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Biochar engineered phase change material: enhancing octadecane for next generation thermal energy storage applications

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ABSTRACT

Phase change materials (PCMs) possess viable solution for thermal energy storage systems in terms of latent heat storage. However, due to insufficient thermal conductivities, these materials cannot be employed effectively for energy storage applications. This work integrated novel combination of octadecane PCM and groundnut shell biochar (GNB) for better thermal transfer efficiency. The bio-waste derived GNB particles were synthesized and combined with octadecane PCM by adopting two-step material preparation technique. As per outcomes of the work, the physiochemical evaluation validated the chemical compatibility of GNB/octadecane composites. Besides, GNB microstructures and its interaction with octadecane PCM for thermal network development were illustrated using Scanning Electron Microscopy (SEM). In addition, latent heat melting enthalpy showed that composite with 0.7 wt% integrated GNB micro/nanoparticles exhibited 244.4 J/g. Further, maximum of 113.5% improvement in thermal conductivity was obtained employing GNB particles. Furthermore, photo-transmittance observation demonstrated 57.8% decrement in transmissibility with increment in photoabsorbance. Moreover, thermal stability of all prepared composites was validated by thermogravimetric evaluation. Therefore, the GNB/octadecane composite significantly enhanced the thermal conductivity, reduced transmissibility, shown chemical and thermal stability along with cyclic stability. The preferred achieved characteristics for prepared composite rendered it a promising composite for efficient thermal energy storage.

1. Introduction

Efficient thermal energy storage is essential element of energy system as it can store energy of intermittent energy sources like solar energy. Sensible heat storage system is type of thermal energy storage system but it requires substantial volume for energy storage and possess change in temperature during charge and discharge cycles [1]. On the other hand, latent heat energy materials for thermal energy storage exhibit significant thermal capacity, higher energy storage density [2], near-constant temperature during charge and discharge cycles [3], elevated temperature range and economical [4]. As a result, phase change materials (PCMs) with substantial latent heat storage capacity

can be employed to develop an efficient thermal management system as a remedy for thermal challenges [5]. The latent heat transmission during the phase change process is markedly greater than sensible heat [6]. The use of appropriate PCMs in energy storage technologies can significantly augment the efficiency of energy harvesting through the phase change procedure [7]. PCMs are classified as organic, inorganic and eutectic [8], among them organic PCMs have prominent choice for energy storage composites over inorganic PCMs because of its capability to store energy for significant temperature range with excessive packing density [9], better chemical, thermal stability [10], non-corrosive in nature, and cost effective. The additional application of PCMs in numerous fields, such as electronic devices [11], cooling vests, solar thermal [12], battery

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thermal management [13], automobiles and others [14], are frequently seen in present scenario. Considering the numerous benefits of PCMs, the majority of organic PCMs have limited thermal conductivity [15], inefficient light absorption and a propensity for combustion, leading to a diminished pace of heat energy transmission. These limitations restrict utilisation of PCM in numerous thermal regulation applications. Thus, escalating the thermal transport of PCMs by synthesizing highly thermal conductive composites is one of the important issue [16]. Diverse nanoparticles, including metals [17], metal oxides [18], and carbon-based [19] nanoparticles, are incorporated into base PCM to create nanocomposites that enhance thermal conductivity, light absorption efficiency, thermal stability, and reduce leakage problems [20].

The consumption of thermally conductive nanoparticles is the prevalent approach to enhance the heat transfer effectiveness of PCMs for thermal energy storage [21]. In literature, comprehensive studies have been devoted to enhancing the thermal conductivity of PCMs by integrating carbon nanoparticles [22] and nanoplatelets [23]. The carbon based nanoparticles have gained significant consideration owing to their lower density and remarkable intrinsic thermal conductivity in comparison to other nanoparticles [24]. Even though nanomaterials hold significant attributes, there are still a few problems associated with them, such as high production costs and hurdles in mass production. This implies that they can only be used on a lab scale and can't be commercialized for real world applications. Additionally, these nanoparticles are often toxic and expensive, and when they are treated, they are released into the environment, which discloses how important it is to find eco-friendly options. The synthesis of biochar by adopting green preparation route presents a novel environmentally sustainable method for altering solid waste (including coconut waste [25], rice husks [26], and other biochar) and industrialized waste (such as sawdust [27] and old tyres [28]) into efficient nanoparticles. Biochar has arisen as an environmentally viable substance resulted from agriculture and forestry byproducts. The biochar based carbon nanoparticles exhibit numerous advantages, such as cost-effectiveness [29], simplicity of preparation, improved sorption capacity, environmental gains stemming from their waste-derived origin, extensive surface area, a three-dimensional porous architecture, and heightened resistance to corrosion and heat. Accordingly, the fabrication of waste derived biochar and its utilization in thermal energy storage have appealed considerable research attention.

Previously, various biochar-derived nanoparticles were combined into PCM to assess thermophysical properties. For example, garlic stems are used to produce biochar microparticles at a temperature of 700 °C. Biochar microparticles have two-dimensional flake-like structures and three-dimensional porosity. The paraffin wax to conduct heat properties were improved by as much as 27.3% with garlic stem derived biochar. Also, dispersing garlic stem-based biochar microparticles made minute changes to the phase change temperatures of PCM, coupled with the latent heat decrement by only 6.1% [30]. Besides, in other related study, carbon-based longan shell (CLS) particles were dispersed inside the paraffin PCM for thermophysical characteristics. The CLS showed three-dimensional structure with high surface area to volume ratio, resulted in improved heat conduction interfaces. As per results, adding 1.0% weight fraction of CLS biochar had substantial effects, increasing thermal

conductivity by 89%. The latent heat enthalpy of energy storage also increased, from 231.25 J/g to 268.75 J/g. Likewise, various studies have assessed the effects of particles derived from carbon-based bio-waste [31]. In the same way, carbon-based bio waste derived particles have been investigated by various studies. However, the present research work introduced novel integration of GNB particles into low temperature commercial organic PCM operating at a temperature range of 29-35 °C for thermophysical characteristics evaluation. As per authors' claim, the combination of groundnut waste derived GNB particles and low temperature commercial grade organic PCM has not been investigated previously highlighting the novelty of present research work alongside the existing literature results as consolidated in Table 1. The prime reason for selecting GNB particles is synthesize from waste products. Besides, groundnut shell is significantly available and easy to get, making it a viable low-cost option for PCM integration. Further, integration of waste derived GNB particles into octadecane composite results in environment-friendly and sustainable option. Besides, octadecane is organic solid-liquid PCM and are extensively utilized due to appropriate thermophysical characteristics [32]. This research work corresponds to thermal energy storage application via sustainable materials for future. Hence, the study of synthesize and utilization biochar from groundnut shells is significantly important. This work focused on synthesize biochar from groundnut shells, which was then used as additive to enhance the thermophysical properties of octadecane PCM. The paper investigated the thermophysical properties of GNB/Octadecane. The results pointed that the GNB/Octadecane PCM composite is sustainable option storing latent heat and have remarkable potential for real-world utilization.

