. One behavior that is strongly linked to inorganic PCMs, like metallic salts, is supercooling. A few investigations found that silver nanoparticles improved the thermal conductivity of these composites while also lowering the degree of supercooling [27, 52].

4.2. Thermal Conductivity Enhancer: Carbon-Based Nanoparticles

The thermal conductivity of carbon-based compounds is higher than that of metal-based additions. Additionally, they are a preferable option for nano-additives in PCMs due to their stability and low density. The only drawback to adding carbon additions is the difficulty of creating structures devoid of flaws, which raises their cost. However, extensive research on NEPCMs has demonstrated superior thermal performance and no discernible impact on heat storage capacity. The formation of percolation networks with high concentrations of carbon-based nanoparticles scattered throughout the base PCM is thought to be the cause of the generally higher thermal conductivity values observed in experiments involving these nanoparticles, such as CNT, graphene, graphene oxide, etc. For instance, Warzoha et al. [53] compared paraffin wax containing graphene, carbon nanotubes, TiO_2 nano-powder, and aluminium nano-powder at a 20 % (by volume) loading level. They discovered that carbon-based nanoparticles accelerated heat transfer rates during melting and freezing, and graphene-paraffin PCM demonstrated the greatest increase in latent heat capacity. This was explained by the fact that better thermal percolation networks are formed when graphene and carbon nanotubes are evenly distributed throughout the base PCM. Carbon nanotubes, carbon nanofibers, and additives based on graphite or graphene are examples of carbon-based nanomaterials. Graphene oxide and reduced graphene oxide, graphite nano-powder, graphene nanoplatelets, and graphene nanosheets are examples of graphite-based nano-additives. Kibria et al. have reviewed in detail how carbon nanotubes and nanofibers affect viscosity, latent heat, and thermal conductivity [31]. Aspect ratios, size, loading levels, and the effects of surface modifications, surfactants, interfacial thermal contacts and resistances, among other parameters, on various thermophysical properties were all examined in the review. Since it was discovered that PCMs with graphite-based nano-additives had superior heat transfer performance, many studies have not been conducted employing CNTs and CNFs. The high heat conductivity of graphite-based materials was identified as the primary cause of this phenomenon. Additionally, research indicated that when the CNTs/CNFs were disseminated in wax, their contact resistance increased. On the other hand, a continuous matrix was supplied by graphite-based materials in the PCM, resulting in an efficient heat transport pathway [28]. Therefore, the performance of PCMs distributed with graphite-based materials as nano-additives is the primary focus of this section.

Table 8. Synopsis of the literature on PCMs distributed with nano-additives based on carbon

PCM	**Nano-additive**	**Loading level (Mass %)**	**Thermal Conductivity Enhancement (%)**		**Latent Heat Enhancement (%)**	**Author**
			Solid	**Liquid**		
Paraffin Wax (67 ^{o}C)	CNFs d = 100nm l = 20mm	1	4.17	Data NA	Data NA	Elgafy et al. [26]
		2	12.5			
		3	20.84			
		4	33.33			
Paraffin Wax (52 - 54 ^{o}C)	MWNTs	0.2	11	18	0.06	Wang et al. [25]
		0.5	16	21	-0.12	
		1	25	28	-0.24	
		2	33	31	-0.91	
Palmitic Acid (58 - 60 ^{o}C)	MWNTs d = 10 - 30nm l = 5 - 15mm	0.1	-0.63	Data NA	-12.4	Zeng et al. [20]
		0.5	-3.8		-7.9	
		1	-0.32		-8.9	
		2	7.23		-9.9	
		5	26.4		-12.9	
Palmitic Acid (58 - 60 ^{o}C)	MWNTs CTAB d = 10 - 30nm l = 5 - 15mm	0.1	-2.5	Data NA	-13.4	Zeng et al. [20]
		0.5	0.63		-13.9	
		1	2.5		-16.4	
		2	6.9		-11.9	
		5	19.5		-11.4	
Palmitic Acid (58 - 60 ^{o}C)	MWNTs SDBS d = 10 - 30nm l = 5 - 15mm	0.1	-11.6	Data NA	-8.5	Zeng et al. [20]
		0.5	-6.3		-8.9	
		1	-3.1		-7.5	
		2	0		-9.5	
		5	9.99		-12.4	
Paraffin Wax	GNPs	1	38.5	Data NA	4.1	Kim et al. [54]
		2	73.1		-	
		3	84.6		2.8	
		5	158		2.09	
		7	204		-	
Palmitic Acid (62.5 ^{o}C)	CNTs d = 30nm l = 50mm	0.2	4	2	-3.65	Wang et al. [59]
		0.5	7.5	12	-4.95	
		1	46	38	-11.54	
Paraffin Wax (52 - 54 ^{o}C)	CNFs	1	24.38	Data NA	No direct data available	Cui et al. [60]
		2	28.44			

