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Thermal behaviour of Paraffin-MWCNT stabilized by Sodium dodecylbenzene sulphonate nano-enhanced phase change material for energy storage applications

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Abstract. The Phase change materials (PCMs) possess the great potential to store renewable and sustainable thermal energy that can mitigate the issue of energy to a great extent. However, the low thermal conductivity hinders the extensive use of PCM in various applications. To alleviate this deficiency, the PCMs are often incorporated with highly conductive nanoparticles. The carbon-based nanoparticles are highly regarded to be a promising option because of their elevated thermal conductivity like Multiwall carbon-nanotube (MWCNT). However, these highly conductive nanoparticles sometimes exhibit the issue of non-uniform dispersion with PCM. In this paper, we report the use of surface-modified MWCNT by using stabilized Sodium dodecylbenzene sulphonate surfactant (SDBS) with Paraffin wax (PW) RT47 at wt% 0.1 and 0.3 of MWCNT. The sample is created by using two-step method. Further, for characterization; chemical composition by Fourier transform infrared spectroscopy (FTIR), thermal conductivity by thermal property analyzer (TEMPOS) and for thermal stability, thermal gravimetric analyzer (TGA) is used. The results showed a significant enhancement in the thermal conductivity of composite PCM, the inclusion of 0.1 and 0.3 wt% of surface-modified MWCNT increased the thermal conductivity up to 51.29% and 76.5% respectively. The FT-IR confirms that the components are physically mixed in NePCM composite, no chemical reaction appeared as no displacement of characteristic peaks or a new peaks appeared. TGA results showed the prepared nano-enhanced phase change material (NePCM) is stable. Thus, surface modification of MWCNT by using SDBS for PW can be the effective method to boost the overall performance of NePCM without losing its basic characteristics. Therefore, based on results, it can be concluded that the surface modified Paraffin/MWCNT NePCM is well suited for applications like energy storage, photovoltaic thermal system, and battery thermal management.



1. Introduction

After the industrial revolution, increasing greenhouse gas emissions and expanding environmental concerns raised a serious concerns about the effective use of energy. At present, critical issue of an energy crisis due to over-looming population growth, shrinking world economy and mismatch of energy supply and demand has opened widespread options for utilization of renewable and sustainable energies in the future, such as clean affordable wind, solar, and water. Since the issue with renewable energies is its intermittent nature, the effective thermal energy storage (TES) system can reduce this issue substantially by using effective advanced phase change materials and devices.

The most abundant and widely available renewable energy is solar energy, it is considered to be a bright prospect for future energy demands. The sporadic nature of solar energy requires necessary thermal energy storage so that extra heat collected during day can be stored for its utilization at night. The most used method to store solar heat in energy applications is a sensible heat storage system (SHSS) but on other hand, the latent heat thermal energy storage system (LHTES) showed better energy density with wide temperature ranges between endothermic and exothermic heat release and absorbed at a constant temperature. The phase change material (PCM) based latent heat thermal energy storage (LHTES) by solid-liquid phase transition can offer an effective alternative method for thermal energy storage. The PCMs store energy by melting and storing heat energy in the liquid stage, this heat storage can be released and utilized later when the PCMs temperature falls below its melting temperature converting it again into crystal form. The PCM-based heat storage system holds significant importance as it has been implemented in practical applications such as solar energy storage, food preservation, cooling of engines, battery thermal management, medical applications, and many more ahead.

The number of PCM materials that have been analyzed for latent heat storage applications the most common of them are organic and inorganic PCMs. The organic paraffin is the most commonly utilized PCM due to its widespread advantages, such as high latent heat, better thermal stability, low vapor pressure, a little supercooling, chemical stability, and easy availability in wide temperature range. However, it lags in small thermal conductivity issues (0.2 W/mK) which substantially limits the heat flow rate through it during the process of melting and solidification. To resolve the issue of smaller thermal conductivity of pure Paraffin, many techniques have been introduced the most common one is the inclusion of high thermal conductive nano-particles in base PCM.

After the inclusion of highly thermal conductive nanoparticles in base PCM the resultant material is named as nano-enhanced phase change material. The various investigations have been analyzed by incorporating pure Paraffin with metal and carbon-based nanoparticles. As compared to metal based nano-particles carbon-based nano-particles like Carbon nanotube (CNT), single wall carbon nanotube (SWCNT), multi-wall carbon nanotube (MWCNT) (3000 W/mK), Graphene, Graphite and others have relatively high thermal conductivity, better porosity, large aspect ratio and thermal stability. The MWCNT is one of the best candidate for thermal conductivity enhancement as it has a high aspect ratio ranging from 100 to 1000 [10] that leads to reduced contact resistance and helps in constructing a 3D thermal conduction network that facilitates phonon and electron transfer rate in NePCM.

