

Investigation of thermal performance and chemical stability of graphene enhanced phase change material for thermal energy storage

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ABSTRACT

Phase change materials (PCMs) have received widespread thermal energy storage (TES) and release properties due to their unique characteristics. However, the PCMs suffer from poor thermal conductivity, resulting in the least thermal performance and heat transfer characteristics. This research focused on enhancing the heat transfer and storage characteristics by developing an organic paraffin wax composite by dispersing highly conductive graphene powder using a two-step technique. The results show that the developed nano enhanced PCM significantly improves the thermal conductivity by 72.2% at 0.6 wt% of graphene powder. Furthermore, the Fourier transform infrared spectrum shows there is no additional peak observed, means physically and chemically stable, and the reduced light transmission capability was enhanced by 32.0% than pure PCM. Due to its extreme characteristics, the developed PCM is an outstanding material for medium temperature solar thermal energy storage applications.

1. Introduction

The impending reduction in fossil fuel resources will induce a shortage of both energy and carbon sources. As a means of averting future energy crises, it is projected that thermal energy storage (TES) will influence a generation of energy in the near future, particularly in renewable energy systems where the discontinuous and unpredictable nature of energy sources are important problems (Chien et al., 2021). TES materials, such as phase change materials (PCMs), have received the most attention in recent years (Boopalan et al., 2021; Kalidasan et al., 2022). This is due to their ability to store and release substantial thermal energy during the process of phase transition (Nizetić et al., 2020). Among all PCMs, organic paraffin wax, PCMs had remarkable attention owing to its excellent latent heat (enthalpy), low supercooling, desirable melting temperature, no toxicity, and excellent physical and chemical stability (Reji Kumar et al., 2020). However, the PCMs in TES applications are greatly affected by their lower thermal conductivity (TC). Owing to their lower value of TC, the heat transfer and storage

capability are not good (Fikri et al., 2022). To overcome this issue, researchers suggested adding highly conductive nano-sized particles with base PCM to alter their thermo-physical characteristics (Jamil et al., 2019). Pandey et al. (2020) studied the thermo-physical properties of paraffin wax with polyaniline for medium-temperature applications. It's ensured that the maximum rise in thermal conductivity was 11.96%, and the decrease in light transmission was found at 89%. The prepared nanocomposites are stable up to 250 °C, thereby an excellent candidate for solar TES applications. R et al. (2022b) compared the performance of Multi-walled carbon nanotubes (MWCNT) and modified MWCNT dispersed inorganic PCM for TES application. It was noticed the prepared modified MWCNT dispersed nanocomposites had better dispersion stability, higher thermal conductivity, and significantly enhanced light absorption capacity than MWCNT dispersed PCM. Kumar et al. (Kumar, 2022) investigated a Copper Oxide (CuO) dispersed inorganic PCM for solar thermal applications. The addition of CuO nanoparticles to the PCM significantly enhanced the thermophysical properties. The TC was improved by 87.39% for 3 wt% CuO particles dispersed in PCM. Also, the formulated nanocomposites are thermally stable up to 475 °C,

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Nomenclature

Composite codes

PW	Paraffin wax
PWGr-0.2	Paraffin wax with 0.2 wt% graphene
PWGr-0.4	Paraffin wax with 0.4 wt% graphene
PWGr-0.6	Paraffin wax with 0.6 wt% graphene
PWGr-0.8	Paraffin wax with 0.8 wt% graphene

Abbreviations

PCM	Phase change materials
TES	Thermal energy storage
CuO	Copper Oxide
PVT	Photovoltaic thermal
TC	Thermal conductivity
MWCNTs	Multi-walled carbon nanotubes
FTIR	Fourier transform infrared
UV-Vis	Ultraviolet-visible spectrum
TiO ₂	Titanium dioxide
MgO	Magnesium Oxide