2. Materials and methods

2.1. Materials information

This study employed octadecane PCM procured from Suzhou Senfeida Chemical Co. Ltd. As per evaluation, the peak phase change temperature of octadecane is 33.5 °C and a melting enthalpy value of 234.5 J/g. The physical properties showed white appearance with purity level exceeding 98% for octadecane PCM. Further, to improve thermal performance of octadecane, the GNB particles are employed in this research work. The GNB particles are synthesized under laboratory conditions from waste groundnut shells obtained from local Malaysian market, as given in Fig. 1. The groundnut shells are easily accessible in South-East Asia region, and it is cultivated commercially in various countries of the region.

2.2. Synthesis of GNB and preparation scheme for PCM composites

This section describes how to turn groundnut shells into valuable particles for PCM composites by employing a material synthesis and preparation method. Initially, the groundnut shells were cleaned and washed with distilled water to get rid of any dirt. Further, for two hours at 150 °C, cleaned groundnut shells were placed in dry oven for drying process. Afterwards, an electric grinding machine changes the dried

Table 1
Carbon biochar filler enhanced phase change materials as on existing literature

| PCM | Carbon biochar source | Loading fraction (%) | Thermal conductivity improvement % | Application | Reference |
|---------------|-----------------------|----------------------|------------------------------------|------------------------------------|-----------|
| PEG1000 | Cotton stalk | 20 | 114 | Leakage Resistance | [33] |
| A46 | Coconut shell | 0.5 | 88.6 | Solar Still | [34] |
| Eutectic PCM | Coconut shell | 0.7 | 54.09 | Optical Absorbance | [35] |
| Paraffin | Garlic stem | 5 | 27.3 | Thermal Performance | [30] |
| Palmitic acid | Pinecone | 40 | 43.76 | Leakage Resistance | [36] |
| PEG1000 | Prosopis juliflora | 0.7 | 75 | Thermal Performance | [37] |
| RT44 | Longan Shell | 1.0 | 89 | Thermal Performance | [31] |
| Beeswax | Rice husk | 0.6 | 48 | Heat Sink | [38] |
| Octadecane | Ground nutshell | 0.7 | 113.52 | Low Temperature Thermal regulation | This Work |

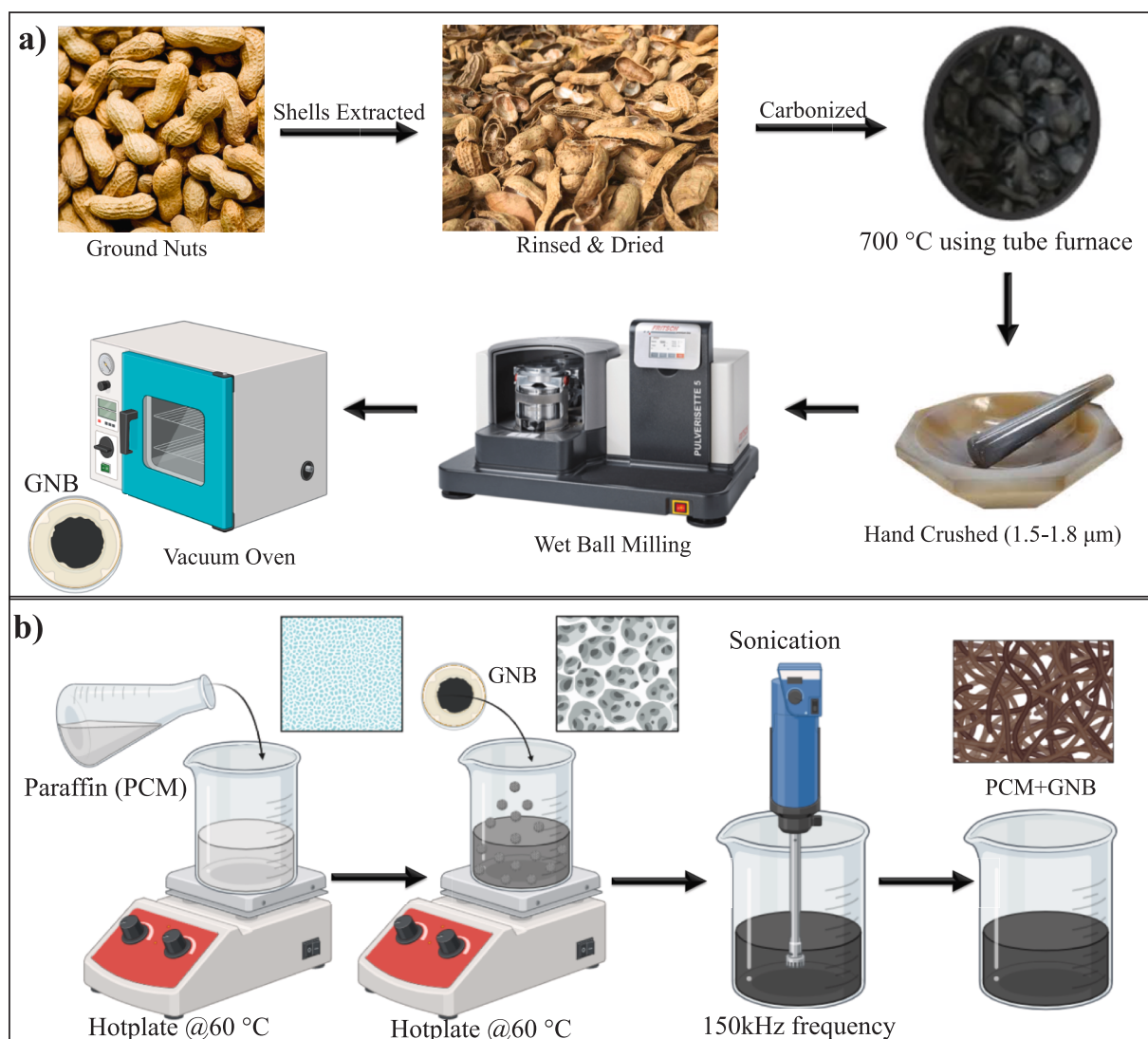


Fig. 1. Synthesize of a) GNB particles and b) PCM composites.

