



Research Article

Investigation of the Enhancement of Thermophysical Properties of New Combinations of MWCNTs with Several PCMs Consisting of a Type of Paraffin in Comparison with Some Mineral Compounds (AN-MN-6H₂O)

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ABSTRACT

Thermal Energy Storage (TES) for solar thermal systems has attracted great attention because of the intermittent availability of solar energy. In the current paper, new combinations of several Phase Change Materials (PCMs) including a type of paraffin and some mineral compounds like ammonium nitrate and magnesium nitrate hexahydrate were examined and their thermophysical properties were compared. This study targets solar heating systems at different temperature intervals for the TES. Another new approach of this study is to determine the effect of Multi-Wall Carbon Nanotubes (MWCNTs) with two diameters (D) of 8 and 10-20 nm on paraffin's thermophysical property to improve these properties. An innovative method was used to measure Electrical Conductivity (EC) as it is easier to measure than thermal conductivity (K) to study the effect of nanoparticles on PCM behavior. The results showed that the highest values of improvement over paraffin properties were related to 5 % nanoparticle additive for both nanoparticle diameters among the percentages studied. The addition of 5 % nanoparticles with 10-20 nm and 8 nm to paraffin at 25 °C increased heat conductivity by 142 % and 156 %, respectively. The addition of nanoparticles to paraffin improved EC several times such that a diameter of 8 nm made a 300 % increase in EC compared to 10-20 nm.

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1. INTRODUCTION

The main problem associated with solar thermal energy is its storage and one of the best solutions is PCMs for storing energy by latent heat thermal energy storage (LHTES). It is considered one of the most efficient thermal energy sources. It is characterized by higher storage density (ρ) and low-temperature difference between the heat storage and release process. Due to the periodical solar energy availability, PCMs represent a proper alternative technique for storing solar energy [1]. Some criteria should be considered to select proper PCM candidates. For example, they should satisfy the operating temperature range for LHTES, high latent heat of fusion, and sizeable specific heat to ensure high storage density of the system. This material must have high thermal conductivity to increase the thermal charging and discharging rate. Besides these criteria, the material with high density is favored as it improves energy storage density and reduces the volume of the TES system. Moreover, the PCM is desired at a low price and abundant availability.

However, it is challenging to select a PCM with a perfect profile property, thermal boundaries, and operation goals for a proper application or to match the thermal conditions and requirements of LHTES design.

Considerations such as thermophysical properties, thermal stability in thermodynamic cycles, and environmental properties should be considered to find a suitable PCM for storing solar energy. Many investigations have been done on the thermophysical properties of various materials to find suitable TES materials at different temperature intervals. Using PCMs in building applications is a novel, sustainable, and efficient solution to improve the energy performance of buildings. Various PCMs such as fatty acids, paraffin, and inorganic salts have been used to improve the energy performance of buildings. The addition of Butyl Stearate (BS) enhances thermal capacity and exhibits corrosion protection of rebar by hindering penetration of chloride ions into the concrete [2]. The use of carbon fiber PCM, including paraffin, to manage the heat of lithium-ion batteries has led to the improved thermal performance of this type of battery [3-5]. PCM's TES technologies have advantages such as high energy storage density, high compactness, simple structure, and ease

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of maintenance. Besides, PCM can also be used as a thermal control for devices that work and generate heat intermittently such as chips [6, 7]. PCMs in solar collectors like flat plates, evacuated tubes, and heat pipes are used to store energy from the collector and benefit it when solar energy is not accessible [8-11]. PCMs have a high storage density (amount of energy stored per unit mass) and a narrow temperature range for

charging and discharging the storage. This range corresponds to the phase transition temperature of the PCM. The compactness of the PCM storage system results in greater flexibility in choosing a location for the storage system [12].

Several PCMs, which many researchers have investigated and can be candidates for solar thermal applications, are presented in Table 1.

Table 1. Thermophysical properties of some appropriate materials for TES

Materials	T_m (°C)	ρ (kg/m ³)	LHM (kJ/kg)	C_p (kJ/kg.K)	K (W/m.K)	References
Formic acid	9	-	245	2.180	0.272	[13]
Polymethyl methacrylate (PMMA)	41	-	54.6-48.7	-	0.16-0.25	[14]
Paraffin wax	52	Liquid 780	210	Liquid 2.9	Liquid 0.15	[15-17]
		Solid 860		Solid 2.1	Solid 0.24	
Paraffin wax	52-54	Liquid 814	266	Liquid 2.95	Liquid 0.15	[1]
		Solid 900		Solid 2.195	Solid 0.232	
Paraffin wax	53-57	0.895	184.48	2.384	0.41	[18]
		0.867	240	3.046	0.148	
Sodium acetatetrihydrate with graphite	58	1.35	210 180-200	2.5	2-5	[19]
Palmitic acid (PA)	60.8	-	148-149	-	0.6	[20]
Mandelic acid	118-121	1300	161	-	-	[21]
Benzoic acid	121-123	1080	114-147	-	-	[21]
Phthalic anhydride	131	1530	159	-	-	[21]
Dimethyl terephthalate	142	1290	170	-	-	[21]
Adipic acid	151-155	1360	260	-	-	[21]

PCMs suffer from defects such as phase separation, slow heat transfer, leakage, and instability [22-24]. One of the significant disadvantages of PCMs is their low thermal conductivity, which is present in all pure materials except metal-based materials [25].

Hence, the low heat conductivity of PCM increases the temperature gradient and time constant, reducing the heat transfer speed [26, 27]. Low thermal conductivity reduces PCM heat storage and release [28, 29], which reduces the performance. The thermal conductivity of PCMs should be improved to enhance the heat transfer rate and the stored energy coefficient utilization [30].

