

Article

Paraffin Wax [As a Phase Changing Material (PCM)] Based Composites Containing Multi-Walled Carbon Nanotubes for Thermal Energy Storage (TES) Development

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Abstract: Thermal energy storage (TES) technologies are considered as enabling and supporting technologies for more sustainable and reliable energy generation methods such as solar thermal and concentrated solar power. A thorough investigation of the TES system using paraffin wax (PW) as a phase changing material (PCM) should be considered. One of the possible approaches for improving the overall performance of the TES system is to enhance the thermal properties of the energy storage materials of PW. The current study investigated some of the properties of PW doped with nano-additives, namely, multi-walled carbon nanotubes (MWCNTs), forming a nanocomposite PCM. The paraffin/MWCNT composite PCMs were tailor-made for enhanced and efficient TES applications. The thermal storage efficiency of the current TES bed system was approximately 71%, which is significant. Scanning electron spectroscopy (SEM) with energy dispersive X-ray (EDX) characterization showed the physical incorporation of MWCNTs with PW, which was achieved by strong interfaces without microcracks. In addition, the FTIR (Fourier transform infrared) and TGA (thermogravimetric analysis) experimental results of this composite PCM showed good chemical compatibility and thermal stability. This was elucidated based on the observed similar thermal mass loss profiles as well as the identical chemical bond peaks for all of the tested samples (PW, CNT, and PW/CNT composites).

Keywords: TES; PCM; paraffin wax; multi-walled CNTs; SEM; EDX; TGA; FTIR

1. Introduction

Intermittent thermal energy, particularly from renewable resources such as solar energy, has entailed the need to develop reliable thermal energy storage (TES) technologies, mainly for heating and cooling applications. Furthermore, the balance of thermal energy supply and demand should be investigated thoroughly, such as the economic deployment of TES technologies, which could be achieved and be successful. In this regard, solar heating and cooling have been considered the most substantial applications requiring TES systems. Although most of the traditional thermal energy systems require short-term thermal storage solutions (i.e., water thermal storage), some significant applications require robust TES technologies, especially for long-term storage requirements in the industrial and commercial sectors.

There are three types of thermal energy storage technologies: sensible storage, latent or, more often, phase change storage, and thermochemical storage [1]. First, sensible thermal storage is based on the capability of storage materials to store thermal energy while varying its temperature without changing its state (i.e., solid or liquid). The most

well-known sensible materials include rock, sand, and water. Meanwhile, latent thermal storage is associated with storing thermal energy by changing the storage material phase or state from solid to liquid or vice versa. Some common examples include molten salt, ice/water, and paraffin wax (PW). The third type (thermochemical storage) is different, as it stores thermal energy through a chemical process called adsorption, which differs from the previous two types associated with physical thermal storage. For example, silica gel and zeolite are considered thermochemical storage materials.

The key to the effective and widespread use of solar energy for low-temperature thermal applications is efficient and cost-effective heat storage. Latent heat storage is mostly desirable because of its capability to deliver a high-level energy storage intensity and its features to store heat at a constant temperature, which are related to the phase transition temperature of the heat storage element. For example, molten salt has been used in concentrated solar power systems to store solar heat. Additionally, ice storage has been widely used for chilled water applications. However, storage capacity and temperature range are the two main factors that determine the suitability of phase change materials for specific applications. Therefore, paraffin wax (PW) has been introduced as a promising PCM, especially for free cooling applications [2–5].

Carbon nanotubes (CNTs) are considered a high thermal conductivity additive due to their huge, homogeneous micropores, matchless physicochemical properties, particular surface area, minimal density, and thermal conductivity at high levels [2000–6000 W/(m K)] [4]. CNTs are being employed as an addition to improve the heat transfer properties of other chemical adsorbents [2,4]. Considering that CNTs are a one-dimensional nano-addition substance, they have a distinguished nano-scale effect, high thermal conductivity, and low mass loss [4]. Corresponding to related studies, CNTs have a thermal conductivity greater than 3000 W/(m K) [5,6]. Based on the previous facts, the mixing of CNTs with paraffin wax (PW) to enhance the thermal conductivity of PCMs has been conducted in numerous studies [7–10].

Wang et al. [10] integrated pristine multi-walled CNTs (MWCNTs) into paraffin and revealed that the thermal conductivity improvement ratios in the composite containing 2.0 wt.% were 35% and 40%, respectively, in solid and liquid states. In alternative research, Wang et al. [11] handled CNTs with a mechano-chemical treatment. Handled CNTs have been effectively spread regarding the palmitic acid solution caused by their chemical functional structure, mainly the hydroxide radical in the shell of said CNTs. Wang et al. [11,12] synthesized separate dual types of MWCNTs and compared the impact of the two variations on the thermal behavior of PW and palmitic acid. The authors mentioned that by adding low amounts of grafted MWCNTs, this modification could improve the PCMs' thermal conductivity at a heat above 60 °C compared to premier MWCNTs. Nevertheless, these modified MWCNT-containing nanocomposites have lower thermal conductivity than premier MWCNTs at lower temperatures.

Teng et al. [13] reported the addition of MWCNTs and graphite to paraffin to improve the properties of PCMs. This investigational outcome showed that the addition of MWCNTs is more efficient than graphite in changing the thermal storage of paraffin.

Ye et al. [14] used Na_2CO_3 , MgO as a PCM, and MWCNTs as supportive substances. The obtained results showed that the thermal conductivity of MWCNTs improves as the mass fraction increases, and likewise raises with the increase in test temperature. Xu and Li [15] manufactured stable paraffin composites modified by diatomite and MWCNTs to produce cement-based thermal energy storage composites. They reported that the thermal conductivity and thermal storage rate increased significantly compared to the blank paraffin. Li et al. [16] combined CNTs with 1-octadecanol to improve the thermal conductivity of the PCM. Tang et al. [17] applied multi-walled CNTs plus n-octadecylamine (f-MWCNTs) to enhance the MWCNT dispersibility of PCMs in paraffin.

