Enhancing thermal energy storage in buildings with novel functionalised MWCNTs-enhanced phase change materials: Towards efficient and stable solutions

Muhammad Aamer Hayat [a,*], Yongkang Chen [a,*], Yongzhen Yang [b], Liang Li [c], Mose Bevilacqua [a]

[a] School of Physics, Engineering and Computer Science, University of Hertfordshire, Hatfield AL10 9AB, United Kingdom
[b] Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, Taiyuan, Shanxi, China
[c] College of Engineering Design and Physical Sciences, Brunel University London, Uxbridge, UB8 3PH, United Kingdom

ARTICLE INFO

ABSTRACT

Phase change materials (PCMs) are a promising panacea to tackle the intermittency of renewable energy sources, but their thermal performance is limited by low thermal conductivity (TC). This pioneering work investigates the potential of organic PCM-enriched surface-modified and un-modified multi-walled carbon nanotubes (MWCNTs) for low-temperature thermal energy storage (TES) applications. The functionalised and un-functionalised MWCNTs enhanced PCM have demonstrated a TC enhancement of 158 % and 147 %, respectively, at 25 °C. However, the TC value of the unmodified MWCNTs-based PCM dropped by 52.5 % after 48 h at 25 °C, while that of the functionalised MWCNTs-based PCM remained stable. A DSC analysis of up to 200 thermal cycles confirmed that the surface-modified and un-modified MWCNTs had no major effect on the peak melting and cooling temperatures of the nano-enhanced PCMs although a minor decrease of 7.5 % and 7.7 % in the melting and crystallisation enthalpies, respectively, was noticed with the inclusion of functionalised MWCNTs. Moreover, functionalised MWCNTs incorporated PCMs have led to increases in specific heat capacity by 23 % with an optimal melting enthalpy value of 229.7 J/g. In addition, no super-cooling, no phase segregation, and a small phase change temperature were noticed with these nano-enhanced PCMs. Finally, no chemical interaction from nano-PCMs was seen in the FT-IR spectra with the incorporation of both functionalised and un-treated MWCNTs. It is evident that the functionalised MWCNT-based PCM has better thermal stability and it offers a promising alternative for improving thermal storage and management capabilities in buildings, contributing to a sustainable and energy-efficient building design.

Introduction

Thermal energy storage (TES) is a crucial component of sustainable energy systems since it enables energy to be stored during periods of low demand and for redeployment during peak times [1–3]. The utilisation of phase-change materials (PCMs) is a highly promising technique to store thermal energy. These substances have the capacity to keep thermal energy in a phase transition in the form of latent heat [4,5]. The poor thermal conductivity (TC) of conventional PCMs, however, restricts their applications and efficiency [6–9]. One effective method for increasing the TC of PCMs is the dispersion of superior thermal conductivity nano additives within PCMs since ordinary millimetre or micron-sized additives have the drawbacks of lower surface energy and a significantly larger density, which are more likely to cause sediments [10–12].

In contrast to metal and metal oxide nanoparticles, carbon-based nanoparticles have recently attracted researchers because their superior TC (i.e., 3000–6600 $W \cdot m^{-1} \cdot K^{-1}$) and their higher surface areas support better intermolecular interaction with PCM molecules [13–15]. Specifically, multi-walled carbon nanotubes (MWCNTs) with excellent TC and significant surface areas have become a possible replacement for the additives of conventional PCMs in recent years [16,17]. In an evaluation of the thermophysical characteristics of carbon and metal oxide nanoparticles enhanced PCMs, Arshad et al. [18,19] discovered that carbon-based nanoparticles outperformed metal oxide particles with a larger increase in TC and an acceptable drop in melting enthalpies. They also incorporated 1 wt% of pristine-MWCNTs (P-MWCNTs) into the organic PCM (paraffin) and found that MWCNTs addition enhanced the TC of the PCM by 66 % with a slight decrease in the enthalpy [20].

Nomenclature

Abbreviations

PAR	Paraffin
MWCNTs	Multiwalled carbon nanotubes
CNTs	Carbon nanotubes
F-MWCNTs	Functionalised-MWCNTs
P-MWCNTs	Pristine-MWCNTs
Nano-PCM	Nanoparticles enhanced PCM
PCM	Phase change material
TES	Thermal energy storage
FTIR	Fourier transform infrared spectroscopy
TC	Thermal conductivity
TEM	Transmission electron microscopy
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
DTG	Derivative thermogravimetry
LH	Latent heat
Conc.	Concentration
Temp.	Temperature

Symbols

ΔH	Latent heat
K	Thermal conductivity
ΔT	Degree of super cooling

Chinnasamy and Cho [21] incorporated MWCNTs into lauryl alcohol as PCM at different concentrations ranging from 1 wt to 5 wt%. The results showed that the degree of supercooling was reduced by the addition of MWCNTs, and the TC was increased by 82.6 % at 5 wt% of CNTs. He et al. [22] investigated the effects of P-MWCNTs on PCM at three different particle concentrations ranging from 1 wt% to 3 wt%. They found that at 3 wt% of MWCNTs, the TC of nano-PCM in solid was raised by 47.30 %, with the reduced supercooling. However, the stability of the nanoparticles, which is a significant aspect of the overall performance of nano-PCMs [23], has been neglected in many previously published studies and needs more investigations.

The major drawback of using MWCNTs is their stability since their hydrophobic nature makes it difficult to disperse in any aqueous solution to obtain a homogeneous mixture [24,25]. The dispersibility of MWCNTs can be improved by functionalising MWCNTs and there are various ways to functionalise MWCNTs with additional groups to improve their dispersibility within enhanced PCMs, including acids [26], amines [27], polymers [28], and other groups. MWCNTs thermal conductivity, stability, and compatibility with PCMs have all been proven to improve by functionalisation [29,30]. Recent studies have shown that acid (H_2SO_4 + HNO_3) functionalisation of MWCNTs improves their thermal conductivity and stability, making them suitable for nano-phase change materials (nano-PCMs). The acid treatment not only increases the surface areas of the MWCNTs but also creates functional groups on their surfaces, which improves their dispersion and interaction with the PCM matrix. These functionalised MWCNTs have been shown to augment the heat transfer properties of PCMs and increase their thermal reliability [31]. Kumar et al. [32] explored pristine multi-walled carbon nanotubes (MWCNTs) and acid functionalised multi-walled carbon nanotubes (F-MWCNTs) as nanoparticles to enhance the thermophysical properties of inorganic salt hydrate PCM. The results showed that the addition of 0.5 wt% MWCNTs improved the thermal conductivity by 50 % compared to pure salt hydrate PCM. Furthermore, the inclusion of 0.5 wt% F-MWCNTs increased TC by 84.78 % compared to pure salt hydrate PCM. In their other investigation [33], they employed varied concentrations of functionalised and un-functionalised MWCNTs with salt hydrate PCM. The incorporation of

0.7 wt% MWCNTs improved the thermal conductivity of PCM to 0.78 W/mK, while 0.7 wt% F-MWCNTs improved the TC of PCM to 0.92 W/m.K, compared to pure salt hydrate PCM, and lowered the light transmittance to 92 % and 93.49 %, respectively. Fikri et al. [34] examined the TC enhancement of organic PCM (A70) by incorporating various mass fractions (0.1 wt–1.0 wt%) of F-MWCNTs. The results found that the thermal conductivity of the composite was enhanced by the addition of 1.0 wt% of F-MWCNTs compared to the pristine PCM. Additionally, it was observed that the nano-PCM was thermally stable up to 200 °C and did not undergo any chemical reactions with the base PCM.

Despite the potential benefits demonstrated by functionalised MWCNTs as nano-enhanced phase change materials (PCMs), a crucial aspect that has received limited consideration is the stability of the MWCNT-enhanced PCM. It is well established that the stability of nanoparticles is a crucial factor in determining the overall performance of nano-PCMs [35,36]. Several methods have been investigated by researchers including pH adjustment, and surfactant addition [37]. However, among these techniques, acid functionalisation was proven as an effective method with better long-term stability of MWCNTs within PCM [12]. In recent literature [29,32–34,38,39], studies on functionalised MWCNTs have emerged, however, the stability of such functionalised MWCNTs has not been fully addressed. Although MWCNTs are not low-cost particles, their exceptional properties such as their high aspect ratio, high TC, and efficient heat transmission properties as compared to other existing nanofillers have the potential to justify their applications in highly efficient nano-PCMs for TES [40].

The novelty of the current research lies in introducing an innovative approach by evaluating the stability and sustainability of the modified and un-modified MWCNTs-based PCM, which has been previously neglected in the literature. Additionally, the primary objective of this study is to conduct a comprehensive examination of the synthesis and thermophysical characterisation of these nano-enhanced PCMs in order to assess their potential for a building's thermal management.

Experimental approaches

Materials

Paraffin (PAR), a typical type of PCM, with a melting temperature range of 27–29 °C, heat storage capacity of 250 kJ/kg, Cp of 2.0 kJ/kg·k and TC of 0.2 W/m·K was utilised and supplied by Rubitherm GmbH, Germany [41]. This particular PCM was chosen because of its closeness to the ideal temperature for the indoor comfort of buildings and its adaptability for various thermal energy storage applications within the specified temperature range. To augment the PCM's thermal conductivity, multi-walled carbon nanotubes (MWCNTs) were selected and supplied by Sigma-Aldrich, UK. A typical MWCNT has an outer diameter of 6–13 nm, a surface area of 220 m^2/g, 98 % trace metals basis, a length range of 2.5–20 µm, and a density of 2.1 g/mL at 25 °C. Furthermore, a surfactant, sodium dodecylbenzene sulfonate (SDBS), bought from Sigma-Aldrich, UK, was used exactly as supplied, with no chemical changes.

