

RESEARCH ARTICLE

Investigation on Thermophysical Properties of Multi-Walled Carbon Nanotubes Enhanced Salt Hydrate Phase Change Material

R. K. Rajamony¹, M. Samykano^{2,*}, A. K. Pandey^{3,4}, S. Ramesh Babu⁵, M. M. Noor², D. Ramasamy², J. K. Siaw Paw¹ and S. K. Natarajan⁶

¹Institute of Sustainable Energy, University Tenaga Nasional (@The National Energy University), Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia

²Faculty of Mechanical & Automotive Engineering Technology, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia

³Research Centre for Nanomaterials and Energy Technology (RCNMET), School of Engineering and Technology, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, Petaling Jaya, 47500 Selangor Darul Ehsan, Malaysia

⁴CoE for Energy and Eco-sustainability Research, 248007 Uttaranchal University Dehradun India

⁵Department of Mechanical Engineering, Nalla Malla Reddy Engineering College, Hyderabad, 500088 Telangana, India

⁶Solar Energy Laboratory, Department of Mechanical Engineering, National Institute of Technology Puducherry, 609609 Karaikal, UT of Puducherry, India

ABSTRACT - Thermal Energy Storage (TES) is a valuable tool for improving the energy efficiency of renewable energy conversion systems. One of the most effective methods for harnessing thermal energy from solar sources is through energy storage using phase change materials (PCMs). However, the thermal performance of PCMs is hindered by their low thermal conductivity. This research focuses on enhancing the thermal performance of salt hydrate PCM using multi-walled carbon nanotubes (MWCNTs) and surfactants. Through experimental investigations, a salt hydrate PCM with varying concentrations of MWCNTs (ranging from 0.1% to 0.9%) was prepared using a two-step technique and their thermophysical properties were thoroughly characterized. Various techniques such as field emission scanning electron microscope, thermal conductivity analyzer, ultraviolet-visible spectrum, thermogravimetric analyzer, and Fourier transform infrared spectroscopy were utilized to study the effect of surfactant on the nanocomposites and examine their morphology, thermal conductivity, optical properties, thermal stability, and chemical stability. The results indicated that the inclusion of MWCNTs with salt hydrate significantly improved the thermal conductivity by 68.09% at a concentration of 0.7 wt %, compared to pure salt hydrate. However, this enhancement in thermal performance was accompanied by a reduction in optical transmittance in the developed nanocomposite PCM. Additionally, the formulated nanocomposite demonstrated excellent thermal and chemical stability up to temperatures as high as 468 °C. As a result, this nanocomposite shows great promise as a potential candidate for solar TES applications, offering favourable characteristics for efficient energy storage from solar sources.

1.0 INTRODUCTION

The pressing issue of global warming and environmental pollution stemming from excessive reliance on fossil fuels has led to a growing emphasis on adopting renewable energy systems [1]. Among various renewable energy sources, solar energy stands out as the most credible, environmentally friendly, and accessible option. Nevertheless, the intermittent nature of solar energy poses a significant challenge to its widespread implementation in energy systems [2]. To enhance the effectiveness of renewable energy conversion systems, thermal energy storage (TES) has proven reliable. Phase change materials (PCMs) [3] offer an efficient technology for harnessing solar energy. These PCMs can absorb, store, and release heat energy during their phase transition from solid to liquid, maintaining isothermal conditions. The key advantages of using PCMs include their wide range of melting temperatures, high latent heat storage (LHS) capacity, thermal stability, and eco-friendliness [4]. However, PCMs do have certain limitations, such as lower thermal conductivity (TC) and suboptimal light absorption properties, which hinder their practical application in solar thermal systems and lead to slower charging and discharging rates [5], [6]. As a solution, some researchers suggest incorporating high-conductive nanoparticles into the PCM to improve its heat conductivity and modify other properties [7]–[9]. Despite an abundance of research on enhancing the performance of PCMs, selecting the most suitable PCM and conductive particles remains a challenging and complex task.

The incorporation of nanomaterials into the base PCM is known as nano-enhanced phase change materials (NePCMs). Some researchers have suggested that adding a small amount of surfactant to the PCM can improve dispersion stability, leading to increased thermal conductivity (TC) [10]–[12]. In recent studies, a salt hydrate PCM with Copper Oxide (CuO) nanoparticles and a surfactant nanocomposite was synthesized using a two-step method at various concentrations (0.1%,

ARTICLE HISTORY

Received	:	22 nd Feb 2023
Revised	:	31 st July 2023
Accepted	:	28 th Aug 2023
Published	:	20th Sept 2023

KEYWORDS

Thermal energy storage; Salt hydrate; Thermal conductivity; Multi-walled carbon nanotubes 0.5%, 1%, 2%, 3%, and 5%). The results demonstrated that at 3.0 wt% CuO with salt hydrate PCM, the TC was enhanced by 87.39%, and the prepared nanocomposites exhibited chemical and thermal stability up to 474°C [13]. Using the T-history method, Qu et al. conducted an experimental characterization of carbon-based nanoparticles dispersed in paraffin PCM. They found that the TC was enhanced by 240% and 108% for the composite with compositions of paraffin: High-density polyethylene: Expanded Graphite: MWCNTs (75:20:5:0) and (75:20:0:5), respectively [14]. Furthermore, Octadecanol (OD) thermophysical properties with MWCNT nanocomposites were synthesized at various concentrations. The outcome indicated that the TC increased from 0.16±0.001 W/mK to 0.82±0.04 W/mK at OD-g-MWCNT (1:1) [15]. Comparing regular MWCNTs with surface-modified MWCNTs dispersed in salt hydrate PCM, it was observed that functionalized MWCNTs exhibited higher dispersion stability, thermal stability, and TC due to the attachment of the COOH group on their surface. The TC was improved from 0.45 W/mK to 0.92 W/mK at 0.7 wt% [16]. These studies demonstrate the potential of nanocomposites in significantly improving the TC of PCMs, which could pave the way for more efficient and practical applications of renewable energy systems utilizing solar energy.