Xiao et al. [18] developed oxidized and grafted carbon nanotubes as a filler to improve the thermal energy storage of palmitic acid (PA). Wherever the grafted type was implanted on the 3-propyltrimethoxysilane based on oxidized type, the composite PCMs' thermal

conductivity with different types of carbon nanotube raised by 34–40% compared to that of ordinary palmitic acid. However, it is worth noting that the latent heat of grafted CNTs doped with palmitic acid is higher than that of ordinary palmitic acid, whereas oxidized CNTs doped with palmitic have lower latent heat than palmitic acid. Tao et al. [3]. Employed single-walled carbon nanotubes, multi-walled carbon nanotubes, graphene, and C60 as fillers to enhance the properties of high-temperature salt PCM. The results showed that the capability of enhancing of thermal conductivity is in the following decreasing order: single-walled carbon nanotubes, multi-walled carbon nanotubes, and graphene, while the composite PCM with C60 has the lowest thermal conductivity. It was concluded that the columnar framework encourages efficient heat conduction pathway connections. Therefore, single-walled carbon nanotubes and multi-walled carbon nanotubes exhibit additional advantages for thermal conductivity improvement. The thermal conductivity of composite PCMs with the load up of 1.5 wt.% of single-walled carbon nanotubes and multi-walled carbon nanotubes increased by nearly 57% and 50%, respectively. Moreover, new sorts of carbon nanotubes were investigated, such as grafted types CNTs. While the combination of high conductive additives into PCM revealed a substantial increase in thermal conductivity, latent heat storage/discharge, and overall performance improvements. However, there are still unanswered problems, such as whether PCM packed in the pores of supporting materials is required to build an effective heat transfer network. As a result, choosing the best heat transfer additive for PCM composites is crucial. This needs a complete research study to examine the performance of various additives and to define the elements impacting PCM composites, filling the knowledge gap in previous studies, as previously described. Our current research focuses on the use of paraffin wax and multi-walled carbon nanotube (MWCNT) composites for thermal energy storage applications.

In this study, paraffin wax was doped with nano additives of Multi-Walled Carbon Nanotubes (MWCNTs), to forming a nanocomposite PCM. The properties of nanocomposite PCM have been investigated such that the thermal energy storage features and capabilities of the new materials can be greatly enhanced and improved. First, an experimental study of the Thermal Energy Storage (TES) system is described. Characterization of Paraffin-Wax doped with Multi-Walled Carbon Nanotubes Composites is then discussed. Furthermore, SEM, EDX, FTIR, and TGA are among the characterization techniques used.

2. Materials

2.1. TES System Evaluation and Experimental Set-Up

A thermal energy storage (TES) system mainly consists of the following parts (see Figure 1): a source of heat, a storage unit, and load resistance. To improve the overall performance and to increase the efficiency of the system, several approaches can be considered.

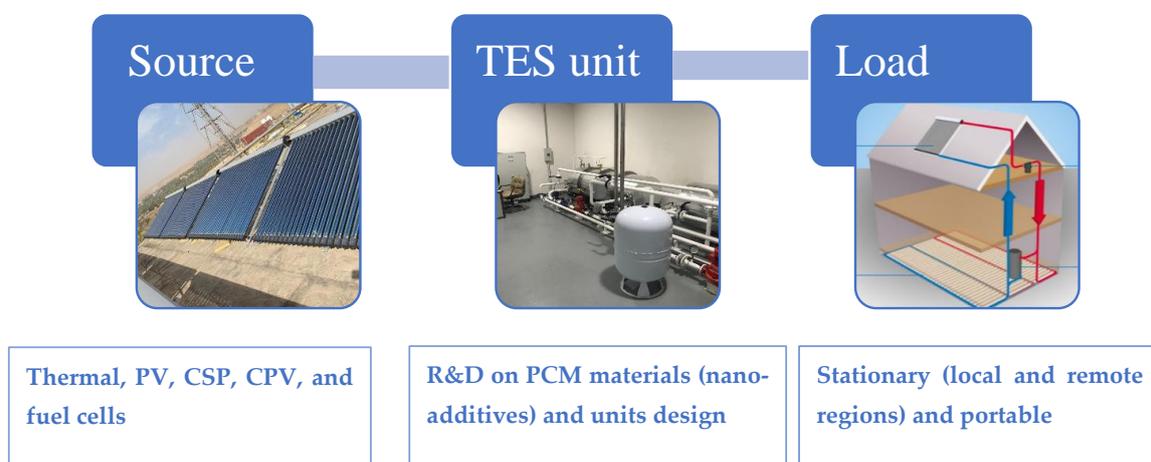


Figure 1. A thermal energy storage system mainly consists of a source of thermal energy (such as solar tubes, as shown) and a TES unit to store the thermal energy for some period of time to be used by a load for domestic or industrial use.

The course of the melting and solidifying process of the PCM was investigated during the experiments. The material was tested as follows: Temperature sensors were installed on the supply and return of the storage tank water system. The flow meter measured the water flow continuously, and the measurement results were saved every 10 s. The mass of the material used to fill the bed, which was used during the test, was 822.3 kg. It should be noted that the calculations did not take into account heat losses due to the environment or the heat accumulated in the structural elements of the tank itself, in which the phase change material was located.

2.2. Materials: Paraffin Wax (PW) and Multi-Walled Carbon Nanotubes (MWCNTs)

A phase change material with the properties described below was used during the tests. The phase change temperature of the PW was 54 °C with the other related properties tabulated, as shown in Table 1. Paraffin wax from the unit bed at our laboratory was provided by NET (New Energy Transfer Company, Poland). The MWCNTs had the following parameters: 9.5 nm in diameter, 1.5 µm in length, and a carbon purity of approximately 90%.

Table 1. Physical properties of the paraffin wax (PW) [5].