Synthesis of functionalised MWCNTs

Fig. 1 shows the schematic of a typical functionalisation process. An acidic treatment of MWCNTs by strong acids was employed, which could effectively introduce oxygen-containing functional groups, such as –COOH on the surfaces of MWCNTs, as shown in Fig. 2. These functional groups can react with the other functional groups which can improve the dispersion of MWCNTs themselves or in a PCM matrix [42]. Three grams of MWCNTs were sonicated for two hours at 60 °C while suspended in a solution of H_2SO_4 and HNO_3 (3:1, v/v). After removing the resulting supernatant, the sediment was neutralised by deionized water washing. The product was then dried for 24 h at 80 °C in a vacuum oven, as shown in Fig. 1, and then ready to be employed.
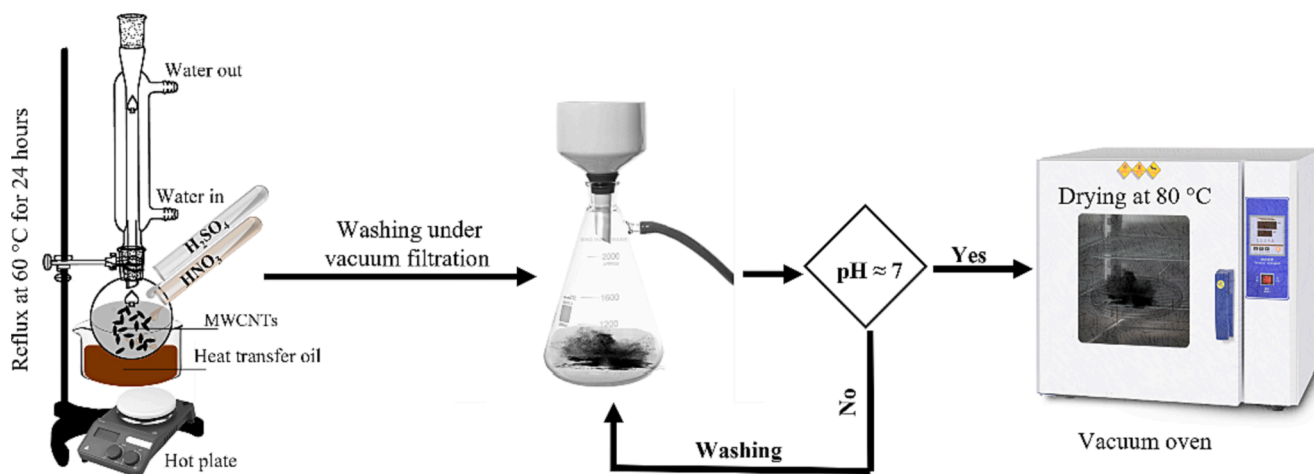
Fig. 1. A typical schematic of functionalisation process of MWCNTs.
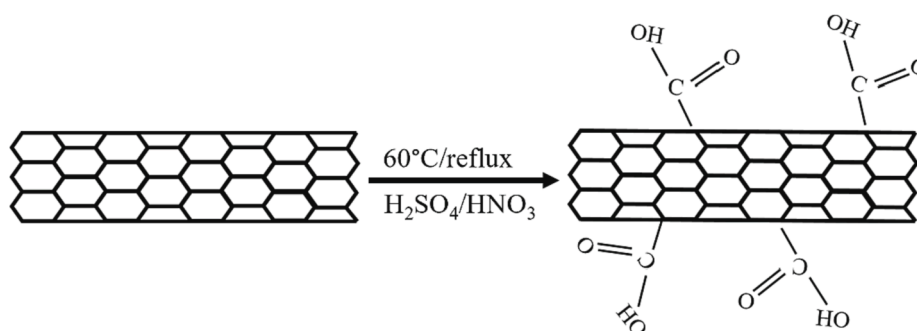

Fig. 2. Schematic grafting of COOH bond after reflux.

Synthesis of nano-paraffin

The nano-enhanced paraffin (nano-PAR) was made by a two-step process, which is widely used in the production of nanofluids [43]. The main objective of this process is to enhance the thermal conductivity of PCM by adding nanoparticles to it, while this newly prepared nano-PCM would have sound stability. The nanoparticles used in this process were functionalised and un-functionalised MWCNTs, which were added at a specific mass concentration. The schematic of a two-step method is shown in Fig. 3.

The first step of the process entailed melting the paraffin in a hot water bath, which was maintained at 65 °C. Then a known quantity of nanoparticles was mixed into a specific amount of PCM. A magnetic stirrer was operated at 500 rpm at 65 °C for 2.5 h to disperse particle clusters and get a homogeneous solution. The purpose of this step is to stir and homogenise the mixture. To improve the dispersion of nano-fillers within the PCM, the mixture was stirred for thirty minutes after adding sodium dodecylbenzene sulfonate (SDBS) separately. Due to its high hydrophilicity, the addition of SDBS during the preparation of nano-PCM served to lower the surface tension of the PCM.

In the second step, samples were sonicated for 40 min at the frequency of 20 kHz and 40 % amplitude with a probe sonicator, to improve nanoparticle dispersion and homogeneity while minimising aggregation and sedimentation. This is an important step that ensures that the nanofillers can be well dispersed and homogeneous in the PCM and that aggregation and sedimentation are minimised. Finally, the temperature of the nano-PCM samples was lowered to 20 °C.

To evaluate the efficacy of the method, visual depictions of the samples were taken before and after they were subjected to a thermal bath for 48 h at 65 °C. Fig. 4(a–b) showed that the untreated MWCNTs
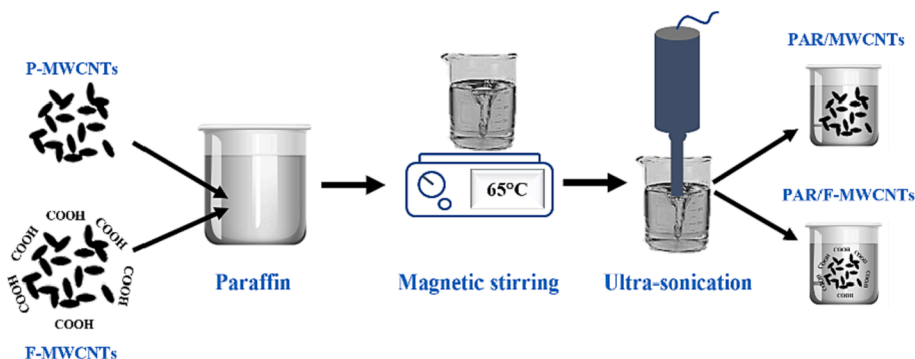

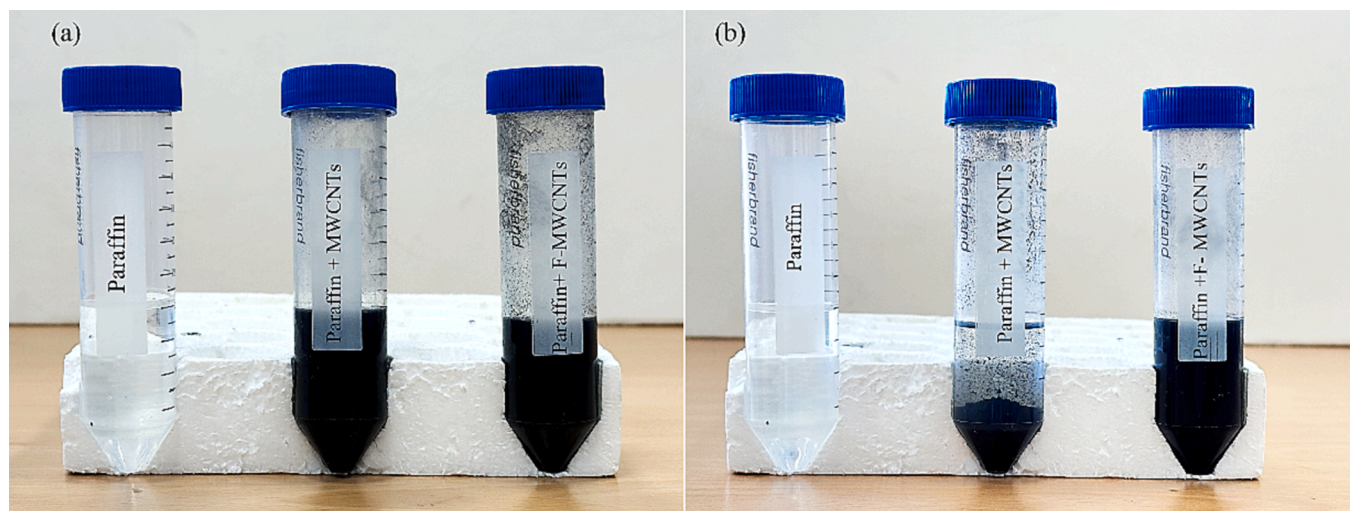**Fig. 3.** Schematic of a two-step method.

Fig. 4. Samples just after sonication (a), and after 48 h of sonication (b).

had been sedimented after 48 h of sonication, while the functionalised MWCNTs remained dispersed, which indicates that the surface modification of MWCNTs may play an important role in the anti-glomeration of MWCNTs themselves and in producing stable and well-dispersed nano-PCMs.

Concentration optimisation

Initially, the pure MWCNTs-based PAR samples were prepared with MWCNT's concentration ranging between 0.2 and 1.0 wt% and then the latent heat (LH) and TC of the prepared samples were measured at 5 °C and 25 °C respectively. An Analysis of Variance (ANOVA) was used to identify the suitable concentration at which TC could be the maximum while an LH reduction was the least. Two responses were analysed in this model; thermal conductivity and latent heat, and both responses were given the same importance. In the analysis, particle concentration (i.e., 0.2 wt% to 1.0 wt%) and temperature (15 °C and 25 °C) have been considered as factors.

