Green synthesized 3D Coconut Shell Biochar/Polyethylene Glycol Composite as Thermal Energy Storage Material

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Abstract

Developing stable, economic, safer and carbon-based nanoparticles from agro solid waste facilitates a new dimension of advancement for eco-friendly nanomaterials in competition to existing nanoparticles. Herewith, a three dimensional highly porous honeycomb structured carbon-based coconut shell (CS) nanoparticle is prepared through green synthesis technique using tube furnace to energies organic phase change material (PCM). CS nanoparticle synthesis using a green approach is incorporated with polyethylene glycol (PEG) using a two-step technique to develop PEG/CS nanocomposite PCM. Thermophysical features of the nanocomposites are characterized using transient hot bridge (ThB), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA), whereas optical property and chemical stability is evaluated using UV-Vis and FTIR spectrometers. Resulting nanocomposite demonstrates higher thermal conductivity by 114.5% (improved from 0.24 W/m·K to 0.515 W/m·K). Energy storage enthalpy increased from 141.2 J/g to 150.1 J/g with 1.0% weight fraction of CS nanoparticles. Optical absorbance of the nanocomposite is improved by 2.14 times compared to base PCM. The developed nanocomposite samples exhibit extreme thermal stability up to 215 °C. The 3D porous structure of CS nanoparticles shows better contact area with PEG, causing low interfacial thermal resistance for improved thermal network channels and pathways for extra heat transfer and phonon propagation.

Keywords: Coconut Shell; Green Synthesise; 3D Nanoparticle; Phase Change Material; Thermal Energy Storage;

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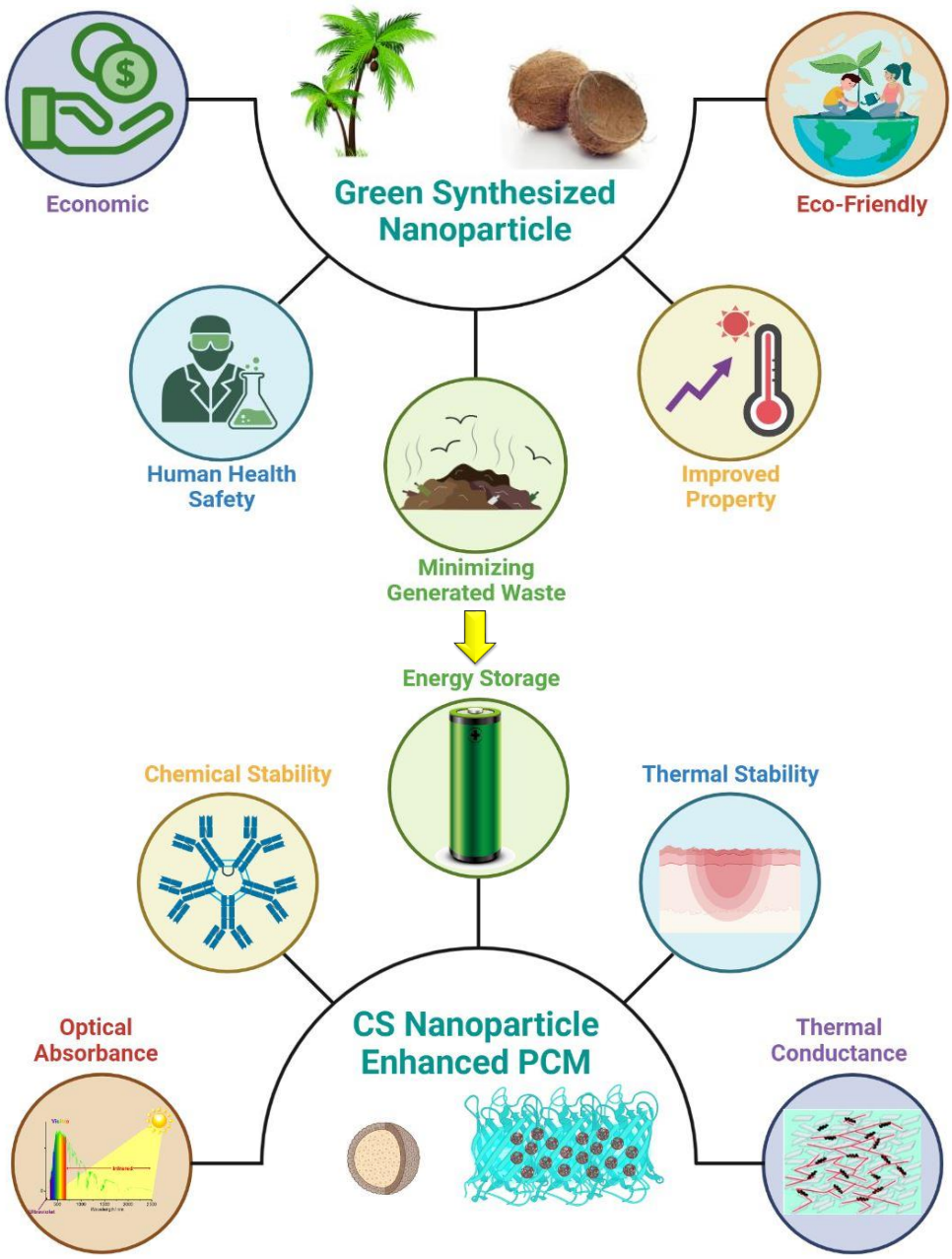
Highlight

- Green synthesised 3Dimensional, highly porous carbon-based nanoparticle
- Up to 114.5% thermal conductivity improvement with CS nanoparticle
- Increase in latent heat capacity (6.3%) from 141.2 J/g to 150.1 J/g
- Optical absorbance increases more than 2 folds and transmissibility falls by 69%
- Excellent thermal cycle stability for 500 thermal cycles.