	Thermal-Related Parameters	Value	Unit
1	Melting temperature	54.32	°C
2	Latent heat of fusion	184.48	kJ/kg
3	Density of PW (liquid phase)	775.00	kg/m ³
4	Density of PW	833.60	kg/m ³
5	Specific heat of PW (liquid phase)	2.44	kJ/kgK
6	Thermal conductivity	0.15	W/mK
7	Viscosity	6.3×10^{-3}	P.S (Pascal Second)
8	Kinematic viscosity	8.31×10^{-5}	m ² /s
9	Prandtl number	1001.23	-
10	Thermal expansion coefficient	7.14×10^{-3}	1/°C

2.3. Preparation of PW Using the Melting Method

Paraffin and Paraffin/MWCNT compounds were prepared separately by adding CNTs and MWCNTs, respectively, to paraffin using a mechanical dispersion method. The first batch of samples was prepared with a different load of nanoparticles corresponding to 0.5% (PW1-CNT), 0.75% (PW-2CNT), and 1% (PW-3CNT) by mass. Paraffin wax was weighted and melted in a beaker on a hotplate stirrer at 70 °C. Magnetic stirring was applied for 1 h after adding different fractions of nanoparticles, followed by sonication for 3 h. Finally, the liquid compounds were cooled at room temperature to obtain a solid (Figure 2). Element analysis for PW from the TES unit and the pristine one from the Techno Pharm Chem company are showed in Appendix A.

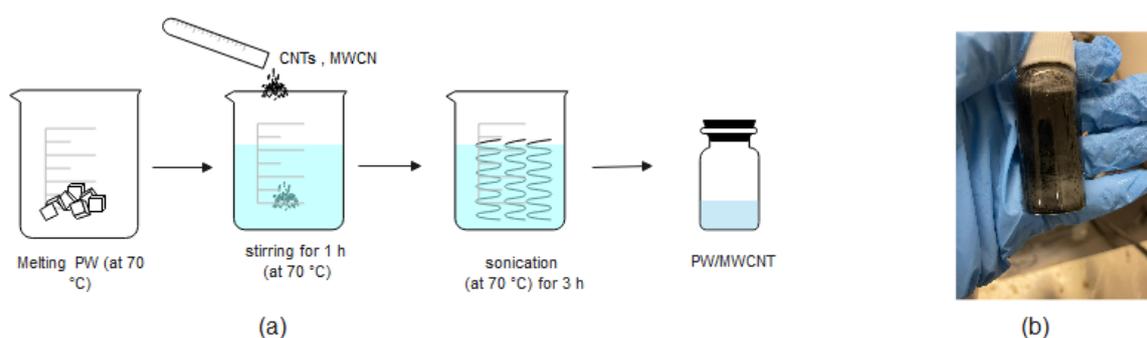


Figure 2. (a) Sample preparation using the mechanical dispersion method. (b) Final product following sample preparation of PCM with MWCNT.

2.4. Theoretical Background of TES System Evaluation

In this section, we review the necessary equations and theoretical foundations to evaluate the thermal energy storage (TES) and the temperature of the feed water, which was calculated at the start using Equation (1):

$$T_{w,aw} = \frac{T_{w1} + T_{w2}}{2} \quad (1)$$

By linearly interpolating the literature data, the density and specific heat of the water were calculated using Equation (2):

$$f(T) = f(T_0) + \frac{f(T_1) - f(T_0)}{T_1 - T_0} \times (T_{w,aw} - T_0) \quad (2)$$

Equation (3) was used to calculate the heat flux transferred from the water to the PCM material throughout the storage loading process as well as the amount of heat according to the dependency:

$$Q = \rho_w \times V_w \times C_w \times (T_{w,1} - T_{w,2}) \quad (3)$$

The heat accumulation during the charging and discharging of the paraffin bed were determined by Equation (4). Finally, we determined the theoretical heat using Equation (5):

$$\eta = \frac{Q}{Q_t} \times 100\% \quad (4)$$

$$Q_t = m_{PCM} \times C_{PCM,S} \times (T_m - T_1) + m_{PCM} \times L + m_{PCM} \times C_{PCM,L} \times (T_2 - T_m) \quad (5)$$

For more information on the abbreviations and symbols for equations, see Appendix B.

3. Results and Discussion

3.1. TES System Evaluation

Based on the obtained results, the heat transferred from the feed water to the PCM material (i.e., PW) when the heat storage was being charged and the heat received by the water from the phase modification material through the heat storage discharge were calculated. Therefore, the feedwater temperature was calculated at the beginning, according to Equation (1).

In order to conduct further analysis of the test results, the density and specific heat of the supply water needed to be determined. However, these values change as a function of temperature, as shown in Table 2. Since the literature data only provide the thermophysical properties of water at selected temperatures, analysis of the obtained test results and the density and specific heat of the water were calculated by linearly interpolating the literature data using Equation (2).

Table 2. The density and specific heat of water as a function of temperature.

Temperature (°C)	Density (kg/m ³)	Specific Heat (J/kg. K)
0.01	999.90	4.212
10.00	999.70	4.191
20.00	998.20	4.183
30.00	995.70	4.174
40.00	992.20	4.174
50.00	988.10	4.174
60.00	983.20	4.179
70.00	977.80	4.187
80.00	971.80	4.195
90.00	965.30	4.208
100.00	958.40	4.220

In Equation (2), T is the actual temperature for which the density or specific heat of the water is determined. T_0 and T_1 are the closest temperatures from the literature data below and above the actual temperature, respectively, while $f(T)$, $f(T_0)$, and $f(T_1)$ are the specific density or heat values for the given temperatures T , T_0 , and T_1 . The average water temperature at the inlet and outlet from the reservoir, calculated according to Equation (1), was used to calculate the density and specific heat of the water.

The heat flux transferred from the water to the PCM material during the storage loading process as well as the amount of heat according to the dependency was then calculated using Equation (3).