Eqs. (1) and (2) demonstrate the mathematical model utilised to establish the relationship between input variables and dependent responses implemented in regression models.

$$TC = -43 - 5.5*(Conc.) + 4.8*(temp.) + 3.1*(Conc.)*(temp.) \quad (1)$$

$$LH = 0.739 - 6.025*(Conc.) + 7.02164E - 18*(temp) \quad (2)$$

Table 1 demonstrates the fit statistics for the initial response, calculated with ANOVA, a Design-Expert software. The regression analysis indicates coefficients of determination (R^2) greater than 0.95 for both responses, with only a small number of data points separating the regression line from the response points. The adjusted R^2 values are also over 0.96, signifying that only a small portion of the variance occurred. To evaluate the model's ability to predict new observations, the

predicted R^2 was examined. The results indicate a correlation of good quality, with a difference of 0.2 between the adjusted and predicted R^2 values. This implies that sufficient signals with satisfactory precision ratios of 61.2354 and 27.6835 for the first and second responses, respectively, could be obtained.

The 3D plot of particle concentration and temperature as a function of TC and LH is shown in Fig. 5. It can be seen that an increase in MWCNT's concentration results in an increase in TC while inducing a slight reduction in LH at both investigated temperatures of 15 °C and 25 °C. It was also observed that the optimal MWCNT concentration for achieving the highest overall TC was 0.984 wt%, which corresponded with a modest decrease in LH by −6.6 %, as shown in Fig. 6. This reduction in LH was deemed acceptable given the significant enhancement in TC of 147.2 % at this concentration. However, since there was no significant difference observed between 0.984 and 1 wt% of MWCNTs, the concentration of 1.0 wt% was chosen for all experiments in this study.

Characterisation techniques

Numerous characterisation techniques were employed to examine the chemical and structural attributes of the base PAR and the PAR augmented with nanofillers, in order to gain a deeper understanding of their properties. These methods included Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential scanning calorimetry (DSC), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and Derivative thermogravimetry (DTG), and Thermal conductivity measurement (TC) apparatus.

TEM (JEOL JEM-F200) was used to examine the microstructures and size distribution of the surface-modified and unmodified MWCNTs. The chemical structures and absorption spectra of the samples at ambient temperature were analysed through FTIR spectroscopy. The FTIR tests were conducted using a Perkin Elmer Frontier spectroscope over a wavelength range of 4000 to 600 cm^{-1}, with accuracy and spectral resolution of 0.01 cm^{-1} and 4 cm^{-1}, correspondingly. The melting and crystallisation temperatures, as well as the enthalpies of PAR and nano-PAR enhanced with un-modified and surface-modified MWNCTs, were investigated using DSC. The Q200 DSC by TA Instrument, UK was utilised to conduct these experiments over a temperature interval of 15–45 °C at a cooling and heating rate of 1 °C min^{-1} in the presence of a nitrogen atmosphere. Calibration of the DSC was performed prior to the experiments by determining the T_{onset} and ΔH_{fusion} of pure indium samples that served as standard references. TGA and DTG were used to test thermal reliability of the pristine PAR and nano-PAR over the
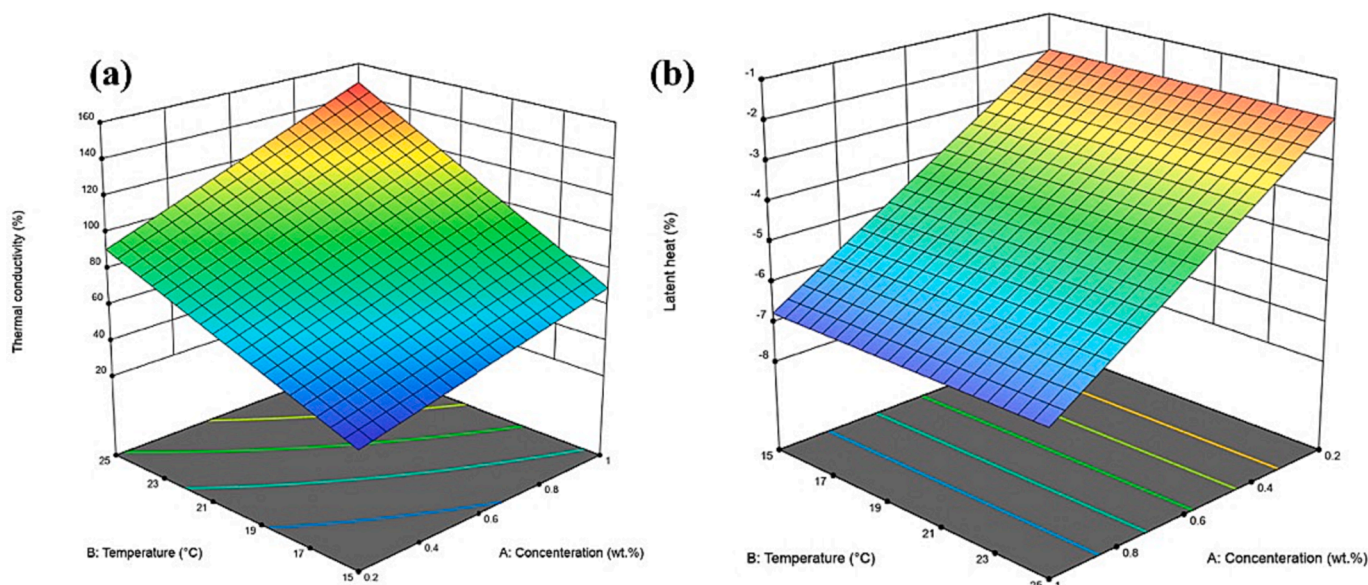
Table 1
The fit statistics for the obtained initial response.

First Response				
	Std. Dev.	2.89	R^2	0.9964
	Mean	86.90	Adjusted R^2	0.9964
	C.V. %	3.32	Predicted R^2	0.9889
			Adequate Precision	61.2354
Second Response	Std. Dev.	0.319	R^2	0.9762
	Mean	−4.35	Adjusted R^2	0.9694
	C.V. %	7.30	Predicted R^2	0.9531
			Adequate Precision	27.6835

Fig. 5. 3D plot of particle concentration and temperature as a function of (a) TC, (b) LH.
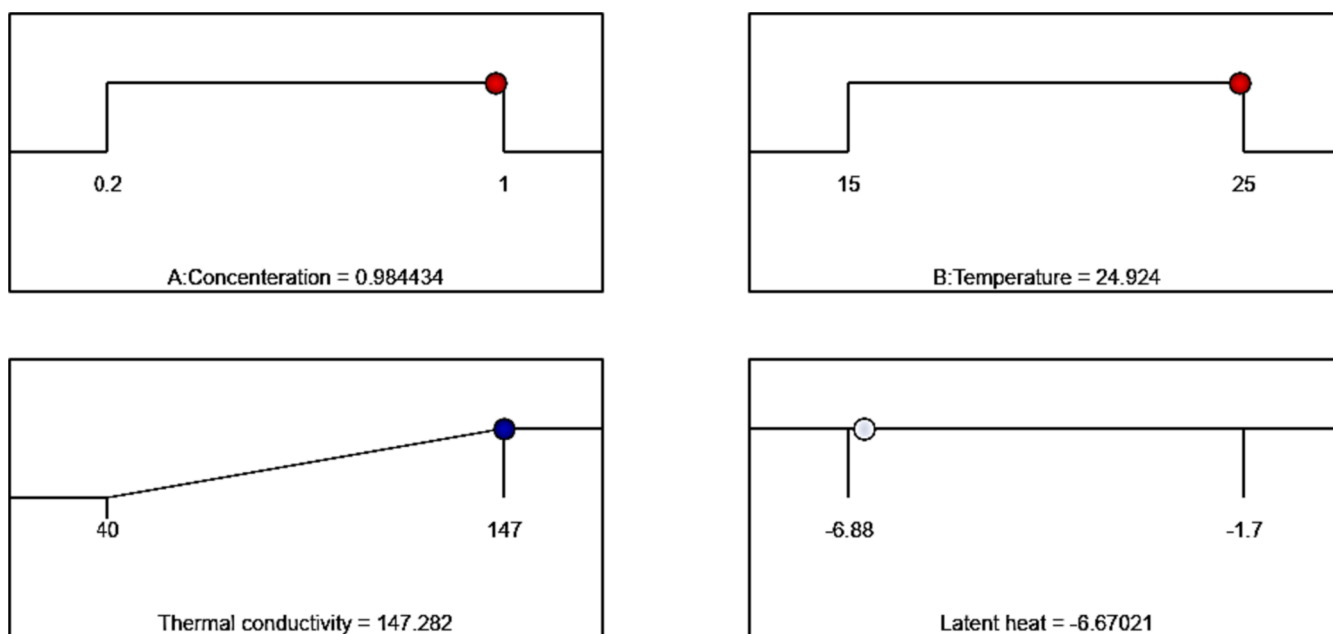

Fig. 6. Typical optimised response predicted by ANOVA.

temperature range of 20–400 °C at a heating rate of $10\,°C\,min^{-1}$ under a nitrogen purge flow rate of 100 mL min^{-1}. The Q-50 TGA by TA Instrument Inc., UK was used for these experiments. The specific heat capacity of the samples was determined using MDSC, by subjecting them to heating over a temperature range of 15 to 45 °C in a DSC instrument with a Tzero hermetic pan and lid (TA Instruments) at a heating rate of 2 °C·min^{-1}. The MDSC yielded Cp data with a precision of approximately ±2 %. The thermal conductivity of all samples was determined using a Hot Disk Thermal Constant Analyzer (TPS-2500S), as shown in Fig. 7. The method is standardised in ISO 22007-2. One sample for each concentration was used and for each sample, measurements were performed three times to ensure the repeatability of results. Then the same samples were left for 48 h in the sample holder to investigate the stability of the results. To test the sample's TC at different temperatures other than the ambient temperature, an aluminium sample holder with a diameter of 2.4 cm, a height of 1.5 cm, and a volume of 7 mL was

developed in accordance with the manufacturer's instructions for the TPS-2500S. The sample's temperature was raised using the sensor 5465 with a radius of 3.089 mm. To ensure an expected accuracy, the instrument was calibrated using manufacturer-supplied stainless-steel samples, and the variation between results obtained experimentally and documented in the instruction manual was below 0.5 %, which is significantly smaller than the equipment measurement error (i.e., ±5 %). Based upon the calibration the uncertainty in measuring thermal conductivity was less than 0.5 %.