Several studies have investigated the enhancement of thermal properties in PCMs using various nanoparticles. For instance, the two-step approach was used to prepare a binary nanoparticle (TiO₂-graphene) dispersed paraffin wax PCM composite at different concentrations. The findings showed that the addition of TiO₂ particles increased the TC by 120% compared to the base PCM at 1.0 wt%. Furthermore, the TiO₂-graphene nanocomposite exhibited a 179% increase in TC compared to the base PCM. This binary composite significantly improved the TC [17]. Similarly, graphene-enhanced erythritol PCM nanocomposites were synthesized using a two-step method at different concentrations (0.1%, 0.5%, and 1.0%). At 1.0 wt%, the developed nanocomposite showed a 53.1% enhancement in TC, and the latent heat storage (LHS) was reduced by 6%. Although the LHS decreased after several thermal cycles, the high TC helped maintain a high value of LHS [18]. In another study by Ranjbar et al. [12], the performance of PCMs (stearic acid and polyethylene glycol) embedded with MWCNTs was examined for TES applications. The TC was enhanced by 16.83% and 16.57% for stearic acid/MWCNT and polyethylene glycol/MWCNT at 1.0 wt%, respectively. Furthermore, the thermal stability and reliability of a nano silica-based PCM composite were analyzed at different concentrations (0.5%, 1.0%, and 2.0%). The results demonstrated that the decomposition temperature of the formulated nanomaterials augmented from 246 °C to 270 °C, indicating higher thermal stability due to the development of thermal barriers with nano PCMs [19]. Investigating the physical and thermal properties of TiO₂-embedded stearic acid PCM composites at various concentrations (0.09%, 0.26%, 0.335, and 0.36%), the findings showed that the addition of TiO₂ particles enhanced the TC by 6.97%, 27.16%, and 17.53% at 30 °C, 60 °C, and 70 °C, respectively, at 0.36 wt%. The Fourier transform infrared (FTIR) curve suggested that the formulated nanomaterials were chemically stable and true composites [20]. Manoj Kumar et al. [21] studied the thermal performance of PCM dispersed with CuO and Al₂O₃. The TC of paraffin/CuO and paraffin/Al₂O₃ was enhanced by 60.56% and 39.44%, respectively, at 1.0 wt%. The paraffin/CuO dispersed PCM performed better than the paraffin/Al₂O₃ dispersed PCM. Additionally, the performance of MWCNT and graphene platelets enhanced PCMs for photovoltaic thermal applications was compared [22]. The TC of paraffin/MWCNTs and paraffin/graphene nanoplatelets was 0.191 W/m°C and 0.169 W/m°C, respectively, at 0.5wt%. The results concluded that MWCNTs enhanced PCM with higher TC, while graphene platelets dispersed PCMs had higher specific heat. An innovative hybrid nanoparticle (MWCNT-CuO) enhanced PCM was fabricated for TES applications in a parabolic dish [23]. The addition of hybrid nanoparticles into the PCM enhanced the TC by 6.125% compared to plain PCM, and the formulated nanocomposites exhibited a higher charging rate. Recently, nano carbon-based paraffin nanocomposites were developed to enhance thermophysical properties at various weight concentrations (0.02%, 0.06%, and 0.1%) [24]. The TC of paraffin/nano coconut shell and paraffin/nano graphite was increased by 0.36 W/m°C and 0.32 W/m°C at 0.02 wt%, and 0.336 W/m°C and 0.326 W/m°C at 0.1 wt%, respectively. Additionally, PW/ TiO₂ nanocomposites were fabricated for TES applications. The results indicated that the addition of a small quantity of nano-size particles enhanced the TC, decomposition temperature, and absorption capability. The TC was improved by 86.36% at 1.0wt% TiO₂, and the decay temperature was increased from 225 °C to 237 °C at 1.0wt% TiO₂ [11]. The thermal and chemical properties of various sizes of carbonbased nanoparticles enhanced the magnesium nitrate hexahydrate PCM for TES [25]. The TC of mesoporous carbon, nano graphite, MWCNTs, carbon sphere, and graphene nanoplatelets with magnesium nitrate hexahydrate was enhanced by 75.0%, 65.0%, 82.4%, 100%, and 72.5%, respectively. The nanocomposite with carbon sphere-enhanced PCM showed the highest reduction in charging time. The research publications that reported the thermal properties of carbon-based nanoparticle-dispersed PCM are summarized in Table 1.

In this study, the researchers aimed to enhance the energy management of solar thermal systems by developing nanocomposites with improved thermal conductivity (TC) and dispersion stability. To achieve this, they used PlusICE S50 salt hydrate as the phase change material (PCM), MWCNT as nanoparticles, and Sodium dodecylbenzene sulfonate (SDBS) as a surfactant. The addition of nanoparticles in PCM has been previously shown to enhance thermal properties, but the effect of using a surfactant in carbon-based nanoparticle-dispersed salt hydrate PCM for solar applications has not been addressed in experimental studies. The research methodology involves collecting the necessary materials and formulating the MWCNT-dispersed salt hydrate at various concentrations using a two-step technique. Subsequently, they investigated the thermal behavior of formulated nanocomposite. The findings indicated an improvement in the thermal properties of inorganic PCM, which is supported by previous studies on nanocomposite preparation and characterization. The novelty of the present research lies in studying the effect of using a surfactant in PCM and MWCNT composites, characterizing the properties of the developed nanocomposites, and evaluating their performance. The study is organized

in a systematic manner, with Section 1 discussing the research purpose and reviewing related literature on nanocomposite preparation and characterization. Section 2 covers the methods used for fabricating the nano PCM composite, the characterization techniques employed, and the materials used in the preparation of the composites. In Section 3, the research delves into the characterization and performance evaluation of the nanocomposites' thermal stability, TC, and chemical stability. Finally, Section 4 depicts the conclusions drawn from the research results, and the study concludes with future recommendations. Overall, this research holds the potential to enhance the application of salt hydrate for TES purposes, aligning with the sustainable development goals (SDGs) set by the United Nations. By exploring the incorporation of surfactant in the nanocomposite preparation, the researchers aim to contribute to advancing solar thermal systems and promoting sustainable energy management.

