

## Enhancement in Thermal Properties of Organic Phase Change Material (Paraffin) via TiO<sub>2</sub> Foam Doping

**Neetu Bora**

Department of Physics,  
Govind Ballabh Pant University of Agriculture and Technology,  
Pantnagar, 263145, Uttarakhand, India.  
*Corresponding author:* neetubora95@gmail.com

**Deepika P. Joshi**

Department of Physics,  
Govind Ballabh Pant University of Agriculture and Technology,  
Pantnagar, 263145, Uttarakhand, India.  
E-mail: deepikakandpal@gmail.com

(Received on February 04, 2023; Accepted on February 17, 2023)

### Abstract

Phase change materials (PCM) can absorb or release a huge amount of latent heat in accordance with the increase or decrease of the surrounding temperature. Among all the studied PCMs, organic PCM paraffin has been chosen due to the large energy storage capacity for thermal energy storage (TES). The present work introduces a thermally modified phase change material by TiO<sub>2</sub> foam impregnation in paraffin. Three TiO<sub>2</sub>/paraffin PCM composites TPCM1, TPCM2, and TPCM3 containing 10 wt.%, 15 wt.%, and 20 wt.% of TiO<sub>2</sub> foam with paraffin have been successfully synthesized for thermal energy storage. The porous TiO<sub>2</sub> foam can provide a high paraffin loading capacity of up to 80 % (TPCM3) due to hollow cavities. TiO<sub>2</sub> foam is uniformly distributed over the inner and outer surface of the paraffin as a nano additive to enhance the thermal conductivity (TC) of the composite PCM. The structural, morphological, and thermal study revealed that doping of the supporting material has potentially modified all the criteria of PCM composite for TES. The highest leakage-proof result was obtained for 20 wt.% of TiO<sub>2</sub> foam impregnated composite (TPCM3) by analysing mass loss across 500 thermal cycles in an oven at 80°C. The thermal reliability of the TPCM3 composite has also been investigated after 500 thermal cycles. The TPCM3 composite maintains its crystalline nature with homogeneous dispersion and thermal stability without affecting the thermal and chemical properties of the PCM. The latent heat of the TPCM3 composite reached 182.87 J/g, and the thermal conductivity has been calculated at 0.71 W/m-K, which is 3.73 times higher than paraffin. The results concluded that synthesized TPCM3 composite could be a potential candidate for TES due to chemical and physical compatibility, easy synthesis process, good thermal and chemical reliability, and acceptable energy storage capacity with enhanced thermal conductivity.

**Keywords-** Paraffin, TiO<sub>2</sub> foam, Latent heat, Thermal conductivity, Thermal stability.

### 1. Introduction

The amount of greenhouse gases significantly increased due to the quick usage of fossil fuels. Since 1751, the amount of carbon dioxide emissions has climbed to over 347 billion tonnes (Prabhu and ValanArasu, 2020). Scientists are therefore making enormous efforts to limit the use of fossil fuels, and to produce energy from renewable sources, such as wind, sunshine, geothermal, and hydropower. Given its abundance and accessibility, solar energy is one of the most promising forms of renewable energy (Prabhu and ValanArasu, 2020; Nie et al., 2021). By 2050, according to the International Energy Agency, solar energy will generate 21 % of the global electricity consumption (Su et al., 2018; Parvate et al., 2021). However, there are many issues with the use of solar energy (Mazinani et al., 2017; Deka et al., 2020). Area, time of day, season, and local meteorological conditions all affect how strong the sun's radiation is at any given location (clear and cloudy sky) (Mitran et al., 2021; Wang et al., 2021). However, bridging

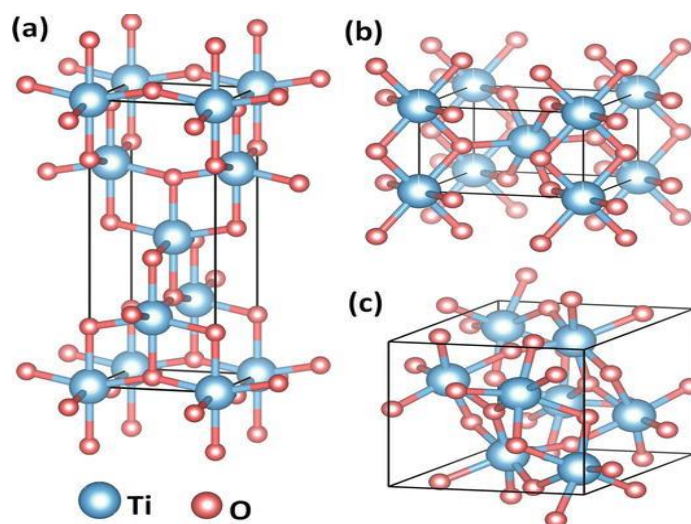
the energy supply and demand gap by employing renewable energy (such wind, solar, and hydroelectric energy) may be seen as a driving factor in this process (Yao et al., 2014). The usage of renewable energy is also subject to some restrictions since it is not always and constantly available (Aulakh and Joshi, 2019). As a result, it makes engineering valuable to store solar energy in various ways, such as electrochemical and thermal energy storage systems (TESS) (Antony et al., 2021). Therefore, the creation of such energy-storing materials that can be used later becomes crucial. In this regard, phase change materials (PCM) have drawn the focus of researchers for thermal energy storage (TES).

There are three different kinds of PCM: eutectic, organic, and inorganic (Prasanna and Deshmukh, 2021). The inorganic PCMs are often hydroxides, alloys, and salt hydrates, which have good thermal conductivity, and latent heat storage capacity. However, unpredictable melting behaviour is less trustworthy (Jebaraj and Iniyar, 2006; Mazinani et al., 2017; Prasanna and Deshmukh, 2021). The majority of the organic PCMs are made of fatty acids, and paraffin has been shown potential candidate as a TES material due to its non-toxic and higher latent heat storage (LHS) fusion capability (Deka et al., 2020; Zhang et al., 2020). For TES, organic PCMs (particularly paraffin) have drawn the most attention out of all the identified PCMs since they can absorb or release a significant quantity of latent heat in response to changes in ambient temperature (Son et al., 2013). Therefore, paraffin has a considerable capability for storing energy (Li et al., 2014). However, the thermo-physical characteristics of paraffin (such as shape, structure, thermal conductivity, reliability, thermal deterioration, and thermal performance) have not been able to meet all of the demands of engineers for TES devices (Hou et al., 2011). To improve the understanding of the thermo-physical characteristics of paraffin, many investigations have been carried out. A review of the literature found that dispersing metal, and their oxide nanoparticles (NPs) in paraffin, such as  $\text{TiO}_2$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{SiO}_2$ , etc., can significantly increase the thermal properties and the thermal conductivity of paraffin (Singh, 2019; Zhou et al., 2020; Wang et al., 2021).