The CNT often entangles with the issue of non-uniform dispersion in base PCM, many techniques of surface modification and functionalization have been adopted by multiple researchers for improvement of interfacial adhesion and uniform dispersion of CNT in base PCM. Avid et al.[1] performed surface modification of pure Paraffin by surfactant octadecyltrimethoxy silane (ODMS) as modifying bonding agent to prepare high-performing stable NePCM. As per results, thermal conductivity of modified Paraffin/MWCNT (PM) with 1 wt% loading found to be 0.261 W/mK as compared to pristine Paraffin 0.256 W/mK, the obvious reason behind it is introduction of ODMS produced the soft layer on MWCNT which impedes the agglomeration of MWCNTs and improved its quality of dispersion. In another study, Bahramnia et al. [2] experimentally investigated the impact of 3-(triethoxy silyl) propyl amine loading on MWCNTs with 25, 75 and 150 wt%, as per results, 75 wt% sily grafted MWCNT is optimized wt% and owns uniform morphology among the samples, TGA also confirms that 75 wt% has higher thermal stability. In another study, Ong et al. [3] introduced novel polyurethane acrylic lacquer and hardener (PALH) as a cohesive additive surfactant using vacuum

filtration assisted drop-casting method for MWCNT, nano graphite, titanium carbide and copper nanowires. As per investigation, MWCNT with 5 wt% with 1 wt% of PALH showed optimized results with 87% increment in thermal conductivity, further thermal cycling tests revealed that surface-modified MWCNT remained stable. Arasu et al. [4] prepared two different surfactants Sodium dodecyl sulfate (SDS) and SDBS to analyze stability of TiO₂ –Ag/water nanocomposite. The results showed 29.6% thermal conductivity improvement of nanocomposite with SDS (0.1 wt%) and whereas SDBS (0.1 wt%) showed poor dispersion with nanofluid with only 2.1% thermal conductivity enhancement. The ratio of MWCNT to SDBS needs to be optimized as a large SDBS ratio will decrease thermal conductivity as it increases the interfacial thermal resistance, and a small amount of SDBS will not impact the thermal conductivity.

Herein, this paper intends to provide research focusing on the surface modification of MWCNT by using SDBS for enhanced thermal conductivity of PW with 0.1 wt% and 0.3 wt%. The MWCNT to SDBS wt% ratio is taken as 1:1. The chemical characterization through Fourier transformed infrared (FT-IR) and thermal stability analysis by TGA are analyzed.

2. Materials and methods

2.1 Materials

The Paraffin wax (PW) RT47 has the melting temperature 47-48 °C was use as PCM, MWCNT nanoparticles of 10-15 nm sized and SDBS as surfactant purchased from RUBITHERM Germany, Phase change materials Products Ltd and (Sigma-Aldrich company) Germany respectively.

2.2 Preparations for PW/Multiwall CNT Composite

The two-step method was used for PW-added MWCNT composites preparation, as shown in **Figure 1**. Paraffin was heated above the melting temperature using a hotplate. Once the Paraffin was appropriately melted, then the concentration of nanoparticles was added to the liquefied Paraffin. In addition, the SDBS was added as the 1:1 with respect to nanoparticles. The addition of SDBS in Paraffin PCM mitigates agglomeration issues in Paraffin. The ratio of surfactant is taken as 1:1 to nanoparticles as reported by previous studies [5][6]. The SDBS surfactant is selected with 1:1 wt% to nanoparticles as it reduces the surface tension between Paraffin PCM and nanoparticles and allowing homogenous dispersion. A probe sonicator was used to properly mix the PCM nanoparticles and SDBS to form the composite. At last, the composite was kept at normal temperature for cooling.

