Thermal conductivity and Thermal properties enhancement of Paraffin/ Titanium Oxide based Nano enhanced Phase change materials for Energy storage

Imtiaz Ali Laghari Faculty of Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia. laghari.imtiaz@quest.edu.pk

Zafar Said Department of Sustainable and Renewable Energy Engineering, University of Sharjah, P. O. Box 27272, Sharjah, United Arab Emirates U.S.-Pakistan Center for Advanced Studies in Energy (USPCAS-E), National University of Sciences and Technology (NUST), Islamabad, Pakistan zsaid@sharjah.ac.ae M.Samykano Faculty of Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia. mahendran@ump.edu.my

K.Kadirgma Faculty of Mechanical & Automotive Engineering Technology, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia <u>kumaran@ump.edu.my</u> <u>A.K</u> Pandey Research Centre for Nano-Materials and Energy Technology (RCNMET), School of Engineering and Technology, Sunway University, No. 5, Jalan Universiti, Bandar Sunway, Petaling Jaya, 47500 Selangor Darul Ehsan, Malaysia adarshp@sunway.edu.my

V.V.Tyagi School of Energy Management, Shri Mata Vaishno Devi University, Katra, 182320, (J&K), India vtyagi16@gmail.coms

Abstract— The Latent heat storage (LHS) based on phase change materials (PCMs) has a critical part to demonstration in preserving and efficiently utilizing energy, resolving demand-supply mismatches, and boosting the efficiency of energy systems. However, they have a low thermal performance inherent in it because the low thermal conductivity (TC) of PCMs. Paraffin organic PCMs have several advantages such as higher LHS, nontoxic, abundant in nature and inexpensive, whereas TiO2 nanoparticle is type of hydrophilic group having tendency to improve TC. In this research TiO_2 in different concentration (0.1, 0.5, 1, and 2 wt percent) with surfactant sodium dodecyl benzene sulphonate (SDBS) added into Paraffin RT44 HC PCM using two step techniques, and the thermophysical properties were broadly discussed. Thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FT-IR) and Thermal property analyzer (TEMPOS) were used for the characterization of prepared composite nano-enhanced phase change materials (NePCM). Additionally, the effect of nanoparticles on TC was investigated. The highest TC was obtained with PW/TiO2-1.0 by an increment of 86.36% as related with base PW. The FTIR spectrum of the composite PW/TiO2 confirmed no interaction between PW and TiO2, resulting in a more chemical stable composite. The addition of TiO₂ to PW enhanced the degradation temperature to 10°C by making it more thermal stable. Grounded on the results it can be concluded that the developed composite is suitable for thermal energy storage (TES), photovoltaic thermal (PVT) systems, and hot water applications.

Keywords— Phase change materials, Paraffin RT44HC, Titanium oxide, Thermal conductivity, Thermal energy storage.

I. INTRODUCTION

Energy is a foremost problem in the globe today because of the fact that around 850 million people do not have access to electrical energy. Global energy consumption is predicted to

grow by approximately 30 percent between now and 2040 as a result of the strong demand for energy services.[1]. The most efficient systems for storing energy are TES, energy storage operations have one overall goal: to lessen the rate incongruity between supply and demand. As a storage medium for LHS systems, phase change materials (PCMs) have shown to be an intriguing solution that is becoming increasingly prevalent [2]. PCMs are categorized as: organic, inorganic, and eutectic. Organic PCMs are comprised of paraffin, non-paraffin, and fatty acids. Organic PCMs are the most often utilized PCMs because of their qualities such as non-toxicity, durability, lack of super cooling effect, and low chemical reaction, among others [3][4]. Chemically, inorganic PCMs are less stable than organic PCMs, which is why inorganic PCM costs less and has a larger LHS capacity. Similar to organic PCM, inorganic PCM exhibits corrosive characteristics and hysteresis. In light of all of this research, it seems apparent that the O-PCMs (which include paraffin polyethylene glycols, fatty acids, and there have been studied thoroughly to store latent heat. Paraffin is the broadest melting point range of any organic PCM[5]. By changing the PCM and increasing the amount of carbon atoms in paraffin wax (alkanes), the melting point and LHS can be increased. One of the most significant constraints of PCMs is their low TC; one technique for increasing the TC of PCMs is to use different nanoparticles as TC enhancers[6]-[8]. The utilization of nanocarbons, nanometals, and nanometal oxides has led to the development of NePCMs with improved thermal properties. [9].