The heat that could theoretically be accumulated in the PCM material (i.e., PW) and the efficiency Equation (4) of heat accumulation during charging and discharging of the paraffin bed were determined. The thermal efficiency during the loading and unloading of the heat storage was also determined. The theoretical heat formula (Equation (5)) consists of three parts: sensible heat accumulated in a solid substance in the range from the initial temperature (T_1) to the material phase change temperature (T_m), which is 54 °C, and the phase change heat and sensible heat accumulated in the liquid from the melting point to the final temperature (T_2) of water flowing from the exchanger.

The heat stored in the material while the paraffin bed was charging was lower than the theoretical heat. This is because some of the PCM material in the tank may not melt, and the properties of PCM materials change over time. PCM material partially degrades during the following cycles, and its heat storage capacity partially decreases. The theoretical thermal capacity of the paraffin bed, which resulted from the scope of the calculations, was 57.39 kWh according to the characteristics of the PCM material used. The heat absorbed by the deposit in the calculations was 35.04 kWh. Thus, the ratio of the heat stored in paraffin to the theoretical heat capacity of the bed equaled 61.07%. The results are presented in Table 3.

Table 3. Process of heat storage loading.

Time (s)	Water Temperature at the Inlet to the Tank (°C)	Water Temperature at the Outlet to the Tank (°C)	Water Flow (kg/s)
10	42.6 ± 0.4	34.6 ± 0.4	1.90
660	46.5 ± 0.4	44.8 ± 0.4	2.85
1340	53.0 ± 0.4	51.2 ± 0.4	2.86
2000	57.4 ± 0.4	55.8 ± 0.4	2.86
2660	62.7 ± 0.4	61.1 ± 0.4	2.86
3340	66.7 ± 0.4	66.0 ± 0.4	2.87
4000	67.7 ± 0.4	66.1 ± 0.4	2.87
4660	68.1 ± 0.4	66.8 ± 0.4	2.88
5340	67.2 ± 0.4	66.0 ± 0.4	2.87
6000	68.1 ± 0.4	66.3 ± 0.4	2.86
6660	67.9 ± 0.4	66.3 ± 0.4	2.87
	Total heat (kWh)		35.04
	Theoretical heat (kWh)		57.39
	Efficiency (%)		61.07
	Average heat flux (kW/m ²)		19.18

As shown in Table 3, the total heat removed from the PCM material was 39.41 kWh, while the heat that could theoretically be removed was 57.39 kWh. Thus, the heat storage discharging efficiency was 70.91%. The discharge efficiency of heat storage with PCM materials ought to be in the range of 45–78%. This value is in the upper range of the discharge efficiency for the paraffin bed, which proves the good performance of the bed.

Figure 3 shows the temperature difference between the water supply and the return from the bed. A sudden drop and increase in the value of the water return temperature from the ex-changer is related to the incorrect reading of the measuring system. The average difference in temperature was 1.93 K. This is an acceptable disparity to ensure greater test accuracy. This can be achieved, for example, by reducing the water flow through the exchanger.

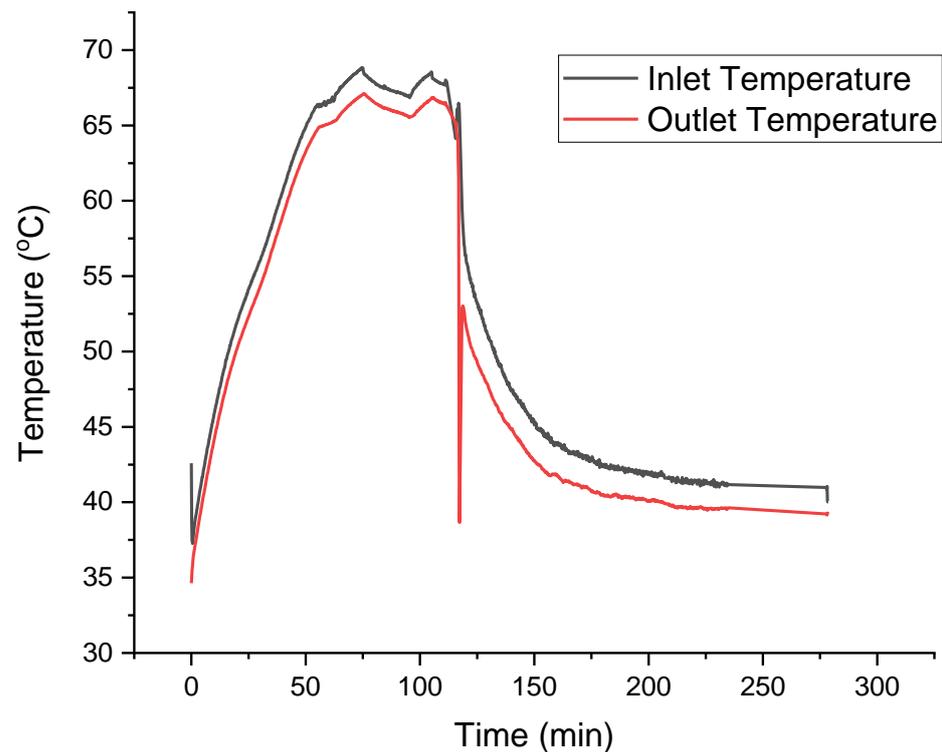


Figure 3. Temperature difference between the supply and return from the paraffin tank.

3.2. Characterizations of Paraffin Wax Containing Multi-Walled Carbon Nanotube Composites

Carbon nanotubes are categorized into single-wall carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT), where SWCNTs have been made of monolayer graphene. The dangling bonds are swiftly incorporated on the boundary while winding the graphene layer into a cylinder, resulting in the axis of CNTs becoming randomly dispersed [5]. When the graphite surface area is lined up lengthwise across the SWCNT axis, a two-dimensional geometry such as a graphene surface with a single layer is produced [6]. On the contrary, multi-walled carbon nanotubes have outstanding characteristics (thermal, electrical, and mechanical), which afford a wide range usage potential opportunities [7]. It has been determined that the thermal conductivity of single multi-walled carbon nanotubes near 37,000 W/(m K) at a temperature of 100 K with the macroscopic thermal conductivity are able to achieve 6000 W/(m K) [8]. The thermal conductivity of single multi-walled carbon nanotubes at room temperature can be comparable to an isotopically pure diamond and can even achieve a greater value [9].