It is necessary to enhance the thermal conductivity to improve the performance of the thermal energy storage system and accelerate the process of charging and discharging energy [31]. Various techniques can enhance the thermal conductivity of PCMs by incorporating fins or extended surfaces, metal matrices, electrospinning, encapsulation, dispersion of high-conductivity particles or nanomaterials in the PCM itself, employing metal foams, using multiple PCMs, and embedding heat pipes [25, 32-37].

Among all the techniques mentioned above, the addition of nanoparticles to enhance the thermal conductivity of PCMs is the topic of the present research. Nano-inclusion-assisted thermal conductivity enhancement has been used for developing nano-enhanced organic PCMs for LHTES [17, 19, 20]. The thermal conductivity increases as nanoparticle size decreases, while surface tension increases as nanoparticle size increases [38].

This study investigates the thermal conductivity effects of adding nanoparticles to paraffin. Addition of nanoparticles improves the thermophysical properties of PCM and increases the PCM's thermal performance by reducing the heat transfer time [39]. Experimental measurements showed that adding

nanoparticles to enhance thermal conductivity could bring about perfect results in optimizing the phase change temperatures and decreasing heat capacity coefficient, leading to a reduction of energy storage [18].

Due to properties of paraffin like high heat of fusion, nonpoisonous, stable properties after 1500 cycles, no phase separation, and the phase process only result in a small volume change. Meanwhile, low thermal conductivity in a solid state and supercooling (liquid state of a body when its temperature is less than the crystallization temperature) are included as the significant disadvantages of organic PCM.

The early mentioned criteria, especially melting point and latent heat, should be considered suitable for heat storage in various solar thermal energy systems [1, 40]. Thus, based on the operating temperature range for solar thermal applications like solar collectors, they are classified according to the type of concentrators listed in Table 2.

Table 2. Classification of solar collectors according to the concentration degree [41]

Category	Example	Temperature range (°C)
No concentration	Flat-plate Evacuated tube	Up to 75 Up to 200
Medium concentration	Parabolic cylinder	150-500
High concentration	Parabolic	1500 and more

Due to some unsuitable paraffin properties including thermal conductivity, two ways to increase the contact surface and add nanoparticles have received much attention [42-44].

In this research, nanoparticles are used to improve the thermal conductivity coefficient.

Past research has shown that at any temperature and concentration of nanotubes, the incorporation of some materials such as metal oxides [45], single-walled carbon nanotubes [46], MWCNTs [47], carbon nanofibers [48], nanoplatelets [49] and graphene [50] into the base fluid at a nanoscale level improves the thermal conductivity. The relative rate of improvement in thermal conductivity depended on the amount of added nanomaterials' thermal conductivity, addition ratio, and mixing quality [51]. Improvements in thermal conductivity are acceptable at limited costs [52].

According to the early mentioned criteria and the results of some reported publications in Table 1, thermophysical properties of new combinations of several PCMs for solar TES applications, especially in terms of melting point and latent heat, are studied and compared in this paper. They include a new commercial type of improved paraffin wax and three combinations of ammonium nitrate and magnesium nitrate hexahydrate (AN-MN-6H₂O).

Previous research has used solutions of PEG, PA6, and various nanoparticles (SiO₂, Al₂O₃, Fe₂O₃, and ZnO) to produce composite PCMs by electrospinning whose fiber diameter strongly depends on the electrical conductivity of the solutions. For example, the fiber diameter is reduced as the electrical conductivity increases [36, 37].

Another new approach adopted in this study is to determine the effect of the diameter of MWCNTs on the thermophysical properties of paraffin. In order to determine the appropriate weight percentage of nanoparticles, an innovative method and unique device have been implicated by measuring EC rather than thermal conductivity (K) as it is easier to measure than K to study the effect of nanoparticles on PCM behavior.

2. EXPERIMENTAL

2.1. Materials

In general, an essential specification of PCMs is to store energy through latent heat during the charging process, which justifies their ability to store heat and keep cold or hot. Considering the fact that one of the primary aims of this study is to investigate PCMs and their properties like melting point and latent heat, as mentioned earlier in the previous section, they are suitable for solar heat energy storage. Then, the measurement and comparison of the properties of four ingredients include an improved type of paraffin by MWCNTs and three mineral compounds provided by the combination of Ammonium Nitrate and Magnesium Nitrate hexahydrate (AN-MN-6H₂O). Their binary phase change diagram is displayed in Figure 1.

The eutectic is a minimum-melting composition of two or more components, as shown in Figure 1; each melts or freezes congruently, forming a mixture of the component crystals during crystallization [53]. The eutectics have a sharp melting point similar to pure substance and volumetric storage density is slightly above organic compounds.

These three selected compounds are considered:

- Eutectic (contains 61.2 % ammonium nitrate and 38.8 % magnesium nitrate hexahydrate)
- Hyper eutectic (contains 55 % ammonium nitrate and 45 % magnesium nitrate hexahydrate)
- Hypo eutectic (contains 79 % ammonium nitrate and 21 % magnesium nitrate hexahydrate)

Merck provides these minerals and Khavaran Company provides paraffin. Table 3 shows the essential characteristics of these materials. Before doing the tests, the ingredients with the specified percentages were melted and mixed with a magnetic stirrer for 15 minutes, and then they were made ready to perform the tests. The basic information about nanoparticles is listed in Table 4.