Results and interpretation

The impact of functionalised and un-functionalised MWCNTs nano-fillers on the thermophysical characteristics and stability of nano-phase change materials was investigated. Fourier-transform infrared spectroscopy (FT-IR), thermal conductivity testing, differential scanning

Fig. 7. Thermal conductivity setup attached to the thermal bath.

calorimetry (DSC), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA) were used to examine the characteristics of these materials. The findings of this study provide a thorough understanding of the thermophysical properties of nano-enhanced PCMs and valuable information on their potential use in thermal energy storage.

Structure analysis

Both the structures and particle size of functionalised and unfunctionalised MWCNTs were examined with a TEM. The results revealed that the untreated MWCNTs had a size range of 6–9 nm as shown in Fig. 8(a), while the functionalised MWCNTs had an increased size range of 12–15 nm as shown in Fig. 8(b). This increase in size indicates the successful attachment of the –COOH group to the MWCNTs as described in Fig. 2. Similar observations reported in numerous studies [32,34] confirmed that the surface modification process has crafted the COOH group to the MWCNTs. In addition, the F-MWCNTs appear straighter and have smoother surfaces than pure MWCNTs, confirming that the COOH attachment to the MWCNT's surface.

Infrared spectroscopy analysis

The sample's chemical interactions and functional groups were studied using FT-IR spectroscopy between 600 and 4000 cm^{-1} spectra transmittance. Fig. 9 depicts the FT-IR bands of MWCNTs, F-MWCNTs, pure paraffin, PAR/MWCNTs, and PAR/F-MWWCNTs, respectively. It can be seen that no stretching or bending peaks appeared in the MWCNTs infrared spectra due to the absence of functional groups. However, F-MWCNTs depict a broad absorption band around 3400 cm^{-1} owing to O–H stretching of the carboxylic group, and a band around 1635 cm^{-1} corresponds to the C=O stretching vibration, and the band around 1410 cm^{-1} is ascribed to C–H bending, which confirms the acid functionalisation of the P-MWCNTs [26]. The pristine paraffin spectra contained three transmittance peaks between 2800 and 3000 cm^{-1}, which demonstrated mild asymmetrical stretching vibrations of –CH$_2$– and –CH$_3$ groups. The peak at 1490 cm^{-1} in PAR revealed a substantial amount of C–H scissoring of the alkane groups. The peak at 750 cm^{-1} was attributed to the rocking vibration of C–H in the long-chain methyl group [44,45]. FT-IR spectra for nanocomposites have been confirmed in recent research with similar patterns [32–34]. The paraffin incorporated with un-functionalised and functionalised MWCNTs did not show any new peak confirming only physical interactions between paraffin and MWCNTs without chemical interactions. Moreover, the PAR/F-MWCNTs showed no peak from F-MWCNTs, which could be due to the very low concentration of F-MWCNTs within the paraffin.

Thermodynamic properties

Thermal properties during melting and crystallisation of pristine PCM and CNTs-enhanced PCM were investigated between the temperature range of 15 °C to 45 °C with a DSC. The solidification and melting phenomena of the pure PAR and the PAR impregnated with the modified and the unmodified MWCNTs are shown in Fig. 10. Moreover, the
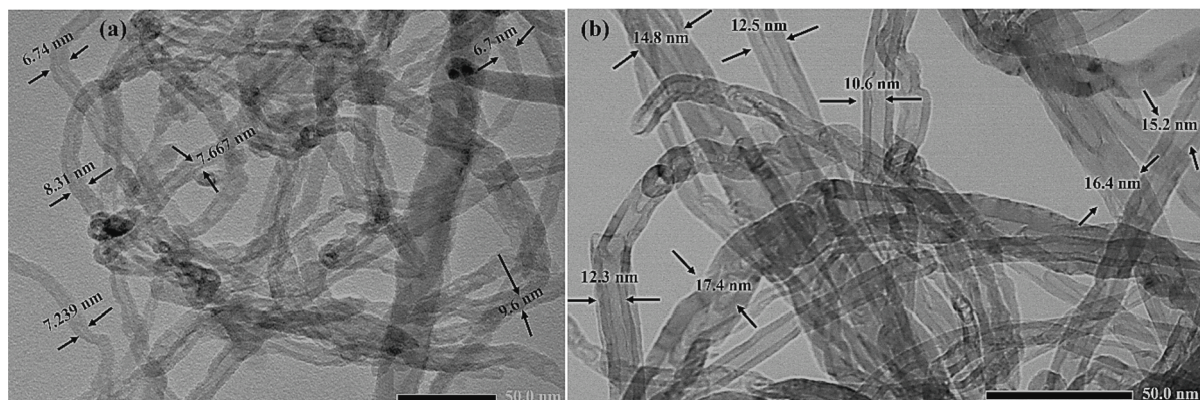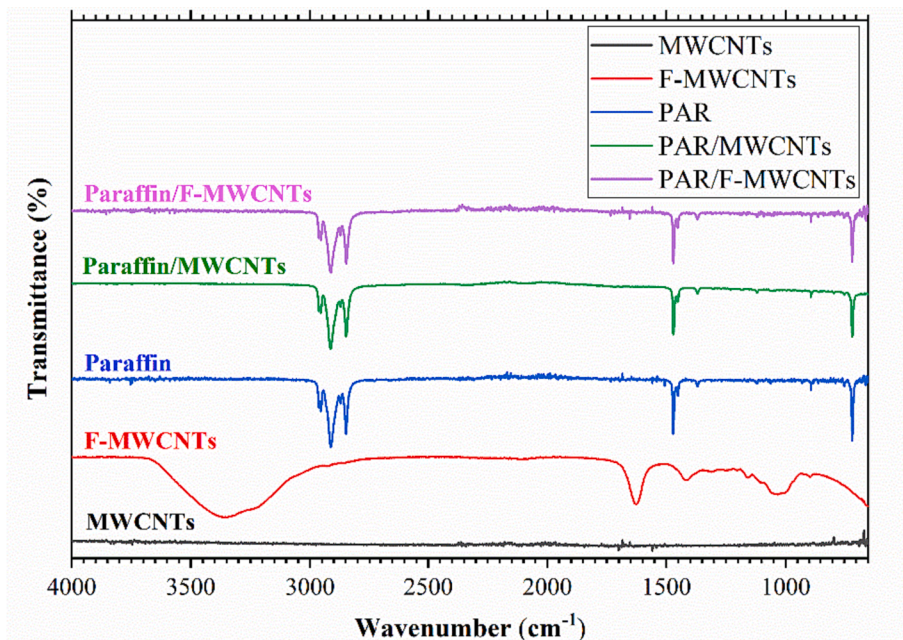

Fig. 8. TEM images of (a) P-MWCNTs, (b) F-MWCNTs.