Zhou et al. (2020) reported the synthesis of  $\text{TiO}_2$  NPs by a facile gas flame combustion method. It has been found that the synthesized  $\text{TiO}_2$  NPs show an anatase phase with a particle size of about 9 nm. Chen et al. (2020) prepared new three-dimensional interconnected hierarchically porous anatase  $\text{TiO}_2$  foam with the mesoporous wall structure, via a sol-gel templating method. Zhu et al. (2022) reported the synthesis of  $\text{TiO}_2$  NPs by sol-gel method, and found that  $\text{TiO}_2$  NPs have excellent chemical and thermal stability, and the band gap and surface area were calculated to be 3.2 eV and  $64.041 \text{ m}^2/\text{g}$ . Nomura et al. (2015) successfully developed the sol-gel synthesis method for  $\text{TiO}_2$  nanoparticles. Khannyra et al. (2022) conducted rutin mediated synthesis method for the development of  $\text{TiO}_2$  nanoparticles (NPs). XRD showed the amorphous nature of titanium dioxide nanoparticles. Mahdi and Kara (2021) successfully prepared nano- $\text{TiO}_2$  paraffin composite. It was found that on increasing the  $\text{TiO}_2$  content, viscosity, density, thermal conductivity increases. However, the composite shows less thermal stability due to the leakage of paraffin from the prepared composite. The dispersion of  $\text{SiO}_2$  NPs,  $\text{TiO}_2$  NPs, copolymers,  $\text{ZnO}$  NPs,  $\text{CuO}$  NPs, and all other NPs in paraffin shows a slightly improvement in thermal conductivity, leakage, and homogeneity, however with a significant decrease in latent heat (Hsu et al., 1993; Small et al., 2005; Wang et al., 2021). To build the optimum material for TES, it is necessary to create shape-stable paraffin composite with high latent heat and high thermal conductivity.

Hence, the present work attempts to develop a novel kind of shape-stable phase change composite material by using  $\text{TiO}_2$  foam with paraffin to prevent leakage problems, and enhance the thermal stability, reliability, and conductivity of paraffin. For achieving all these properties, titanium dioxides ( $\text{TiO}_2$ ) foam have been synthesized (Khannyra et al., 2022). Titanium dioxide ( $\text{TiO}_2$ ) semiconductor nanoparticles, a classic inorganic metal oxide material that naturally occurs on the earth and it has a different crystal structure rutile, anatase, and brookite (Hsu et al., 1993; Mahdi and Kara, 2021). Due to their PH

dependence ( $\sim 1.5$ ),  $\text{TiO}_2$  nanoparticles form aggregated cluster-type and tetragonal structures as shown in Figure 1 (Small et al., 2005). Anatase  $\text{TiO}_2$  NPs have a relevant band gap of 3.23 eV, while rutile has a band gap of 3.06 eV (Hairrom et al., 2021). Metal oxide has been used as a shell matrix due to its thermal conductivity promoter property, porous nature, non-toxic, and relatively cost-effective in comparison to other metals and metal oxides (Kandpal et al., 2007; Sharma et al., 2022). In addition to these,  $\text{TiO}_2$  is nonreactive with organic PCM (Sharma et al., 2009; Mugundan et al., 2022; Razak et al., 2022). Synthesized  $\text{TiO}_2$  foam has been used for preparing  $\text{TiO}_2$ /paraffin composites via direct mixing of  $\text{TiO}_2$  in paraffin with various wt.% (i.e., 10 %, 15 %, and 20 %). Direct mixing synthesis is a low-cost, facile, and very effective method for preparing paraffin composites. Different techniques have been used to characterize the manufactured TES materials, including the Leakage test, XRD, FESEM, FTIR, DSC, TGA, and LFA.



**Figure 1.** Crystal structure of  $\text{TiO}_2$  (a) Anatase (tetragonal) (b) Rutile (tetragonal) (c) Brookite (orthorhombic) micrograph.

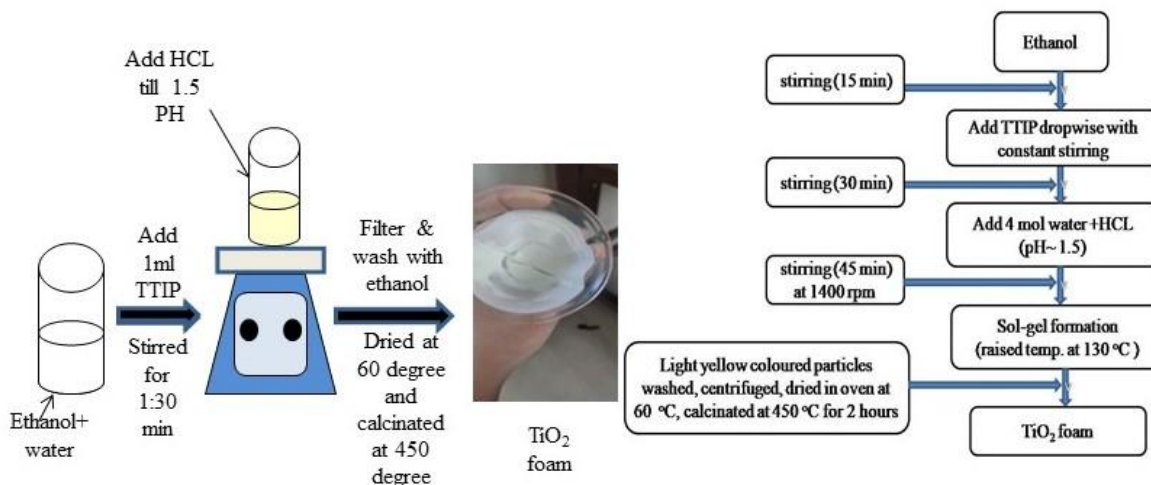
## 2. Materials and Method

### 2.1 Materials Used

Chemical used in this experiment, are Titanium (IV) iso-propoxide (TTIP, 98+%), purchased from Sigma Aldrich. Acetonitrile (98 %), ammonium hydroxide (29 % in water), absolute ethanol (99.5 %), and paraffin have been received from Hi-media. Distilled water (DI water) used in experiment, collected from laboratory water distiller.

### 2.2 Synthesis of $\text{TiO}_2$ Foam

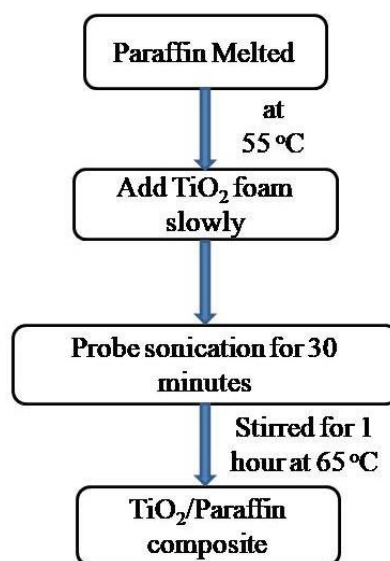
$\text{TiO}_2$  foam has been synthesized via the Sol-gel method as shown in Figure 2. First TTIP is added dropwise with ethanol and water with continuous stirring. Using diluted  $\text{H}_2\text{SO}_4$  to keep the PH at 1.5, 4 moles of water have been added to the solution after 35 minutes, and the mixture then magnetically agitated for 45 minutes at 1200 rpm. A gel-like solution has been obtained after 50 minutes it has been treated at  $130^\circ\text{C}$  for one hour. Yellow-coloured particles have been received, and washed with DI water. Further, the washed particles have been centrifuged at 10,000 rpm, and the obtained light yellow-coloured foamy particles have been dried at  $60^\circ\text{C}$  in hot air oven (Su et al., 2018; Mazinani et al., 2017; Deka et al., 2020). The final  $\text{TiO}_2$  foam has been obtained after being calcinated at  $450^\circ\text{C}$  for 2:30 hours.