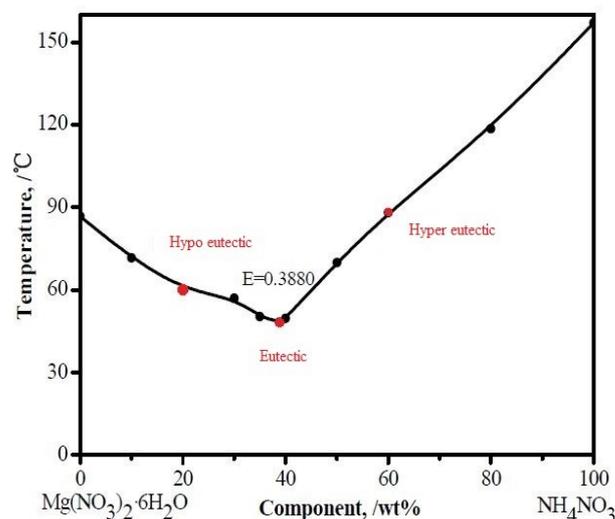


Figure 1. The binary phase change of AN-MN-6H₂O in composition

Table 3. The materials studied and the essential information including melting point and density

Materials	T _m (°C)	ρ (kg/m ³)
Paraffin	59	931
Eutectic	44.8	1561.4
Hypo eutectic	60	1577
Hyper eutectic	118	1665.4

Table 4. Specification of nanoparticles

Material	Paraffin	MWCNTs (8 nm)	MWCNTs (10-20 nm)
Purity (%)	95	> 95	> 95
-COOH content (wt %)	-	3.86	2.00
OD (nm)	-	< 8	10-20
ID (nm)	-	2-5	5-10
Length (μm)	-	10-30	10-30
Special surface area (m ² /g)	-	> 500	> 200
ρ (g/cm ³)	0.931	2.1	2.1
EC (S/cm)	-	> 100	> 100

2.2. Nanocomposite preparation

Nanofluid is generally prepared in two ways. In the one-step method, nanoparticles are prepared and dispersed directly into the fluid. The nanoparticles are provided in powder form and then added to the base fluid by the two-stage method. On the other hand, the suspension, surfactants, diffusers' pH controls, and ultrasonic oscillations are used to stabilize the

nanoparticles and prevent agglomeration and particle deposition. The second method has been used to prepare the nanocomposite in this research. Ultrasonic agitator, mechanical agitator, and toluene as a solvent have been used to disperse and homogenize the compound. After weighing the material with 5 grams of paraffin and the desired percentage of nanoparticles, it is dissolved in 50 ml of toluene and stirred for 15 minutes with an ultrasonic stirrer (three times, each time for five minutes with one-minute intervals for device rest and mixing). The solution is mixed with a mechanical stirrer for 20 minutes (twice for ten minutes at one-minute intervals to rest the device and mix). To improve the paraffin's thermal storage properties and find the optimal combination of nanoparticles with the PCM, different percentages of MWCNT such as 0.5 wt %, 1 wt %, 2.5 wt %, and 5 wt % were selected to add the PCM. Each ingredient was mixed with the base material (as mentioned) in a cylindrical glass container with a 52 mm diameter. Due to the accumulation of electric charge at sharp points and the negative impact on measuring electrical conductivity, a cylindrical container was used, as displayed in Figure 2. An electrical circuit setup was arranged to test the electrical resistance of all the samples, as displayed in Figure 3. The specific resistance of the nanoscale compound was measured, with a voltage range of 200 v to 200 kV.



Figure 2. Picture of the cylindrical glass container for electrical resistance testing



Figure 3. Picture of the electrical circuit setup

Determination of the thermo-physical properties of PCM is the basic required information for the research and applications. The properties mainly include density, melting point, fusion latent heat, thermal conductivity, specific heat capacity (C_p), viscosity, and thermal expansion coefficient. Generally, the phase change properties such as melting point, fusion latent heat, and specific heat capacity can be measured by Differential Scanning Calorimetry (DSC) [54]. A DSC was used to determine the thermos-physical properties of the binary system. Depending on the DSC settings throughout the measurements, varying results were obtained. In this research, a heating rate of 5 °C per minute was used.

Furthermore, the correct phase transition temperature range was almost impossible to obtain simply from DSC measurement. Combining phase equilibrium considerations with DSC measurements presents a reliable design method to incorporate phase-change heat and temperature range [12]. Various thermo-physical properties of the mentioned materials like density, viscosity of liquid phase, thermal conductivity, heat capacity, and heat release rate (HR) were measured by standard methods described in detail. Materials' density was measured by the Immersion method at different temperatures in the liquid and solid phases with the accuracy of 10 %. The experiments for thermal analysis of materials were carried out by the DSC1 model, with a heating/cooling rate of 5 °C/min. The neutral atmosphere in this device is nitrogen gas and the atmosphere is reactive with oxygen gas. This device monitors the sample's thermal behavior with Topem software and in the form of modulating. This device is based on measuring the heat flux between the sample and the reference, measured by temperature changes and sinusoidally. This device is capable of operating in the temperature range of -130 to 600 °C (if this temperature does not destroy the sample). The DSC tests were performed as melting-solidification-melting. The conductivity of PCM samples was measured by the KD2 Pro thermal properties analyzer based on the transient hotwire method.

The materials' thermophysical properties such as specific heat capacity, latent heat (L), and thermal conductivity (K) for the temperature range of 25-55 °C were measured based on their standard code. The instruments for measuring the properties are shown in Figure 4 and their specifications and standard methods are listed in Table 5.