3.2.1. SEM and EDX Characterizations

SEM images of carbon nanotube and carbon nanotube–paraffin nanocomposites were used to describe their micromorphology using Scanning Electron Microscope manufacturing by JEOL Ltd., model: JSM-7100F, Tokyo, Japan.

The multi-walled carbon nanotubes were made of a black powder with a laminar architecture and loosely packed particles, as shown in Figure 4, displaying PW-based MWCNTs nanocomposites. Figure 4 confirms that the MWCNT layers were distributed in the PW in various paths and spots. The MWCNTs created a framework that supports heat transfer. Moreover, the layers of the MWCNTs were totally and regularly covered by paraffin, where the MWCNTs and PW were strongly integrated as the content of the MWCNTs increased, without any microcracks or loose interfaces. These observations have been confirmed by the EDX Elemental Analysis (see Figure 5), of the spatial distribution of various elements.

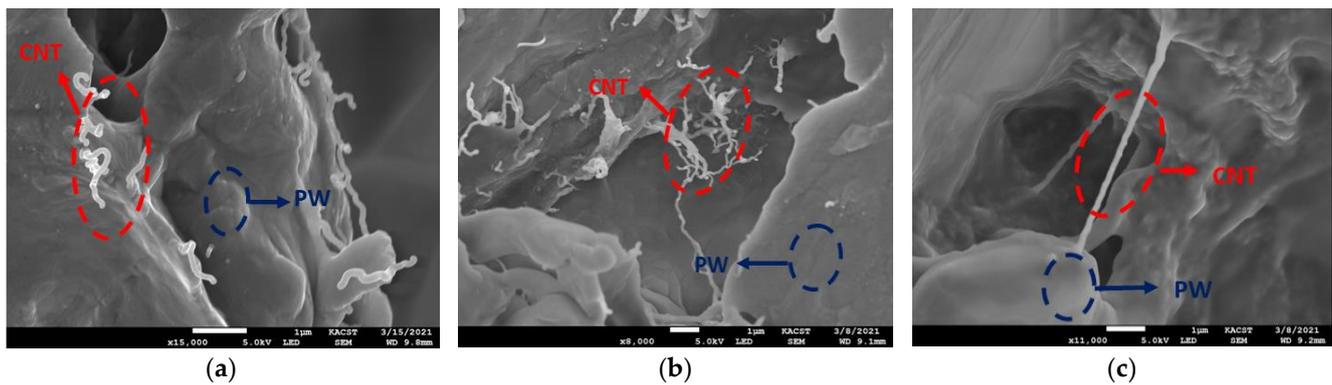


Figure 4. SEM images of the paraffin wax/MWCNT composites: PW-1CNT (a), PW-2CNT (b), and PW-3CNT (c). Scale bars of Figures 4 and 5 are the same (see Figure 5).

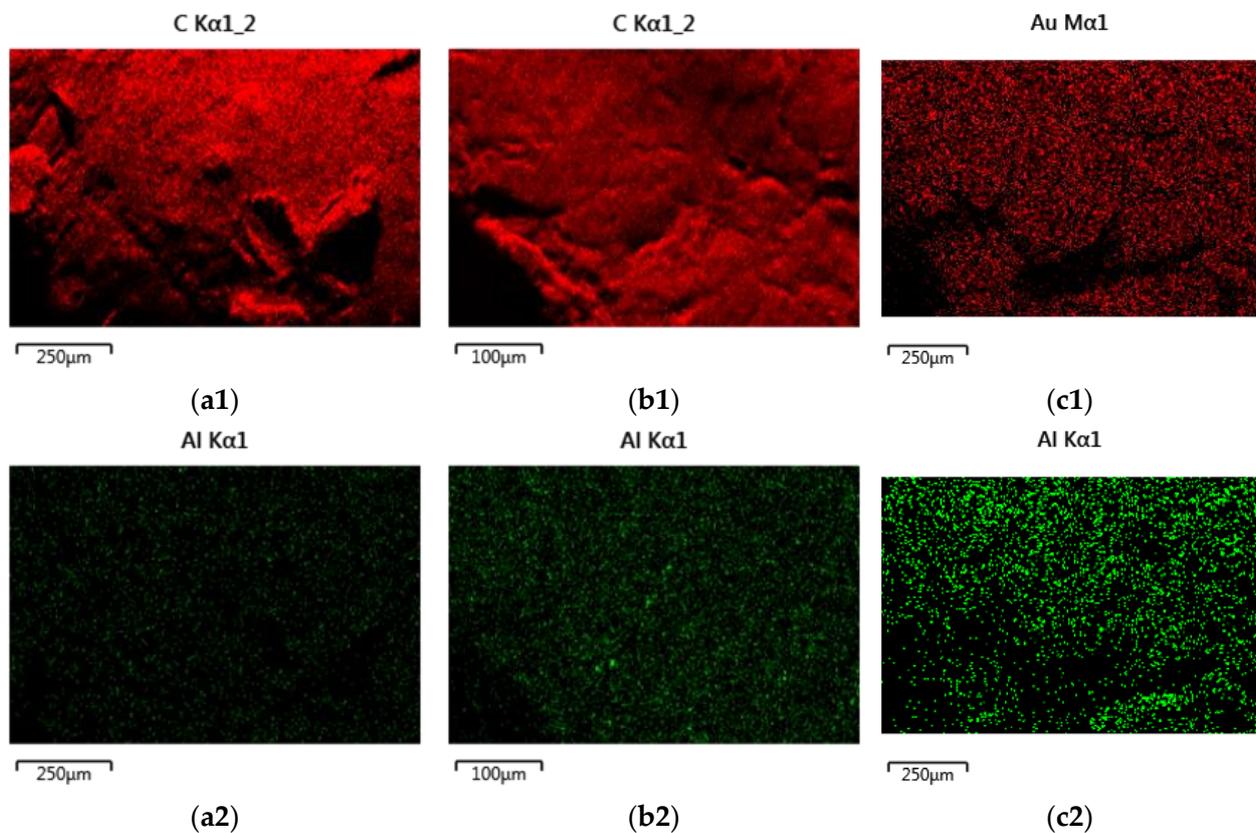


Figure 5. EDX images of the paraffin wax/MWCNT composites: (a1,a2) PW-1 CNT, (b1,b2) PW-2 CNT, and (c1,c2) PW-3 CNT.