PCMs composites have been broadly studied by numerous researchers by dispersing nano particles (NPs) as they offer a noteworthy ability for improving the TC at lower concentrations [10]. The result indicated that they have a

significant impact on enhancing rate of heat transfer. This study examined the effects of TES on the newly produced composites palmitic acid added titanium dioxide (TiO₂) [11]. Different nanoparticle wt fractions (0.5, 1, 3, and 5%) were dispersed into the base and their influence on the thermophysical characteristics was examined. Palmitic acid's TC steadily increased by 12.70%, 20.4%, 46.60%, and 80.0% for the addition of nano sized particles, respectively. A novel method was used to make a nanoparticle enhanced PCM stearic acid SA TiO₂ [12]. They exhibited greater TC values than the base PCM, according to the findings. NEPCM composites were developed with weight concentrations of 0.09, 0.26, 0.33, and 0.36 wt%. As compared to pure SA PCM, the greatest TC was determined to be 27%. Kenisarin et al.[13] investigated PW/EG composite with mass fractions of 2 percent, 4 percent, and 6 percent were created by absorbing molten organic material into the EG structure. The PW/EG composites have higher TC's as the EG content is increased. Kumar et al. [14] investigated on increasing the TC of PW using copper oxide (CuO) nanoparticles can be utilized as an effective TES. Five samples of PW were created by dispersing CuO nanoparticles in paraffin wax at weight percentages of 0, 0.5, 1.0, 1.5, and 2.0. The results shown that combining CuO and paraffin wax significantly increased the TC and LHS performance of the PW. Paraffin with polyaniline nanocomposite was created by dispersion with simple sonification [15]. LHS increased by 15.9 percent due to enhanced dispersion of conducting polymer-based nanocomposite. When the LHS is enhanced, the PCM will store more thermal energy. Because lower interfacial resistance interprets in better PCM efficacy, the TC improved by 20.4 percent, resulting in improved charging performance. From the above literature found that the incorporation of nanoparticles increases PCM's TC. The TiO2 nanoparticles have the capability to significantly increase the thermal conductivity of PW RT44 HC and are very inexpensive in comparison to other nanoparticles. There are a few research on the development of stable nano-TiO2 composites, thermal reliability and energy storage capabilities. Thus, the primary aim of this work is: a) to develop a stable NePCM with high TC foe use in TES by employing SDBD as a surfactant; and b) to examine the thermal stability, chemical stability, and effective TC of the material thus produced. This investigation intends to use the prepared composite for the application such as solar still heating, solar water and air heaters, solar collectors and photovoltaic thermal systems [16][17].

II. MATERIALS AND METHODS

A. Materials

Paraffin RT44 HC was acquired from Rubitherm phase change materials. It has a melting point of 44-45 °C, LHS capacity of 250 kJ/kg, and TC of 0.20 W/mK. Sigma– Aldrich, Germany, provided titanium dioxide (TiO₂) nanoparticles in the anatase form with a diameter of 25nm. Sodium dodecyl benzene sulphonate (SDBS) acquired from Sigma-Aldrich (M) Sdn Bhd and employed as a surfactant during the development of NePCM to ensure homogenous dispersion. Table 1 summarizes the thermophysical properties of RT44 HC, SDBS, and TiO₂ were presented.

TABLE 1 THERMOPHYSICAL PROPERTIES OF *RT44HC*, *Ti*O₂ AND SDBS

Properties	RT44 HC	SDBS	TiO ₂
Thermal conductivity (W/mK)	0.20	-	4.8 - 11.8
Density (kg/l)	0.8	1.09	4.26
Latent heat(kJ/kg)	220	-	-
Color	White	White	White
Melting temperature(°C)	44	214-217	2103-2123
Size(nm)	-	-	25
Appearance	-	Flakes	-
Molecular weight (g/mol)	-	348.48	-

B. Preparation of NePCM

A nanocomposite composed of Paraffin RT44 HC with a melting point of 44 to 45 degrees Celsius and TiO₂ was created using probe sonicator. RT44 was melted using hotplate maintained at a temperature more than 65 degrees Celsius for the duration of the process. Using an analytical microbalance, the required weight of TiO₂ in the 25nm size range was calculated (Model: EX224, OHAUS). TiO₂ was added to melted PW for 30 minutes and the solution probe sonicated to get the appropriate dispersion. To conduct additional testing following sonication, the mixture was cooled to room temperature, as seen in Fig 1. The PW and PWT1 are used throughout the paper to refer to base Paraffin RT44HC and 1% weight composition NePCM, respectively.



Fig. 1. Preparation methods of nano enhanced PCM.