		5	37.19			
		10	40.63			
Soy Wax (52 - 54 ^{o}C)	CNFs	1	5.86	Data NA	No direct data available	Cui et al. [60]
		2	9.26			
		5	21.91			
		10	24.38			
Octadecanol	Graphene	1	31.6	Data NA	-8.3	Yavari et al. [58]
		2	71		-10.1	
		4	140		-18	
n-Hexadecane	MWCNTs d = 10 - 20nm l = 0.5 - 1mm	0.1	Data NA	Data NA	-13.45	Zang et al. [61]
		0.2			12.83	
		1			4.74	
		2			7.78	
		10			3.31	
Palmitic Acid (62.5 ^{o}C)	MWCNTs d = 20 - 40nm l = 10 - 15mm	1	45	Data NA	No direct data available	Ji et al. [62]
		2	47			
		3	49			
		5	55			
		7	64			
Paraffin Wax (20 ^{o}C)	MWCNTs	0.15	19	20	5.97	Kumaresan et al. [55]
		0.3	35	23	-0.93	
		0.45	39	30	1.24	
		0.6	41	43	1	
Paraffin Wax (58 - 60 ^{o}C)	GNPs	1	Data NA	17	Data NA	Yu et al. [56]
		2		44.9		
		3		55.6		
		4		92.2		
Paraffin Wax (58 - 60 ^{o}C)	S MWCNTs d = 20nm	1	Data NA	1.33	Data NA	Yu et al. [56]
		2		6.67		
		3		6.67		
		4		13.33		
Paraffin Wax (58 - 60 ^{o}C)	f - S MWCNTs d = 20nm	1	Data NA	2.77	Data NA	Yu et al. [56]
		2		6.67		
		3		10		
		4		20		
Paraffin Wax (58 - 60 ^{o}C)	L MWCNTs d = 40nm	1	Data NA	0	Data NA	Yu et al. [56]
		2		0.67		
		3		1.33		
		4		5.33		
Paraffin Wax (58 - 60 ^{o}C)	CNFs d = 100nm	1	Data NA	3.33	Data NA	Yu et al. [56]
		2		6.67		
		3		10		

		4		20		
Paraffin Wax	CNTs	7	66.33	48.17	Data NA	Babaei et al. [57]
Paraffin Wax	Graphene	7	86.66	51.8	Data NA	Babaei et al. [57]
Paraffin Wax	SLG	1	5900	Data NA	Data NA	Goli et al. [58]
Paraffin Wax	MWCNTs	20 (% by vol)	832	Data NA	4.06	Warzoha et al. [53]
Paraffin Wax	Graphene	20 (% by vol)	2800	Data NA	12.5	Warzoha et al. [59]
Stearic Acid	MWCNTs	0.1 (% by vol)	Data NA	8.27	Data NA	Choi et al. [60]
Stearic Acid	Graphene	0.1 (% by vol)	Data NA	15.2	Data NA	Choi et al. [60]
Paraffin Wax	Graphene	3	30.8	Data NA	Data NA	Huang et al. [61]
Paraffin Wax	Graphene Oxide	3	35.7	Data NA	Data NA	Huang et al. [61]
Paraffin Wax	MWCNTs d = 65nm	0.005 (% by vol)	125	Data NA	Data NA	Warzoha et al. [53]
		0.01	145			
		0.025	170			
		0.05	270			
Beeswax	Graphene	0.05	340	Data NA	7.9	Amin et al. [62]
		0.1	500		9.02	
		0.15	620		15.4	
		0.2	740		15.5	
		0.25	780		27.3	
		1	1060		0.32	