**Figure 2.** Schematic block diagram of the synthesis of  $\text{TiO}_2$  foam.

### 2.3 Synthesis of $\text{TiO}_2$ /Paraffin Composite

Paraffin wax has been melted at  $65^\circ\text{C}$  in a water bath. An analytical microbalance has been used to measure the wt.% of the synthesised  $\text{TiO}_2$  foam (10 %, 15 %, 20 %). After adding  $\text{TiO}_2$  foam to the heated paraffin wax stirred for 1 hour, after stirring the probe sonication has been performed for 30 minutes. After sonication, the  $\text{TiO}_2$ /paraffin composite has been allowed to cool at ambient temperature (Hairom et al., 2021). Finally, samples have been moulded in a hydraulic press with a diameter of 10.2 mm and a thickness of 3 mm. In this way, a series of composite PCMs have been prepared, which contain 10 wt.%, 15 wt.%, and 20 wt.% of  $\text{TiO}_2$  foam in paraffin viz. TPCM1, TPCM2, and TPCM3, respectively. Schematic block diagram of the synthesis of  $\text{TiO}_2$ /paraffin composite has been summarized in Figure 3.



**Figure 3.** Schematic block diagram of the synthesis of  $\text{TiO}_2$ /paraffin composites.

Using X-ray light at the  $2\theta$  range from an XRD (X-ray diffractometer), the crystal structure of  $\text{TiO}_2$  foam has been studied at  $10^\circ$  to  $80^\circ$ . Fourier transformation infrared spectroscopy (FTIR) has been used to analyze the chemical composition of  $\text{TiO}_2$  foam (FTIR, Bruker,  $600\text{--}4000\text{ cm}^{-1}$ ). Field emission scanning microscope (FESEM) is used to conduct the morphological assessment. The seepage test has been conducted to determine the TPCM3 composite's trustworthiness and reusability.

### 3. Result and Discussion

#### 3.1 Leakage Test

The current work is an attempt to investigate the leakage-bearing property of various synthesized PCM composites. To achieve minimal paraffin leakage for many TES applications, the ratio of impregnation of prepared  $\text{TiO}_2$  foam in paraffin has been optimized through the leakage test. That modifies the leakage property of paraffin and convert it into a shape stable PCM for TES applications.

The leakage performance and shape stability of produced composite samples have been assessed by placing the TPCM1, TPCM2, and TPCM3 samples in a hot air oven set at  $80^\circ\text{C}$ . The samples are thermally treated for 500 thermal cycles while being wrapped in filter paper.

##### 3.1.1 Seepage Analysis

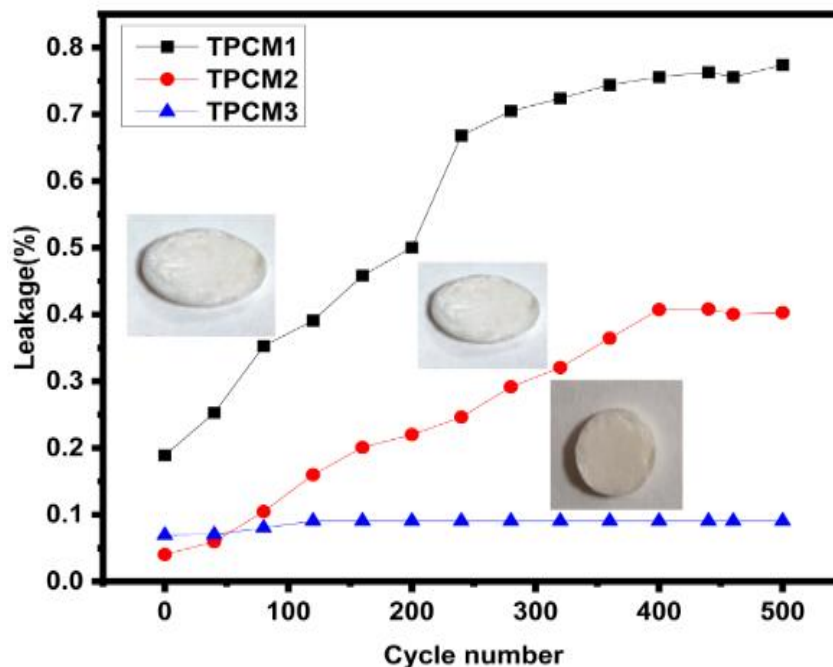
The formula used to determine the paraffin leakage rate, is denoted by Equation 1 (Aulakh and Joshi, 2019).

$$L = \frac{W_o - W_n}{W_o} \times 100\% \quad (1)$$

where,  $W_o$  and  $W_n$  are the weight of the sample before and after thermal treatment.

Figure 4 displays the weight loss curves for the sample TPCM1, TPCM2, and TPCM3, which shows the leakage rate, is 0.77 %, 0.40 %, and 0.08 %, respectively. The TPCM3 sample shows negligible leakage of 0.08 % of paraffin due to the porous nature of  $\text{TiO}_2$  Foam. Paraffin is absorbed into the porous structure of  $\text{TiO}_2$ , and so this cross-linked network-like shape limits paraffin's momentum within the matrix. Therefore, a certain rigidity caused by  $\text{TiO}_2$  foam has effectively stopped the smooth running of paraffin when the temperature is increased over the melting point of paraffin (Khannyra et al., 2022). Additionally, the inclusion of  $\text{TiO}_2$  foam shows a favourable impact on the paraffin composite's leakage tendency (Hairrom et al., 2021). It can help to improve the leakage problem during the phase change process and stabilize the PCM due to the surface tension, capillary force, and other interactions between the porous network of  $\text{TiO}_2$  foam and PCM (Yao et al., 2014). Figure 4 makes it abundantly evident that there is no sign of leakage in the filter paper surrounding the composites after numerous heat treatment cycles, which is a positive finding for establishing the leakage-proof PCM successfully.





**Figure 4.** Leakage test analysis of TPCM1, TPCM2 and TPCM3 composites.

### 3.2 XRD Analysis

To investigate the crystalline property of the TiO<sub>2</sub> foam, paraffin and TiO<sub>2</sub>/paraffin composite (TPCM3), XRD has been performed. The results are presented in Figure 5 (a), (b) & (c) respectively). The diffractogram for TiO<sub>2</sub> foam shows sharp peaks at (110), (101), (200), (111), (210), (211), (220), (002), (310), (301), (112). This confirms the anatase phase and rutile phase of TiO<sub>2</sub> foam at 450°C temperature which are in good agreement with the literature (Zhou et al., 2020). Paraffin shows two sharp and intense diffraction peaks at miller indices (110) and (200), respectively and some other small peaks which show the crystalline nature of pure paraffin wax. According to the XRD data of TiO<sub>2</sub>/paraffin (TPCM3) composite materials, all of the miller indices (110, 110), (101), (200), (111), (210), (211), (220), (002), (310), (301), and (112) diffraction peaks of TiO<sub>2</sub> foam and paraffin are present in the TPCM3 composites, and no additional new peaks are found (Mahdi and Kara, 2021). It suggests that there is not any chemical interaction between paraffin and TiO<sub>2</sub> foam.