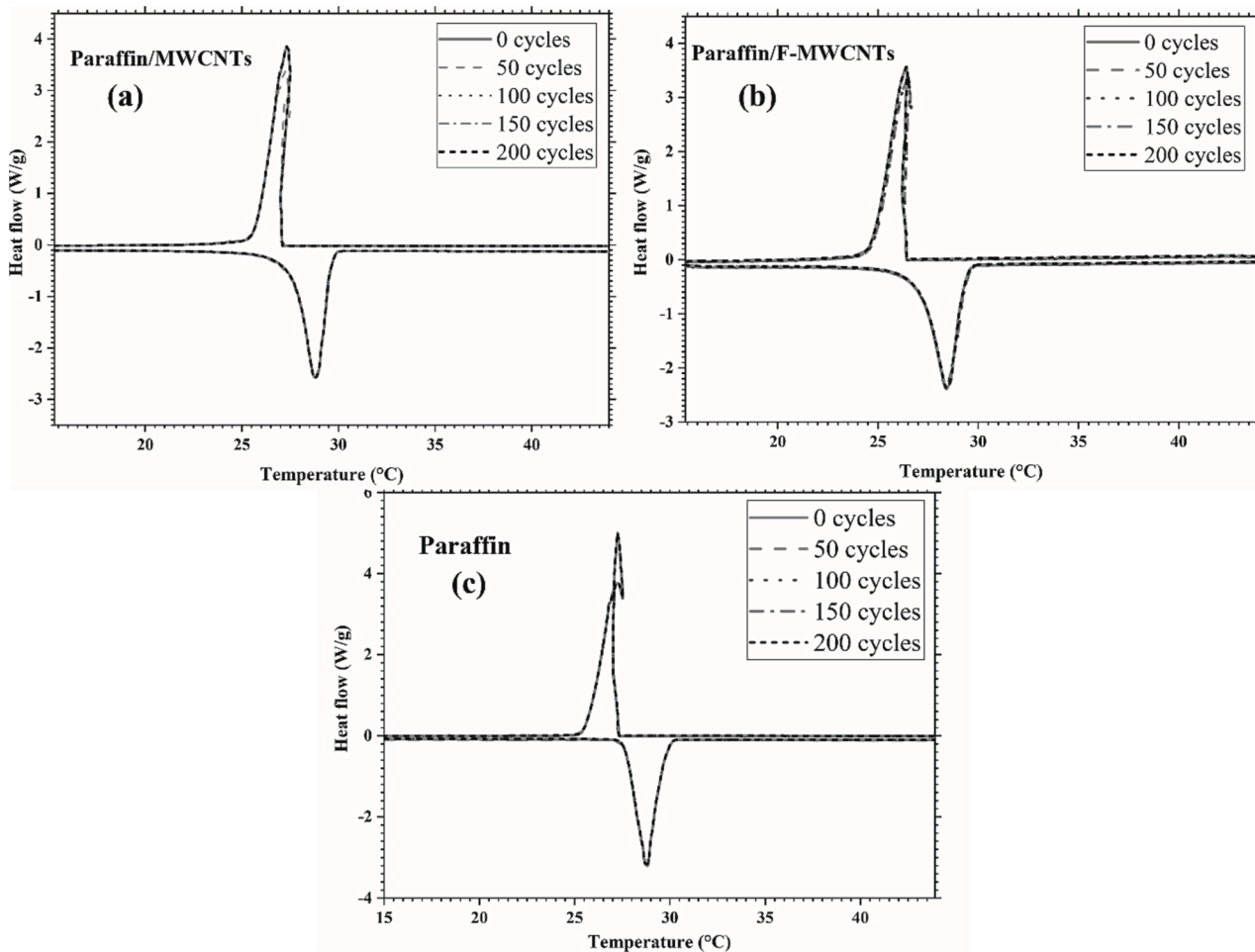**Fig. 9.** FT-IR spectra of functionalised and untreated samples.

Fig. 10. DSC curves of (a) PAR/MWCNTs, (b) PAR/F-MWCNTs and (c) pure PAR.

Table 2
Thermal properties of samples.

Sample	Melting		Crystallisation		
	T_{peak}	ΔHm	T_{peak}	ΔHc	ΔT
PAR	28.92	248.4	27.26	251.7	1.66
PAR/MWCNTS	28.96	231.3	27.35	233.3	1.61
PAR/F-MWCNTS	28.46	229.7	26.78	232.2	1.68

T_{peak}: peak temperature (°C), ΔHm: latent heat of melting (J/g), ΔHc: latent heat of crystallisation (J/g), ΔT: super–cooling degree (°C).

melting and crystallisation values of latent heat, temperatures, and degree of supercooling for all samples are provided in Table 2. It was observed that the inclusion of functionalised and un-functionalised MWCNTs into the PCM has only a minute impact on melting and crystallisation temperatures. However, because of the non-melting enthalpies of the CNTs a small decline in the melting and solidification enthalpies was noticed with the incorporation of treated and untreated CNTs [46]. In the melting process, only one endothermic peak was observed for all the samples, which shows the isomorphous crystalline structure of the pristine PCM and the CNTs-enhanced PCM. Similarly, one exothermic peak can be seen during the cooling of treated and untreated CNTs based PCM, which confirms that the addition of both additives does not affect the solidification process. Two peaks were noted for pure PCM during the solidification process, and this could be due to the metastable rotator phase, which appears prior to final crystallisation due to heterogeneous nucleation [47,48]. To further verify the thermal stability of all the samples they were exposed to 200 thermal cycles with a DSC. There was no significant change which was reflected in the thermal properties of the pure PCM and nano-PCMs, as shown in Fig. 10 (a–c). Overall, less than 1 % variation in the phase transition temperatures and enthalpies was observed after 200 cycles, suggesting a promising stability level for TES applications in buildings.

The supercooling degree (ΔT) of pure paraffin and composites is stated in Table 2. ΔT was reduced slightly by the incorporation of pristine MWCNTs into the PCM and for modified MWCNTs-based PCM a minor increase in ΔT, which is almost negligible [49]. The overall decline in ΔT shows the significance of nanomaterials as nucleating agents for efficient surface adsorption and homogenous nucleation.

The specific heat capacity (Cp) was measured in the liquid and solid forms when the temperature rises from 15 °C to 45 °C as shown in Fig. 11 (a-b). The Cp is usually ignored by researchers since it has a low thermal energy density during a sensible heat storage process and a

comparatively little effect on the total amount of thermal energy that can be retained using these materials. However, the Cp still influences other variables that influence the total amount of stored heat in a given temperature range when such materials are used [44].

It can be seen from Fig. 11 that in the solid phase, from 15 °C to 25 °C the Cp of the pure PAR and nano-PAR improved steadily with an increase in temperature. On the other hand, it remained constant during the liquid state from 35 °C to 45 °C. Furthermore, the results showed that the nano-enhanced PCM depicts higher Cp compared to the pure PCM. The Cp values of the pure PAR and PAR with treated and untreated MWCNTs at 25 °C and 45 °C were 3.132 J/g °C, 3.838 J/g °C, 3.858 J/g °C and 1.89 J/g °C, 2.505 J/g °C, 2.525 J/g °C, respectively.

Thermal durability

The thermal stability of pristine PCM and nano-PCMs was analysed with TGA and DTG. Fig. 12 (a-b) show typical TGA and DTG curves of the PAR and nano-PAR. It can be seen from the TGA analysis in Fig. 12 (a) that neither the PAR nor its composites exhibit any noticeable reduction in mass up to ~ 130 °C. Then the weight loss became more prominent as the temperature continuously increased, achieving its highest degradation temperature while having left a fixed residue behind. The degradation temperature for PAR impregnated with MWCNTs and F-MWCNTs was 228.46 with 1.438 % residue and 230.39 °C with 1.861 % residue, respectively. The decomposition occurred as a result of paraffin evaporation, in which hydrocarbon chains disintegrated into monomers. In addition, the incorporation of pure and modified MWCNTs increased the maximum degradation temperature of the nano-PAR because the highly thermally conductive nanoparticles had fastened and uniformed the heat transfer. In essence, the nanoparticles formed a shielding layer on the surface of the PAR preventing vaporisation during thermal deprivation. The DTG analysis in Fig. 12b shows that pure PAR and nano-PAR have almost analogous thermal decompositions. TGA and DTG tests revealed that the functionalised nano-PCMs remained stable and did not lose weight until 130 °C, confirming that the produced new materials have the potential to be used for TES. For their application in buildings, they could be encapsulated in a suitable material or supporting structure that ensures the confinement of leakage problems while allowing controlled charging and discharging of thermal energy as needed.

Thermal conductivity
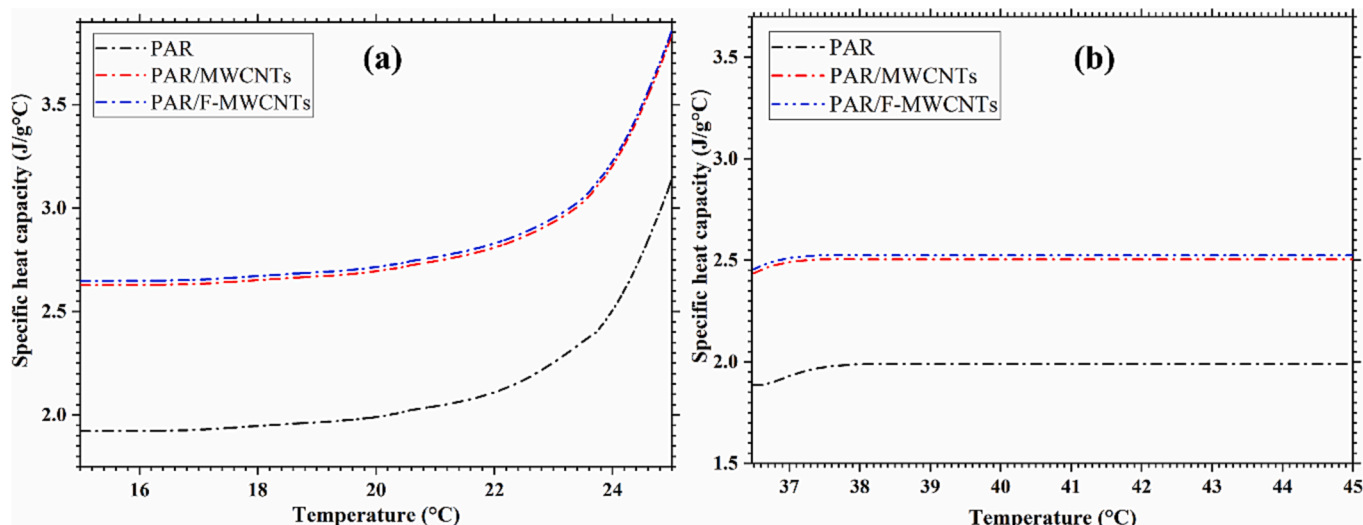
Thermal conductivity is an important thermal property that