Amaral et al.'s evaluation [2] of PCMs with carbon nanostructures explained how a number of factors, such as shape, porosity, aspect ratio, etc., improved the underlying PCM's thermal characteristics. PCMs' increased thermal conductivity is dependent on the type of filler used. For instance, Jiang et al. [63] found that graphene oxide dispersed in paraffin wax had a higher thermal conductivity value than graphene itself. The augmentation of thermal conductivity was examined using non-equilibrium molecular dynamics simulations. When graphene and CNT were used to distribute n-octadecane (OD), comparable outcomes were observed. This suggested that the alignment of nanofillers in the wax's alkane molecules is directly related to the improvement in thermal conductivity [57].

The thermal conductivity values varied significantly depending on whether the fillers were orientated perpendicular to the alkane molecules or alongside them. Again, the previously mentioned factors may be responsible for the greater heat conductivity that graphene/OD provided compared to CNT/OD. Dispersing graphene nano-additives into the PCM increased thermal conductivity, but there was a risk of limited molecular heat transfer, which would have reduced latent heat. According to Kim et al. [54], this circumstance could be resolved with a decent dispersion. Exfoliated GNPs were employed in their investigation to improve the thermal performance of n-docosane in mass fractions ranging from 1 to 7 %. A substantial boost (> 200 %) in thermal conductivity was noted with minimal changes in latent heat. Better heat transfer rates were also made possible by network development and effective phonon transport, which were made possible by a good dispersion. This was further supported by another study that discovered that at a loading level of 10 mass percent, eicosane's thermal conductivity rose by around 400 % [64].

A study by Yavari et al. [65] similarly credited a strong dispersion between graphene and 1-octadecanol for the ~140 % increase in thermal conductivity. Graphene-based additives have a large interfacial contact area and a high aspect ratio, just like CNTs and CNFs. Even while graphene-based fillers are naturally very thermally conductive (k ~ 4800 - 5300 W/mK), this study also described the Kapitza, or thermal resistance, which is the primary reason why they did not produce nanocomposites with exceptionally high thermal conductivity values. In their investigation of the impact of graphite flakes on Sodium Acetate Trihydrate (SAT) composites, Dannemand et al. [66] found that adding 5 % graphite flakes could increase the SAT composite's thermal conductivity by up to 1.1 W/mK. The study also found that graphite flakes outperformed the same amount of graphite powder when it came to improving thermal conductivity. The longer heat conductivity of the flakes, as opposed to the powder, was the reason the authors gave for this behavior. For five months, graphite powder at a loading level of 1 mass percent was discovered to provide SAT composites with stable supercooling and a 39% increase in thermal conductivity.

When CNFs, graphene nanoplatelets, and graphite nano-powder were added as fillers to paraffin wax up to 10 % loading fraction, Bahiraei et al. [28] carried out a thorough investigation of thermophysical parameters and heat transport characteristics. When adding more additives, the solid-state enhancement was significantly greater than the liquid-state enhancement, according to the study, which considered the temperature dependency of the thermal conductivity of paraffin wax with various nanofillers. Internal stress created in the nanocomposite during solidification improved the contact area between the wax molecules and the additives, increasing solid-phase thermal conductivity. When the NEPCM melted, this stress was released, resulting in a decrease in the thermal conductivity of the liquid phase. When herringbone-style graphite nanofibers were distributed in a PCM at varying volume fractions (0.05 – 11.4 %), this behavior was also noted. While the liquid phase thermal conductivity was improved only after a specific loading level, the solid phase thermal conductivity was shown to be growing exponentially with the loading level. This showed that heat flow, which is crucial for increasing the solidification rate, is not encouraged in a liquid composite at lower loading levels. Bahiraei et al. [28] also noted that latent heat improved marginally at a 2.5 % loading level compared to pure paraffin wax. The intermolecular interactions between the filler and wax molecules were the reason given by the authors for this event. Initially, Shaikh et al. [46] suggested this method after observing that the latent heat capacity may be increased by modest amounts of carbon nano additions. This study provided a thorough hypothesis of how the phase change and, consequently, the system's latent heat capacity was affected by the intermolecular interactions between the base PCM and CNT. When the system absorbs heat, the weak van der Waals forces that hold molecules together break down, causing a phase change phenomenon without causing a temperature change. The effect on latent heat capacity can change in different systems since the intermolecular interactions between the nano-additives and the PCM can be influenced by several factors, including the base PCM employed, the size and shape of the nano-additives, the concentration of the nanoparticles, etc.