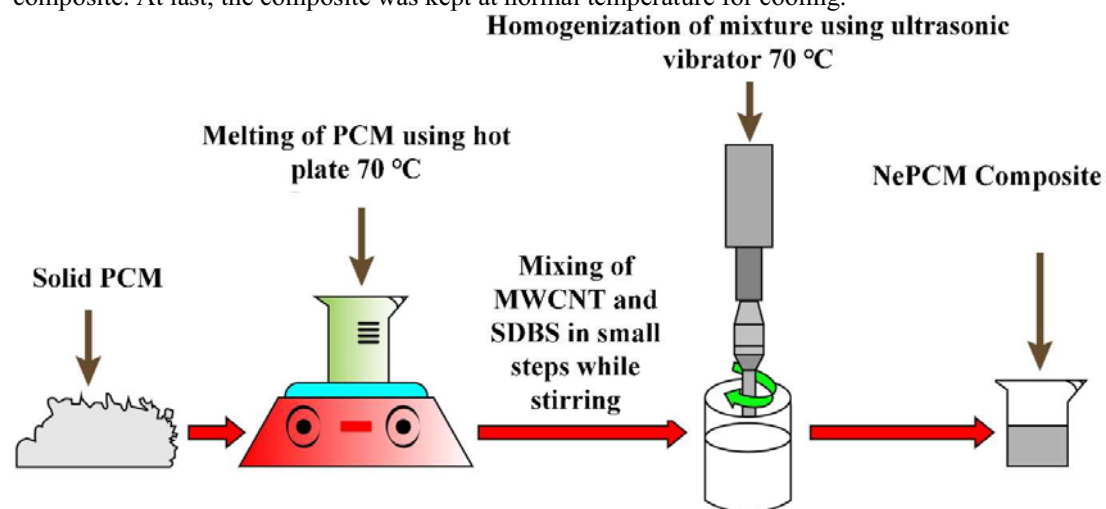


Figure 1: Preparation PW/Multiwall CNT NePCM composite

3. Results and discussion

This part of paper discussed the characterization results, including chemical composition analysis, thermal stability analysis and thermal conductivity for PW and formulated composites.

3.1 Chemical Composition analysis

To observe the reaction between MWCNT and coupling agent of SDBS the FT-IR of NePCM is measured. FT-IR characterization for MWCNT showed no obvious peak, as seen in **Figure 2**, for PW, the strong absorption peaks at 2920 cm^{-1} and 2848 cm^{-1} were belonging to the C-H stretching vibration of -CH₃ and -CH₂, respectively. The third and fourth obvious peaks were 1466 cm^{-1} and 724 cm^{-1} . The strong absorption peak of 1466 cm^{-1} was due to the plane bending vibration of -OH. The fourth peak, 724 cm^{-1} , showed plane swing vibration of the hydroxyl group. For Paraffin and Multiwall carbon nano tube 0.1% (PM-0.1) and Paraffin and Multiwall carbon nano tube 0.3% (PM-0.3), the same peak can be seen as the PW. It can be concluded from the results of PM-0.1 and PM-0.3 that both the composite has the same peaks as the PW obvious peaks. Results indicate that PW with two support materials are physically mixed, and no chemical reaction has occurred.

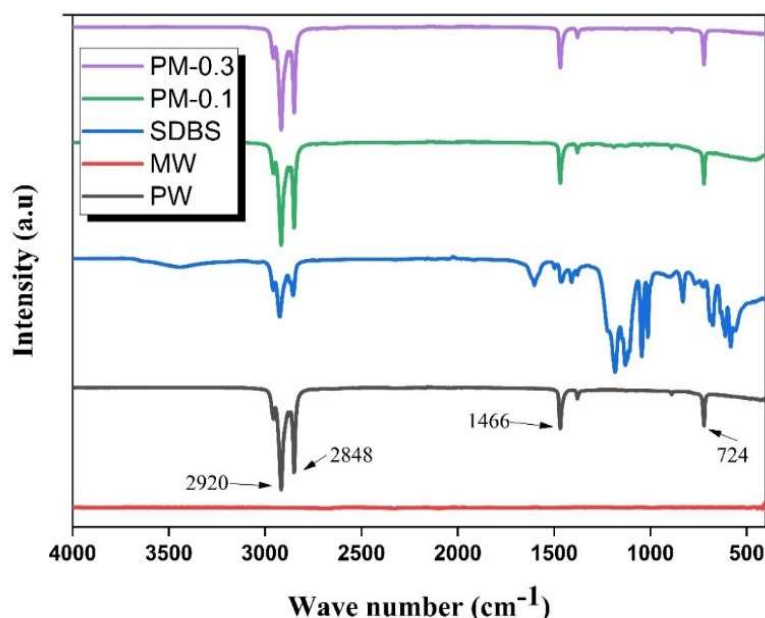


Figure 2: FTIR spectra of PW and its composites

3.2 Thermal stability of composite

Thermal stability of the PW and prepared composites PM-0.1 and PM-0.3 were examined using TGA. The **Figure 3** shows the TGA curve, which demonstrates the thermograph of the PM-0.1 and PM-0.3. The TGA of composites were tested within the range of 30 to 400°C temperature. The PW exhibited high stability up to 320 °C without a noticeable degradation. The enhancement in thermal stability is because of the thermal barrier of MWCNT and PW added composite. Further, the onset degradation temperature for PW, PM-0.1 and, PM-0.3 are 314.6 °C, 326.8 °C and 330.5 °C, respectively.