C. Characterizatin of NePCM

Extensive testing of the NePCM characterization, the thermal stability of the prepared samples was verified using TGA to determine the initial and final degradation temperatures. This was performed using a PerkinElmer TGA that operated between around 40 and 350°C and heated at a rate of approximately 20°C/min. The chemical composition of the NEePCMs was determined using FT-IR, the Perkin Elmer instrument were taken transmittance mode with 64 scans from 4000-400 cm⁻¹. TEMPOS thermal properties analyzer is used to evaluate the TC of PCM and NePCM composites in the solid phase (SH-3 sensor, Meter group). It

should be distinguished that the TC value was measured at temperatures lesser than the melting point of PCM/ NePCM in order to prevent the possibility of natural convection in the mushy zone during melting. To avoid differences in the results, the measurement is performed five times, and the average value is presented here. The maximum variance in TC measurement is reported to be 10%.

III. RESULTS AND DISCUSSION

The thermal stability, chemical stability, and thermal conductivity of the produced composite NePCM are described in detail in this section.

A. Thermal Stability Analysis

The TiO₂ has been reported to enhance the thermal decomposition resistance of the materials, the degradation of PW and NePCM is shown in fig 2. When the temperature reaches 225 °C PW start to decompose and when the temperature rises to 274 °C it completely decomposes. The TGA curve of NePCM have shown the same trend as that of base PW, but the decomposition temperature is higher than that of base PW. The onset degradation temperature for PWT0.1, PWT0.5, PWT1 and, PWT2 are 223.89 °C, 229.33°C, 231.91°C and 237.32°C respectively. When the mass proportion of Np's rises to certain extent the thermal stability of the NePCM was increased as displayed in fig 2. At temperatures higher than pure paraffin PW, excellent thermal stability is seen, whereas a lower value indicates a decrease in thermal stability[18]. This is most likely because nano TiO₂ increases the physical bonding connection between PW molecules, increasing the heat resistance of the nanocomposites, when heated, the TiO₂ NPs form a thermal barrier, which may account for the enhanced thermal stability. The findings indicate that nano TiO_2 is an appropriate additive for improving the thermal stability of PW/TiO₂ nanocomposite.

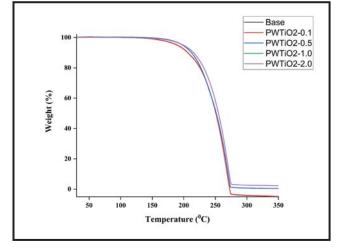


Fig. 2. TGA curve wt% vs Temperature for PW and NePCM Composite

B. Chemical Stability Analysis

The FTIR spectroscopy was used to determine the composition of developed composites PW/TiO_2 in the range 4000-400 cm⁻¹. The figure no 3 illustrates the infrared spectrum of paraffin PW base, TiO₂ nanoparticles, SDBS surfactant, and its composite PW/TiO_2 . Based on the

indication, observed composites exhibit four distinct visible peaks at various wavelengths. Major peaks were seen at 2958cm⁻¹,2910 cm⁻¹, 2850cm⁻¹, 1471cm⁻¹, and 716cm⁻¹. The first, second, and third peaks, 2958, 2910, and 2850 cm⁻¹, respectively, are centered between 2800 and 3000 cm⁻¹ and correspond to the symmetric stretching vibrations of the single bond CH3 and CH2 groups, respectively. [19]. The peak, 1471 cm⁻¹, represents the deformation of the single bond CH3 and CH2 groups, whereas the last peak, 716 cm⁻¹, represents the rocking of the single bond CH2 group and is located between 710 and 725 cm⁻¹. Single bond CH2 group associated with deformation at 710-725 cm⁻¹ peaks region; single bond CH3 and single bond CH2 group seen at 1350-1470 cm⁻¹ peaks region; symmetric stretching vibration seen at 2800-3000 cm⁻¹ peaks region; single bond CH3 and single bond CH2 group seen at 2800-3000 cm⁻¹ peaks region. Evidently, no additional peak was identified in the FTIR of PW/TiO₂ as compared to pure PW. As a result, no chemical interaction took place between PW, TiO2 nanoparticles, and the surfactant SDBS.