Fig. 11. The specific heat capacity (Cp) of PAR and nano-PAR (a) solid, and (b) liquid.
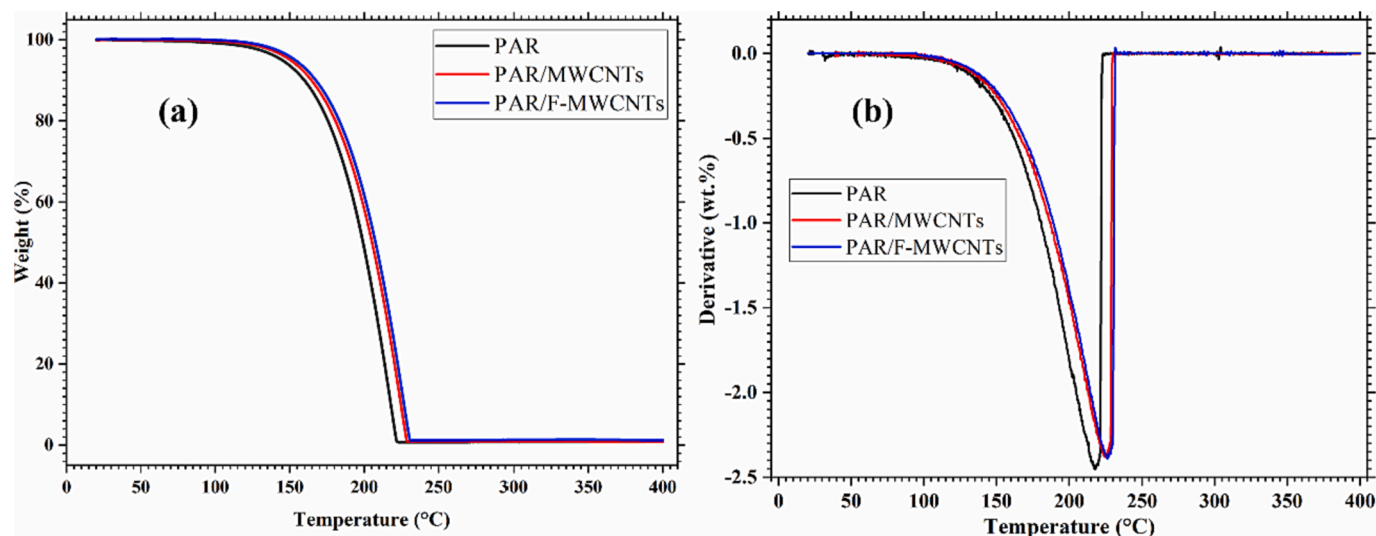
Fig. 12. Analysis of thermal durability of pure PCM and nano-PAR (a) TGA curves, (b) DTG curves.

influences the performance of nano-PCMs. The higher TC accelerates the heat transfer and improves the heating and cooling performance of the PCMs, while low TC slows the charging and discharging rates of the PCM, which results in the poor performance of the TES materials [50]. The TC of the pristine PCM, PCM/MWCNTs, and PCM/F-MWCNTs was measured for freshly prepared samples and on samples that had been stored in a thermal bath for 48 h, to assess the reproducibility of the results. The tests were carried out in both liquid and solid states at temperatures varying from 5 °C to 55 °C, to provide a comprehensive understanding of the TC behaviour of these investigated materials.

As shown in Fig. 13, at 5 °C, the TC value of the pure PAR was recorded as 0.195 W/m.K. However, freshly produced nano-PCM samples with untreated MWCNTs and treated MWCNTs demonstrated a 69.2 % and 79.4 % rise in TC, respectively. At 15 °C, the TC remained relatively unchanged for all the freshly prepared samples as they were in a solid state and displayed their orderly microstructure. After being kept in a water bath for 48 h, the TC of the PAR with untreated MWCNTs reduced significantly, with values of 0.233 W/m.K and 0.236 W/m.K at 5 °C and 15 °C, correspondingly, possibly due to their hydrophobicity. In contrast, the PAR with functionalised MWCNTs showed little to no change in their TC after the same period, as shown in Fig. 13.

As can be seen in Fig. 13, an abrupt increase of TC at 25 °C, occurred for all the samples apart from the measurement taken for the untreated

MWCNTs after 48 h. Such a sudden increase near the melting temperature of PCM was because near melting temperature the crystalline arrangement of the PAR became unstable, and a rise in temperature accelerated the molecular vibration in the lattice, so the TC values of pristine PAR and nano-PAR increased brusquely near the melting temperature (i.e., 25 °C). In the liquid state at 35 °C, 45 °C and 55 °C the TC values taken for all samples were below 0.2 W/m.K. This is because the organised microstructure present in the solids changes to a disorganized one in the liquids. Heat conduction in solids is primarily due to lattice vibrations, where molecules move within their lattice structures. Solids have a greater TC value compared with liquids as they possess greater free-electron motion and lattice vibrations. Overall, F-MWCNTs outperformed P-MWCNTs in terms of stability and TC. This is due to the –COOH groups adhesion to the surfaces of MWCNTs, which results in improved dispersion and bonding strength with the PCM matrix. Furthermore, functionalisation reduces surface resistance and improves the interaction between nanoparticles and PCM, hence increasing heat conductivity [33].

The thermal conductivity improvement after the addition of MWCNTs was also calculated and expressed as a percentage enhancement at various temperatures from 5 °C to 55 °C, as depicted in Fig. 14. The TC enhancement ratio was determined using Equation (3).
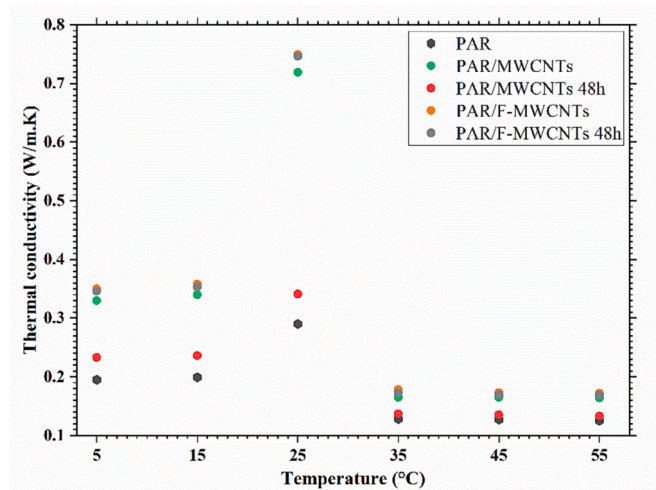

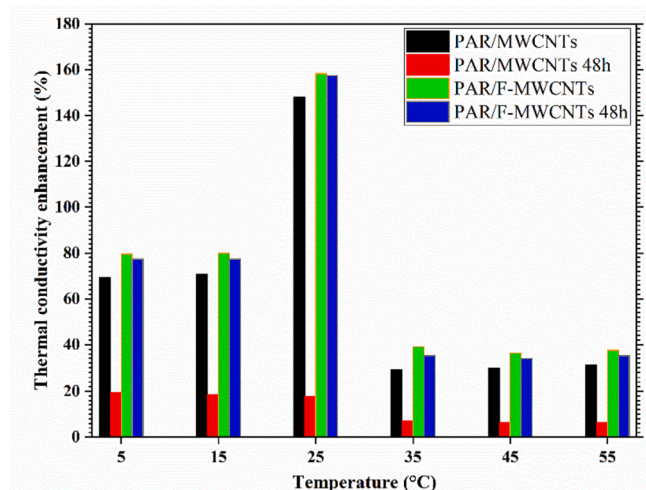**Fig. 13.** Thermal conductivity of fresh samples and samples after 48 h.

Fig. 14. Thermal conductivity enhancement of fresh samples and after 48 h.

$$\eta = \frac{K_{nano-PCM} - K_{PCM}}{K_{PCM}} * 100 \qquad (3)$$

where, $K_{nano-PCM}$ and K_{PCM} are the thermal conductivities of nano-PCMs and pure PCM, correspondingly.

The percentage enhancement of the TC values of pristine MWCNTs was 69.23 % at 5 °C and 70.85 % at 15 °C, whereas the percentage enhancement of F-MWCNTs was 79.49 % at 5 °C and 79.90 % at 15 °C. The TC enhancement of the P-MWCNTs after 48 h reduced significantly which demonstrates the poor stability of pristine MWCNTs. However, the functionalised MWCNTs maintain the TC level of the PCMs after 48 h and no significant change was noticed, indicating a good stability of functionalised MWCNT PCM. The maximum enhancement of the TC was observed for functionalised MWCNTs at 25 °C with an enhancement factor of 158 %.

At 35 °C, the thermal conductivity value of the pristine MWCNTs decreased by 28.9 % compared to its original value. The functionalised MWCNTs, on the other hand, showed a 39.06 % enhancement in thermal conductivity. At 45 °C and 55 °C, the improvement in TC for both pristine MWCNTs and functionalised MWCNTs showed a similar trend, with the functionalised MWCNTs exhibiting a higher thermal conductivity value compared to the pristine MWCNTs. Overall, the F-MWCNTs demonstrated greater enhancement since acid modification of MWCNTs lowed the surface resistance and increased the contact between PCM and nanofillers which improves the TC enhancement. In addition, the covalent connection formed by functionalised MWCNTs between nanoparticles and PCM is also an important factor in improving the TC [32]. This demonstrates how functionalised MWCNTs can improve PCMs thermal conductivity and preserve the TC level over time.

Furthermore, the greater TC achieved with F-MWCNTs may be ascribed to physical changes in the MWCNTs during the functionalisation procedure. Since functionalization caused structural changes in the F-MWCNTs which may have resulted in reduced agglomeration and improved alignment. These modifications have led to uniform dispersion of MWCNTs within PCM, improved thermal channels within the PCM, lowering thermal resistance and increasing TC of nano-PCM.