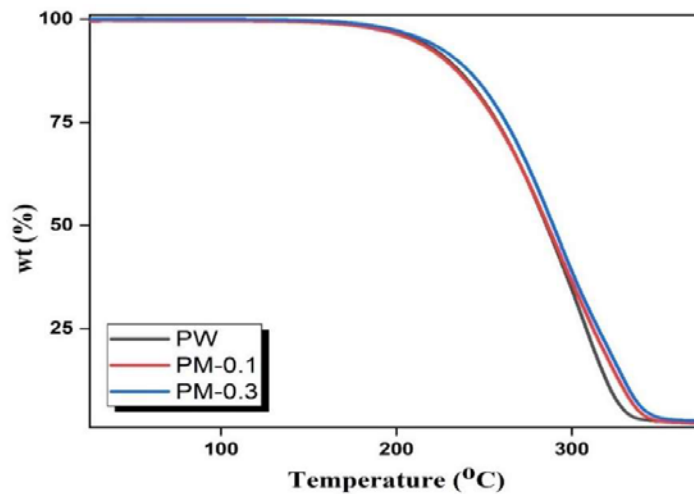


Figure 3: TGA curve PW and its composites

3.3 Thermal conductivity of composite

The value of thermal conductivity of PW and its composites PM-0.1 and PM-0.3 were shown in **Figure 4**. The thermal conductivity of PW recorded as 0.1983 W/mK. While, the thermal conductivity value for the composites PM-0.1 and PM-0.3 were 0.3092 W/mK and 0.3548 W/mK, respectively. The composites PM-0.1 and PM-0.3 have a higher thermal conductivity of 51.29%, 76.5% higher than the PW. The increase in thermal conductivity was observed because addition of nanoparticles.

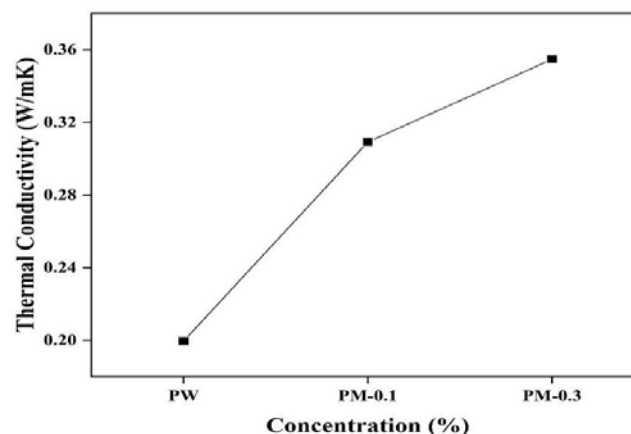


Figure 4. Thermal conductivity Curve of PW and it's composite

The highest increment in thermal conductivity was reported as 76.5% for composite (PM-0.3) as compared to PW. The thermal conductivity in composite PCM is linked with collective motion of phonons over long distance and molecular alignment in the NePCM. The increase in thermal conductivity was seen in PM-0.1 and PM-0.3 composite is because of the higher crystallinity and aspect ratio of MWCNT, further individualization of 3D networks in Paraffin matrix that enhanced the phonon-phonon transmission and created better molecular alignment.

4. Conclusion

In this study, surface-modified NePCM was synthesized by using Paraffin RT47 as base PCM and MWCNT nanoparticles. The surfactant Sodium dodecylbenzene sulphonate was used for surface modification of MWCNT with 1:1 wt%. Various thermal characteristics of NePCM were investigated with surface modification and without surface modification including chemical stability, thermal conductivity, and thermal stability analysis. As per results, the FTIR exhibited no chemical reaction occurred, the TGA confirmed that the thermal stability of MWCNT/SDBS ameliorated the thermal stability of Paraffin RT47. In addition, the composite PM-0.1 and PM-0.3 showed increased thermal conductivity of 51.29 % and 76.5 % as compared to base PW. The surface-modified MWCNT with

PCM showed enhanced thermo-physical properties. Therefore, it might be the candidate for energy storage and other thermal practical applications in future.

5. Author Contributions

Yasir Ali Bhutto: conceptualization, investigation, writing original draft. A.K. Pandey: supervision, methodology. R. Saidur: supervision, review and editing. Imtiaz Ali Laghari: review and editing. D. Buddhi: formal analysis, writing-review and editing. V.V. Tyagi: writing-review and editing.

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Declaration-of-interests

It is declared by the authors that they do not have any known personal relationships or competing financial interests that may have influenced described work presented in this research paper.