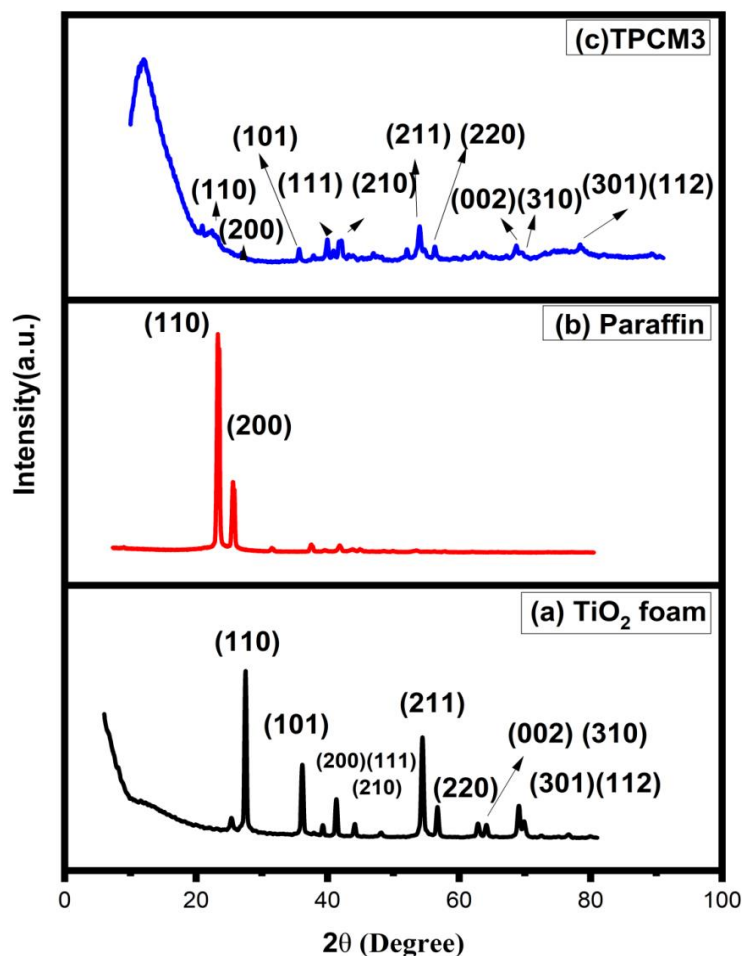
Utilizing the following formulas, the average crystallite size, strain, and dislocation density of the samples have been determined (Antony et al., 2021).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

$$\varepsilon = \frac{\beta}{4 \tan\theta} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

where,  $\beta$ ,  $D$ ,  $\varepsilon$ ,  $\delta$ ,  $\theta$ ,  $k$ , and  $\lambda$  are the full width at half maximum (FWHM) of the peaks, average crystallite size, strain due to distortions, contents of dislocations, Bragg's angle, shape function (0.98) and X-ray wavelength (1.541Å), respectively.



**Figure 5.** XRD patterns of (a) TiO<sub>2</sub> foam, (b) paraffin and (c) TPCM3 composite.

For TiO<sub>2</sub> foam, average crystallite size has been estimated at approximately 17.07 nm. This shows that TiO<sub>2</sub> foam has a finer structure. In addition, it is also observed that as the particle size decreases, the micro-strain increases. The strain, crystallite size, and micro-strain of synthesized samples are tabulated in Table 1. The results of XRD initially proved the successful synthesis of the TiO<sub>2</sub> foam.

**Table 1.** XRD data of TiO<sub>2</sub> foam.

Compound	Crystalline size (nm)	Micro-strain ( $10^{-3}$ )	Dislocation density ( $\delta \times 10^{-3}$ )
TiO <sub>2</sub> foam	17.07	1.61	0.343
Paraffin	16.5	0.859	0.367
TPCM3	17.2	0.99	0.338

### 3.3 FTIR Analysis

Figure 6 (a), (b), & (c) respectively) shows the infrared (IR) spectra of TiO<sub>2</sub> foam, paraffin, and TPCM3 composite, respectively. The spectrum of the TiO<sub>2</sub> foam, as shown in Figure 6(a), represents the stretching spectra of Ti-O and Ti-O-Ti with a distinctive wide band at 500-700 cm<sup>-1</sup>. The stretching vibrations of -

CH<sub>2</sub> and -CH<sub>3</sub> could be attributed to the absorption peaks in the paraffin FTIR spectrum at 2917.95 cm<sup>-1</sup> and 2852.64 cm<sup>-1</sup>, while the stretching vibration of C=O could be attributed to the absorption peak at 1681.39 cm<sup>-1</sup> (Li et al., 2014). The absorption peaks at 1536.51 cm<sup>-1</sup> and 714 cm<sup>-1</sup> might be attributed to -CH<sub>3</sub> in-plane bending and swing vibrations, respectively. The IR spectra of the TPCM3 composite may be seen to contain the entire features of TiO<sub>2</sub> foam and paraffin. However, the TPCM3 composite shows no new distinctive absorption bands, indicating that the absorption of paraffin into the porous TiO<sub>2</sub> foam network is just a physical contact and not a chemical reaction. This conclusion is further corroborated by the XRD results.