(a)

(b)

Figure 4. Picture of the DSC testing machine manufactured by (a) Mettler toledo and (b) KD2 testing device from Decagon company

3. METHOD

3.1. Measurement of properties

Table 5. The measurement tools and their specifications

Properties	Producer and model	Standard	Accuracy (%)
Latent heat	Mettler toledo DSC 1	ASTM D3418	0.52
Specific heat	Mettler toledo DSC 1	ASTM E1269:2018	0.52
Thermal conductivity	Decagon KD2	EN55022:1987	5
Density	-	-	5

An insulated flask was used to measure the materials' heat release rate (the flask was insulated up to 6 cm thickness of polyurethane foam), as shown in Figure 5. The insulated flask container was filled with 200ml water and PCM was filled in a 10 ml spherical glass container and immersed in the water. Two thermocouples (K type) were used to measure the temperatures and were recorded by the data logger, one in the glass container for PCM and one in the water flask. After melting the PCM entirely in the glass container at a constant temperature, it was placed inside the flask and the temperature changes were recorded. Due to the flask insulation, all the heat released from the PCM was absorbed by the water and finally, it reached the equilibrium temperature.

**Figure 5.** Picture of the insulated flask and measuring heat release rate test setup

4. RESULTS AND DISCUSSION

4.1. Comparison of mineral PCMs

One of the desirable features of PCM is the low volume expansion coefficient (α_L), which is obtained here by examining PCM volume in both liquid and solid states. This value was 1 % for paraffin and is 5.08 and 1.2 % for the combination of eutectic and hypo, respectively. Table 6 shows the density values and volumetric expansion coefficients of the test materials.

Table 6. Density and thermal expansion coefficient of materials

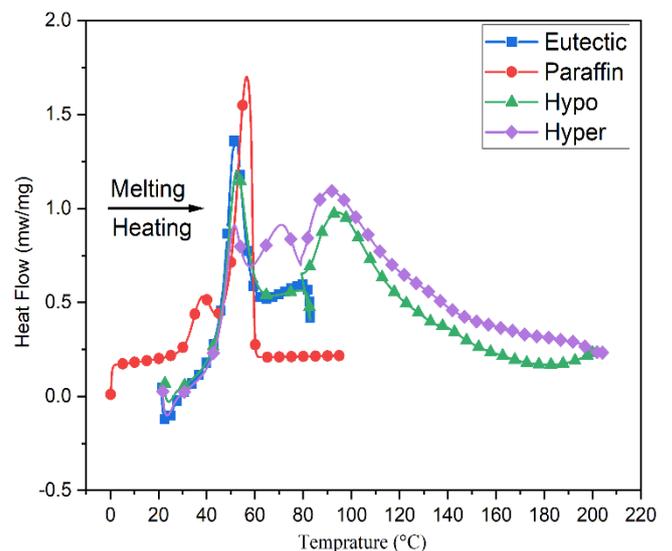
Material	T_m (°C)	ρ_{solid} (kg/m ³)	ρ_{liquid} (kg/m ³)	α_L (%)
Paraffin	59	931	911	1
Eutectic	44.8	1596	1515	5.08
Hyper	118	1665	-	-
Hypo	60	1577	1558	1.2

The DSC test results for the materials have been reviewed, as shown in Figure 6, and compared with each other considering the importance of latent heat and specific heat capacity in selecting PCMs. The amount of Latent Heat during the Melting (LHM) process or the enthalpy change of phase transition (storage density) is possible to estimate by using the area under the peak level of the DSC diagram [12]. The Origin software automatically calculates the total peak area, i.e., the total enthalpy change (Q_{PC}) phase transition. It can be calculated theoretically using the following equation:

$$Q_{pc} = \int_{t_1}^{t_2} \left(\frac{\delta Q}{dt} \right)_{pc} dt \quad (1)$$

As per Figure 6, it is seen that the peak of each curve is near the melting point of the corresponding material. For the paraffin, the amount of LHM obtained was 187.78 kJ/kg in the temperature range of 48.01 to 59.82 °C. Alternatively, for the eutectic, hypo, and hyper composition, the amount of latent heat content obtained was 152.2 kJ/kg, 416 kJ/kg, and 559 kJ/kg, respectively, for the temperature range of 28-58 °C, 50-120 °C, and 75-150 °C.

The higher the amount of latent heat, the more the ability of PCM's TES. As demonstrated by the results, the highest amount of latent heat was obtained for the hyper eutectic composition, but due to its high melting point (118 °C), it could be applied to the solar collectors rather than flat plate ones. The lowest amount of latent heat was for the eutectic composition. The comparative layout of the DSC results of all the investigated materials in a single diagram is shown in Figure 6.

**Figure 6.** Comparative diagram of DSC analysis of the materials

DSC tests were employed to measure the variations of specific heat capacity corresponding to the temperature obtained from materials' three states (solids, liquid, and phase changes). The comparative results of the materials' specific heat capacity in a single diagram are shown in Figure 7. This figure indicates that the most remarkable value of all these materials is obtained during the phase change period and the most significant value is for the eutectic compound.

The test results of obtaining the heat release of a particular volume of material during the solidification process (discharging PCM) in an insulated flask within 1000 Sec are shown in Figure 8. The results show that the hypereutectic

compound has the highest discharge time and the most extended duration related to heat release; after that, paraffin, hypo, and eutectic compounds are in the following order.