Symbols

∇T	Temperature gradient
ρ	Density of PCM
α	Diffusivity of PCM
Cp	Specific heat capacity

which is very suitable for solar energy applications. A binary nanoparticles (TiO₂-Graphene) dispersed paraffin wax PCM was analyzed by Laghari et al. (2022). Initially, the researcher dispersed TiO₂ nanoparticle with paraffin wax, the optimized nano PCM composites is 1.0 wt %. Afterwards, graphene nanopowder was dispersed with the optimized nanocomposite. It was found 1.0 wt% graphene had optimum thermal conductivity, afterwards, the TC decreases, maybe the agglomeration of nanoparticles. Also, the light transmission of the binary composite was considerably reduced. Fikri et al. (Fikri et al., 2022) compared the performance of MWCNT and modified MWCNT dispersed PCM for TES applications. Literature reports that the presence of MWCNT into the PCM improves the TC, light absorption and is chemically and thermally stable. Also, it was found the modified MWCNT dispersed PCM had better performance than the pure MWCNT dispersed PCM composite. A Polyaniline@Cobalt enhanced PCM was prepared and characterized for TES. It was found that the TC increases with an increase in nanoparticle concentration. Also, the light absorption was improved with an increase in nanoparticle concentration (B et al., 2021). A Fe₂O₃-based paraffin wax nanocomposite is prepared and characterized by Lu et al. (2022) for TES utilization. The thermal conductivity was enhanced by 79% and 53% at liquid and solid phases of PCM. Further, latent heat decreased by 12% and 8.33% at solidification and melting, respectively. the carbon-based nanoparticles enhanced PCM was developed and analyzed by He et al. (2019) for energy storage applications. The TC conductivity was increased by 47.3%, 176% and 44% for MWCNTs, graphene nanoplatelets and nano graphite dispersed myristic acid PCM. furthermore, the developed nanocomposites have thermal stability up to 240 °C. recently, nano copper enhanced lauric acid PCM composites are prepared and characterized by Wen et al. (2022) for solar energy storage applications. The TC was effectively enhanced by 0.46 W/mK and 0.33 W/mK for Lauric acid/Cu and Lauric acid/Cu/attapulgitite composites. Also, researcher reported that, due to the higher TC, thermal stability the nanocomposites have potential candidate for energy conversion for buildings. A graphene and MWCNT dispersed PCM composites are prepared and examined the thermal performance of nanocomposite integrated photovoltaic thermal system done by Abdelrazik et al. (2022).

The TC of paraffin/MWCNT was enhanced by 13.6% compared to paraffin/graphene nanocomposites. Researcher reported that integration of paraffin wax/MWCNTs and paraffin wax/graphene nanocomposite PCM integrated rear side of the PVT system effectively enhances the electrical and thermal energy, because of the higher TC of nanocomposites, the heat transfer rate increases between PCM and PVT system. So that the temperature of the panel decreases and enhances the electrical efficiency. Recently MgO NPs enhanced paraffin PCM at various concentration (0.25 wt%, 0.5 wt%, 0.75 wt% and 1.0 wt%) were developed and characterized TES applications (Samiyammal et al., 2023). The TC was enhanced 55.5% compared to base paraffin PCM at 1.0 wt% MgO. Besides that, the prepared all nanocomposites are thermally stable and it can be used up to 291 °C in solar TES applications.

From the above literature, it is noticed that incorporating nano-sized particles into the PCM improves thermal conductivity. Furthermore, incorporating carbon-based nanoparticles into the base PCM gives excellent properties than other nanoparticles like metal and metal oxides. However, few researchers (Abdelrazik et al., 2022; He et al., 2019; R et al., 2022b) have analyzed the thermo physical properties of carbon-based PCMs in the melting temperature range of 50 °C for solar TES applications. This research uses organic RT50 as a PCM and graphene as a nanoparticle. The foremost objective of this research study is to improve the TC, decrease light transmission and increase light absorption of the base matrix. This study investigates the chemical stability, TC, and light transmission of the paraffin wax with graphene nanoparticles. The chemical stability was analyzed by Fourier transform infrared (FTIR), thermal inductivity was examined by TEMPOS thermal conductivity analyzer, and light transmission was examined by Ultraviolet-visible (UV-Vis) spectrum. Due to the various excellent thermal and chemical properties, the prepared nanocomposites are used for medium-temperature solar thermal applications like desalination (R et al., 2022a), photovoltaic thermal systems (Islam et al., 2021), (Samuel Hansen et al., 2020), battery thermal management (Murali et al., 2021), electronics (Hayat et al., 2020), textiles (Salaün et al., 2010), medical field (Seddiqi et al., 2021) water heating (Pandey et al., 2021) and food industries (Gin and Farid, 2010). The manuscript is organized in such a way that section 1 explores the background, the previous study of various nano dispersed PCM characterization and its applications, section 2 displays the resources and methods used in this study, and section 3 discusses the various characterize techniques used to analyze the thermophysical properties and finally section-4 briefly discusses the remarkable results and further research scope on the study.