РСМ	Melting temperature (°C)	Nanoparticle	Size (nm)	Weight percentage (%)	Thermal conductivity enhancement (%)	Reduction in light transmittance (%)	Reference
Stearic acid	55-62	MWCNT	10- 20	-	16.83	-	[12]
Inorganic	50	FMWCNT	10- 23	0.3	58.7%	89.8%	[16]
Paraffin	50	Graphene and silver	20	0.8	53.7		[26]
Paraffin	53	MWCNT	30	2	35%	-	[27]
Paraffin	50	Graphene	8	0.6	72%	32%	[28]
Paraffin	40-42	MWCNT	2-8	0.5	15.75	-	[22]
Inorganic	58-60	MWCNT+CuO	-	-	6.125	-	[23]
Salt hydrate	50	MWCNT	10- 20	0.7	68.09	89	Present work

Table 1. Thermal properties investigation of some major work with MWCNTs

2.0 MATERIALS AND METHODS

This section discusses the various materials used to prepare the nanocomposites, the preparation methods and characterization techniques.

2.1 Materials

The selection of the appropriate PCM and nanoparticles is a critical step in TES applications, and it depends on factors such as the specific application and the operating temperature range. For this research, a commercial-grade inorganic PCM called PlusICE S50 was obtained from PCMs Ltd, United Kingdom. The phase transition temperature range is 50°C, making it suitable for the intended application. To improve the thermal properties of the PCM, MWCNT were chosen as the nanoparticles. These MWCNTs were procured from Cheap Tubes Inc., USA, and they have a diameter of 10-20 nm with 95% purity. MWCNTs are expected to improve the nanocomposite's thermal conductivity and overall performance. Additionally, a surfactant/stabilizer called SDBS was acquired from Sigma Aldrich Sdn Bhd. The surfactant plays a crucial role in the dispersion and stability of the MWCNTs within the PCM matrix, preventing agglomeration and ensuring uniform distribution. This can lead to better enhancement of thermal properties and improved performance of the developed nanocomposite. Table 2 provides the properties of the SDBS, MWCNT, and salt hydrate PCM, which are essential for understanding their characteristics and how they might interact within the nanocomposite to achieve the desired performance for solar thermal applications.

Table 2. Properties of salt hydrate PCM, MWCNT and surfactant

Property	MWCNTs	SDBS	PCM
Melting temperature (°C)	3650-3700	204-207	50
Thermal conductivity (W/mK)	3000	-	0.45
Latent heat (J/g)	-	-	100
Colour	Black	white	white
Density (kg/m ³)			1600
Size	Diameter:10-20 nm and length: 10-30 µm	-	-

2.2 Sample Preparation

The synthesis of the nanocomposites is carefully carried out by dispersing MWCNT into PCM. The preparation method is outlined in Figure 1 and involves a two-step process. The following equipment was used for the formulations: an analytical balance machine UNIBLOC, TX323L, a hot plate for heating the PCM, a magnetic stirrer for mixing, and a bath ultrasonic (Model: EASY 60H, ELMASONIC) for sonication. The procedure starts by placing the salt hydrate PCM

in a beaker and heating it to a temperature above 70 degrees Celsius using the hot plate. Next, the required amount of SDBS is added to the liquid PCM, and the mixture is stirred for five minutes using the magnetic stirrer. Subsequently, a pre-measured weight concentration of MWCNT is added to the mixture and stirred for an additional 10 minutes. This step aims to ensure uniform dispersion of the MWCNT within the PCM matrix. To further improve the dispersion and minimize nanoparticle agglomeration, the beaker is placed in the bath ultrasonic, and sonication is carried out for one hour. Throughout the sonication process, the temperature is maintained at 70 °C to facilitate effective dispersion and enhance the interaction between the MWCNT and PCM. After completing the one-hour bath sonication, the nanocomposite is allowed to cool down to room temperature. This procedure is repeated for various weight concentrations of MWCNT (0.1%, 0.7%, and 0.9%) to prepare nanocomposites with different compositions. Once the nanocomposites are prepared, they are subjected to characterization to investigate various thermophysical properties. This step is crucial for understanding the performance and suitability of the developed nanocomposites for solar thermal applications. The nanocomposites' thermophysical properties were assessed to determine how the addition of MWCNT and surfactant influences their thermal conductivity, stability, and other relevant characteristics.