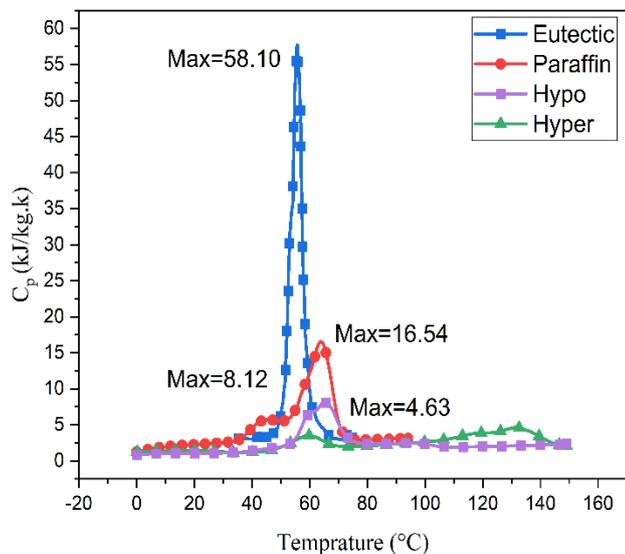


Figure 7. Comparative diagram of specific heat capacity variations versus the temperature of the materials

The heat released rate values for a given volume of 10 ml of the substance in 200 ml of water are given in Table 7. The results are compared with the amount of DSC calculation of the total enthalpy change of phase transition (latent heat) (Q_{PC}) using Equation 1. The results indicate that the higher the heat release rate, the higher the material's latent heat and the greater the melting point. In addition, it is clear that the hyper composition is suitable for higher-temperature applications of solar thermal energy. Others including hypo composition, paraffin, and eutectic composition have the capability to be used for the lower temperature of solar thermal energy applications. Moreover, the amounts of specific heat capacity in each state in Table 7 show that this

Table 7. The values of specific heat capacity (C_p) in different states and the latent heat content of materials

Materials	L (kJ/kg)	HR (J/s)	$C_{p,Liquid}$ (kJ/kg.K)	$C_{p,Max}$ (kJ/kg.K)
Paraffin	187.78	0.7954	3.23	16.5409
Eutectic	152.2	0.5775	3.5564	58.102
Hypo	416	1.419	2.02898	8.12041
Hyper	559	2.3119	2.05435	4.63736

The hyper composition shows the highest amount of K factor at 0.727 while paraffin content shows the lowest value of 0.328 w/m.K. They are almost identical to the values reported in the references [55].

Table 8. The results for the conduction heat transfer coefficient of the materials

Materials	$K_{55^\circ C}$ (w/m.K)
Paraffin	0.328
Eutectic	0.635
Hypo	0.532
Hyper	0.727

In summary, the variation of all the tested materials' measured properties including density, latent heat, and

property is not proportional to the material's latent heat. It could not be the only proper criterion for selecting PCM.

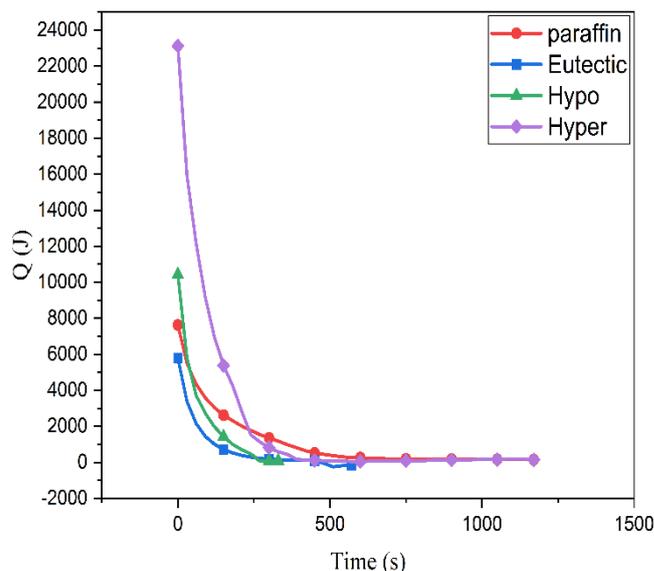


Figure 8. Comparative diagram of the heat released within 1000 seconds for materials

A cylindrical mold with an outer diameter of 10 mm, a length of 6.5 cm, and an inner diameter of 2 mm was prepared to measure the conduction heat transfer coefficient (K factor) of solid-state PCMs for the Hyper and Hypo composition tests. In the liquid state of paraffin and eutectic composition, a quantity of 50 ml of the substance is placed inside the container and the probe measures the K factor. The thermal conductivity values measured at 55 °C for the materials can be seen in Table 8. The excellent value of this factor accelerates the heat transfer rate and shorter melting time to absorb energy storage. The lower heat transfer coefficient helps longer solidification time and provides thermal stability for designing a TES system.

thermal conductivity corresponding to the melting point is illustrated in Figure 9. It is vital to notice that the properties of all the PCMs consisting of density, latent heat, and thermal conductivity proportionally change with the melting point except for the eutectic compound. Finally, it is worth mentioning that the eutectic composition shows the minimum melting point.

4.2. Effect of adding nanoparticles to paraffin

This part of the study examines the effect of adding MWCNTs with two different diameters and different weight percentages on the properties of paraffin which aims to determine the optimal percentage of nanoparticles based on the output current through nanocomposite with increasing voltage at the ambient temperature of about 25 °C. The results shown in

Figure 10 are for output currents through paraffin nanocomposites versus the input voltages with different weight percentages of 0.5, 1, 2.5, and 5 for the two size nanocomposites 8 and 10-20 nm. The applied voltage changes from 0 to 12000 volts and the output current changes from 0 to 20 mA. It is observed that the electrical conductivity increases with the percentage of adding nanoparticles for both sizes, 8 and 10-20 nm. It shows excellent electrical conductivity even at low voltages of about 15 volts. The currents that passed through the 8 and 10-20 nm nanocomposites are 20 mA and 0.52 mA, respectively.