groundnut shells into coarse powder. Subsequently, the groundnut shell powder material goes through a carbonisation process in nitrogen (N_2) at $700\text{ }^\circ\text{C}$ for three hours, while the heating rate of the tube furnace to reach $700\text{ }^\circ\text{C}$ was $20\text{ }^\circ\text{C}/\text{min}$. The obtained carbonised GNB shell particles were further processed by hand-crushing and wet ball milling to attain smaller size of particles. Similarly, carbon waste from groundnut shells size was further reduced by hand-crushing and then wet ball milling them for 6 hours at 500 rpm, with a 5-minute break every 10 minutes of operation. The obtained biochar was subsequently subjected to crushing and wet ball milling for particle size reduction with ball-to-powder-to-water ratio of 300 gram of Zirconia ball to 20 grams of GNB sample to 20 ml of water to achieve homogeneous refinement and improved dispersion characteristics. Wet ball milling is done with 1 mm balls and water to break up the groundnut shell particles. To get the final particles, the ball-milled particles were dried in the oven at $200\text{ }^\circ\text{C}$, as shown in Fig. 1. Additionally, octadecane PCM was mixed with synthesized GNB particles for heat transfer properties improvement by applying two-step preparation method. The Fig. 1 displayed all the steps to prepare GNB particles added octadecane PCM composites. Furthermore, we carefully measured out 25 g of octadecane and different amounts of nanoparticles (0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, and 0.9 wt.%) using an analytical microbalance (MODEL: EX 224 OHAUS) and placed them into sample containers. Then, the octadecane base PCM

was heated to $60\text{ }^\circ\text{C}$ on a hot plate (RCT, BASIC IKA) to change its phase from a solid to a liquid, which is necessary for getting the nanoparticles to spread out evenly in the composite. After the PCM had completely melted, GNB particles at the right concentrations were added one at a time in the melted PCM. The resultant mixture was consequently exposed to sonication for 30 minutes with a probe sonicator (Model: FS 1200 N) to ensure uniform and comprehensive dispersal of the nanoparticles inside the PCM. Following the sonication process, the samples were permitted to equilibrate to ambient temperature before testing.

3. Results and discussions

3.1. Morphological evaluation of PCM and GNB/octadecane composite

The morphology and microstructure of octadecane phase change material, GNB particles, and octadecane/GNB composites are examined using scanning electron microscopy. Fig. 2a illustrates the surface morphology of octadecane phase PCM. The surface exhibited an uneven and fibrous texture, in contrast to the flat crystalline plates. This PCM has a sponge-like network-driven shape. The little black areas signified the existence of micropores. Further, GNB particles exhibited a structured heterogeneous surface shape as shown in Fig. 2b and c. The GNB particles displayed an uneven and rough morphology, characterised by

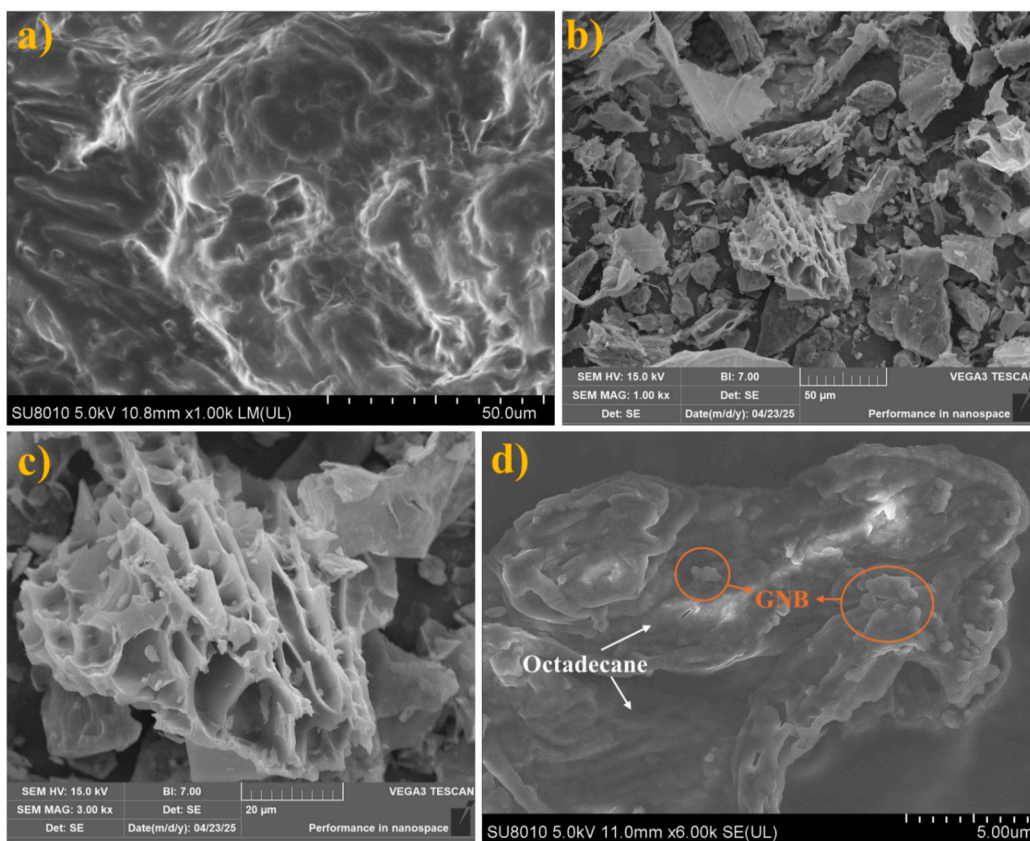


Fig. 2. Morphological evaluation a) octadecane b) groundnut shell biochar c) groundnut shell biochar zoomed image d) groundnut shell biochar based PCM composite

micropores and channels. The existence of smaller fractured particles distributed throughout a broad porous structure leads to structural brittleness due to carbonisation. Morphological images of GNB-dispersed octadecane composite samples are illustrated in Fig. 2d.

A uniform spreading of waste derived GNB particles throughout the octadecane matrix is evident, devoid of agglomeration or clustering processes. Octadecane infiltrates the micropores of GNB particles and interstitial spaces between lamellar structures, facilitating improved energy storage. The biochar particles appear to be embedded within the octadecane, as emphasised in the Fig. 2c. The rough topography of GNB particles enhances the surface area for thermal contact, thereby improving the heat transfer rate. However, to enhance the dispersal

stability of GNB particles in the base PCM, a further reduction in particle size is necessary.