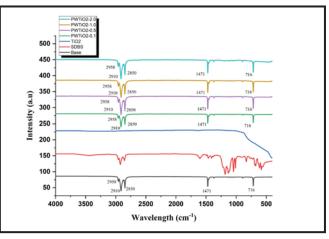


Fig. 3. Physical and chemical stability analysis of RT44HC and TiO₂ based enhanced composite PCM

C. Thermal stability Analysis

The TC is one of the important constraints to evaluate the distinction of NEOPCM composite. As shown in the fig, the TC of PW/TiO₂ composites is greater than that of base PW, with a TC of 0.1980 W/ mK. The combination of TiO_2 and PW further enhances the TC of NePCM. The outcomes revealed that the TC of PWT0.1, PWT0.5, PWT1 and PWT2 are 0.2616, 0.3357, 0.3690 and 0.2852 W/ mk respectively. The highest TC was obtained with 1.0-PWTiO₂ by an increment of 86.36% as related with base PW. Beyond a specific limiting weight %, we found TC saturation and a declining trend in TC with increasing concentration. The decrease in TC at high nanoparticle concentrations might be ascribed to NPs agglomeration. The agglomeration of the NPs results in the creation of non-uniform composites, which reduces overall thermal efficiency. The major cause of decreasing effectiveness is agglomeration, which causes the thermal network to break down and decrease TC.

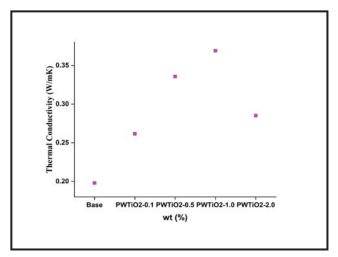


Fig. 4. Thermal conductivity of RT44HC and $\rm TiO_2$ based enhanced composite PCM

IV. CONCLUSIONS

The preparation of TiO₂ nanoparticle-in-paraffin RT44, which is a solid-liquid phase transition material, was accomplished using two step methods. The nanocomposites based on paraffin RT44 HC and TiO₂ prepared for thermal management applications with NPs wt fractions ranging from 0.1, to 2%. Experimental investigations have been carried out on a variety of thermophysical characteristics, including thermal stability, chemical stability, and TC. The TC was enhanced up to 2.0 wt % afterward decreasing trend. The highest increase in TC of NePCM is obtained by adding a 1% mass fraction of TiO₂, the effective TC increases 86% in comparison to base paraffin. The FTIR outcome showed that the developed composite is well mixed physically and no additional peak was observed which result no chemical reaction appears in the composite PCM. The TGA results presented the prepared composites have the higher thermal stability than PW, it can be observed that higher thermal stability with PW/TiO2 composite. Additionally, introducing a small quantity of nanoparticles resulted in a significant rise in the degradation temperature. From the above findings it can be determined that developed composite is chemically and thermal stable and can be utilized for the solar thermal applications and water heating applications.

ACKNOWLEDGMENTS

The authors would like to thank Universiti Malaysia Pahang (UMP) and Ministry of Higher Education Malaysia for the financial provision given under Fundamental Research Grant Scheme: FRGS/1/2021/STG05/UMP/02/5 and Sunway for the research facilities provided University via Individual Research Grant (IRG) 2021 (GRTIN-IRG-10-2021).