It was anticipated that as the mass fraction of multi-walled carbon nanotubes rises, the thermal conductivity slowly rises, while the latent heat drops, which would indicate that the increase in the PCM's thermal conductivity using MWCNTs complements the decreased latent heat of the PCM composite. Consequently, further thermal measurements are required, with a fitting mass fraction of multi-walled carbon nanotubes needing to be measured, based on the application.

3.2.2. FTIR Analysis

The FTIR spectra of the paraffin, carbon materials, and composites are shown in Figure 6.

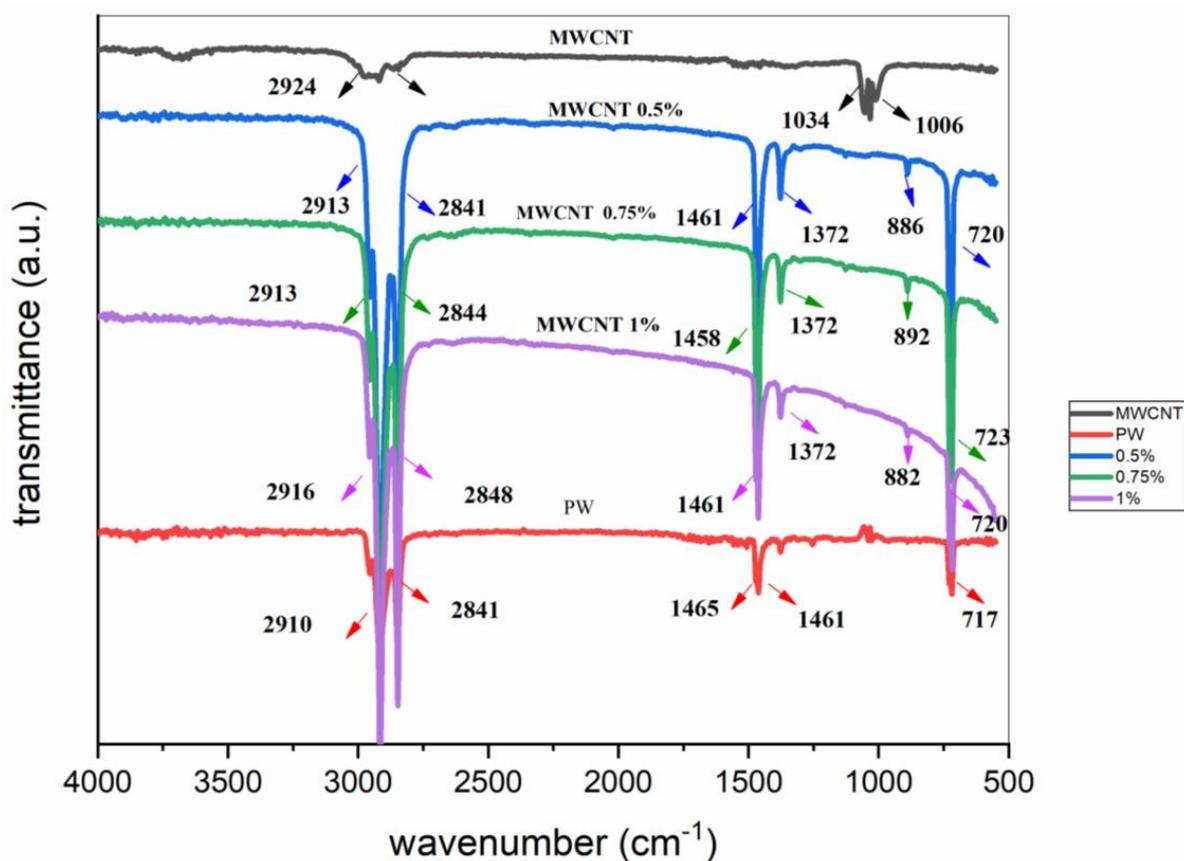


Figure 6. FTIR spectra of paraffin wax, CNTs, PW-1CNT (0.5% CNT), PW-2CNT (0.75% CNT), and PW-3CNT (1% CNT).

The PW-1CNT, PW-2CNT, PW-3CNT, and PW spectra displayed four remarkable peaks, corresponding to the presence of PW. The bonds detected at around 2800 cm^{-1} are designated to the C-H stretching vibration of the CH_3/CH_2 groups. The peak near 1500 cm^{-1} is assigned to the bending vibration of C-H. The 717 cm^{-1} absorption band is credited to the in-plane deformation rocking vibration of the PW molecule [19,20]. The spectra corresponding to the CNT showed a band of absorption around 3000 cm^{-1} , which can be accredited to the stretching of the C=C bonds. Bonds corresponding to the stretching of the C-C of the CNT structure were observed at around 1000 cm^{-1} [19,21–23].

The addition of CNT to the PW did not form any new peaks, and the PW-1CNT, PW-2CNT, and PW-3CNT only displayed a combination of peaks corresponding to the PW and CNT.