3.2. Brunauer-Emmett-Teller (BET) analysis for surface area

Influence of biochar derived micro/nanoparticle with PCMs for effective energy storage and PCM impregnations are characterized based on the surface area, porosity and the pore volume distribution patterns of GNB, and this is determined using BET technique. Herein, the surface area, DFT pore size, particle size, and pore width of the synthesis GNB biochar microparticles are discussed. Fig. 3 presents the adsorption-desorption isotherms of GNB alongside their pore size distribution

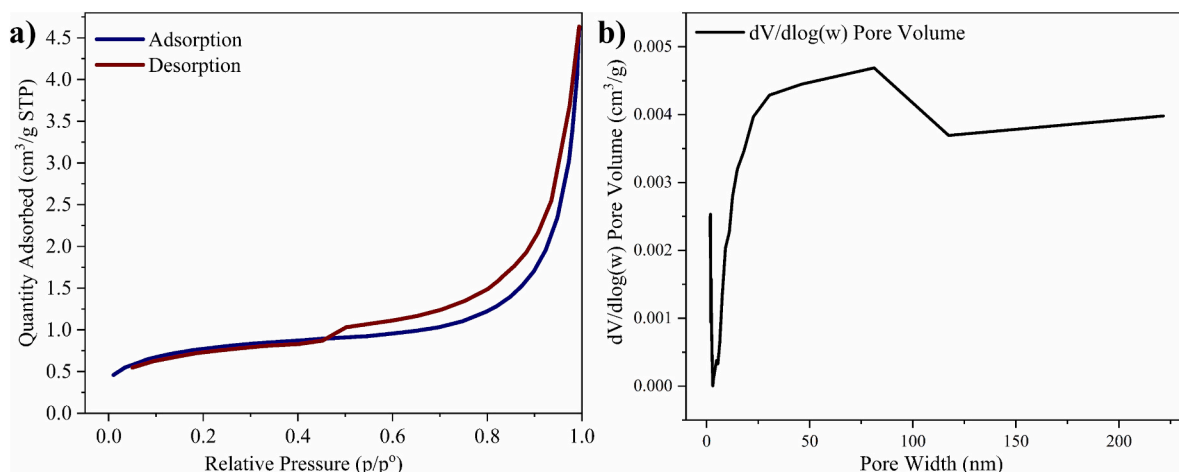


Fig. 3. BET analysis a) adsorption-desorption isotherms of GNB; b) pore size distribution.

which is determined via BET surface analyser that employs N_2 as an adsorbate. Fig. 3a reflects that the maximum N_2 adsorbed within GNB sample is $4 \text{ cm}^3/\text{g}$ as inferred from the graph; this reflects low specific surface area of the synthesised sample which is noted to be of $2.82 \text{ m}^2/\text{g}$; this is owing to the long duration ball milling process of the developed GNB. The factor to note with passage of with N_2 there is no collapse of the porous support, and this ensures better structural framework architecture, which increases the dimensional stability. As well, the developed composite is expected to resist moisture absorbance which will pave strong affinity got stable thermal properties. Subsequently, Fig. 3b presents information of the pore size and its distribution within the sample space, its inference that the maximum of pore is of the width range 2-100 nm with low internal void structures. As there are no sharp peak patterns observed, it reflects that the GNB samples reflects more interparticle voids rather than intrinsic pores. As the air gaps are comparatively higher, this reduces the thermal boundary resistance and improves heat transfer. However, certain research work emphasis on the treatment of KOH towards activation of biochar's for enhancing their porosity, thereby opting them as a Supporting Material to develop form stable PCM nanocomposites.

Subsequently on comparison with biochar-based fillers such as a) garlic stem biochar [30] and b) longan shell biochar [39] with surface area of $201.72 \text{ m}^2/\text{g}$ for garlic stem biochar and $121.15 \text{ m}^2/\text{g}$ for longan shell biochar reported in previous studies with thermal conductivity increment of 27.3% and 97.9%, the present GNB system demonstrates competitive thermal conductivity enhancement despite its lower surface area.

This indicates that thermal conductivity enhancement is not directly proportional to BET surface area alone but rather depends on the combined influence of carbon microstructure, degree of carbonization, filler dispersion, interfacial compatibility, and conductive network formation. The present results therefore suggest that low-cost agricultural biochar with optimized carbon architecture can effectively function as a sustainable thermal conductivity enhancer without requiring extremely high surface area characteristics.

3.3. Chemical stability evaluation utilizing FTIR and XRD techniques

The chemical properties of octadecane and octadecane-integrated PCM structures were meticulously analysed using the Fourier Transform Infrared (FTIR) spectrum, as depicted in Fig. 4. An intense peak in absorption was seen at a frequency of 2918, and 2844 cm^{-1} owing to the aliphatic C-H stretching vibration. The peaks at around 1476 and 720

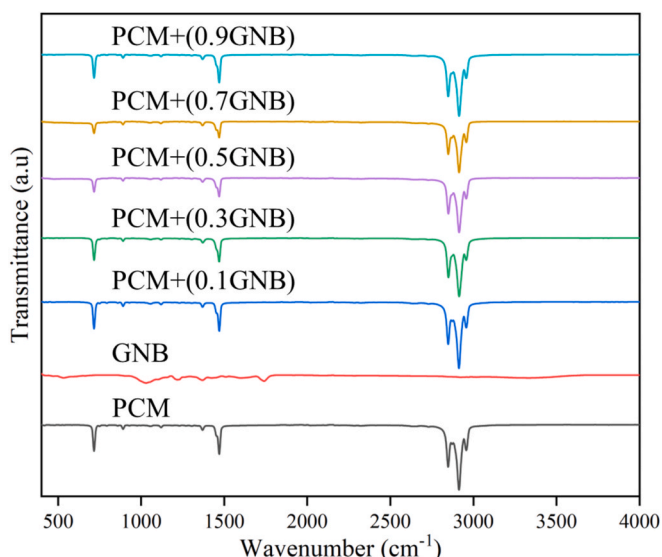


Fig. 4. Chemical stability evaluation of PCM and composites using FTIR

cm^{-1} are attributed to CH bending vibration, as evidenced in the spectrum of octadecane and its composites [40]. The GNB spectrum exhibits highly impoverished or almost featureless transmittance over the scanned range, as anticipated for carbonized microparticles with limited IR-active activities. All significant peaks observed in the FTIR spectra of GNB/octadecane specimens were congruent with those identified in the spectra of the base PCM. This signifies that no novel connections were established between GNB and octadecane.