REFERENCES

- T. Kober, H. Schiffer, M. Densing, and E. Panos, "Global energy perspectives to 2060 – WEC's World Energy Scenarios 2019," *Energy Strateg. Rev.*, vol. 31, no. December 2019, p. 100523, 2020, doi: 10.1016/j.esr.2020.100523.
- [2] L. F. Cabeza, *Thermal energy storage*, vol. 3. 2012.
- [3] P. K. S. Rathore and S. K. Shukla, "Enhanced thermophysical properties of organic PCM through shape stabilization for thermal energy storage in buildings: A state of the art review," *Energy Build.*, vol. 236, p. 110799, 2021, doi: 10.1016/j.enbuild.2021.110799.
- [4] J. Qin, Y. Chen, C. Xu, and G. Fang, "Synthesis and thermal properties of 1-octadecanol / nano-TiO 2 / carbon nanofiber composite phase change materials for thermal energy storage," *Mater. Chem. Phys.*, vol. 272, no. July, p. 125041, 2021, doi: 10.1016/j.matchemphys.2021.125041.
- [5] H. Jouhara, A. Żabnieńska-Góra, N. Khordehgah, D. Ahmad, and T. Lipinski, "Latent thermal energy storage technologies and applications: A review," *Int. J. Thermofluids*, vol. 5–6, 2020, doi: 10.1016/j.ijft.2020.100039.
- [6] R. P. Singh, J. Y. Sze, S. C. Kaushik, D. Rakshit, and A. Romagnoli, "Thermal performance enhancement of eutectic PCM laden with functionalised graphene nanoplatelets for an efficient solar absorption cooling storage system," *J. Energy Storage*, vol. 33, no. October 2020, p. 102092, 2021, doi: 10.1016/j.est.2020.102092.
- [7] W. Q. Li, S. J. Guo, L. Tan, L. L. Liu, and W. Ao, "Heat transfer enhancement of nano-encapsulated phase change material (NEPCM) using metal foam for thermal energy storage," *Int. J. Heat Mass Transf.*, vol. 166, 2021, doi: 10.1016/j.ijheatmasstransfer.2020.120737.
- [8] S. Wu, T. Yan, Z. Kuai, and W. Pan, "Thermal conductivity enhancement on phase change materials for thermal energy storage: A review," *Energy Storage Mater.*, vol. 25, no. October 2019, pp. 251–295, 2020, doi: 10.1016/j.ensm.2019.10.010.
- [9] A. Al-Ahmed, M. A. J. Mazumder, B. Salhi, A. Sari, M. Afzaal, and F. A. Al-Sulaiman, "Effects of carbon-based fillers on thermal properties of fatty acids and their eutectics as phase change materials used for thermal energy storage: A Review," *J. Energy Storage*, vol. 35, no. December 2020, p. 102329, 2021, doi: 10.1016/j.est.2021.102329.
- [10] Y. Chen, Y. Liu, and Z. Wang, "Preparation and characteristics of microencapsulated lauric acid as composite thermal energy storage materials," *Medziagotyra*, vol. 26, no. 1, pp. 88–93, 2020, doi: 10.5755/j01.ms.26.1.21303.
- [11] R. K. Sharma, P. Ganesan, V. V. Tyagi, H. S. C. Metselaar, and S. C. Sandaran, "Thermal properties and heat storage analysis of palmitic acid-TiO2 composite as nano-enhanced organic phase change material (NEOPCM)," *Appl. Therm. Eng.*, vol. 99, pp. 1254–1262, 2016, doi: 10.1016/j.applthermaleng.2016.01.130.
- [12] H. Masoumi, R. Haghighi, and S. M. Mirfendereski, "Thermochimica Acta Modification of physical and thermal characteristics of stearic acid as a phase change materials using TiO 2 -nanoparticles," *Thermochim. Acta*, vol. 675, no. February, pp. 9–17, 2019, doi: 10.1016/j.tca.2019.02.015.
- [13] M. Kenisarin, K. Mahkamov, F. Kahwash, and I. Makhkamova, "Solar Energy Materials and Solar Cells Enhancing thermal conductivity of para ffi n wax 53 – 57 ° C using expanded graphite," Sol. Energy Mater. Sol. Cells, vol. 200, no. July 2017, p. 110026, 2019, doi: 10.1016/j.solmat.2019.110026.
- [14] P. M. Kumar, R. Anandkumar, D. Sudarvizhi, K. Mylsamy, and M. Nithish, "ScienceDirect Experimental and Theoretical Investigations on Thermal Conductivity of the Paraffin Wax using CuO Nanoparticles," *Mater. Today Proc.*, vol. 22, pp. 1987–1993, 2020, doi: 10.1016/j.matpr.2020.03.164.
- [15] K. B et al., "Synthesis and Characterization of Conducting Polyaniline@cobalt-Paraffin Wax Nanocomposite as Nano-Phase Change Material: Enhanced Thermophysical Properties," *Renew. Energy*, vol. 173, pp. 1057–1069, 2021, doi: 10.1016/j.renene.2021.04.050.
- [16] I. A. Laghari, M. Samykano, A. K. Pandey, K. Kadirgama, and V. V. Tyagi, "Advancements in PV-thermal systems with and without

phase change materials as a sustainable energy solution: energy, exergy and exergoeconomic (3E) analytic approach," *Sustain. Energy Fuels*, vol. 4, no. 10, pp. 4956–4987, 2020, doi: 10.1039/d0se00681e.

- [17] 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," *Renew. Sustain. Energy Rev.*, vol. 133, no. April, p. 110341, 2020, doi: 10.1016/j.rser.2020.110341.
- [18] H. Masoumi, R. Haghighi khoshkhoo, and S. M. Mirfendereski,

"Modification of physical and thermal characteristics of stearic acid as a phase change materials using TiO 2 -nanoparticles," *Thermochim. Acta*, vol. 675, no. February, pp. 9–17, 2019, doi: 10.1016/j.tca.2019.02.015.

[19] N. Mekaddem, S. Ben Ali, M. Fois, and A. Hannachi, "Paraffin/expanded perlite/plaster as thermal energy storage composite," *Energy Procedia*, vol. 157, pp. 1118–1129, 2019, doi: 10.1016/j.egypro.2018.11.279.