2. Materials and methodology

2.1. Materials

In present research, Paraffin wax RT50 as a PCM with 50 °C melting temperature and graphene powder as a nanoparticle. The Paraffin RT50 had an excellent heat storage enthalpy of 160.0 J/g is acquired from RUBITHERM, Germany. Graphene nanopowder 8 nm-sized were procured from a graphene supermarket. The thermophysical properties of RT50 and graphene powder used in the research are represented in Table 1.

Table 1
Characteristics of PCM and nanoparticles.

Properties	Paraffin wax-RT50	Graphene
Melting temperature	50 °C	3550 °C
Thermal conductivity	0.2 W/mK	4000 W/mK
Heat storage enthalpy	160 kJ/kg	–
Density	0.88 kg/l (s) and 0.76 kg/l (l)	2267 kg/m ³
Specific heat capacity	2 kJ/kg K	2.1 kJ/kg K
Color	Blueish white	Black
Solubility	Insoluble in water	Insoluble

2.2. Preparation method of nano-enhanced PCMs

A two-step strategy is adopted for forming the Paraffin wax enhanced graphene nanocomposite PCM. Fig. 1 shows the step-by-step procedure of preparing the nanocomposites with different weight concentrations of graphene powder. First, a required amount of Paraffin wax and nanoparticle (0.2 wt%, 0.4 wt%, 0.6 wt% and 0.8 wt%) was measured by the analytical microbalance (EX224, OHAUS). The measured paraffin wax was heated at 70 °C using a hot plate (RCT, BASIC IKA), followed by graphene nanopowder added to the liquid PCM and sonicated using ULTRASONIC BATH (EASY 60H, ELMASONIC) for 60 min for dispersing uniformly. After sonicating, the sample could cool at room temperature. The same method was used to prepare the remaining weight concentration of the nanoparticles. The various concentration of the nanocomposite was represented by PW, PWGr-0.2, PWGr-0.4, PWGr-0.6 and PWGr-0.8 for paraffin wax, paraffin wax with 0.2 wt% graphene, paraffin wax with 0.4 wt% graphene, paraffin wax with 0.6 wt% graphene and paraffin wax with 0.8 wt% graphene.

2.3. Characterization technique

Various thermal-sensitive instruments were used to examine developed nanocomposite PCM's thermal, chemical and light transmission characteristics. The chemical characteristics of developed nanocomposite PCM were characterized by FTIR, Model: FTIR SPECTRUM TWO, PERKIN ELMER. The wave number range of 400 cm^{-1} -4000 cm^{-1} , a wave number precision of 0.01 cm^{-1} and spectral resolution of 0.01 cm^{-1} were used to examine the functional groups and chemical composition. An optical absorbance and transmittance was examined by using UV-Vis spectroscopy (Model: LAMBDA 750, PERKIN ELMER, USA). The readings were taken wavelength 200 nm–800 nm at room temperature. The thermal properties like thermal diffusivity and TC was analyzed by using Thermal property analyzer (TEMPOS), dual needle SH-3, at normal room temperature.

3. Results and discussions

The results on chemical stability, light transmission, thermal conductivity, and thermal diffusivity are discussed in this section.

3.1. Chemical analysis

FTIR spectrometer is used to analyze the chemical composition of paraffin PCM and graphene nanoparticles. Fig. 2 shows the FTIR spectrum graph of graphene dispersed paraffin PCM. Generally, the chemical formula for organic paraffin wax is $\text{C}_n\text{H}_{2n+2}$, three peaks are dominate in paraffin wax, like a peak between 719 and 725 cm^{-1} denotes the stunning motion of $-\text{CH}_2$ groups, the $-\text{CH}_2$ and $-\text{CH}_3$ groups deforms the wavelength ranges 1350 cm^{-1} to 1470 cm^{-1} , and the symmetrical stretch in the wavenumber of 2800 cm^{-1} and 3000 cm^{-1} indicates $-\text{CH}_2$

and $-\text{CH}_3$.