Figure 1. Schematic diagram of nanocomposite preparation method

2.3 Characterization Techniques

In this research, detailed morphological analysis of both the salt hydrate and nanocomposites was performed using TEM (FEI Tecnai G2 20 TWIN, 200 kV) and Field Emission Scanning Electron Microscope (FESEM) (TESCAN, VEGA3). To determine the thermal conductivity (TC) of the formulated nanocomposites, a Thermal Property Analyzer (Model: METER group, TEMPOS, SH-3, two-needle) was utilized at room temperature. The sensor (needle) was inserted into the centre of a 10 ml beaker containing the nanocomposite to measure the TC in its solid phase. Each sample's experiment was repeated ten times to obtain average values for more accurate results. Fourier Transform Infrared Spectroscopy (Model: Perkin Elmer) was used to identify the interaction between the PCM and nanoparticles. KBr pellets were used to create samples for analysis, and the wavenumber range of 400 – 4000 cm⁻¹ was scanned. The thermal decomposition behaviour of the nanocomposite PCM was analyzed using Thermogravimetric Analysis (TGA). The TGA was conducted by heating the samples from 30 °C to 600 °C at a heating rate of 10 °C/min under an N₂ atmosphere. A UV-Vis spectrometer (model: Lambda 750) was used to study the light transmission capability of the samples. The spectrum. These characterization techniques gave the researchers insights into the nanocomposite's morphology, thermal properties, interaction between components, and light transmission capability. The obtained data would be vital for understanding the performance and potential applications of the developed nanocomposites for solar thermal systems.

3.0 EXPERIMENTAL RESULTS

In this section, the formulated nanocomposite's morphology, chemical stability, TC, thermal stability, and optical performance were characterized by FESEM, FTIR, Thermal property analyzer, TGA and UV-Vis.

3.1 Morphology of MWCNT, Salt Hydrate and Nanocomposite

Figure 2 displays the morphological behaviour of MWCNT, salt hydrate PCM, and the resulting nanocomposite as observed under FESEM. In Figure 2(a), the microstructure of MWCNT is shown, with tube sizes ranging between 10-24 nm. The MWCNTs exhibit a characteristic tubular structure with a nanoscale diameter. Figure 2(b) illustrates the microstructure of the pristine salt hydrate PCM. It shows a sticky nature with tight bonding among the adjacent PCM molecules. This sticky nature is typical of the salt hydrate PCM. Figure 2(c) reveals the microstructure of the nanocomposite, where MWCNTs are uniformly distributed within the salt hydrate PCM matrix. The well-dispersed mixture of MWCNT nanomaterials with the base PCM is observed. The tubular structure of the MWCNT nanoparticles is adequately dispersed and can be identified by marked blue colour circles in the image. The successful dispersion of MWCNT within the salt hydrate PCM matrix indicates that a homogeneous composite has been formed. The large surface area and tubular structure of MWCNTs contribute to their proper dispersion, allowing them to mix effectively with the

salt hydrate PCM. This uniform distribution of MWCNTs within the PCM matrix is advantageous for enhancing the thermal properties of the nanocomposite, as well as its overall performance in solar thermal applications.



Figure 2. Morphology of (a) MWCNT, (b) salt hydrate and (c) MWCNT dispersed salt hydrate PCM

3.2 Fourier Transform Infrared Spectrum Analysis

FTIR analysis was conducted to evaluate the chemical stability of the formulated nanocomposites at various concentrations of MWCNTs with surfactant. The FTIR analysis covered a range from 400 1/cm to 4000 1/cm. Several characteristic peaks were observed for the pure salt hydrate PCM (blue-coloured line in Figure 3). The peaks at 3240 1/cm correspond to O-H stretching, 1643 1/cm to N=O bending, 1324 1/cm to a mixture of N-O stretching and bending, N=O bending, and 822 1/cm to NO₃-. Additionally, a peak at 1040 1/cm represents C-O, indicating the presence of the ester group. Similarly, for the salt hydrate/MWCNT with surfactant nanocomposite in Figure 3, the peaks showed similarity to those of the pure PCM. There were no additional peaks related to the base PCM observed, indicating no new chemical bonds formed between the PCM and MWCNTs. This suggests that the newly created nanocomposite is chemically stable, and the MWCNTs indicates that the formulated nanocomposites are stable and well-suited for solar energy storage applications. This chemical stability is essential for reliable and efficient energy storage materials in solar thermal systems. Therefore, the nanocomposites developed in this research show promising potential for enhancing solar energy storage and contributing to sustainable energy solutions.



Figure 3. FTIR graph of MWCNT dispersed salt hydrate with SDBS at various concentrations

3.3 Thermal Conductivity

Thermal conductivity (TC) is a crucial property of PCM as it directly affects the heat absorbing and releasing rate of LHS materials. In the present study, the TC of the formulated PCM with different concentrations of MWCNT with SDBS and without SDBS was evaluated at room temperature, and the findings are described in Figure 4. The TC of the salt

hydrate PCM was measured to be 0.47 Wm⁻¹.K⁻¹. On the other hand, the TC of the nanocomposites SH0.1MWS, SH0.7MWS, and SH0.9MWS, which contain different weight concentrations of MWCNT with SDBS, were found to be 0.56 Wm^{-1} .K⁻¹, 0.79 Wm⁻¹.K⁻¹, and 0.68 W/mK, respectively, at room temperature. The findings demonstrate that the TC value increases with MWCNT concentrations up to 0.7 wt%. Beyond this concentration, there is a decreasing trend in the TC. The maximum TC of the MWCNT dispersed salt hydrate with SDBS was achieved at 0.7 wt%, with a value of 0.79 Wm⁻¹.K⁻¹. The percentage enhancement in the TC of the formulated nanocomposites was calculated using Eq. (1). This calculation allows researchers to quantify and compare the improvement in TC achieved with the addition of MWCNTs and SDBS. Overall, these findings indicate that the inclusion of MWCNTs with SDBS to PCM significantly enhances the TC of the nanocomposite. The optimized concentration of MWCNTs was found to be 0.7 wt%, leading to the highest enhancement in TC.