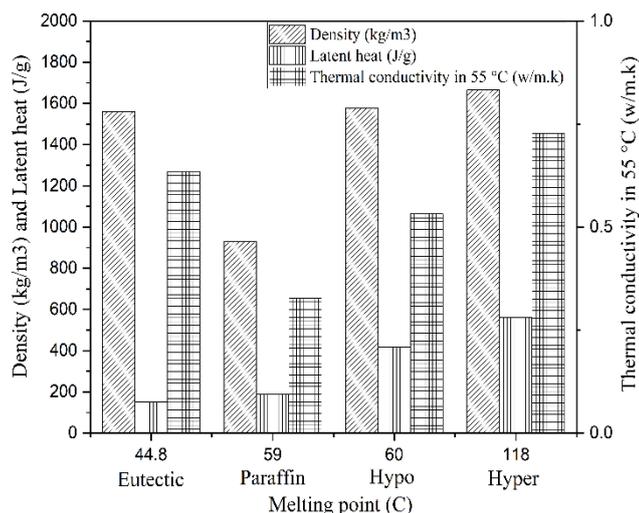


Figure 9. Comparative diagram of density, latent heat, and thermal conductivity of tested materials

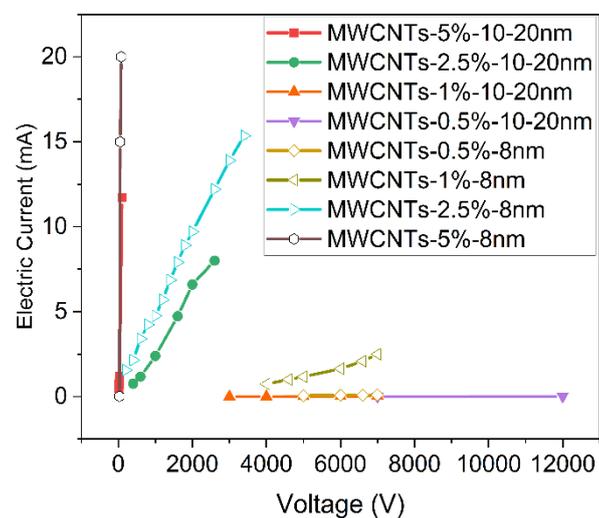


Figure 10. Comparative diagram of changes in electrical current through nanocomposites with increasing voltage

In Figure 11, nanocomposites' electric conductivity with different percentages is visible for both nanoparticles 10-20 and 8 nm, indicating an increase in its value from zero to 0.12721 and 0.38121 S/cm, respectively, as per Figure 12. Among the four different percentages nominated for review, 5 % addition of each of the nanoparticles shows the best behavior based on the electrical conductivity. This weight percentage addition (5 %) has been used for further experiments due to the highest electrical conductivity in nanocomposites shown in Table 9.

Table 9. Specifications of nanocomposites

Base material	Nano particle	Particle diameter r (nm)	Particle weight percentage (wt %)	Nano-paraffin composite symbol
Paraffin	MWCNTs	< 8	5	A
Paraffin	MWCNTs	10-20	5	B

Moreover, the higher conductance rate for Nanoparticles 8 is higher than 10-20 nm due to their higher specific surface.

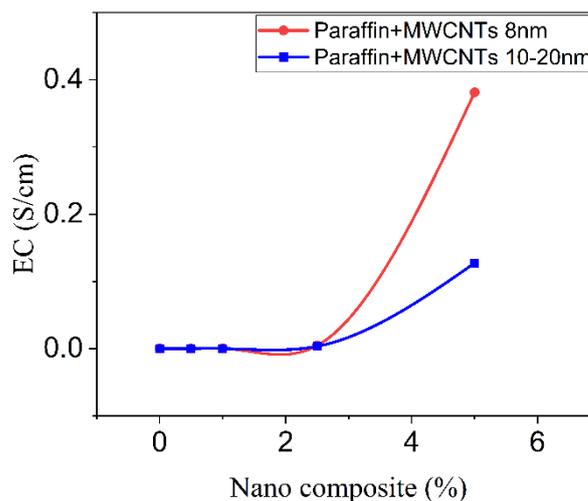


Figure 11. Comparative diagram of changes in electrical conductivity of compounds with different percentages of nanoparticles

As shown in Figure 12, adding nanoparticles to paraffin does not change the shape of the DSC diagram. However, it reduces the maximum value, which leads to a decrease in the subsurface area of the diagram, thus reducing the amount of latent heat. For the paraffin, the amount of LHM obtained was 187.78 kJ/kg in the temperature range of 48.01 to 59.82 °C. In comparison, addition of nanoparticles with diameters of 10-20 and 8 nm reduces the LHM to 162.02 and 168.58 kJ/kg in the same temperature range, respectively.

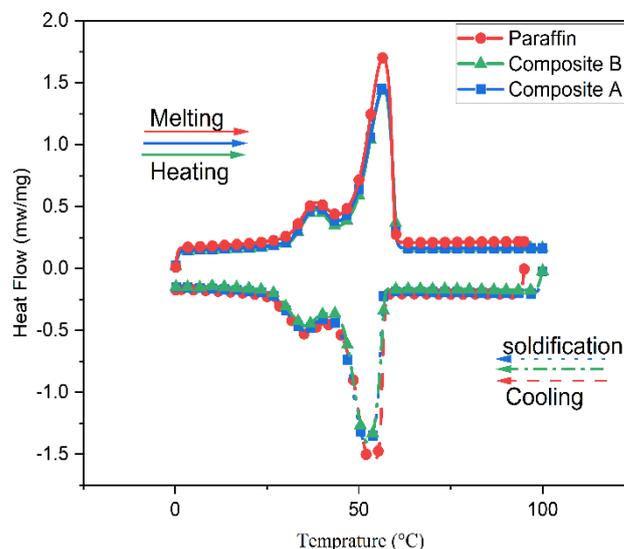


Figure 12. Comparative diagram of DSC analysis of the paraffin and nano-paraffin composites

Due to the uniformity of C_p as per Figure 13, the diagram shows that in the case of paraffin and its nanocomposite, the maximum specific heat value is selected as a suitable criterion for comparative analysis of their behavior. Adding 8 nm diameter nanoparticles reduces the maximum amount of specific heat to 13.9379 kJ/kg.K. In comparison, adding nanoparticles with 10-20 nm diameter increases this amount to 17.5034 kJ/kg.K.