From the graph the available peaks are 2916 cm^{-1} , 2847 cm^{-1} , 1464 cm^{-1} & 720 cm^{-1} . The peak 720 cm^{-1} specifies rocking vibration of $-\text{CH}_2$ and $-\text{CH}_3$ as it lies between the range 719 and 725 cm^{-1} , the peak 1464 cm^{-1} ensures the deformation vibration of $-\text{CH}_2$ and $-\text{CH}_3$ and it lies in the range of 1350 and 1470 cm^{-1} wavenumber and a peak at wavenumber 2916 cm^{-1} denote symmetrical stretching vibration of $-\text{CH}_2$ and $-\text{CH}_3$ it lies between the range of 2800–3000 cm^{-1} . It clearly shows no additional peak formed when the incorporation of nanoparticles dispersed into the PCM, which means there is no chemical reaction takes place in the prepared nano PCM composites.

3.2. Light transmissibility

Fig. 3 shows the transmission of graphene-based PCM and its composites. It was found that adding nanoparticles decreases the transmission and increases the absorbance. The decrease in light transmission may be attributed to the light absorption of graphene nanoparticles. The deterioration in light transmission increases light absorption. Therefore, it is an excellent resource for solar energy applications. It was found that the percentage transmission is 21.18.4%, 14.25%, 16.18%, and 14.83% and 14.87% for PW, PWGr-0.2, PWGr-0.4, PWGr-0.6 and PWGr-0.8 respectively. This percentage can be calculated by using the solar spectrum by NREL (Gueymard, 2004). From the graph, it was found that the increase in reduction percentage of transmission 32%, 23.6%, 29.98% and 29.79% for PWGr-0.2, PWGr-0.4, PWGr-0.6 and PWGr-0.8 than pure paraffin wax PCM. Fig. 4 illustrates the light absorptivity of PW and graphene-enhanced PCM composites. It was found that with the addition of graphene nanoparticles into the paraffin wax, the absorption capacity is increased. Also, observed that the absorption cure is indirectly proportional to the light transmission curve (B et al., 2021). The results concluded that the increase of graphene powder significantly decreases the light transmission and increases the absorption capability, making it appropriate for direct solar thermal applications..

3.3. Thermal conductivity and thermal diffusivity

The thermal conductivity was evaluated by TEMPOS dual needle SH-3 analyzer. The TC and the thermal diffusivity of developed paraffin with various weight percentages of graphene were plotted in Fig. 5. The TC is the ability of a material to conduct heat. Thermal diffusivity assesses a materials ability to conduct. The TC and diffusivity can be measured using equations (1) and (2).

$$\alpha = \frac{k}{\rho C_p} \quad (1)$$

$$q = -k \nabla T \quad (2)$$

where, α = thermal diffusivity (mm^2/s), k = thermal conductivity (W/mK), ρ = density (kg/m^3), C_p = specific heat capacity (J/kgK), q = heat

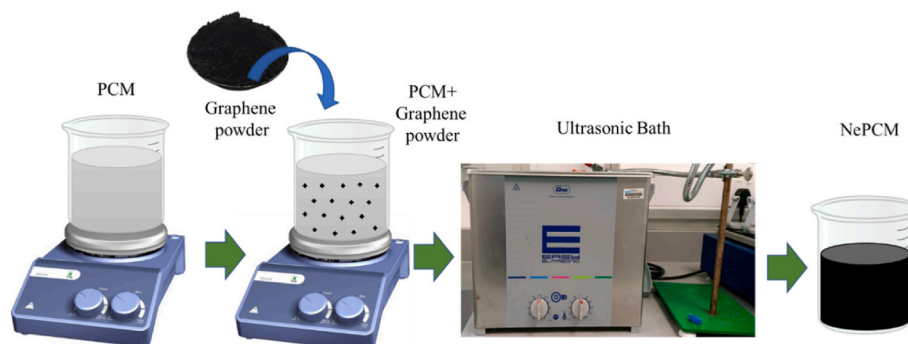


Fig. 1. Step by step method of preparation of nano enhance PCM.