$$k_{enh} = \left[\frac{k_{NePCM} - k_{base PCM}}{k_{base PCM}}\right] \tag{1}$$

The percentage improvement in TC of SH0.1MWS and SH0.7MWS nanocomposites compared to the base PCM was found to be 19.15%, 68.09%, and 44.68%, respectively. The TC increases with the weight fraction of MWCNTs in the nanocomposite increases. This enhancement in TC can be attributed to two main mechanisms: electron transport and phonon transport. Electron transport is more prominent in metals, but in the case of salt hydrate and MWCNTs, the major contribution to TC enhancement is through phonon-phonon transfer. Phonon transport involves energy transfer through lattice or phonon vibrations. The mean free path of phonons needs to be increased to improve phonon transport. However, scattering between phonons, phonons and impurities, and phonons and barriers can limit the mean free path of phonons. As the thermal path lengthens and the temperature rises, one of these factors might become the limiting factor [29]. In this study, the addition of MWCNTs in the salt hydrate increased the phonon transport mechanism, leading to an increase in TC. At lower concentrations of MWCNTs, the combining of nanoparticles may not occur, resulting in a decrease in the mean free path of phonons due to phonon-boundary scattering. On the other hand, at higher concentrations, the coupling of nanoparticles creates a continuous thermal network in the sample, resulting in a higher TC. MWCNTs have a hexagonal structure with no functional groups or other bonds. The enhancement in TC may be attributed to the addition of the surfactant, which reduces surface resistance and enhances the relations between the base PCM and nanoparticles. The surfactant plays a critical role in improving the dispersion and stability of MWCNTs in the nanocomposite. However, at higher weight concentrations of MWCNTs, nanoparticle agglomeration can occur, disrupting the thermal network and reducing electron thermal transport. Moreover, impurities tend to increase linearly with concentration, leading to increased phonon-impurity scattering, which reduces the mean free path length and, ultimately, the thermal conductivity. From the discussion, it is evident that the optimum TC was achieved in the SH0.7MWS nanocomposite, where the enhancement was significant due to a balanced combination of phonon transport, appropriate nanoparticle coupling, and the presence of surfactant for improved interaction between the components.





3.4 Thermal Stability

Figure 5 illustrates the decay temperature of the base PCM and the formulated nanocomposites at various weight concentrations. Based on the literature, salt hydrate PCMs typically decompose in two steps. The first step involves the decomposition of water molecules at around 300°C, while the second step involves the decomposition of salt particles like magnesium nitrate (Mg(NO₃)₂) at around 460°C. The water molecules decompose in two stages, with a portion degrading at around 160°C and the remaining water molecules decomposing in the second stage at around 300°C. After decomposition, some MgO and carbon residues may be left as byproducts. The TGA profile of the base salt hydrate PCM

shows that degradation begins at 56°C, with 28% of the water molecules degrading at 166°C and the remaining water molecules degrading at 298°C. The magnesium nitrate Mg(NO₃)₂ decomposes at 456°C, leaving behind 8.63% residue, possibly MgO. Figure 5 displays the TGA profiles of the SH0.1MWS, SH0.7MWS, and SH0.9MWS nanocomposites. These nanocomposites' onset temperatures were 62°C, 63°C, and 61°C, respectively. The water molecules in these nanocomposites decompose at higher temperatures than the base PCM, with weight reductions of 21%, 24%, and 25.4% for SH0.1MWS, SH0.7MWS, and SH0.9MWS, respectively. The remaining water molecules decompose at higher temperatures (295°C, 298°C, and 296°C) than the base PCM. The remaining mass (residue) decomposition occurs at higher temperatures (464°C, 468°C, and 464°C), with leftovers of 14%, 12.6%, and 12.4%, respectively. It is observed that adding various weight concentrations of MWCNT into the salt hydrate composites increases the decomposition temperature, leading to improved stability. The enhancement in stability can be attributed to two main factors: the creation of oxygen vacancies and free oxygen in MWCNTs, which causes thermal excitation, and the creation of a thermal barrier [8]. The creation of a thermal barrier in the nano PCMs happens due to the addition of MWCNTs, which may delay the breakage of the polymer chains to monomers, resulting in increased thermal stability. This combination of factors contributes to the overall improvement in the thermal stability of the formulated nanocomposites. Overall, the addition of MWCNTs in the salt hydrate PCM nanocomposites positively impacts the decomposition temperature and stability of the materials, making them more suitable for TES applications and contributing to their potential for solar thermal systems.



Figure 5. TGA profile of SH, SH0.1MWS, SH0.7MWS and SH0.9MWS nanocomposites

3.5 Optical Performance Analysis through UV-Vis

In solar TES applications, PCM plays a crucial role in actively storing thermal energy during phase changes and releasing it as required for specific applications. PCMs are chosen for their high transmissibility and transparency to electromagnetic waves, including solar energy, to ensure efficient solar radiation absorption. In this study, UV-Vis experiments were conducted to determine the optical absorptance and transmittance of the salt hydrate PCM and MWCNT-enhanced salt hydrate PCM, and the transmittance results are presented in Figure 6. The irradiation is categorized into ultraviolet (280-380 nm), visible (380-740 nm), and near-infrared regions (740-1400 nm) based on their maximal availability [30]. The transmittance percentage was calculated for a wavelength range of 250-1700 nm to realize the light transmission characteristics of the developed composites related to the solar spectrum data from NREI [31]the transmittance percentage of the base PCM was found to be 62.0%. However, the transmittance of the nanocomposites SH0.1MWS, SH0.7MWS, and SH0.9MWS decreased significantly to 15.9%, 6.64%, and 6.12%, respectively. This remarkable reduction in transmittance is attributed to the incorporation of MWCNT into the salt hydrate PCM. The reduction in transmittance percentages for SH0.1MWS, SH0.7MWS, and SH0.9MWS were 74.3%, 89%, and 90%, respectively. When radiation interacts with a medium, the particles can be transmitted, absorbed, or reflected. The decrease in transmittance of the PCM when MWCNT is dispersed can be compensated by an increase in absorbance. Inorganic PCMs are often transparent mediums that allow radiation to pass through. A higher absorptivity of the nanocomposite provides the ability to respond more favourably to the solar radiation it receives, leading to a larger thermal energy storage capacity at a relatively faster rate. Due to the higher absorbance capability of the developed nanocomposite PCM, it has become a promising material for solar thermal applications. The reduction in transmittance signifies that the nanocomposite absorbs more solar radiation, making it an efficient choice for storing solar energy and facilitating its utilization in solar thermal systems. This property makes the MWCNT-enhanced salt hydrate PCM a potential substance for solar TES applications.