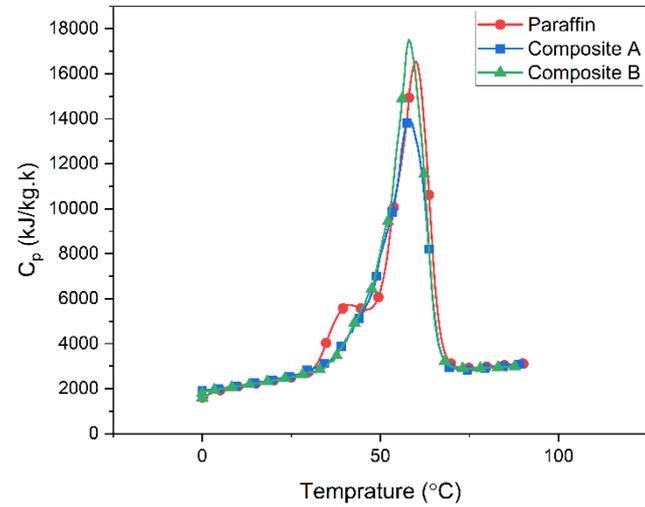


Figure 13. Comparative diagram of specific heat capacity variations versus the temperature of paraffin and nano-paraffin composites

A decrease in heat release in 1000s was observed by adding nanoparticles to paraffin and 0.7525 and 0.6253 (J/s) for nanoparticles with diameters of 10-20 and 8 nm, respectively. These changes are observed in Figure 14.

Thermal diffusivity shows the heat transfer rate of material from the hot end to the cold end. By placing the measured

values of K , ρ , and C_p at 55 °C in Equation 2, α values are obtained for paraffin and nanocomposites.

$$\alpha = \frac{K}{\rho C_p} \tag{2}$$

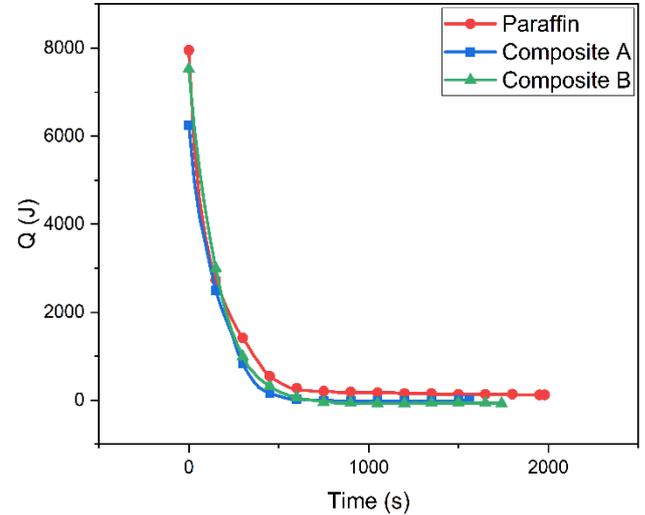


Figure 14. Comparative diagram of heat released within 1000 seconds for paraffin and nano-paraffin composites

The addition of nanoparticles with diameters of 8 and 10-20 nm shows an increase in the thermal diffusivity by 35.68 % and 4.88 %, respectively, as displayed in Table 10.

Table 11 shows the obtained results achieved by some other researchers where the elements affect thermal conductivity and the percentages of different nanoparticles were added with different diameters. It can be concluded that the results are superbly similar to the present study findings.

Table 10. Thermal properties of paraffin and nano-paraffin composites

Materials	L (kJ/kg)	$C_{p,Max}$ (kJ/kg.K)	$K_{25^\circ C}$ (w/m.K)	$K_{55^\circ C}$ (w/m.K)	$EC_{25^\circ C}$ (S/cm)	$\alpha_{L,55^\circ C}$ (mm ² /s)	HR (J/s)
Paraffin	187.78	16.5409	0.088	0.328	-	0.021719	0.7954
Composite A	168.58	13.9379	0.138	0.375	0.38121	0.029469	0.6253
Composite B	162.02	17.5034	0.125	0.364	0.12721	0.022778	0.7525

Table 11. Improvement in thermal conductivity of different nanocomposites with specified weight percentage by the researchers

Nanoparticle	MWCNTs	MWCNTs	nano-Al ₂ O ₃ nano-ZnO ₂ nano-SiC
Base material	Myristic acid (MA)	Paraffin	Paraffin
OD (nm)	< 8	20 50	
length (µm)	10-30	0.52 515	
fraction (vol %)	1 2 3	5	1
K (w/m.K)	0.1913 0.2026 0.2083	0.324 0.309	0.2
K Improvement (%)	3.63 9.75 12.84	23 17	3.3 1.8 4.2
References	[56]	[57]	[51]

According to Figure 15, Both composites have improved thermal and electrical conductivity. On the other hand, adding nanoparticles to paraffin has reduced the amount of latent heat, which is not desirable for energy storage systems. Furthermore, it is obvious that composite A has shown the highest value of $EC_{25^{\circ}C}$, $K_{55^{\circ}C}$ and $C_{p,Max}$.