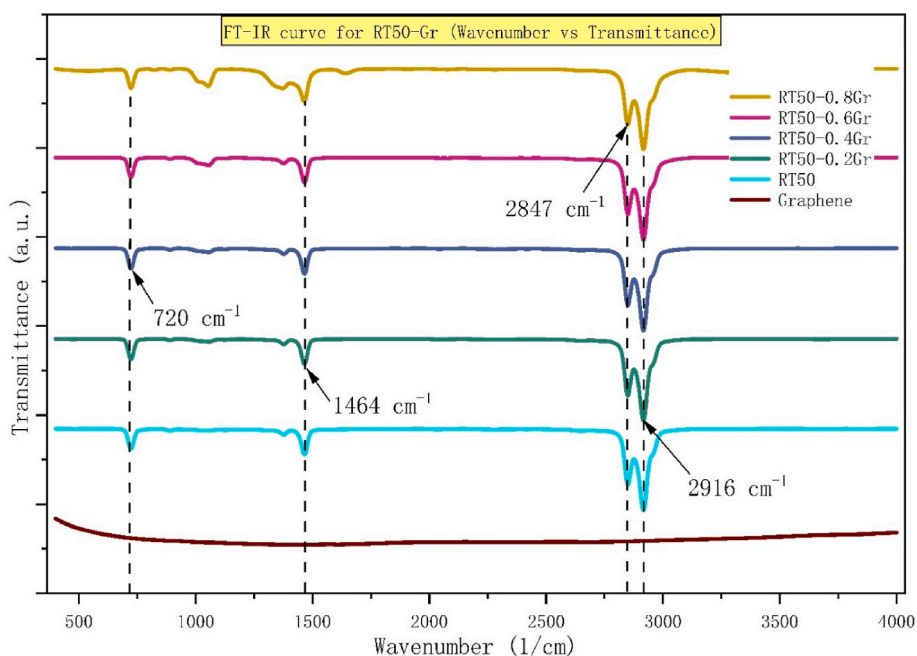


Fig. 2. FTIR spectrum of graphene dispersed PCM.

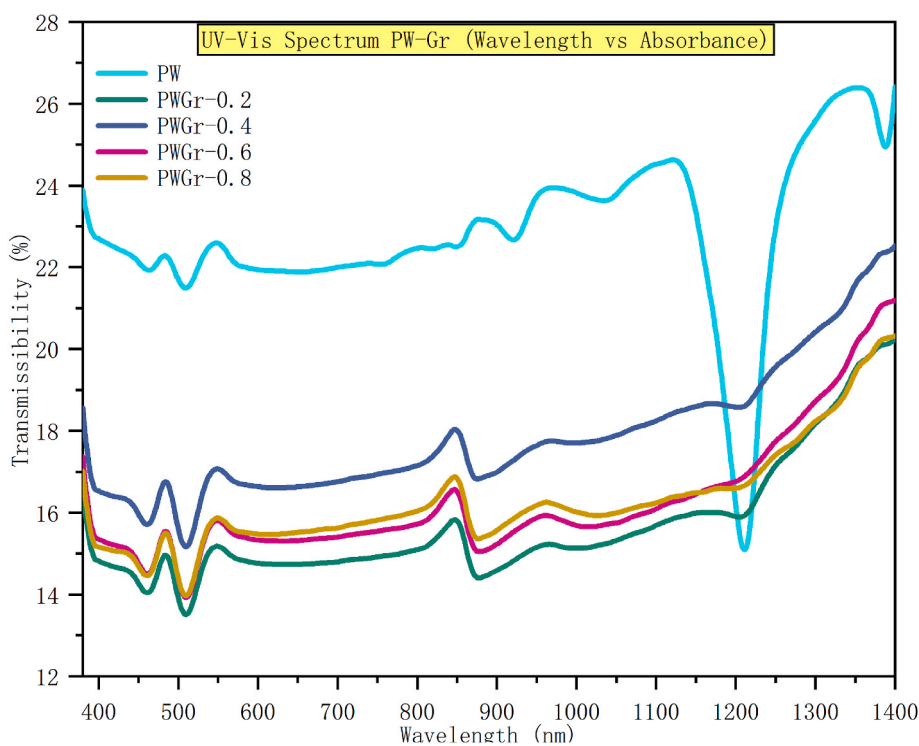


Fig. 3. Light transmission of graphene dispersed PCM.