Figure 6. Transmittance of salt hydrate and nanocomposites

3.6 Determination of Bandgap of Nanocomposites using UV-Vis Spectra

The UV-vis spectroscopy's absorption peak reveals that electrons absorb energy at a specific wavelength. This absorption suggests that these electrons are transitioning from their ground to an excited state. Such transitions indicate the presence of a band gap in the material, where electrons move from the lower energy state to a higher one when exposed to the absorption wavelength. The material's absorption wavelength can determine the band gap's magnitude.

The energy equation of quantum mechanics:

$$Eg = h^*C/\lambda \tag{2}$$

where, Eg is Bandgap (eV), h is Plank constant, $6.626*10^{-34}$ Joules sec, C is velocity of light, $2.99*10^8$ m/s, and λ (Wavelength) is absorption peak (nm)—also, $1eV=1.6810^{-19}$ Joules [32].

Figures 7(a) and 7(b) provide the means to measure the peak absorption and corresponding wavelengths of salt hydrate and nanocomposites. The band gap values can be calculated using Eq. (2), presented in Table 3, for both the salt hydrate and the composites. Remarkably, introducing MWCNTs in the nanocomposites has led to a significant reduction in the band gap values. Specifically, SH0.1MWS, SH0.7MWS, and SH0.9MWS exhibit reductions of 5.0%, 6.87%, and 13.73%, respectively, when compared to the base salt hydrate's band gap. Moreover, an alternative method to examine the band gap is plotting the Tauc plot, which involves (α hv)2 versus hv. This analysis further confirms that the dispersion of MWCNTs can excellently reduce the band gap, with a maximum reduction of 13.73%. The presence of MWCNT scaffolds in the nanocomposites has resulted in a narrower band gap, creating a more photo-responsive region. This region becomes highly favourable for photon production and utilization, making the materials more conducive to photon-related processes.



Figure 7. Bandgap value of (a) Sat hydrate and (b) SH0.7MWS nanocomposite

Table 3. Bandgap values of nanocomposites				
Samples Bandgap (eV)		Decrement in band gap (%)		
SH	3.64			
SH0.1MWS	3.46	5.00		
SH0.7MWS	3.39	6.87		
SH0.9MWS	3.14	13.73		

3.7 Thermal Effusivity

Thermal effusivity measures the ability of a substance to exchange heat with its immediate surroundings at a surface. Moreover, the thermal effusivity can be calculated as the product of the square root of thermal conductivity and volumetric heat capacity λ [33].

$$e = \sqrt{k\rho c} \tag{3}$$

where, *e* is thermal effusivity (Ws^{1/2}/m²K), *k* is thermal conductivity (W/mK), ρc is volumetric heat capacity (J/m³K), ρ is density (kg/m³) and *c* is specific heat capacity (J/kg K).

As observed in Table 4, the thermal effusivity of the developed nanocomposites demonstrates continuous improvement within the MWCNT loading range of 0.1-0.9 wt%. The trend suggests that as the MWCNT content increases, the thermal effusivity increases, potentially reaching a peak value at a specific MWCNT loading. Beyond this optimal loading point, the thermal effusivity might start to decline. Thermal effusivity holds significant importance in guiding the design of nanocomposites for various applications, particularly in thermal management scenarios. These nanocomposites show great potential for enhancing thermal management in diverse fields, such as batteries, buildings, solar energy harvesting, and electronics. By understanding and utilizing the concept of effusivity, researchers and engineers can optimize the composition of nanocomposites to achieve the desired thermal properties required for specific applications. This knowledge could lead to the development of more efficient and effective materials that can efficiently handle heat dissipation and thermal regulation in various technological and industrial settings.

Table 4. Effective thermal effusivity of developed nanocomposites

Sample	SH	SH0.1MWS	SH0.7MWS	SH0.9MWS
Thermal effusivity (Ws ^{1/2} /m ² K)	38.28	41.79	49.64	46.05

4.0 CONCLUSIONS

The current study explores the chemical and thermal performance of MWCNTs enhanced PCM by adding a surfactant. A comparison was made between these nanocomposites' thermal and chemical performance and the base PCM, leading to significant improvements. The FTIR spectrum demonstrated that the formulated nanocomposites are chemically stable, showing no presence of additional functional groups. This confirms that the prepared NePCMs are indeed composites. The decomposition temperature of the developed nanocomposites was notably increased compared to the base salt hydrate PCM. The enhancement in decomposition temperature was observed as follows: from 456 °C to 464 °C for SH0.1MWS, 469 °C for SH0.7MWS, and 464 °C for SH0.9MWS. After decomposition, the leftover weight percentage of the samples indicates the presence of MgO and carbon residues, contributing to the excellent thermal stability achieved in these nano PCMs. The improved thermal stability can be attributed to the formation of a thermal barrier within the nanocomposites.