According to Fan et al. [8], a thicker molten layer caused by an increase in viscosity altered the rates of heat conduction. The influence of nano-additives on the mushy region was theoretically investigated, and the solidification of NEPCM was regarded as a Stefan problem. GNP dispersion in dodecanol (0.5 - 1 mass %) was modelled. Because the liquidus and solidus temperatures changed as additives were loaded, it was found that the thickness of the mushy area increased. Temirel et al. [67] investigated the solidification of eicosane distributed with exfoliated graphene nanoplatelets at various volume fractions in a spherical container. Convective cooling air and water cooling were applied to the enclosure, and it was discovered that as the volume fraction increased, the solidification time decreased significantly. Convective and conductive resistance was characterized by establishing a correlation with non-dimensional solidification time as a function of Biot number.

The thermal behavior of carbon-based NEPCMs can generally be influenced by a wide range of factors, including the type of nano-fillers, their sizes and structures, aspect ratios, alignment, and the synthesis method (oxidation, thermal exfoliation, etc.). These factors all have an impact on the interactions and thermal resistances in the nanocomposites.

4.3. Other Nanoparticles as Thermal Conductivity Enhancers (TCEs)

Researchers became interested in examining the impact of novel nanomaterials on the thermal performance of PCMs as they were being studied for their effectiveness in heat transfer in working fluids. These materials include mesoporous silica, hexagonal boron nitride, hybrid nanoparticles, etc. The thermophysical characteristics of PCMs containing these nanomaterials are listed in Table 9.

At a high loading level of 20 vol. %, a study investigating graphene aerogel impregnated with octadecanoic acid by capillary forces discovered a substantial increase in thermal conductivity (~14 times) with a negligible decrease in latent heat [67]. Mesoporous silica (MPSiO$_2$) was employed as the nano-enhancer in another study. Similar to silica nanoparticles, mesoporous silica also demonstrated a slight increase in thermal conductivity, around 6 % at 5 % mass percentage of n-octadecane additions [68]. Additionally, it was discovered that the viscosity augmentation at the same mass fraction was greater than 60 %, which had a detrimental effect on the PCM's thermal performance. According to a thorough analysis of the rheological behavior of NEPCM, the PCM ceased to operate as a Newtonian fluid above the 3 mass percent loading level of $MPSiO_2$ and instead lived as a power-law liquid with shear thinning behavior. Another work using the same base PCM dispersed with n-hexagonal boron nitride observed a similar thermal conductivity increase at the same mass fraction [21]. Curiously, the authors of this experimental investigation attempted to enhance the dispersion of nano-additives by producing a eutectic by employing stearic acid, another organic PCM, at 2 mass percent.

Table 9. An overview of the research on PCMs mixed with other nanomaterials

PCM	**Nano-additive**	**Loading level (Mass %)**	**Thermal Conductivity Enhancement (%)**		**Latent Heat Enhancement (%)**	**Author**
			Solid	**Liquid**		
n-octa-decane (26.5 °C)	MP SiO_2	1	1.2	1.4	Data NA	Motahar et al. [68]
		3	4.3	3.4		
		5	3.3	4.8		
n-octa-decane / SA	n - HBN	5	6.2	4.9	-3.8	Su et al. [21]
		10	8	16.7	-7.2	
		15	12.7	23.2	-15.5	
Paraffin Wax	Cu_2O-Cu-MWCNT	3.4	Data NA		-26.5	Xu et al. [69]
		6			-35.2	
Methyl Cinnamate	Cu-TiO_2	0.05	8.6	2.9	-1.18	Suresh et al. [70]
		0.08	21.9	8.3	-2.28	
		0.1	32.4	21.4	-3.85	
		0.3	50	40.3	-5.46	
		0.5	65.2	56.8	-7.38	