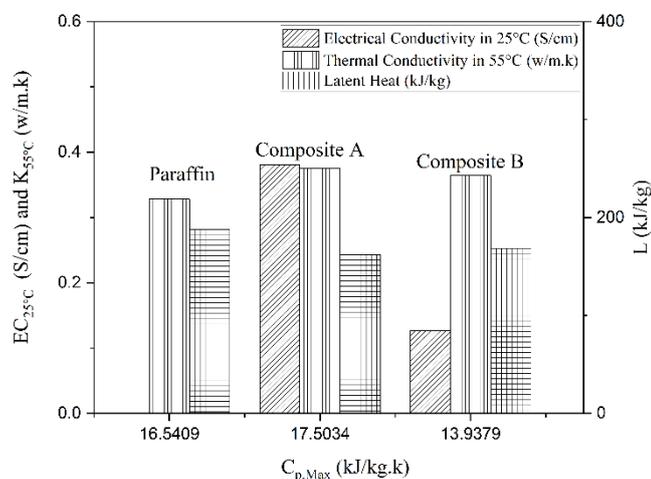


Figure 15. Comparative diagram of latent heat, electrical and thermal conductivity of nanocomposite and paraffin in maximum specific heat capacity

In summary, the investigation on adding nanoparticles to paraffin on its thermophysical properties reduces the LHM. However, it is deduced that adding nanoparticles to paraffin improves the base material's thermal conductivity, electrical conductivity, and thermal diffusivity. Adding nanoparticles with diameters of 10-20 and 8 nm, decreases latent heat by 10.22 % and 13.71 %, increasing thermal conductivity by 10.975 % and 14.329 % at 55 °C, relatively. Adding nanoparticles with a diameter of 8 nm reduces the maximum amount of specific heat by 15.77 %. In comparison, adding nanoparticles with a diameter of 10-20 nm is 5.8 %. An increase in this amount was detected.

5. CONCLUSIONS

Several PCMs have been studied in this experimental investigation based on thermophysical properties to introduce proper TES materials for solar heating systems applications.

To select the proper PCM candidates, a set of criteria that are supposed to be followed for storing energy includes; Phase change temperature in the desired range, fusion's latent heat, thermal conductivity, specific heat, and density, which is considered and tested, and the obtained results can be deduced from this research as follows:

- The operating temperature range of applications based on melting temperature is between 44.8 °C and 118 °C for paraffin wax, eutectic, hypo, and hyper eutectic combination AN-MN-6H₂O. The results indicate that all tested materials' melting points and latent heat proportionally increase or decrease. The rational conclusion would express that the higher the latent heat of the material, the greater the melting point.
- The properties of all the PCMs, like density, latent heat, and thermal conductivity, proportionally change with the melting point except for the eutectic compound. The eutectic composition has a minimum melting point among all the tested materials.

- All the materials investigated in this research have almost a low thermal conductivity coefficient, slowing down the conduction heat transfer, which is advantageous in many TES areas.
- The other criterion was the latent heat of fusion, in which the amount should be high enough to ensure the system's high storage density. The DSC analysis showed that the highest latent heat was obtained for the hyper eutectic composition (118 kJ/kg). The smallest one was obtained for the eutectic composition (44.8 kJ/kg).
- Comparing the amounts of latent heat with the specific heat capacity for three states (solids, liquid, and phase changes) of materials shows that this property is not proportioned to the material's latent heat. It could not be the only criterion for selecting PCM.
- According to the properties such as; high heat release rate, high thermal capacity, and high latent heat, paraffin would be suitable for storing thermal energy in applications below 60 °C, as in solar thermal heating systems. Its low thermal conductivity helps longer solidification time and provides thermal stability for its design's TES system. However, the low density of this type of paraffin reduces its potential for heat storage capability.
- By adding nanoparticles to paraffin, a latent heat reduction has been observed for both nanoparticle diameters, notably lesser in 8 nm-diameter nanoparticles. On the other hand, increasing the amount of thermal and electrical conductivity in 8 nm diameter nanoparticles is more. Suppose latent heat and a reduction in specific heat capacity are not considered. In that case, adding 8 nm-diameter nanoparticles is a better choice between the two diameters of nanoparticles nominated to improve paraffin's performance.
- By reducing the nanoparticle diameter from 10-20 to 8 nm, PCM's proper properties improved even further, one of the reasons being the increase in the surface area of the nanocomposite.
- Finally, since none of the PCMs has a perfect property profile, each application has unique thermal boundaries. Operation goals and the excellent variety of PCMs make it challenging to select one to match the thermal conditions and LHTES design requirements.

Nanoparticles' effect on electrical conductivity has been much more significant than thermal conductivity and other thermophysical materials' properties.

6. ACKNOWLEDGEMENT

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NOMENCLATURE

TES	Thermal Energy Storage
ASTM	American Society for Testing and Materials
DSC	Differential Scanning Calorimetry
LHM	Latent Heat During the Melting
LHTES	Latent Heat Thermal Energy Storage
PCMs	Phase Change Materials
MWCNTs	Multi-Wall Carbon Nanotubes
SEM	Scanning Electron Microscopy
T_c	The temperature that the PCM start to phase change (°C)
T	Temperature (°C)

T_m	Melting point temperature (°C)
C_p	Specific heat capacity (kJ/kg.K)
C_{max}	Maximum specific heat capacity (kJ/kg.K)
Q	Heat release (kJ)
HR	Heat release rate (J/s)
m_{pcm}	Mass of PCM (g)
m_{water}	Mass of water (g)
C_{PCM}	Specific heat of PCM (kJ/kg.K)
C_{water}	Specific heat of water (kJ/kg.K)
T_{PCM}	The temperature of PCM (°C)
T_{water}	The temperature of water (°C)
t	Time (s)
EC	Electrical Conductivity (S/cm)
K	Thermal conductivity (w/m.k)
L	Specific latent heat (kJ/kg)
ρ	Density (kg/ m ³)
α	Thermal diffusivity (m ² /s)
α_L	Thermal expansion coefficient

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