Similarly, Fig. 5 represented the XRD evaluation of octadecane PCM, GNB, and GNB/octadecane composite. The diffraction pattern of base octadecane displays distinct and pronounced peaks at approximately 2θ 21.4°, 23.7°, 35.9°, and 40.3°, indicative of the crystalline alkane structure. Conversely, the XRD spectrum of GNB exhibits an expansive and diffuse hump centred around 2θ 20-24° with minor peak at 26.6°, lacking distinct diffraction peaks. This behaviour substantiates the mostly amorphous characteristics of GNB. Besides, the diffraction pattern of the PCM-GNB composite exhibits the distinctive peaks of octadecane at roughly 21.4°, 23.7°, 26.6°, 27.8°, and 40.3°, though with diminished intensity relative to base PCM. The presence of these peaks indicates that octadecane PCM preserves its crystalline structure following its integration into biowaste derived GNB particles.

No novel diffraction peaks are identified in composite structure, indicating that no chemical interaction or novel crystalline phase occurs amid octadecane and GNB while composite formation. This verifies that the interaction involving PCM and GNB is predominantly physical amalgamation. The XRD results indicate that GNB successfully supports octadecane without modifying its crystalline phase, demonstrating good structural compatibility.

3.4. Photoabsorbance and transmissibility evaluation

Optical absorbance and transmittance analysis of PCM and the nanomaterial dispersed nanocomposite PCM are insightful in understanding the ability of the PCM to behave under the electromagnetic spectrum. Application of the developed PCM composites towards solar thermal energy-based application systems are determined based on this analysis. The spectrum of solar radiation is primarily made up of ultraviolet (UV) rays, visible rays, and near-infrared (IR) rays, which represent 7%, 44%, and 37% of the total, respectively. Therefore, the optical characteristics of the developed composites are assessed within the wavelength range of 280-1400 nm [41]. The patterns of photoabsorptivity and transmittance for the PCM nanocomposites are analyzed using a UV-Visible spectrometer and are presented in Fig. 6a and Fig. 6b.

Fig. 6a displayed an optical absorbance spectral curve resulting from base PCM octadecane and its GNB particles-based composites. As per evaluation, average absorbance value measured between 280-1400 nm

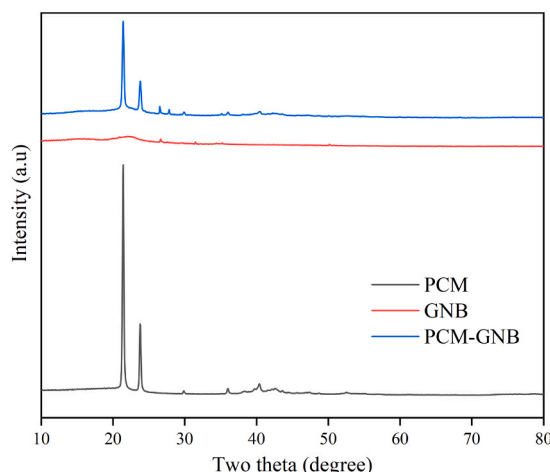


Fig. 5. Chemical stability evaluation of PCM and composites using XRD

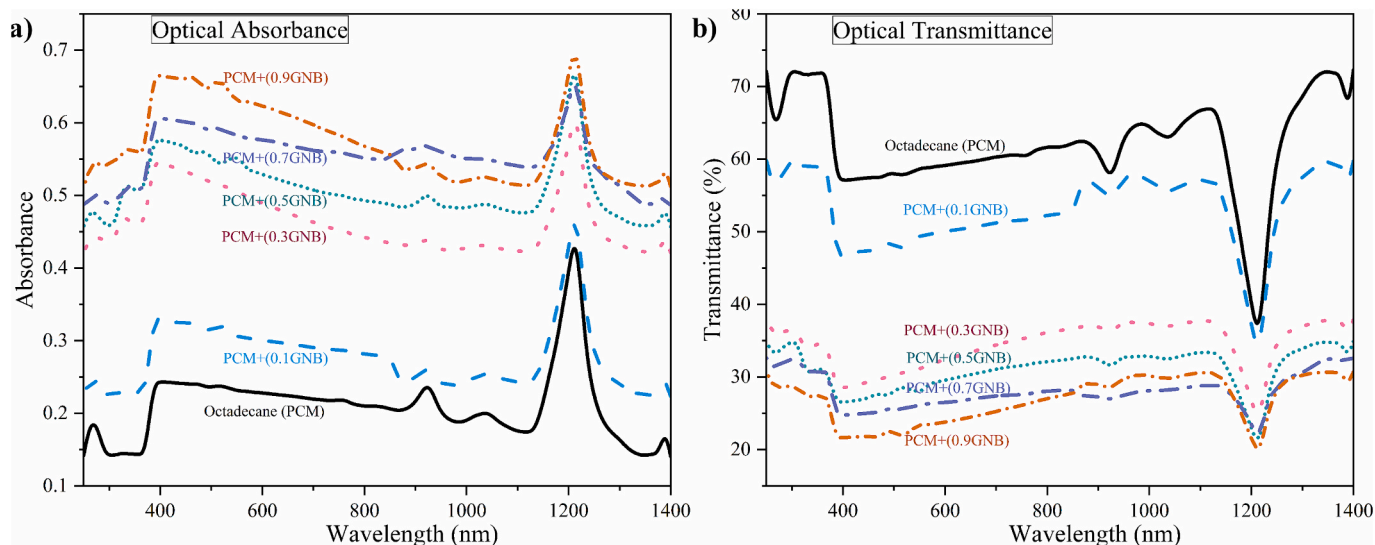


Fig. 6. Optical features of developed nanocomposite PCM a) absorbance and b) transmittance.

wavelength showed the optical absorbance value of 0.212 (the value is considerably low for utilization energy harvesting and solar thermal applications). Additionally, octadecane composite with GNB particles of 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.% and 0.9 wt.%, the optical absorbance of octadecane improved to 0.279, 0.465, 0.511, 0.555 and 0.575, respectively. The increment promotes an increase in absorbance of about 31.60%, 119.34%, 141.03%, 161.79% and 171.22% respectively, which is due to following scientific implications. a) the GNB biochar carbon material is characterized by π -conjugated carbon structures, which effectively boost optical absorption in the UV-Vis-NIR spectrum; b) surface morphology of GNB is characterized by its porous and irregular nature, which facilitates light scattering and trapping, ultimately boosting the optical absorbance of the octadecane-biochar composite; and also c) the even distribution of biochar in octadecane results in a heterogeneous mixture that interferes with light transmission and enhances absorbance through interfacial polarization effects. On a positive note, the rise in optical absorbance influences the optical transmittance of octadecane, which can be seen in the optical transmittance curve in Fig. 6b. GNB efficiently enhances absorbance with considerable positive effects by reducing the transmittance of the developed composite. Based on the optical transmissibility curve in Fig. 6b, the comparison for the transmissibility from UV-Vis analysis to the solar spectrum value can be find. It was observed that octadecane PCM has an optical transmissibility of 60.75%. Besides, adding GNB carbon particles at different weight percentages (0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, and 0.9 wt.%) demonstrated the optical transmissibility to decrease. The measurements were found as 51.7%, 33.5%, 30.3%, 27.2%, and 25.6%, respectively. On a sharp note, while the increase in absorbance of octadecane with 0.9 wt.% of GNB is 171.22%; the decrease in transmittance only accounts for about 57.8%. The absorbance values follow a logarithmic relationship with transmittance according to the Beer–Lambert law.