Heat transfer analysis

The thermal performance of pure PCM and nano-PCMs was evaluated using infrared thermography (IRT). Typical IR thermal images of pure PCM and PCM incorporated with MWCNTs and F-MWCNTs are shown in Fig. 15, which shows the temperature distribution during a melting process of samples at 5 W for different time durations. The temperature of nano-PCMs was observed higher than that of pure PCM during the first 20 min, which shows that pure and functionalised MWCNTs improved the TC of composite PCMs. The pure paraffin fully melts after 80 min, and its temperature is substantially greater than the nano-PCMs, which are not fully melted. This is because the inclusion of MWCNTs improves viscosity while decreasing convective heat transfer. The phase transition duration of nano-PCMs is substantially longer than that of pure PCM since the high thermal conductive MWCNTs reduced the convection heat transfer and the consistently lower temperature of nano-PCMs is advantageous for TES applications in buildings [51]. In the early phases of melting, when the temperature differential between the PCM and the heat source is most significant, conductive heat transfer is important. The significance of convective heat transfer, which gains prominence as the phase change proceeds, is not inherently diminished, but it does highlight the importance of thermal conductivity in the initial phases of melting.

Conclusions and future work

In this experimental investigation thermal, chemical, and physical characterisation analyses have been performed for the functionalised and un-functionalised MWCNTs-based organic PCMs. The critical
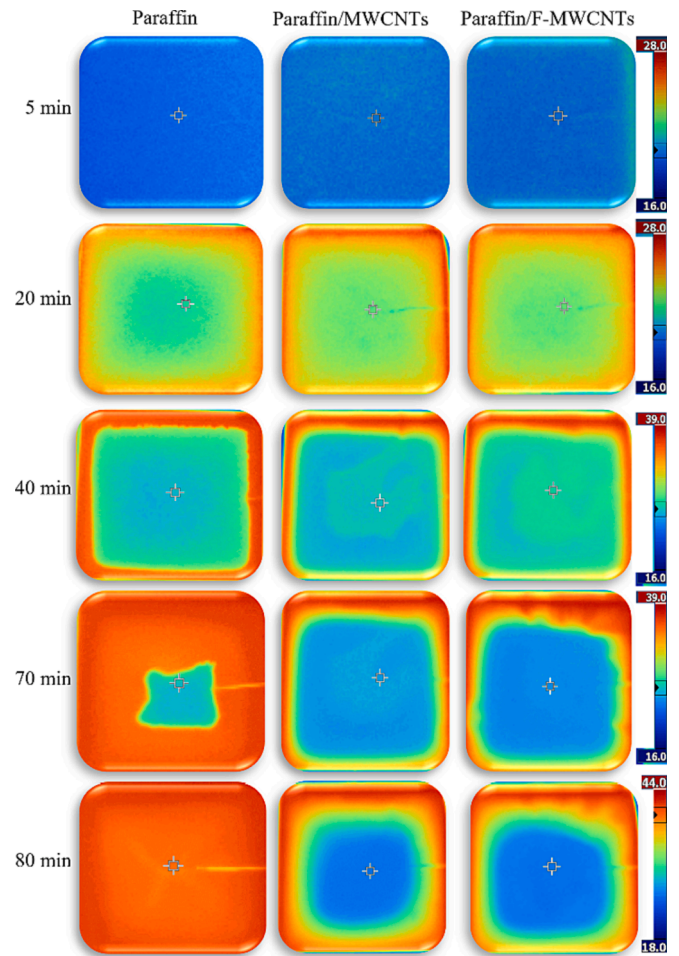

Fig. 15. Images of infrared thermography during melting of pure PCM and nano-PCMs.

findings from this study are as follows:

- The physical observation of the nano-PCM samples has shown that surface-modified MWCNTs remain dispersed in the paraffin after 48 h but pristine MWCNTs were sedimented in the paraffin. It is evident that surface modification of MWCNTs with an acidic treatment has resulted in uniform and sustainable dispersibility within a PCM.
- The FT-IR spectrum has indicated that the inclusion of pristine and functionalised MWCNTS into PCMs has no chemical interactions between MWCNTs and PCMs since no new peak was noticed from the nano-PCMs spectra.
- DSC analysis depicted that up to 200 thermal cycles both the melting and crystallisation temperatures of the nano-enhanced PAR samples remained almost the same compared to those of the pristine PAR, indicating good stability of this new functionalised MWCNT-enhanced PCM. Nevertheless, the latent heat of melting and cooling was reduced by 6.8 % and 7.3 % with the addition of untreated MWCNTs respectively and by 7.3 % and 7.7 % with functionalised MWCNTs, correspondingly. The melting enthalpy of functionalised and un-functionalised MWCNTs-based PCMs was 229.7 J/g and 231.3 J/g, respectively.
- The specific heat capacity was enhanced with the inclusion of MWCNTs, with a maximum enhancement of 23 % by functionalised MWCNTs-based PAR. This improvement is critical since it indicates that this type of nano-PCM will be capable of storing more thermal energy per unit mass, which improves this material's capacity to absorb and release heat while maintaining a relatively constant

temperature, and thus enhances their potential in thermal energy storage systems.

- TGA and DTG investigation showed that the thermal and chemical stability of PAR increased with the incorporation of MCNTs, as there was no weight loss noticed in the samples up to 130 °C.
- The thermal conductivity (TC) values of all the samples after 0 and 48 h of sonication revealed that the untreated MWCNTs significantly dropped their TC value from 0.719 W/m.K to 0.341 W/m.K (i.e., 52.5 %) after 48 h, and the TC value of surface-modified MWCNTs remained almost the same after 48 h. The maximum improvement of 158 % in TC was noticed for F-MWCNTs at 25 °C with a TC value of 0.749 W/m.K.
- IR thermographic images of all samples revealed homogeneous melting and temperature distribution. Because of the uniform dispersion of nanofillers, the addition of MWCNTs resulted in an increase in melting time.

Finally, the functionalised MWCNTs-based PCM showed long-term stability and maximum increase in the thermal conductivity with a minimum effect on its latent heat even after 200 thermal cycles, these exceptional thermal characteristics of F-MWCNTs-based PCM depict that the developed nano-PCM has the potential to significantly improve thermal management and energy efficacy in buildings. F-MWCNTs could be investigated further by inserting them into inorganic PCM or by combining them with other low-cost nano additives to improve the thermophysical properties of PCM. The enhancement of certain properties such as specific heat capacity, density, latent heat, and TC are important for an ideal nano-PCM. It is very challenging to balance these properties while ensuring cost-efficacy, stability over repeated thermal cycles, compatibility with other system components, and environmentally friendly characteristics. To address these challenges, advanced thermal engineering techniques, optimised thermal energy storage system design, and novel approaches to controlled energy input and extraction are required.

CRediT authorship contribution statement

Muhammad Aamer Hayat: Conceptualisation, Writing - original draft, revising the manuscript. **Yongkang Chen:** Review, editing & supervision. **Yongzhen Yang:** Supervision. **Liang Li:** Supervision. **Mose Bevilacqua:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

References

[1] M.M. Farouq, C. Jimenez-Bescos, S. Riffat, P.A. Mirzaei, Development and thermal characteristic study of an integrated phase change material earthbag unit for temporary housings, Energy Build. 284 (2023), 112852.

[2] P.D. Lund, J. Lindgren, J. Mikkola, J. Salpakari, Review of energy system flexibility measures to enable high levels of variable renewable electricity, Renew. Sustain. Energy Rev. 45 (2015) 785–807.

[3] A. Evans, V. Strezov, T.J. Evans, Assessment of utility energy storage options for increased renewable energy penetration, Renew. Sustain. Energy Rev. 16 (2012) 4141–4147.

[4] H. Liu, K. Sun, X. Shi, H. Yang, H. Dong, Y. Kou, P. Das, Z.-S. Wu, Q. Shi, Two-dimensional materials and their derivatives for high performance phase change materials: emerging trends and challenges, Energy Storage Mater. 42 (2021) 845–870.

[5] B. Cárdenas, N. León, High temperature latent heat thermal energy storage: Phase change materials, design considerations and performance enhancement techniques, Renew. Sustain. Energy Rev. 27 (2013) 724–737.

[6] Z.-R. Li, N. Hu, L.-W. Fan, Nanocomposite phase change materials for high-performance thermal energy storage: A critical review, Energy Storage Mater. (2022).

[7] K. Guedri, F. Riaz, B.M. Fadhl, M.K. Agrawal, N.A. Shah, B.M. Makhdoum, H. M. Youshanlouei, Use of nano-encapsulated phase change material mixed with water for natural convection cooling in combination with nickel foam, Therm. Sci. Eng. Prog. (2023), 101934.

[8] M.A. Hayat, Y. Chen, M. Bevilacqua, L. Li, Y. Yang, Characteristics and potential applications of nano-enhanced phase change materials: A critical review on recent developments, Sustain. Energy Technol. Assess. 50 (2022) 101799.

[9] I. Afaynou, H. Faraji, K. Choukairy, A. Arshad, M. Arıcı, Heat transfer enhancement of phase-change materials (PCMs) based thermal management systems for electronic components: A review of recent advances, Int. Commun Heat Mass Transfer. 143 (2023), 106690.

[10] Z. Ge, Y. Li, D. Li, Z. Sun, Y. Jin, C. Liu, C. Li, G. Leng, Y. Ding, Thermal energy storage: challenges and the role of particle technology, Particuology. 15 (2014) 2–8.

[11] H. Nazir, M. Batool, F.J.B. Osorio, M. Isaza-Ruiz, X. Xu, K. Vignarooban, P. Phelan, A.M. Kannan, Recent developments in phase change materials for energy storage applications: A review, Int. J. Heat Mass Transf. 129 (2019) 491–523.