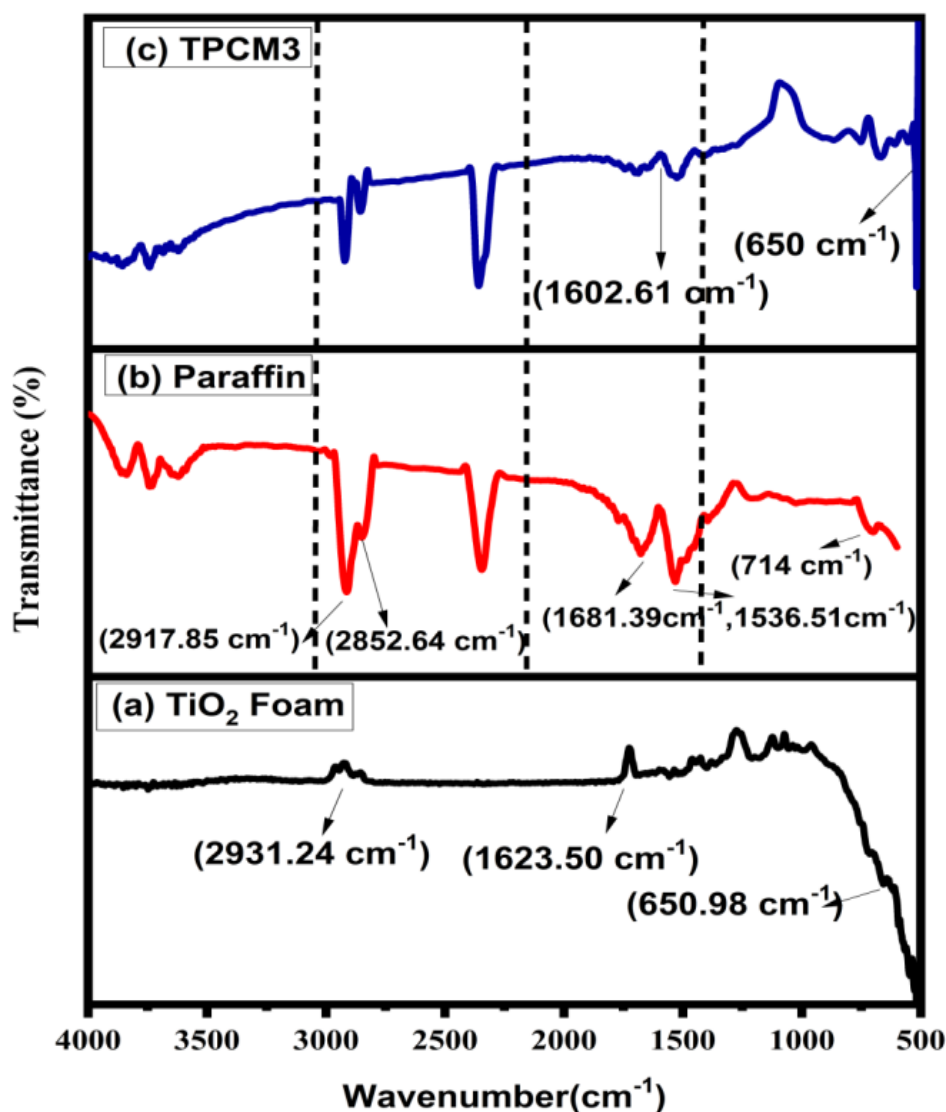


Figure 6. FTIR analysis of the samples (a) TiO<sub>2</sub> foam (b) paraffin and (c) TPCM3 composite.



### 3.4 FESEM Analysis

The surface morphologies of the  $\text{TiO}_2$  foam and TPCM3 composite are shown in Figure 7 (a) & (b).  $\text{TiO}_2$  foam has a typically porous foam/cluster like structure as shown in Figure 7 (a). It contains several regular tetragonal networks (Figure 1) and reticulates pores on the surface, which shows consistency with the existing literature of  $\text{TiO}_2$  foam (Chen et al., 2020; Zhou et al., 2020). The rich micro pore structure of the  $\text{TiO}_2$  foam has relatively high thermal conductivity, excellent chemical stability, and the robust mechanical properties make it a better candidate material for thermal energy storage (Zhang et al., 2020). Figure 7 (b) depicts the surface morphology of the TPCM3 composite; it is evident that after adding paraffin into  $\text{TiO}_2$  foam, the surface structure of  $\text{TiO}_2$ /paraffin composite has become regular. A similar-phenomenon is observed by other researchers (Hairom et al., 2021). As a result, there is no sign of immiscibility between  $\text{TiO}_2$  foam and paraffin in the FESEM pictures, indicating that the uniform paraffin dispersion into the  $\text{TiO}_2$  network is required for creating leakage-proof PCM.

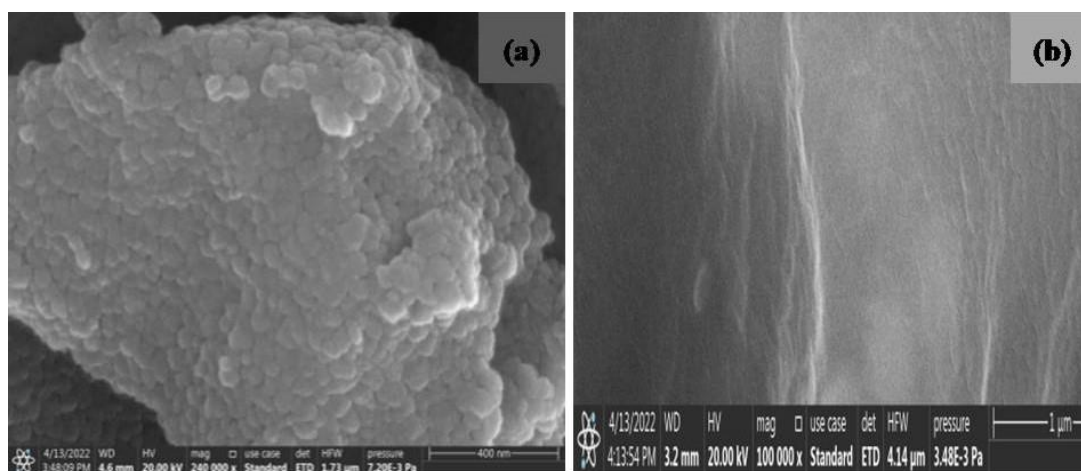


Figure 7. FESEM images (a)  $\text{TiO}_2$  foam (b) TPCM3 composite.

### 3.5 Thermal Stability

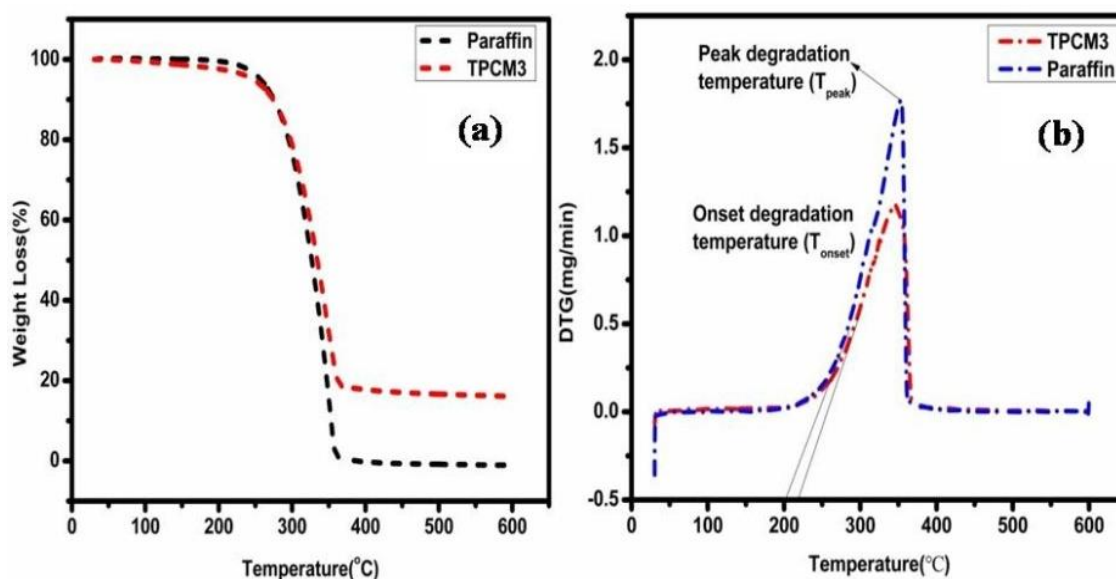
The thermal stability of composite PCMs has been analysed using thermogravimetry (TGA). Figures 8(a) and 8(b) show the TGA and DTG (Derivative thermogravimetry analysis) curves of paraffin and TPCM3 composites, respectively. The weight loss curve of paraffin and TPCM3 composites exhibits one-step heat degradation, as can be shown in Figure 8 (a). Paraffin began to degrade thermally at about  $220^\circ\text{C}$  and is fully destroyed at  $350^\circ\text{C}$ . The DTG curve is depicted in Figure 8 (b), and at  $345^\circ\text{C}$ , the highest degradation rate has been noted (Hairom et al., 2021). The TGA profile of the TPCM3 sample shows one-step degradation up to  $600^\circ\text{C}$ , which is typical for immiscible mixes with various degradation temperatures. The first step, corresponding to paraffin degradation, starts at roughly  $150^\circ\text{C}$  and ends at roughly  $380^\circ\text{C}$ . The amount incorporated in the composites, is proportional to the rate of weight reduction throughout this phase. The TGA in this study has been conducted between 27 and 600 degrees Celsius, and as indicated in Figure 8 (a), the residue in the TPCM3 composite can be recognised as  $\text{TiO}_2$  foam. The residue amount and the wt.% of  $\text{TiO}_2$  foam in the  $\text{TiO}_2$ /paraffin (TPCM3) composite are comparable. In light of these findings, it can be concluded that PCM is effectively synthesised and has great thermal stability up to  $80^\circ\text{C}$ .