3.2.3. TGA Analysis

Thermogravimetric analyses (TGAs) were performed in alumina crucibles under nitrogen (flow rate, 100 mL/min) using a thermobalance Discovery SDT 650 from TA Instruments with a heating rate $10\text{ }^\circ\text{C/min}$.

Thermogravimetric analysis method: Figure 7 shows the measured TGA curves. The clear mass loss that is observed is due to paraffin degradation. Furthermore, the nearly overlapping TGA curves in Figure 7 not only reveal the close paraffin impregnation amount but also the CNTs' exceptionally stable thermal performance. In addition, the mass loss that is seen in the thermal behaviour curves and as calculated in Table 4 confirm that the CNT disperses well in the paraffin wax. In other words, CNT is known to be chemical inert and shows resistance to thermal degradation of the thermal decomposition of paraffin wax nanocomposites after the addition of CNT particles, as shown in Table 4 and Figure 7. It is shown that the thermal decomposition of paraffin wax nanocomposites gradually moves to a slightly higher temperature with increasing amounts of MWCNT particles. Even though

the CNT interaction with PW is weak due to the fact that CNT did not functionalize, the CNT can still interact with the surrounding matrix and can improve the overall thermal stability of the PW/CNT nanocomposite. The residual weight at 600 °C, after considering the CNT weight loss and considering that the PW temperature was completely decomposed at this point, as well as the fact that the CNT showed a little degradation, was close to the initial loadings 0.5, 0.75 and 1 wt.% [24–26]. Also as seen in Figure 7, occurrences of rapid degradation of all nanocomposites are shown at around 210 °C due to the degradation of PW, but each single composite experienced different weight loss.

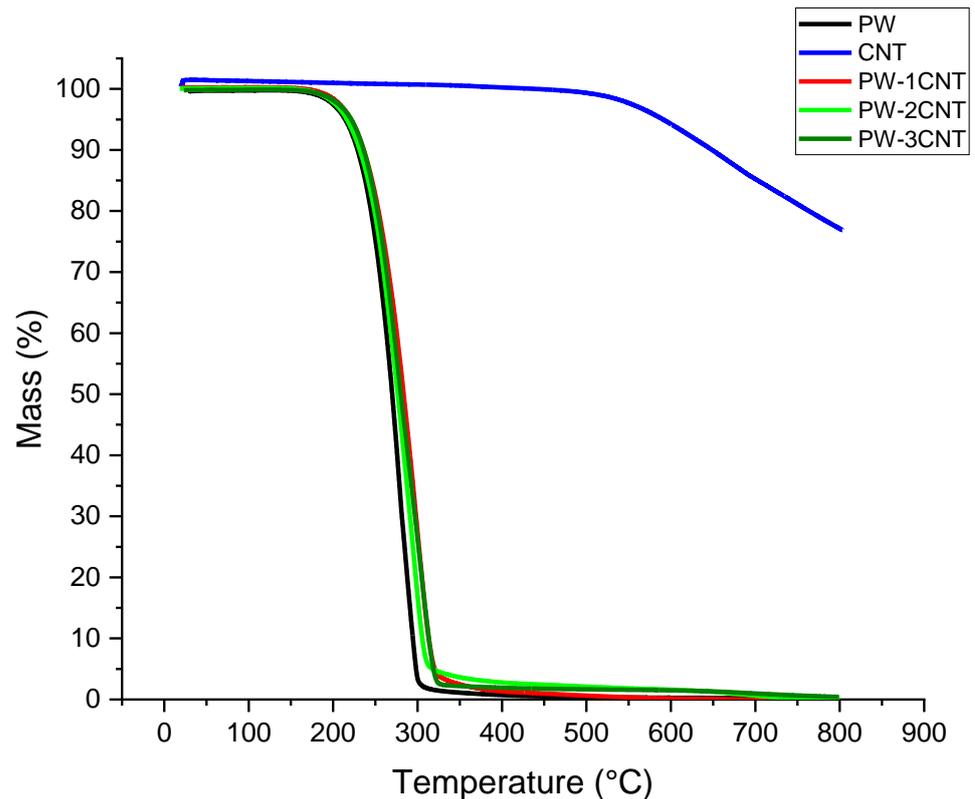


Figure 7. TGA thermogram of the paraffin wax/MWCNT and composites (PW-1CNT, PW-2CNT, and PW-3CNT).

Table 4. Mass loss of the PW, CNT, and composites 1, 2, and 3.

Sample Code	Onset Temperature °C	Mass Loss at 600 °C	Mass Loss % at 700 °C
CNT	533.56	94.237	85.234
PW (2)	243.12	0.281	0.195
Composite 1	249.26	0.171	−0.043
Composite 2	244.56	1.603	0.639
Composite 3	239.97	1.493	0.98

Weighing Accuracy for thermobalance Discovery SDT 650 = $\pm 0.5\%$; Standard uncertainty (mK) of electronic thermometer = ± 1.0 .

It was reported by Kuziel et al. [27] that in MWCNT (0.5 wt.%)–paraffin nanocomposites, the thermal conductivity is enhanced by 37%, in addition to increasing by 6.3% to the enthalpy phase change (ΔH_m), compared to the paraffin, which has brilliant cycling stability. Individual and fibrous ultra-long MWCNTs have superior properties due to the faster nucleation of larger crystallites by MWCNTs via short- and long-range templating as well as the intrinsic properties of individual and fibrous ultra-long MWCNTs [28–30].