conduction (W), and ∇T = temperature gradient (K/m). The TC and thermal diffusivity of PW, PWGr-0.2, PWGr-0.4, PWGr-0.6, PWGr-0.8 are 0.23 ± 0.02 W/mK, 0.308 ± 0.02 W/mK, 0.347 ± 0.025 W/mK, 0.395 ± 0.20 W/mK, 0.3203 ± 0.030 W/mK, and 0.099 ± 0.01 mm²/s, 0.115 ± 0.01 mm²/s, 0.121 ± 0.01 mm²/s, 0.133 ± 0.01 mm²/s, 0.11 ± 0.01 mm²/s. These nanocomposites have higher thermal conductivity and thermal diffusivity relatively to base PCM. The optimum enhancement in TC and thermal diffusivity of 71.74% and 34.35% for PWGr-0.6. The thermal conductivity of nanoparticles of developed nano PCM

composites increases up to 0.8 wt% afterwards, decreasing trend. A similar trend was observed in thermal diffusivity. The reduction in thermal conductivity in higher concentrations may be attributed to that agglomeration of nanoparticles. The agglomeration of the nanoparticles causes non-uniform composites structure, thereby resulting in a decline of TC. This clustering of nanoparticles breakdown the thermal connectivity and reduces the thermal efficiency (R, Samykano, et al., 2022). Electron transport and phonon transport are the two mechanisms for thermal transport. In general, TC in paraffin wax occurs due to phonon-

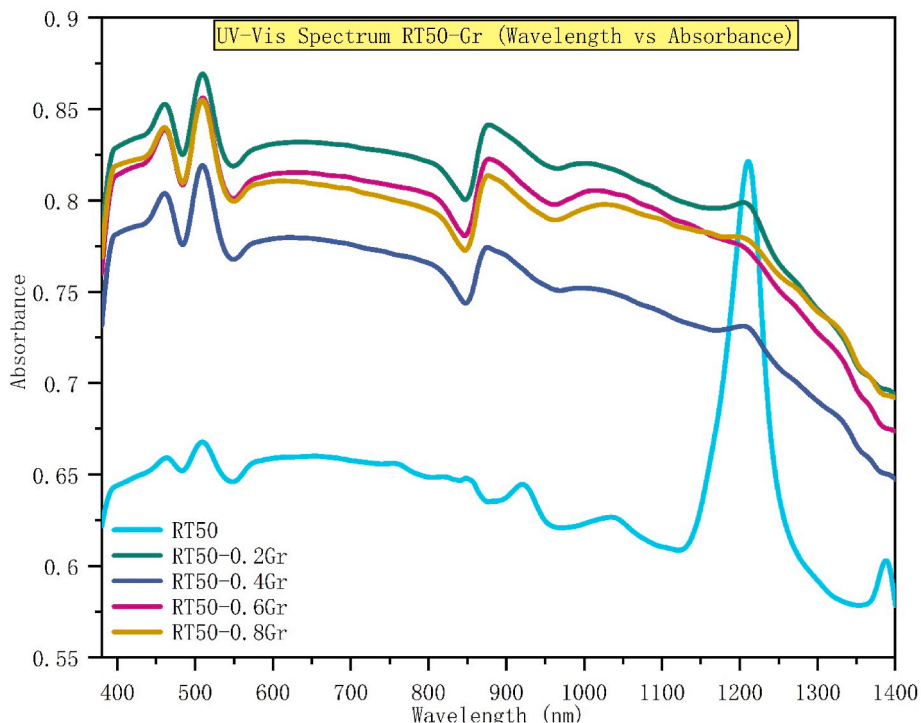


Fig. 4. Light absorption graph of PW and graphene enhanced PCM.