The usage of hybrid nanoparticles as nano-enhancers was documented in relatively little research. Compared to pure Paraffin Wax (PW) and MWCNT/PW, the melting time was significantly shortened by Cu2O-Cu-MWCNT hybrid particles in paraffin produced by the in-situ approach at various mass ratios [68]. The melting time was ~29% shorter than that of pure PW and ~10% shorter than that of MWCNT/PW at 3.4% mass fraction, despite the fact that MWCNT/PW and Cu2O-Cu-MWCNT/PW had comparable thermal conductivity values [70, 71]. Due to their intended use in light-heat conversion systems, the hybrid and MWCNT nanocomposites' light absorption properties were assessed. According to the authors, the former produced better results, which could be because of the decreased interface thermal resistance and boundary scattering losses that made phonon conduction more efficient.

Experimental research was done on the phase change characteristics and thermal performance of another nanocomposite that used methyl ester embedded with copper-titania hybrid nanoparticles [71]. Even at a low concentration of 0.5 mass percent, a significant increase in thermal conductivity was detected (about aprox 65 % in the solid phase and about aprox 57 % in the liquid phase). The morphology of the hybrid nanoparticles demonstrated that the Cu nanoparticles that developed on the titania nanoparticle surface resembled finned structures and offered additional heat transfer surfaces, which improved thermal conductivity and facilitated the early exploration of phase transition processes.

5. Conclusion

Latent heat capacity falls, and thermal conductivity rises with increasing nano-additives concentrations. However, given the overall performance of the PCMs, the increase in thermal conductivity at high loading levels of nano-additives at the expense of heat storage capacity may not always be advantageous. In real-world applications, high concentrations may also cause dispersion instability of systems with many melting and freezing cycles. The impact of nano-additives on the viscosity of the NEPCM has been the subject of very few investigations, making it outside the purview of this literature review. Since the melting cycle is essentially a natural convection-driven process impacted by variations in viscosity, measuring viscosity is crucial to research nano-additives' impact.

While most investigations showed that modest loading levels of nano-fillers increased thermal conductivity and decreased latent heat capacity, a few studies did report exceptions. When designing thermal systems with NEPCMs, ambiguity in the fluctuations in latent heat capacity should be addressed, particularly with low concentrations of nano-additives. Despite the fact that the literature offers some broad explanations for these differences, this review concludes that they do not apply to all systems. The interaction between the scattered nano-additives and PCM molecules is the main cause of the trend disparity. Because a wide range of base PCMs, different nano-additives' sizes, shapes, and compositions, as well as variable heating rates, are used in the research, it is challenging to draw a specific theory from the experimental results found in the literature. A deeper comprehension will be achievable if several nano-additives are distributed throughout the same PCM at varying loading levels and under comparable operating conditions.

An analysis of the literature demonstrates that NEPCMs containing pure metal and carbon-based nanoparticles can improve thermal conductivity more than those including other nanoparticles. Graphene-based nanoparticles are more appealing for creating NEPCMs due to the high density and chemical instability of metallic nanoparticles, even though both kinds of nanoparticles are costly.

5.1. Future Extent

Optimizing thermal performance with low additive concentrations is the main objective of this paper, which utilizes NEPCMs. Few researchers have documented the use of hybrid nanoparticles on PCMs, even though they have the potential to achieve this goal. Finding the ideal loading level for nano-additives is crucial and may involve numerous experimental repetitions. The T-history approach has not been investigated for characterizing NEPCMs despite being suggested as an easy, affordable, and trustworthy way to ascertain the thermophysical characteristics of pure PCM. The thermophysical characteristics of recently created NEPCMs can be better described using this technique.

However, a feasibility study should be conducted by contrasting the T-history method's results with those obtained via TPS measurements and DSC analysis. The majority of research focusses on creating new materials to increase PCM-based systems' effective thermal conductivity. There is a research gap between developing NEPCMs for various applications and phase change heat transfer.

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