4. Conclusions

Phase change materials (PCMs) are considered efficient for storing thermal energy due to their high latent temperature and slight temperature variation during the phase change process. Based on a literature review of PCM type, nanoparticle type, and fraction, as shown in Table 5, we started studying PW (as a PCM) as a material for storing thermal energy, as it has several advantages, including latent fusion, chemical stability, negligible supercooling, no phase separation, and low cost. The thermal storage performance of a TES bed system was approximately 71%, which can be considered relatively high. In order to enhance the thermal conductivity of the PW, the dispersion of high thermal conductivity materials such as MWCNTs was employed. The prepared composites of PW and MWCNTs of various weights were characterized by using various techniques, namely, SEM, EDX, FTIR, and TGA. First, the SEM and EDX results showed significant improvement in the molecular structure of the PW/MWCNT composites. When PW and MWCNTs were mixed, the MWCNT layers were distributed evenly and were integrated with paraffin layers through strong interfaces without microcracks. The FTIR results showed that adding CNT to PW did not form any new peaks, and the prepared composites only displayed a combination of peaks corresponding to the PW and CNT, such that a physical combination can be intuitively expected. TGA analysis elucidated that the addition of MWCNT to paraffin enhanced its thermal properties toward better thermal conductivity. At 700 °C, composites 1, 2, and 3 showed a mass loss of −0.043, 0.639, and 0.98, respectively. Moreover, it can be deduced that the relatively coinciding mass loss profiles (PW, CNT, and PW/CNT composites) could be due to the fact that a uniform distribution of the CNT layers within PW was accomplished.

Table 5. Summary of the previous work on PCM type, nanoparticle type, and fraction.

Authors (Year)	PCM	Type of Additives	Fraction of Additives	Comments
Wang et al. (2009) [10]	Paraffin	MWCNTs	0.2, 0.5, 1 and 2	The composite containing 2.0 wt.% had a higher thermal conductivity of 35% and 40%, respectively, in solid and liquid states.
Wang et al. (2011) [12]	Paraffin Palmitic acid	G8-CNT G18-CNT	-	The thermal conductivity of paraffin and palmitic acid were improved by adding a small amount of G8-CNT. The results showed that the thermal conductivity of CNTs is clearly affected by the length of the grafted chain.
Teng et al. (2013) [13]	Paraffin	MWCNTs Graphite	1, 2 and 3	MWCNTs were more effective in enhancing paraffin performance in all experimental parameters compared to graphite.
Ye et al. (2014) [14]	Na ₂ CO ₃ / MgO	MWCNTs	0.1%, 0.2%, 0.3% and 0.5%	As the weight percentage of the MWCNTs increased, the thermal conductivity of the composite PCMs increased by approximately 96% (the highest) for 0.5% of MWCNTs.

Table 5. Cont.

Authors (Year)	PCM	Type of Additives	Fraction of Additives	Comments
Xu and Li (2014) [15]	paraffin (R27, Rubitherm)	MWCNTs Diatomite materials	0.26% -	The thermal conductivity of PCM-DP600-CNTs was substantially improved, with an improvement level of up to 42.45%.
Li et al. (2014) [16]	Paraffin	CNTs CNTs-SA	-	The thermal conductivity of MicroPCMs/CNTs-SA with 4% CNTs increased by 79.2% when compared to MicroPCMs.
Tang et al. (2014) [17]	Paraffin	(f-MWCNT)	1, 5 and 10%	With 10 wt.% of f-MWCNTs, the thermal conductivity and the heat transfer of the paraffin/f-MWCNTs composite PCMs increased by 86.7%.
Xiao et al. (2015) [18]	Palmitic acid	CNTs, oxidized CNTs and grafted CNTs	1/100	CNTs, O-CNTs, and G-CNTs improved the palmitic acid thermal conductivity, but G-CNT composites had the highest latent heat.
Tao et al. (2015) [3]	Salt	SWCNT, MWCNT, graphene and C60	0.1%, 0.5%, 1.0%, 1.5%, 2.5%	SWCNTs and MWCNTs exhibited significant enhancement in the PCMs' thermal conductivity with mass fractions near 1.5% by 57% and 50%, respectively.

The main suggestions for future work drawn in the light of the obtained results are as follows:

1. Studying the effect of PW/MWCNT composites (of various lengths and diameters) on the thermal conductivity and diffusivity of PW nanocomposites.
2. Comparing the effect of MWCNTs on heat storage/release rates to pristine PW.
3. Investigating the durability of these composites considering the number of possible circular (heating/cooling) applications and any possible degradation of PCM over time.

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Appendix A. Element Analysis for PW from the TES Unit and the Pristine One from the Techno Pharm Chem Company

PW (TES Unit Bed)	
Element	Conc (mg/kg)
Li	0.022 ± 0.001
B	1.83 ± 0.011
Na	545 ± 0.2
Mg	7.88 ± 0.2
Al	31 ± 0.15
Si	85 ± 0.2
Ca	191 ± 0.5
Sc	0.02 ± 0.003
Ti	1 ± 0.005
V	0.058 ± 0.001
Cr	11 ± 0.05
Mn	0.8 ± 0.04
Fe	21 ± 0.1
Co	0.065 ± 0.005
Ni	0.33 ± 0.005
Cu	0.66 ± 0.007
Zn	2 ± 0.05
Se	0.22 ± 0.005
Sr	0.3 ± 0.015
Mo	0.29 ± 0.005
Ag	0.048 ± 0.001
Sn	107 ± 0.2
Sb	0.044 ± 0.001
Ba	0.29 ± 0.005
W	0.11 ± 0.004
Pb	0.11 ± 0.003
Ge	UDL
Sb	UDL
Cs	UDL

Appendix B. Nomenclature of Quantities Used in Equations

T_{w1}	—water inlet temperature
T_{w2}	—water outlet temperature
$T_{w,av}$	—average temperature of the water supply and return
T_m	—phase change temperature of a phase change material
$F(T)$	—the actual density or specific heat of the water
$F(T_0)$	—the density or specific heat of water at a stationary point
$F(T_1)$	—the density or specific heat of water at another known stationary point
ρ_w	—average water density at constant pressure
V_w	—water volume flow
C_w	—specific heat at constant pressure
Q	—real heat capacity
Qt	—theoretical heat capacity
m_{PCM}	—mass of the phase change material
$C_{PCM,S}$	—the sensible heat of a phase change material (solid)
$C_{PCM,L}$	—the sensible heat of a phase change material (liquid)
L	—the latent heat of a phase change material

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