$$A = \log_{10} \left(\frac{1}{T} \right) \tag{1}$$

This larger increase arises from the logarithmic nature of absorbance rather than a direct linear proportionality. Subsequently, radiation can be transmitted, absorbed, or reflected when it passes through a medium. Octadecane is an organic substance that is usually clear and transparent, which lets radiation to easily pass through it. Further, there is a negative relationship between absorbance and transmissibility. This means that integrating GNB to PCMs makes them less able to transmit light, which makes them more able to absorb light. This higher absorptivity makes

the material more responsive to solar radiation, which paces up the rate of thermal energy storage capabilities.

3.5. Thermal conductivity assessment

The charging and discharging rates of PCM depends upon thermal conductivity value. PCMs with higher thermal conductivity values exhibit enhanced heat utilisation efficiency [42]. Thermal conductivity denotes the rate of heat transport in composites. Normally, organic PCMs present relatively low heat conductivity [43]. This study investigates octadecane PCM and endeavours to improve the thermal properties of the PCM composite by adding together bio-waste-developed GNBs particles at levels of 0.1%, 0.3%, 0.5%, 0.7%, and 0.9% to perceive how much better the thermal conductivity is achieved. Besides, to keep the sample solid throughout the characterisation process, the room temperature was kept at 20 °C. Fig. 7 demonstrates the bar graphs of base octadecane and GNB particle-dispersed composites. The thermal conductivity of octadecane PCM is determined at 0.139 W/m.K, representing low thermal energy charging and discharging efficiency. Formed composites of octadecane with GNB particles at weight fractions of 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, and 0.9 wt.% present thermal conductivities of 0.156, 0.187, 0.232, 0.268, and 0.216 W/

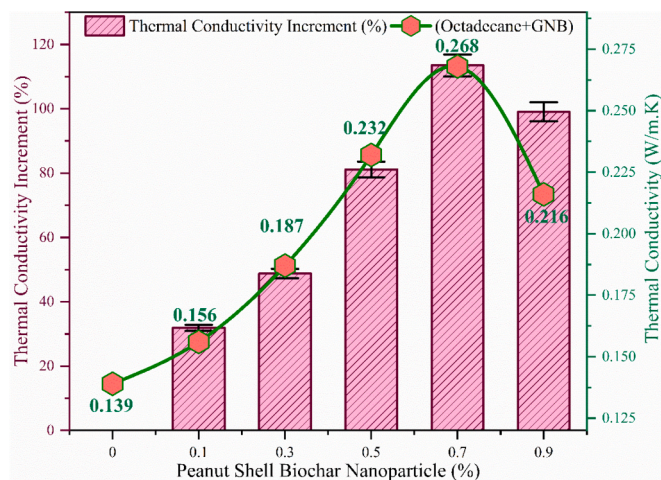


Fig. 7. Thermal conductivity enhancement evaluation for GNB particles added octadecane.

m-K, respectively. The carbonization process at 700 °C promotes the development of partially graphitized domains and interconnected carbon frameworks, which facilitate phonon transport and reduce thermal resistance across the composite system. The incorporation of GNB promotes the development of interconnected thermally conductive networks within the octadecane matrix, facilitating phonon transport and reducing interfacial thermal resistance. The partially graphitized carbon structure of the biochar also contributes to enhanced heat transfer efficiency, particularly at optimized filler concentrations [44]. Nevertheless, at elevated concentrations, following phenomena occurs; cohesive forces of attraction among GNB particles strengthen, directing to creation of clusters. These clusters progressively expand to form dense molecules, and owing to agglomeration, they settle throughout the frequent phase change, disrupting uniform distribution necessary for optimal thermal conduction [45].

The Table 2 showed thermal conductivity advancement of composites when added with GNB particles. The SEM observations presented in Fig. 2c primarily indicate that the composites generally exhibit good dispersion and interfacial integration without severe macroscopic agglomeration. However, at higher filler loading (0.9 wt.%), localized particle clustering and partial sedimentation may still occur at the microscopic scale, which may not be fully distinguishable in low-magnification SEM observations. Such localized aggregation can interrupt the continuity of thermally conductive pathways and increase interfacial thermal resistance, thereby reducing the effective heat transport efficiency of the composite.

3.6. Latent heat enthalpy evaluation

The DSC technique was employed to determine the latent heat heating and cooling curve. Fig. 8 shows the latent heat values endothermic and exothermic curves of PCM and PCM/GNB composites during phase change process. The endothermic peak in the heating curve shows that heat is absorbed when the material changes from solid to liquid. The exothermic peak shows that heat is released when the substance transforms from liquid to solid. According to results interpretations, the octadecane displayed peak melting temperature of 33.5 °C with latent heat enthalpy value of 244.5 J/g. The present work shows that bio-waste derived GNB particles enhances the latent heat enthalpy value of GNB/PCM composites, consequently improving thermal energy storage performance.

The latent heat value ranges from 240 J/g to 245.4 J/g with the incorporation of GNB filler at a concentration of 0.1 to 0.9 wt.%. The maximum latent heat of melting was observed as 245.4 J/g at 0.3 wt.% addition of GNB particles to PCM. Further, at concentrations over 0.3 wt.%, the latent heat value is higher than that of base PCM but lower than that of the composite with 0.3 wt.% GNB addition, as depicted in Table 3. The improvement in energy storage results from the uniform distribution of GNB particles within the PCM matrix, which promotes productive energy absorption and release throughout phase transitions. Additionally, it serves as a nucleation site, aiding in the homogeneous dispersion amid melting and crystallisation phase transitions [46]. The observed enhancement in heat storage efficiency suggests the potential for incorporating biowaste derived microparticles into phase change

Table 2
Evaluation of thermal conductivity at distinct GNB particles wt.% addition.