[12] M.A. Kibria, M.R. Anisur, M.H. Mahfuz, R. Saidur, I. Metselaar, A review on thermophysical properties of nanoparticle dispersed phase change materials, Energy Convers. Manag. 95 (2015) 69–89.

[13] J. Wang, H. Xie, Z. Xin, Y. Li, L. Chen, Enhancing thermal conductivity of palmitic acid based phase change materials with carbon nanotubes as fillers, Solar Energy 84 (2010) 339–344.

[14] K.W. Shah, A review on enhancement of phase change materials-A nanomaterials perspective, Energy Build. 175 (2018) 57–68.

[15] A.K. Gupta, G. Mishra, S. Singh, Numerical study of MWCNT enhanced PCM melting through a heated undulated wall in the latent heat storage unit, Therm. Sci. Eng. Prog. 27 (2022), 101172.

[16] U.N. Temel, S. Kurtulus, M. Parlak, K. Yapici, Size-dependent thermal properties of multi-walled carbon nanotubes embedded in phase change materials, J. Therm. Anal. Calorim. 132 (2018) 631–641.

[17] A.G. Olabi, T. Wilberforce, K. Elsaid, E.T. Sayed, M. Ramadan, S.M.A. Rahman, M. A. Abdelkareem, Recent progress on carbon-based nanomaterial for phase change materials: prospects and challenges, Therm. Sci. Eng. Prog. 23 (2021), 100920.

[18] A. Arshad, M. Jabbal, Y. Yan, Preparation and characteristics evaluation of mono and hybrid nano-enhanced phase change materials (NePCMs) for thermal management of microelectronics, Energy Convers. Manag. 205 (2020), 112444.

[19] A. Arshad, M. Jabbal, L. Shi, J. Darkwa, N.J. Weston, Y. Yan, Development of TiO2/RT–35HC based nanocomposite phase change materials (NCPCMs) for thermal management applications, Sustain. Energy Technol. Assess. 43 (2021), 100865.

[20] A. Arshad, M. Jabbal, L. Shi, Y. Yan, Thermophysical characteristics and enhancement analysis of carbon-additives phase change mono and hybrid materials for thermal management of electronic devices, J. Energy Storage 34 (2021), 102231, https://doi.org/10.1016/j.est.2020.102231.

[21] V. Chinnasamy, H. Cho, Investigation on thermal properties enhancement of lauryl alcohol with multi-walled carbon nanotubes as phase change material for thermal energy storage, Case Stud. Therm. Eng. 31 (2022), 101826.

[22] M. He, L. Yang, W. Lin, J. Chen, X. Mao, Z. Ma, Preparation, thermal characterization and examination of phase change materials (PCMs) enhanced by carbon-based nanoparticles for solar thermal energy storage, J. Energy Storage 25 (2019), 100874.

[23] R. Bharathiraja, T. Ramkumar, M. Selvakumar, Studies on the thermal characteristics of nano-enhanced paraffin wax phase change material (PCM) for thermal storage applications, J. Energy Storage 73 (2023), 109216.

[24] U. Yogeswaran, S.-M. Chen, Separation and concentration effect of f-MWCNTs on electrocatalytic responses of ascorbic acid, dopamine and uric acid at f-MWCNTs incorporated with poly (neutral red) composite films, Electrochim. Acta 52 (2007) 5985–5996.

[25] G.K. Amudhalapalli, J.K. Devanuri, Synthesis, characterization, thermophysical properties, stability and applications of nanoparticle enhanced phase change materials–A comprehensive review, Therm. Sci. Eng. Prog. 28 (2022), 101049.

[26] Z. Cao, L. Qiu, Y. Yang, Y. Chen, X. Liu, The surface modifications of multi-walled carbon nanotubes for multi-walled carbon nanotube/poly (ether ether ketone) composites, Appl. Surf. Sci. 353 (2015) 873–881.

[27] A. Rahimpour, M. Jahanshahi, S. Khalili, A. Mollahosseini, A. Zirepour, B. Rajaeian, Novel functionalized carbon nanotubes for improving the surface properties of polyethersulfone (PES) membrane, Desalination 286 (2012) 99–107.

[28] C.-C. Teng, C.-C.-M. Ma, C.-H. Lu, S.-Y. Yang, S.-H. Lee, M.-C. Hsiao, M.-Y. Yen, K.-C. Chiou, T.-M. Lee, Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites, Carbon N.Y. 49 (2011) 5107–5116.

[29] S. Shen, S. Tan, S. Wu, C. Guo, J. Liang, Q. Yang, G. Xu, J. Deng, The effects of modified carbon nanotubes on the thermal properties of erythritol as phase change materials, Energy Convers. Manag. 157 (2018) 41–48.

[30] Q. Tang, J. Sun, S. Yu, G. Wang, Improving thermal conductivity and decreasing supercooling of paraffin phase change materials by n-octadecylamine-functionalized multi-walled carbon nanotubes, RSC Adv. 4 (2014) 36584–36590.

[31] L. Han, X. Zhang, J. Ji, K. Ma, Research progress on the influence of nano-additives on phase change materials, J. Energy Storage 55 (2022), 105807.

[32] R. Kumar, A.K. Pandey, M. Samykano, Y.N. Mishra, R.V. Mohan, K. Sharma, V. V. Tyagi, Effect of surfactant on functionalized multi-walled carbon nano tubes enhanced salt hydrate phase change material, J. Energy Storage 55 (2022), 105654.

[33] R. Kumar, M. Samykano, A.K. Pandey, K. Kadirgama, 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 Mater. Solar Cells 240 (2022), 111697.

[34] M.A. Fikri, A.K. Pandey, M. Samykano, K. Kadirgama, M. George, R. Saidur, J. Selvaraj, N. Abd Rahim, K. Sharma, V.V. Tyagi, Thermal conductivity, reliability, and stability assessment of phase change material (PCM) doped with functionalized multi-wall carbon nanotubes (FMWCNTs), J. Energy Storage. 50 (2022), 104676.

[35] H. Babar, H.M. Ali, Towards hybrid nanofluids: preparation, thermophysical properties, applications, and challenges, J. Mol. Liq. 281 (2019) 598–633.

[36] H.M. Ali, H. Babar, T.R. Shah, M.U. Sajid, M.A. Qasim, S. Javed, Preparation techniques of TiO2 nanofluids and challenges: a review, Appl. Sci. 8 (2018) 587.

[37] M.U. Sajid, H.M. Ali, Thermal conductivity of hybrid nanofluids: a critical review, Int. J. Heat Mass Transf. 126 (2018) 211–234.

[38] P. Ji, H. Sun, Y. Zhong, W. Feng, Improvement of the thermal conductivity of a phase change material by the functionalized carbon nanotubes, Chem. Eng. Sci. 81 (2012) 140–145.

[39] J. Wang, H. Xie, Z. Xin, Y. Li, Increasing the thermal conductivity of palmitic acid by the addition of carbon nanotubes, Carbon N.Y. 48 (2010) 3979–3986.

[40] T.-P. Teng, C.-M. Cheng, C.-P. Cheng, Performance assessment of heat storage by phase change materials containing MWCNTs and graphite, Appl. Therm. Eng. 50 (2013) 637–644.

[41] Rubitherm, (n.d.). https://www.rubitherm.eu/media/products/datasheets/Techda ta_-RT28HC_EN_09102020.PDF.

[42] J.H. Lehman, M. Terrones, E. Mansfield, K.E. Hurst, V. Meunier, Evaluating the characteristics of multiwall carbon nanotubes, Carbon N.Y. 49 (2011) 2581–2602.

[43] H. Babar, H.M. Ali, Airfoil shaped pin-fin heat sink: potential evaluation of ferric oxide and titania nanofluids, Energy Convers. Manag. 202 (2019), 112194.

[44] M.A. Hayat, Y. Yang, L. Li, M. Bevilacqua, Y.K. Chen, Preparation and thermophysical characterisation analysis of potential nano-phase transition materials for thermal energy storage applications, J. Mol. Liq. (2023), 121464.

[45] X. Zhang, C. Zhu, G. Fang, Preparation and thermal properties of n-eicosane/nano-SiO2/expanded graphite composite phase-change material for thermal energy storage, Mater. Chem. Phys. 240 (2020), 122178.

[46] X. Liu, Z. Rao, Experimental study on the thermal performance of graphene and exfoliated graphite sheet for thermal energy storage phase change material, Thermochim. Acta 647 (2017) 15–21.

[47] A.M. Taggart, F. Voogt, G. Clydesdale, K.J. Roberts, An examination of the nucleation kinetics of n-alkanes in the homologous series C13H28 to C32H66, and their relationship to structural type, associated with crystallization from stagnant melts, Langmuir 12 (1996) 5722–5728.

[48] M.J. Oliver, P.D. Calvert, Homogeneous nucleation of n-alkanes measured by differential scanning calorimetry, J. Cryst. Growth 30 (1975) 343–351.

[49] W. Aftab, J. Shi, M. Qin, Z. Liang, F. Xiong, A. Usman, S. Han, R. Zou, Molecularly elongated phase change materials for mid-temperature solar-thermal energy storage and electric conversion, Energy Storage Mater. 52 (2022) 284–290.

[50] M.A. Hayat, H.M. Ali, M.M. Janjua, W. Pao, C. Li, M. Alizadeh, Phase change material/heat pipe and copper foam-based heat sinks for thermal management of electronic systems, J. Energy Storage 32 (2020), 101971.

[51] K.W. Shah, P.J. Ong, M.H. Chua, S.H.G. Toh, J.J.C. Lee, X.Y.D. Soo, Z.M. Png, R. Ji, J. Xu, Q. Zhu, Application of phase change materials in building components and the use of nanotechnology for its improvement, Energy Build. 262 (2022), 112018.