Additionally, the maximal breakdown (DTG) rate for paraffin and TPCM3 is revealed by the DTG curve of composite around 1.76 mg/min, and 1.35 mg/min at temperatures 345°C and 330°C, respectively. It has been observed that TiO<sub>2</sub> foam has a positive effect on the degradation of composite resulting in a substantial rise in the degradation temperature. This might be because the porous TiO<sub>2</sub> foam network slows down the process of deterioration, and increases the thermal stability of composites by hindering the release of volatile paraffin (Hairrom et al., 2021). Table 2 contains the DTG overview of PCM blends.

**Table 2.** Specific data of TGA/DTG curve.

Sample	T <sub>onset</sub> (°C)	T <sub>offset</sub> (°C)	Δw(%)	DTG(mg/min)	Residue (%) (600°C)
Paraffin PCM	200 ± 0.20	350 ± 0.20	100	1.76	0
TPCM3	240 ± 0.20	380 ± 0.20	80	1.35	20

where, T<sub>onset</sub>, T<sub>offset</sub>, and Δw (%) denotes onset degradation temperature, offset degradation temperature, and paraffin wt.% in the sample.



**Figure 8.** (a) TGA and (b) DTG curves for paraffin and TPCM3 composite.

### 3.6 DSC Results

Through DSC analysis, the phase - transition properties of paraffin and the compositions made from TiO<sub>2</sub> foam have been investigated. Figure 9 (a) & (b) depict the findings of the heating and cooling images obtained, and Table 3 summarises the relevant parameters obtained from DSC measurements. As seen in the picture, paraffin has two transition region peaks: the first at around 36.90-50.20°C for solid-solid phase transition and the second at around 52.23-69.77°C for liquid phase change process. During phase transition process, the main peak around 62.77°C may be traced to the heterogeneously nucleated rotator liquid. It indicates the paraffin's strong solid-liquid phase transformation. The peak to the left of the primary peak results from a change in the homogeneously nucleated crystal rotator, which shows that paraffin's solid-solid phase, has been adjusted (Chen et al., 2020; Zhu et al., 2022). Most likely, this peak is associated with the rebuilding of the orthorhombic to the hexagonal crystal structure, which often occurs in various paraffin waxes.

The TPCM3 composite has been heated during the DSC test from ambient temperature to 600°C. For the composite comprising 20 wt.% of TiO<sub>2</sub> foam, the exothermic process has been seen. The melting/freezing peak temperatures of paraffin and TPCM3 composite have been observed around 62.77°C/ 52.52°C, and 63.3°C /55.96°C, respectively. TPCM3 composites peak temperatures differ slightly from those of pure paraffin. This variation is caused by the entrapment of the liquid paraffin into the porous network of TiO<sub>2</sub> foam. The Gibbs-Thomson equation, which describes the pore size of a porous material, significantly impacts on the phase change temperature of PCM (Sharma et al., 2022).

$$\Delta T \propto \frac{1}{r-t} \quad (5)$$

where,  $\Delta T$  is the difference in melting temperature (due to shifting),  $t$  is the PCM thickness in pores, and  $r$  is pores radius.  $\Delta T$  has an inverse relationship with  $r$ , therefore, melting temperature is depressed with increasing pore size (Jebaraj and Iniyan, 2006; Prabhu and ValanArasu, 2020).

Additionally, the latent heat storage capacities of pure paraffin, and TPCM3 composite during the melting/freezing processes have been found 224/195.5 J/g, and 182.87/113.62 J/g, respectively.

The incorporation rate (%) of paraffin in TPCM3 has been calculated by using the relation (Prabhu and ValanArasu, 2020).

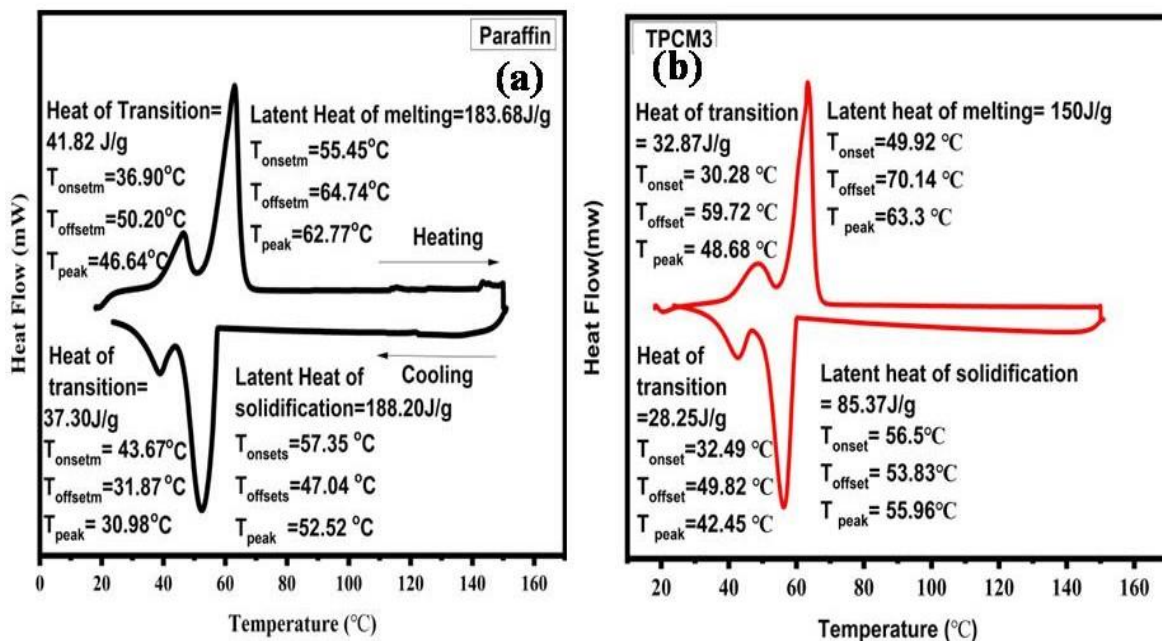
$$\eta(\%) = \frac{\Delta L_{com}}{\Delta L_{para}} \times 100\% \quad (6)$$

where,

$\eta$  -Incorporation rate (wt.%),

$\Delta L_{com}$ - Latent heat of composite,

$\Delta L_{para}$ - Latent heat of pure paraffin.