| PCM | Nanoparticle | Weight % (wt.%) | Thermal Conductivity (W/m-K) | % Improvement |
|------------|--------------|-----------------|------------------------------|---------------|
| Octadecane | - | - | 0.139 | - |
| | GNB | 0.1 | 0.156 | 31.89 |
| | GNB | 0.3 | 0.187 | 48.79 |
| | GNB | 0.5 | 0.232 | 81.16 |
| | GNB | 0.7 | 0.268 | 113.52 |
| | GNB | 0.9 | 0.216 | 99.03 |

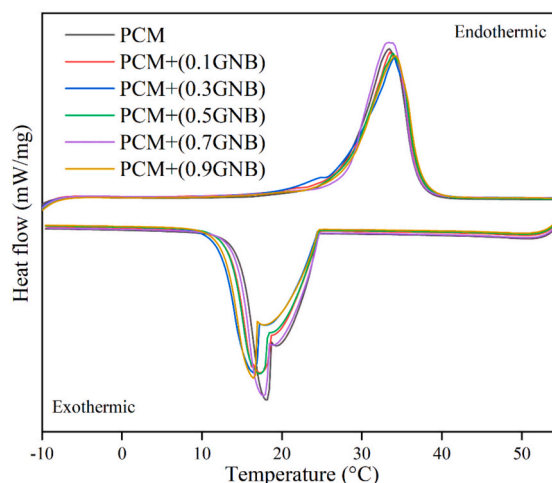


Fig. 8. Latent heat enthalpy evaluation of PCM and GNB integrated PCM composite.

Table 3
Comparative evaluation latent heat enthalpy of prepared composites

| Composite | Latent heat during melting (J/g) | Latent heat during solidification (J/g) |
|----------------|----------------------------------|---|
| PCM | 244.5 | 240.9 |
| PCM + (0.1GNB) | 242.8 | 236.2 |
| PCM + (0.3GNB) | 245.4 | 241.5 |
| PCM + (0.5GNB) | 242.1 | 236.4 |
| PCM + (0.7GNB) | 244.4 | 238.1 |
| PCM + (0.9GNB) | 240.1 | 234.7 |

materials to improve their efficacy. This advancement presents a favourable chance to enhance efficient reliable TES systems.

3.7. Thermal stability analysis

To test the thermal degradation of GNB/PCM composites, the thermogravimetric (TGA) instrument was employed in this work. The obtained samples are heated at a rate of 10 °C per minute, and the temperature starts from 30 °C to 400 °C in a controlled nitrogen atmosphere. The TGA curve shows that both octadecane and its composite break down in one step. Fig. 9a shows that the composite samples are very stable up to 90 °C, without any weight loss. After 90 °C octadecane and its composites break down as the temperature rises. It is observed that Octadecane base PCM breaks down by about 95% when the temperature is between 91 °C and 197 °C. This breakdown process in PCM and its composite occurs when the long-chain polymer breaks down into its smaller parts, which happens proportionally as the temperature rises. The prepared composites are more thermally stable than the base PCM. The composite samples show good thermal stability up to 90 °C, with no weight loss seen in the composites. Fig. 9b shows that the final degradation temperature of all the composites was between 225 and 250 °C. The inherent structure and properties of synthesized GNB microparticles make it easier for them to combine with octadecane, which raises molecular interactions. In the same way, GNB particles impedes the degradation kinetics, suspending the thermal degradation process in composites due to their higher melting temperatures as observed the TGA evaluation. The main cause of thermal degradation of composites is the solid presence of van der Waals and capillary forces formed between octadecane PCM and GNB particles in the composite. This phenomenon

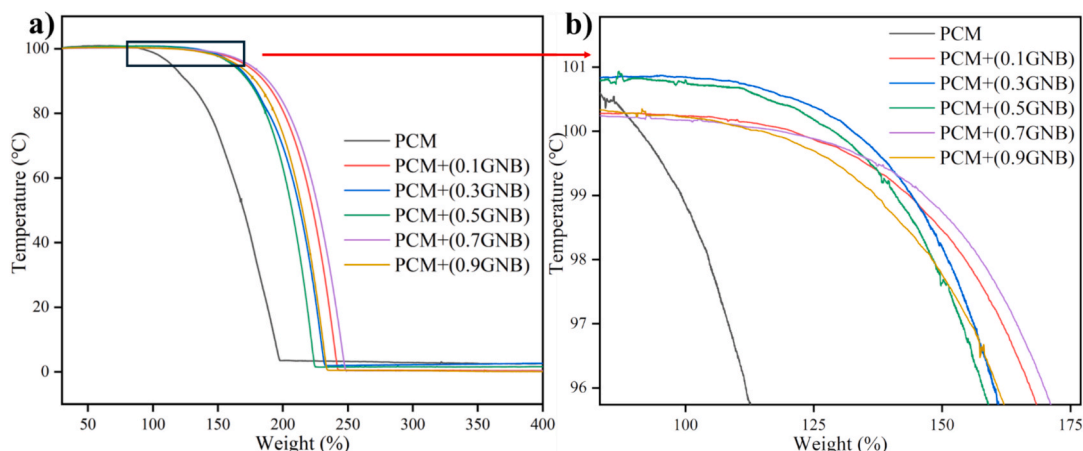


Fig. 9. Thermal degradation evaluation a) PCM and GNB integrated composites b) zoomed image of PCM and GNB integrated composites

function as a thermal barrier against temperature variations, potentially supporting in the creation of thermal barriers in the prepared composites [47]. As per observations, the weight loss tendencies reported in octadecane, and composite materials establish a similar pattern, with the highest rate of weight decline occurring between 90 °C and 250 °C. Moreover, the obtained findings agree with prior research on octadecane PCM supporting successful preparation of composites [48]. The left-over residue after the thermal degradation until 400 °C represents the ash content and the other impurities in the developed composite sample.

3.8. Thermal reliability analysis

To ensure the prolonged reliability of prepared composites a thermal cycling assessment was employed. The extended thermal cyclic stability assessment helps to determine change in important insights of composites. To apply reliability evaluation, this work utilized specialized thermal cyler with concurrent sample processes. The prepared composites were placed in crucibles of thermal cyler to apply continuous heat and cool operations. The process was repeated for 500 heat and cool cycles, and placed samples were then analysed for chemical stability and latent heat enthalpy evaluation. The chemical stability was observed using FTIR spectra after 500 thermal cycles having functional

groups demonstrated in Fig. 10a. As per observations, the samples exhibited different peaks at 292 cm⁻¹, 722 cm⁻¹, 1463 cm⁻¹, and 2852 cm⁻¹. The obtained peaks after 500 cycles of heating and cooling look like those of the base PCM, which implies that the samples are chemically stable. DSC measured the energy storage capacity and other associated factors. Fig. 10b shows the DSC curves for heating and cooling 500 cycled samples. There has been a drop in the melting and cooling enthalpy values. This could take place when the material is charged and discharged repeatedly at different temperatures, which could cause it to break down a little. After thermal cycling, the composite with the utmost thermal conductivity value, PCM + (0.7GNB), had a latent heat of melting of 226 J/g and a peak melting temperature of 33.1 °C. However, before thermal cycling, it had 244.4 J/g latent heat of melting. Similarly, the base PCM exhibited 232.4 J/g of latent heat of melting after 500 cycles. The main reason for the minor degradation is that moisture and other pollutants from external environment absorbed into the material along with pressure of continuous charge discharge cycles. Further, latent heat enthalpy can be affected by interfacial interactions between PCM and biochar. The intense adsorption of PCM on GNB biochar confinement can limit the molecular mobility causing restricted phase transition. This confinement can be intensified over repeated cycles due to structural rearrangement within composites. The melting temperatures and latent heat values of the samples still corresponds with prior