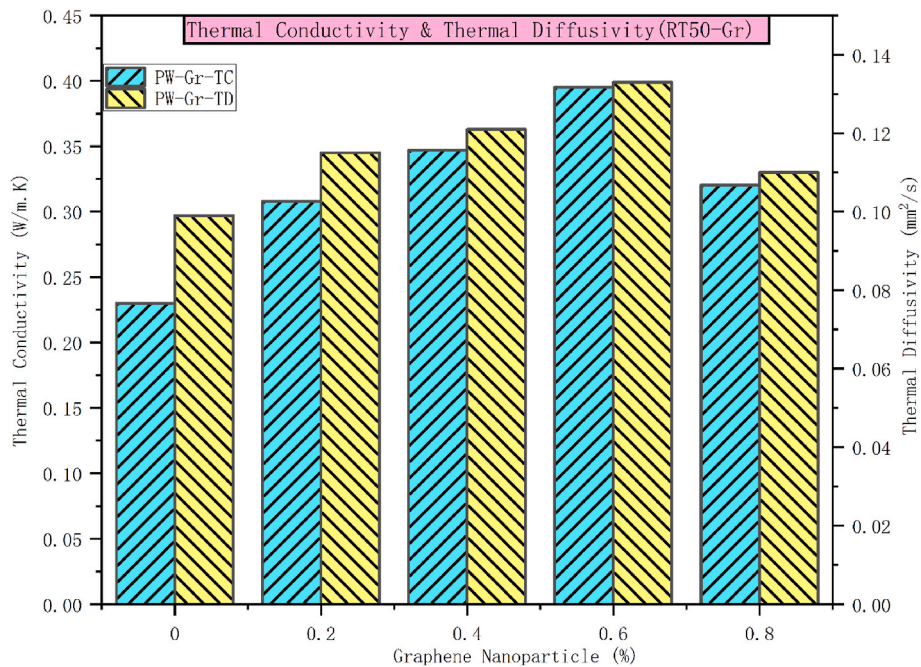


Fig. 5. Thermal conductivity and Thermal diffusivity of graphene dispersed PCM.

phonon thermal movement, whereas in polymers and metals TC occurs due to electron movement. To increase the electron thermal movement of nanocomposite PCM, a linked thermal network must be established by dispersing nanomaterial without hampering the phonon transfer within paraffin wax. Phonon-phonon thermal movement can be improved by a larger mean path of phonons and by hindering the free mean path by phonon-boundary interaction, phonon impurities scattering and phonon-phonon interface (Navarrete et al., 2018). Any of the above parameters can dominate and create a noteworthy effect in thermal

conductivity. The increase of TC in graphene dispersed paraffin wax PCMs relative to paraffin may be attributed to improving the thermal connectivity within the PCM matrix due to the dispersion of extremely conductive nanoparticles. But when the concentration of nanoparticles increases beyond 0.6% the nanoparticles are agglomerated, due to that, the thermal network breaks, hence declining the electron thermal transference. Thus, the optimum thermal conductivity was obtained for PWGr-0.6 nanocomposite.

4. Conclusions

In this research, graphene dispersed organic paraffin wax was prepared, and chemical and thermal properties were analyzed. The FTIR results proved that the developed nanocomposites were chemically stable, and no additional peaks were observed. A significant reduction in light transmission occurs when the nanoparticle concentration increases. It was noted that the transmissibility decreases with respect to the solar spectrum by 14.25%, 16.18%, 14.83%, 14.87% for PWGr-0.2, PWGr-0.4, PWGr-0.6, and PWGr-0.8, respectively. The thermal conductivity was enhanced up to 72.2% for PWGr-0.8 composite afterwards, decreasing trend. The reduction in thermal conductivity in higher concentrations may be attributed to that agglomeration of nanoparticles. The agglomeration of the nanoparticles causes non-uniform composites structure, thereby resulting in the decline of TC. The enhancement in thermal conductivity is attributed that the dispersing nanomaterial must establish a thermal network link without hampering the phonon transfer within paraffin wax. Based on the results measured and evaluated, PWGr-0.6 composite has an optimized composite with a 72.2% increment in TC and 14.83% reduction in solar spectrum transmission. Owing to the excellent thermal, light absorption, and chemical properties, the developed nanocomposites are potential candidature for medium-temperature solar thermal storage applications. The future work will investigate the morphology, thermal stability, and thermal reliability of prepared composites through a scanning electron microscope, thermogravimetric analysis, and thermal cycling.

Author statement

Reji Kumar: Writing - Original Draft, Data Curation, Investigation. M. Samykanoo: Data Curation, Writing - Review & Editing. W.K. Ngui: Investigation, Writing - Review & Editing. A. K. Pandey: Visualization, Writing - Review & Editing. Kalidasan B: Methodology, Data Curation, Investigation. K. Kadrigama: Writing - Review & Editing. V. V. Tyagi: Writing - Review & Editing.

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.

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