The addition of MWCNTs may have caused the breakage of polymer chains into monomers, thereby increasing thermal stability. Regarding thermal conductivity (TC), the base salt hydrate PCM exhibited a TC of 0.47 W/mK. The formulated nanocomposites, SH0.1MWS, SH0.7MWS, and SH0.9MWS, demonstrated remarkable enhancements in TC by 19.15%, 68.09%, and 44.68%, respectively. This improvement can be attributed to increased intermolecular attraction between nano-sized particles and the PCM due to the presence of a surfactant. The nanocomposites also showed enhanced light absorbance and reduced light transmission, particularly significant in the SH0.7MWS composite, which saw an 89% reduction in light transmission. The bandgap of the nanocomposites decreased considerably, resulting in improved absorption capabilities. Future research will investigate the optical performance, morphology, elemental analysis, latent heat storage (LHS) capabilities, and the formulated NePCM's thermal reliability. These formulated nanocomposites hold potential applications in thermal management and TES systems, such as PVT (Photovoltaic-Thermal) systems, cooling electronic components, and battery thermal management in buildings. The higher TC, chemical and thermal stability up to 468 °C make these nanocomposites promising candidates for such applications. Furthermore, this research aligns with the United Nations' SDG 7 and 13, which focus on affordable and clean energy and climate action, contributing to sustainable and environmentally friendly technologies.

5.0 ACKNOWLEDGEMENT

The authors would like to thank Universiti Malaysia Pahang (UMP) for the financial support under Research Grant: RDU223302.

6.0 **REFERENCES**

- K. Baz, J. Cheng, D. Xu, K. Abbas, I. Ali, H. Ali, and C. Fang, "Asymmetric impact of fossil fuel and renewable energy consumption on economic growth: A nonlinear technique," *Energy*, vol. 226, p. 120357, 2021.
- [2] S. F. Moosavian, D. Borzuei, and A. Ahmadi, "Energy, exergy, environmental and economic analysis of the parabolic solar collector with life cycle assessment for different climate conditions," *Renewable Energy*, vol. 165, pp. 301–320, 2021.
- [3] S. Nižetić, M. Jurčević, M. Arıcı, A. V. Arasu, and G. Xie, "Nano-enhanced phase change materials and fluids in energy applications: A review," *Renewable and Sustainable Energy Reviews*, vol. 129, no. April, 2020.
- [4] R. Kumar, A. K. Pandey, S. Mahendran, B. Aljafari, Z. Ma, et al., "Phase change materials integrated solar desalination system: An innovative approach for sustainable and clean water production and storage," *Renewable and Sustainable Energy Reviews*, vol. 165, no. 5, p. 112611, 2022.
- [5] V. Goel, A. Dwivedi, R. Kumar, R. Kumar, A.K. Pandey, K. Chopra, and VV Tyagi, "PCM-assisted energy storage systems for solar-thermal applications: Review of the associated problems and their mitigation strategies," *Journal of Energy Storage*, vol. 69, no. May, p. 107912, 2023.
- [6] R. Reji Kumar, M. Samykano, A. K. Pandey, K. Kadirgama, and V. V. Tyagi, "Phase change materials and nano-enhanced phase change materials for thermal energy storage in photovoltaic thermal systems: A futuristic approach and its technical challenges," *Renewable and Sustainable Energy Reviews*, vol. 133, no. September, p. 110341, 2020.
- [7] A. S. Abdelrazik, R. Saidur, F. A. Al-Sulaiman, A. Al-Ahmed, and R. Ben-Mansour, "Multiwalled CNT and graphene nanoplatelets based nano-enhanced PCMs: Evaluation for the thermal performance and its implications on the performance of hybrid PV/thermal systems," *Materials Today Communications*, vol. 31, no. May, p. 103618, 2022.
- [8] M. George, A. K. Pandey, N. Abd Rahim, V. V. Tyagi, S. Shahabuddin, and R. Saidur, "A novel polyaniline (PANI)/ paraffin wax nano composite phase change material: Superior transition heat storage capacity, thermal conductivity and thermal reliability," *Solar Energy*, vol. 204, no. April, pp. 448–458, 2020.
- [9] A. K. Pandey, M. George, N. A. Rahim, V. V. Tyagi, S. Shahabuddin, and R. Saidur, "Preparation, characterization and thermophysical properties investigation of A70/polyaniline nanocomposite phase change material for medium temperature solar applications," *Energy and Built Environment*, vol.2, no. 3, pp. 1–7, 2020.
- [10] S. Usharani and V. Rajendran, "Morphologically controlled synthesis, structural and optical properties of CeO2/SnO2 nanocomposites," *Journal of Science: Advanced Materials and Devices*, vol. 2, no. 3, pp. 333–339, 2017.
- [11] L. Yang, J. nan Huang, and F. Zhou, "Thermophysical properties and applications of nano-enhanced PCMs: An update review," *Energy Conversion And Management*, vol. 214, no. April, p. 112876, 2020.
- [12] S. Ranjbar, H. Masoumi, R. Haghighi Khoshkhoo, and M. Mirfendereski, "Experimental investigation of stability and thermal conductivity of phase change materials containing pristine and functionalized multi-walled carbon nanotubes," *Journal of Thermal Analysis and Calorimetry*, vol. 140, no. 5, pp. 2505–2518, 2020.
- [13] R. R. Kumar, "Experimental investigations on thermal properties of copper (II) oxide nanoparticles enhanced inorganic phase change materials for solar thermal energy storage applications," In 2022 Advances in Science and Engineering Technology International Conferences (ASET), Dubai, United Arab Emirates, 2022, pp. 1-6.
- [14] Y. Qu, S. Wang, D. Zhou, and Y. Tian, "Experimental study on thermal conductivity of paraffin-based shape-stabilized phase change material with hybrid carbon nano-additives," *Renewable Energy*, vol. 146, pp. 2637–2645, 2020.
- [15] A. Al-Ahmed, A. Sarı, M. A. J. Mazumder, G. Hekimoğlu, F. A. Al-Sulaiman, and Inamuddin, "Thermal energy storage and thermal conductivity properties of Octadecanol-MWCNT composite PCMs as promising organic heat storage materials," *Scientific Reports*, vol. 10, no. 1, pp. 1–15, 2020.
- [16] R. K. R, M. Samykano, A. K. Pandey, K. Kadirgama, and V. V Tyagi, "A comparative study on thermophysical properties of functionalized and non-functionalized multi-walled carbon nano tubes (MWCNTs) enhanced salt hydrate phase change material," *Solar Energy Materials and Solar Cells*, vol. 240, no. March, p. 111697, 2022.
- [17] I. A. Laghari, M. Samykano, A. K. Pandey, K. Kadirgama, and Y. N. Mishra, "Binary composite (TiO₂Gr) based nanoenhanced organic phase change material: Effect on thermophysical properties," *Journal of Energy Storage*, vol. 51, no. 5, p. 104526, 2022.
- [18] M. Vivekananthan and V. A. Amirtham, "Characterization and thermophysical properties of graphene nanoparticles dispersed erythritol PCM for medium temperature thermal energy storage applications," *Thermochimica Acta*, vol. 676, no. April, pp. 94–103, 2019.
- [19] P. T. Saravanakumar, S. P. Arunkumar, B. B. Mansingh, P. M. Kumar, R. Subbiah, and V. K. Eswarlal, "Investigating the effect of thermal cycling on thermal characteristics of the nano-silica based phase changing material (PCM)," *Materials Today: Proceedings*, vol. 50, pp. 1502–1507, 2021.
- [20] H. Masoumi, R. Haghighi khoshkhoo, and S. M. Mirfendereski, "Modification of physical and thermal characteristics of stearic acid as a phase change material using TiO 2 -nanoparticles," *Thermochimica Acta*, vol. 675, no. December 2018, pp. 9–17, 2019.
- [21] P. Manoj Kumar, D. Sudarvizhi, P.M.J. Stalin, A. Aarif, R. Abhinandhana, et al., "Thermal characteristics analysis of a phase change material under the influence of nanoparticles," *Materials Today: Proceedings*, vol. 45, pp. 7876–7880, 2021.
- [22] A. S. Abdelrazik, R. Saidur, F. A. Al-Sulaiman, A. Al-Ahmed, and R. Ben-Mansour, "Multi-walled CNT and graphene nanoplatelets based nano-enhanced PCMs: Evaluation for the thermal performance and its implications on the performance of hybrid PV/thermal systems," *Materials Today Communications*, vol. 31, no. May, p. 103618, 2022.
- [23] V. P. Kalbande, G. Fating, M. Mohan, K. Rambhad, and A. K. Sinha, "Experimental and theoretical study for suitability of hybrid nano enhanced phase change material for thermal energy storage applications," *Journal of Energy Storage*, vol. 51, no. February, p. 104431, 2022.
- [24] X. Sun, L. Liu, Y. Mo, J. Li, and C. Li, "Enhanced thermal energy storage of a paraffin-based phase change material (PCM) using nano carbons," *Applied Thermal Engineering*, vol. 181, no. March, p. 115992, 2020.
- [25] N. Gupta, A. Kumar, H. Dhasmana, A. Kumar, A. Verma, et al., "Effect of shape and size of carbon materials on the thermophysical properties of magnesium nitrate hexahydrate for solar thermal energy storage applications," *Journal of Energy Storage e*, vol. 41, no. March, p. 102899, 2021.