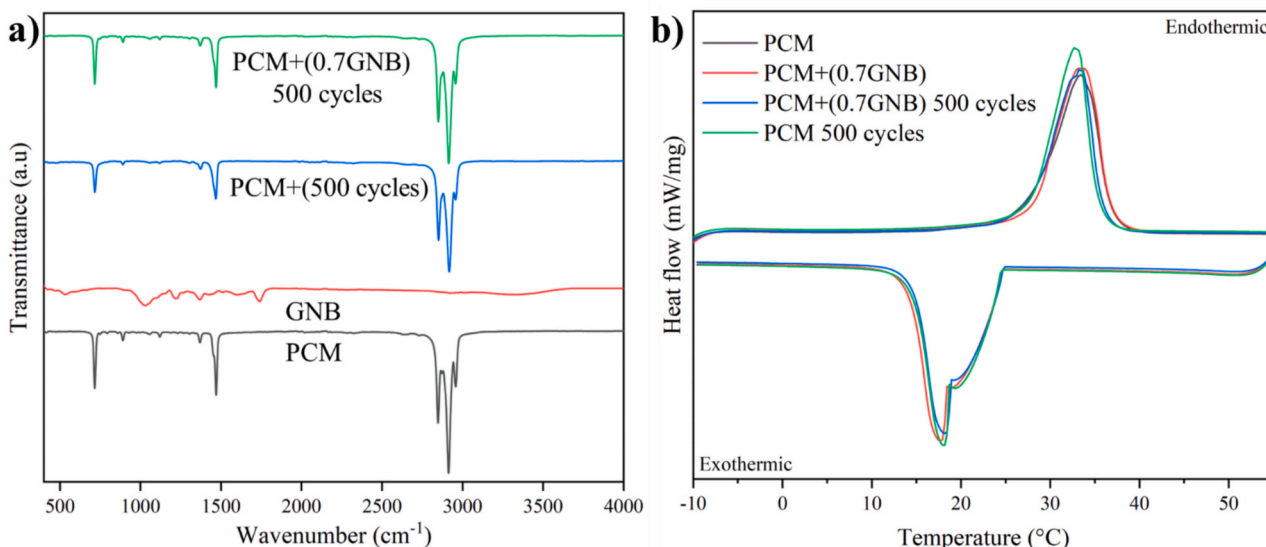


Fig. 10. Thermal cycling evaluation a) FTIR curves b) DSC curves

thermal cycling results. Therefore, the cyclic test results show that the GNB/octadecane composite formulation is reliable for long-term use.

4. Conclusion

The present work conducted thermophysical evaluation of synthesized groundnut shell biochar (GNB) particles integrated with octadecane phase change material (PCM) and distinct weight% (wt.%). The composite preparation adopted two-step material preparation scheme. The prepared composites were tested for thermophysical evaluation such as heat transfer, chemical, thermal stability, photoabsorbance and morphological evaluation. The morphological examination demonstrates presence of uniformly distributed GNB particles without considerable agglomeration. The below given are principal observations obtained in the research work.

- 1) The chemical stability of prepared composites was identified with FTIR techniques. The result elaborated the chemical stability of prepared composite indicating no additional peaks were found in the composites. The peaks achieved matched with base PCM peaks, confirming GNB particles did not alter the internal structure of the base PCM.
- 2) The photo-absorbance and transmittance characteristics analysed by UV-Vis showed substantial decrement in photo-transmittance. The photo-transmittance decreases with increase in GNB particles addition. Further, the 0.7 wt.% integrated PCM composite exhibited 161.7% increment in photo-absorbance.
- 3) The thermal conductivity studies showed significant improvement in heat transmission abilities. As per observation when octadecane PCM was mixed with 0.7 wt.% GNB particles demonstrated the largest boost in thermal conductivity value, about 113% more than the base PCM.
- 4) The latent heat enthalpy values given by DSC evaluation exhibited minor differences in base PCM and GNB particles integrated composites. As per observations. The maximum latent melting enthalpy was obtained for 0.3 wt.% GNB particles addition to PCM. The 0.3 wt.% added composite showed 245.4 J/g of latent heat of enthalpy in comparison to 244.5 J/g for base PCM.
- 5) The TGA confirmed superior thermal stability of prepared composites. The thermal stability of the synthesised composites exceeds that of the underlying PCM. The composites exhibit thermal stability up to 90 °C, with no detectable weight loss. Further, final breakdown temperature of all composites ranged from 225 to 250 °C.

In conclusion, the thermophysical qualities of composite PCM make it a good option for utilization in medium temperature heat storage. The produced GNB particle-based composite PCM exhibits significant potential for application in building energy and thermal energy storage utilization. The sustainable biochar-based conductive framework developed in this work provides a promising pathway toward low-cost and environmentally friendly thermal energy storage materials. The combination of thermal conductivity and thermal dependability satisfactorily fulfils the dual demands of high efficiency and longevity in medium temperature thermal management.

CRedit authorship contribution statement

B. Kalidasan: Conceptualization, Methodology, Data curation, Formal Analysis, Project Administration, Funding Acquisition, Writing - Original Manuscript, Writing - Review & editing. **A.K. Pandey:** Writing - review & editing, Supervision, Project administration, Funding acquisition, Formal analysis. **Yasir Ali Bhutto:** Writing - review & editing, Writing - original draft, Formal analysis. **Wenye Lin:** Writing - review & editing, Project administration, Formal analysis. **Imansyah Ibnu Hakim:** Writing - review & editing, Project administration, Formal analysis. **Fadia Ramadhania Nurhakim:** Writing - review & editing,

Formal analysis. **Nabil Fadlurahman Raynorasaki:** Writing - review & editing, Formal analysis.

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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