**Figure 9.** DSC profiles of melting and solidification curve (a)Paraffin (b) TPCM3 composite.

The impregnation of TiO<sub>2</sub> foam into paraffin has not shown any positive effect on latent heat. However, there is a small decrement in latent heat. That is admissible in comparison to thermal property enhancement. In the Table 3 and Table 4, some thermal properties, such as the peak temperature and latent heat of pure paraffin and TPCM3 composite for melting and solidification process have been reported and compared.

**Table 3.** DSC results of heating of Paraffin, TPCM3 composite.

Sample	T <sub>peak</sub> (°C)	T <sub>m</sub> (°C)		ΔH <sub>p,Expm</sub> J/g	ΔH <sub>p,theoretical</sub> J/g	Encapsulation Ratio (%)	Encapsulation Efficiency (%)
		T <sub>onsetm</sub>	T <sub>offsetm</sub>				
Paraffin	62.77	36.90	64.74	224	225	-	-
TPCM3	63.3	30.28	70.14	182.87	-	81.61	.76

Here, T<sub>peak</sub> is melting peak temperature, T<sub>m</sub> melting temperature, T<sub>onsetm</sub> and T<sub>offsetm</sub> are melting onset and offset temperature during solidification process. ΔH<sub>p,exps</sub>, and ΔH<sub>p,theoretical</sub> are latent heat; Exp- Experimental; Theoretical during solidification process.

**Table 4.** DSC results of cooling of paraffin, TPCM3 composite.

Sample	T <sub>peak</sub> (°C)	T <sub>s</sub> (°C)		ΔH <sub>p,Exps</sub> J/g	ΔH <sub>p,theoretical</sub> J/g
		T <sub>onsets</sub>	T <sub>offsets</sub>		
Paraffin	52.52	43.67	47.04	195.5	225
TPCM3	55.96	56.5	49.82	113.78	-

where, T<sub>peak</sub> is melting peak temperature, T<sub>m</sub> is melting temperature, T<sub>onsets</sub> is melting onset temperature, and T<sub>offsets</sub> is melting offset temperature during solidification process. ΔH<sub>p,exps</sub> and ΔH<sub>p,theoretical</sub> are latent heat; Exp- Experimental; Theoretical during solidification process.

### 3.7 Thermal Conductivity

Thermal conductivity of the pure paraffin PCM and TPCM3 composite have been investigated through the LFA method. The calculated value of the thermal conductivity for TPCM3 composite is found to be increased from 0.19 W/m°C to 0.71 W/m°C in comparison to pure paraffin . The thermal conductivity is calculated by equation 7.

$$K = \alpha \rho C_p \quad (7)$$

where, α= Thermal diffusivity, ρ=Density, C<sub>p</sub>= Specific heat, K=Thermal conductivity

**Table5.** Thermal diffusivity, density, specific heat has been obtained from LFA.

Sample	Diffusivity (mm <sup>2</sup> /sec)	Specific heat (J/g/K)	Density(g/cm <sup>3</sup> )	Thermal Conductivity (W/m°C)
Paraffin	0.171±0.003	2.1	0.54	0.19
TPCM3	0.181±0.002	0.99	3.96	0.71

## 4. Conclusions

In present work, the TPCM3 composite has been synthesised via a direct adsorption approach using three different wt.% of TiO<sub>2</sub> foam with paraffin as samples TPCM1 (10 %), TPCM2 (15 %), and TPCM3 (20 %). The leakage performance of sample TPCM3 (20 %) has been found the best compared to all three samples.

From the seepage test 0.08 % leakage of paraffin has been found. Therefore, this sample has been studied for its structural, morphological, and thermal properties. FESEM images confirm the cluster/foam formation  $\text{TiO}_2$ . The DSC measurement shows that for TPCM3 composite, the change in melting and solidification temperature are  $62.77/64.44^\circ\text{C}$  and  $52.52/51.58^\circ\text{C}$ , respectively, however it shows slight reduction in latent heat as compared to pure paraffin. The presence of  $\text{TiO}_2$  foam in paraffin leads to an increase in the conductivity from  $0.19 \text{ W/m}^\circ\text{C}$  to  $0.71 \text{ W/m}^\circ\text{C}$ . The integration of  $\text{TiO}_2$  foam increases the thermal stability of PCM due to its porous structure.

Finally, it can be concluded that the proposed material TPCM3 has the great potential to be a better material for storing thermal energy in solar air/water heating systems, building comforts applications.

#### Conflict of Interest

No potential conflict of interest was reported by the author(s).

#### Acknowledgements

The authors would like to thank the DES (Director of Experiment Station) G. B. Pant University of Agriculture and Technology, Pantnagar, India for providing financial support for conducting the research work.

#### References

- Antony, A.J., Kala, S.M.J., Joel, C., Bennie, R.B., & Praveendaniel, S. (2021). Enhancing the visible light induced photocatalytic properties of  $\text{WO}_3$  nanoparticles by doping with vanadium. *Journal of Physics and Chemistry of Solids*, 157, 110169.
- Aulakh, J.S., & Joshi, D.P. (2019). Thermal and heat transfer performance of leakage-proof phase change material. *Journal of Emerging Technologies and Innovative Research*, 6(2), 176-179.
- Chen, X., Tang, Z., Liu, P., Gao, H., Chang, Y., & Wang, G. (2020). Smart utilization of multifunctional metal oxides in phase change materials. *Matter*, 3(3), 708-741.
- Deka, P.P., Ansu, A.K., Sharma, R.K., Tyagi, V.V., & Sari, A. (2020). Development and characterization of form-stable porous  $\text{TiO}_2$ /tetradecanoic acid based composite PCM with long-term stability as solar thermal energy storage material. *International Journal of Energy Research*, 44(13), 10044-10057.
- Hairom, N.H.H., Soon, C.F., Mohamed, R.M.S.R., Morsin, M., Zainal, N., Nayan, N., Zulkifli, C.Z., & Harun, N. H. (2021). A review of nanotechnological applications to detect and control surface water pollution. *Environmental Technology & Innovation*, 24, 102032.
- Hou, Y., Vidu, R., & Stroeve, P. (2011). Solar energy storage methods. *Industrial & Engineering Chemistry Research*, 50(15), 8954-8964.
- Hsu, W.P., Yu, R., & Matijević, E. (1993). Paper whiteners: I. Titania coated silica. *Journal of Colloid and Interface Science*, 156(1), 56-65.
- Jebaraj, S., & Iniyan, S. (2006). A review of energy models. *Renewable and Sustainable Energy Reviews*, 10(4), 281-311.
- Kandpal, D., Kalele, S., & Kulkarni, S.K. (2007). Synthesis and characterization of silica-gold core-shell ( $\text{SiO}_2@Au$ ) nanoparticles. *Pramana - Journal of Physics*, 69, 277-283.
- Khannayra, S., Luna, M., Gil, M.A., Addou, M., & Mosquera, M. J. (2022). Self-cleaning durability assessment of  $\text{TiO}_2/\text{SiO}_2$  photocatalysts coated concrete: Effect of indoor and outdoor conditions on the photocatalytic activity. *Building and Environment*, 211, 108743.