- [26] B. Kalidasan, A. K. Pandey, S. Rahman, A. Yadav, M. Samykano, and V. V. Tyagi, "Graphene-silver hybrid nanoparticle based organic phase change materials for enhanced thermal energy storage," *Sustainability*, vol. 14, no. 20, pp. 13240, 2022.
- [27] J. Wang, H. Xie, and Z. Xin, "Thermal properties of paraffin-based composites containing multi-walled carbon nanotubes," *Thermochimica Acta*, vol. 488, no. 1–2, pp. 39–42, 2009.
- [28] R. Kumar R, M. Samykano, W.K. Ngui, A.K. Pandey, B. Kalidasan, et al., "Investigation of thermal performance and chemical stability of graphene enhanced phase change material for thermal energy storage," *Physics and Chemistry of the Earth, Parts* A/B/C, vol. 128, no. September, p. 103250, 2022.
- [29] L. Qiu, Y. Ouyang, Y. Feng, and X. Zhang, "Review on micro/nano phase change materials for solar thermal applications," *Renewal Energy*, vol. 140, pp. 513–538, 2019.
- [30] J. Wang, H. Xie, Z. Guo, L. Guan, and Y. Li, "Improved thermal properties of paraffin wax by the addition of TiO2 nanoparticles," *Applied Thermal Engineering*, vol. 73, no. 2, pp. 1541–1547, 2014.
- [31] C. A. Gueymard, "The sun's total and spectral irradiance for solar energy applications and solar radiation models," *Solar Energy*, vol. 76, no. 4, pp. 423–453, 2004.
- [32] P. Makuła, M. Pacia, and W. Macyk, "How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV-Vis spectra," *Journal of Physical Chemistry Letters*, vol. 9, no. 23, pp. 6814–6817, 2018.
- [33] G. Liang, J. Zhang, S. An, J. Tang, S. Ju,, *et al.*, "Phase change material filled hybrid 2D / 3D graphene structure with ultrahigh thermal effusivity for effective thermal management," *Carbon*, vol. 176, pp. 11–20, 2021.