- Li, H., Chen, H., Li, X., & Sanjayan, J.G. (2014). Development of thermal energy storage composites and prevention of PCM leakage. *Applied Energy*, 135, 225-233.
- Mahdi, M.T., & Kara, I.H. (2021). Thermophysical characteristic of nano  $\text{-TiO}_2$  paraffin wax composite material. *Journal of Mechanical Engineering Research and Development*, 44(6), 48-58.
- Mazinani, B., Beitollahi, A., Masrom, A.K., Samiee, L., & Ahmadi, Z. (2017). Synthesis and photocatalytic performance of hollow sphere particles of  $\text{SiO}_2\text{-TiO}_2$  composite of mesocellular foam walls. *Ceramics International*, 43(15), 11786-11791.
- Mitran, R.A., Ioniță, S., Lincu, D., Berger, D., & Matei, C. (2021). A review of composite phase change materials based on porous silica nanomaterials for latent heat storage applications. *Molecules*, 26(1), 241.
- Mugundan, S., Praveen, P., Sridhar, S., Prabu, S., Mary, K.L., Ubaidullah, M., Shaikh, S.F., & Kanagesan, S. (2022). Sol-gel synthesized barium doped  $\text{TiO}_2$  nanoparticles for solar photocatalytic application. *Inorganic Chemistry Communications*, 139, 109340. <https://doi.org/10.1016/j.inoche.2022.109340>.
- Nie, C., Liu, J., & Deng, S. (2021). Effect of geometry modification on the thermal response of composite metal foam/phase change material for thermal energy storage. *International Journal of Heat and Mass Transfer*, 165, 120652.
- Nomura, T., Zhu, C., Sheng, N., Tabuchi, K., Sagara, A., & Akiyama, T. (2015). Shape-stabilized phase change composite by impregnation of octadecane into mesoporous  $\text{SiO}_2$ . *Solar Energy Materials and Solar Cells*, 143, 424-429.
- Parvate, S., Singh, J., Dixit, P., Vennapusa, J.R., Maiti, T.K., & Chattopadhyay, S. (2021). Titanium dioxide nanoparticle-decorated polymer microcapsules enclosing phase change material for thermal energy storage and photocatalysis. *ACS Applied Polymer Materials*, 3(4), 1866-1879.
- Prabhu, B., & ValanArasu, A. (2020). Stability analysis of  $\text{TiO}_2\text{-Ag}$  nanocomposite particles dispersed paraffin wax as energy storage material for solar thermal systems. *Renewable Energy*, 152, 358-367.
- Prasanna, Y.S., & Deshmukh, S.S. (2021). Significance of Nanomaterials in solar energy storage applications. *Materials Today: Proceedings*, 38, 2633-2638.
- Razak, K.A., Halin, D.C., Abdullah, M.M.A., Salleh, M.M., Mahmed, N., Azani, A., & Chobpattana, V. (2022). Factors of controlling the formation of titanium dioxide ( $\text{TiO}_2$ ) synthesized using sol-gel method—a short review. In *Journal of Physics: Conference Series* (Vol. 2169, No. 1, p. 012018). IOP Publishing, Malaysia.
- Sharma, A., Tyagi, V.V., Chen, C.R., & Buddhi, D. (2009). Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews*, 13(2), 318-345.
- Sharma, R., Kumar, R., Sharma, D.K., Sarkar, M., Mishra, B.K., Puri, V., Priyadarshini, I., Thong, P.H., Ngo, P.T.T., & Nhu, V.H. (2022). Water pollution examination through quality analysis of different rivers: a case study in India. *Environment, Development and Sustainability*, 24, 7471-7492.
- Singh, R.P. (2019). Nanocomposites: Recent trends, developments and applications. In: Singh, R.P. (ed) *Advances in Nanostructured Composites* (pp. 16-47). Boca Raton.
- Small, A., Hong, S., & Pine, D. (2005). Scattering properties of core-shell particles in plastic matrices. *Journal of Polymer Science Part B: Polymer Physics*, 43(24), 3534-3548.
- Son, S., Hwang, S.H., Kim, C., Yun, J.Y., & Jang, J. (2013). Designed synthesis of  $\text{SiO}_2/\text{TiO}_2$  core/shell structure as light scattering material for highly efficient dye-sensitized solar cells. *ACS Applied Materials & Interfaces*, 5(11), 4815-4820.
- Su, X., Jia, S., Lv, G., & Yu, D. (2018). A unique strategy for polyethylene glycol/hybrid carbon foam phase change materials: morphologies, thermal properties, and energy storage behavior. *Materials*, 11(10), 2011.



- Wang, T., Liu, Y., Meng, R., & Zhang, M. (2021). Thermal performance of galactitol/mannitol eutectic mixture/expanded graphite composite as phase change material for thermal energy harvesting. *Journal of Energy Storage*, 34, 101997.
- Yao, Q., Lu, Z.H., Zhang, Z., Chen, X., & Lan, Y. (2014). One-pot synthesis of core-shell Cu@ SiO<sub>2</sub> nanospheres and their catalysis for hydrolytic dehydrogenation of ammonia borane and hydrazine borane. *Scientific Reports*, 4, 7597. <https://doi.org/10.1038/srep07597>.
- Zhang, W., Tian, Y., He, H., Xu, L., Li, W., & Zhao, D. (2020). Recent advances in the synthesis of hierarchically mesoporous TiO<sub>2</sub> materials for energy and environmental applications. *National Science Review*, 7(11), 1702-1725.
- Zhou, J., Zhao, J., Cui, Y., & Cheng, W. (2020). Synthesis of bifunctional nanoencapsulated phase change materials with nano-TiO<sub>2</sub> modified polyacrylate shell for thermal energy storage and ultraviolet absorption. *Polymer International*, 69(2), 140-148.
- Zhu, L., Opuencia, M.J.C., Bokov, D.O., Krasnyuk, I.I., Su, C.H., Nguyen, H.C., Mohamed, A., Zare, M.H., Zwawi, M., & Algarni, M. (2022). Synthesis of Ag-coated on a wrinkled SiO<sub>2</sub>@ TiO<sub>2</sub> architectural photocatalyst: New method of wrinkled shell for use of semiconductors in the visible light range and penicillin antibiotic degradation. *Alexandria Engineering Journal*, 61(12), 9315-9334.



Original content of this work is copyright © Prabha Materials Science Letters. Uses under the Creative Commons Attribution 4.0 International (CC BY 4.0) license at <https://creativecommons.org/licenses/by/4.0/>

**Publisher's Note-** Ram Arti Publishers remains neutral regarding jurisdictional claims in published maps and institutional affiliations.