Graphical Abstract



1.0 Introduction

Application of phase change materials (PCMs) as an energy storage technology can improve the efficiency of energy utilisation through the phase transition process, which is a cost effective passive technology [1]. Generally, PCM are of three types a) Organic (fatty acid, sugar alcohol, paraffin); b) Inorganic (salt hydrate); c) Eutectic (blend of organic & inorganic) [2]. Organic PCMs are predominantly preferred as thermal energy storage materials over inorganic PCM owing to their ability to store energy at wide range of temperature, high heat storage density [3], better chemical & thermal stability [4], isothermal behaviour, no issue of supercooling [5], non-corrosive in nature [6], eco-friendly and economical. Despite numerous advantages of PCM, most of the organic PCM lack thermal conductivity, poor optical absorbance and leakage issue; which limits their applications for many thermal regulation solutions. Nonetheless, to improve the thermal characteristics of organic PCM, different dimensional nanoparticles like carbon nanotubes [7], graphene [8], expanded graphite, hybrid conducting polymers [9] and tetrapods [10] has been explored. In majority of the case the optical absorbance of organic PCM matrix are enhanced by the nanomaterials dispersed with PCM to enhance the thermo-physical characteristics. Likewise, to overcome leakage issue core PCM are encapsulated using silica gel [11]; as well shape stabilized via wood powder/high density polyethylene [12]. However, all the aforementioned nanomaterials continue to confront challenges with high manufacturing costs and difficulty in mass production, resulting in the development of most nanomaterials remaining at the laboratory stage, making large-scale manufacture and use challenging. In addition, these nanoparticles are toxic and costlier. After usage, these nanoparticles are eventually dispersed into the environment, henceforth there is an utmost need for eco-friendly nanoparticle.

Green synthesis of biochar nanoparticle is an emerging eco-friendly technology adopted in converting solid waste (e.g. manure, corn cub, rice husk, eggshell, bamboo) and industrial waste (e.g. waste tyre, sawdust) into nanoparticle. The nanoparticles synthesised via green technology contain more functional groups of C−O and C=O rather than activated carbon. A derivative of charcoal, and activated carbon holds the merit of large specific surface area, chemical stability, ample availability and low density [13]. Nevertheless, usage of activated carbon suffers owing to a) non-renewable nature; b) higher cost and c) difficult to regenerate [14]. Whereas, biochar is an emerging environmentally friendly safer material; and can be prepared from agro & forest residues [15]. Other benefits of green synthesised biochar carbon nanoparticle includes a) cheaper; b) renewable; c) ease of preparation; d) large sorption potential; e) protect environment as can be developed from waste; e) high surface area [16]; f) 3D porous structural framework; g) superior resistance to corrosion and heat and h) higher thermal and electrical conductance [17]. Henceforth, numerous research works on

biochar preparation and their utilisation with energy storage domains were explored. Sheng et al. [18] dispersed biochar derived from sisal fibre (1D carbon bundles) with paraffin to enhance the thermal conductivity from 0.25 W/m·K to 1.73 W/m·K at carbon ratio of 12.8%. Significant improvement in thermal conductivity of the composite was attributed by the anisotropic one dimensional arrangement of sisal fibres exhibited better thermal networks. Likewise, Das et al. [19] dispersed biochar of water hyacinth (PCM: biochar of 4:6; 5:5; 6:4; 7:3; 8:2; 9:1 wt%) to develop form stable PCM with improved thermal conductivity of composite PCM by 13.8 times (PCM: biochar of 6:4 wt%). Conversely, Xiong et al. [20] green synthesised biochar nanoparticles using garlic stem and dispersed the developed nanoparticle with paraffin at a weight fraction of 1wt%, 3wt% and 5wt%. Owing to the two dimensional flake structure of garlic stem nanoparticle and thermally conductive networks within the matrix of paraffin PCM, the thermal conductance improved from 0.19 W/m·K to 0.24 W/m·K with 5% weight fraction of garlic stem nanoparticle. Similarly Lv et al. [21] experimentally investigated the thermal performance of a variety of PCM like paraffin, stearic acid and PEG using biochar developed from phoenix leaf. The PCM:biochar proportion was 75:25 wt%. Interestingly, results depicted that biochar pyrolyzed at higher temperature caused higher graphitization and increased the thermal conductivity of nanocomposites, rather than the biochar nanoparticle pyrolyzed at lower temperature. Conversely, Wan et al. [22] prepared a form stable PCM using palmitic acid and biochar of pinecone at different mass ratios of 4:7, 4:6, 5:5, 6:4 and 6.5:3.5. Increase in thermal conductivity for palmitic acid: biochar of pinecone at 6:4 was about 43.76% as palmitic acid was impregnated within the pores of pinecone biochar resulting in better thermal network channels. Pinus resinosa fruit was pyrolyzed to develop biochar with high porosity and surface area by Mandal et al. [23]. Developed biochar was dispersed with dodecanoic acid to fabricate a shape stabilised composite PCM to overcome the issue of leakage with 3:1 proportion of dodecanoic acid to biochar. Hybrid of graphene oxide and biochar corn straw was developed into nanoparticle to improve the thermal conductivity and shape stability of polyethylene glycol operating at 410 °C [24]. Similarly Atinafu et al. [25] developed hybrid nanoparticle with a mixture of carbon nanotube and biochar of bamboo via hydrothermal method. Above synthesised nanoparticle was dispersed with liquid dodecane to prepare a thermally interconnected heat transfer composite PCM with leak proof and improved thermal conductivity. Goud et al. [26] developed a shape stable PCM for thermal regulation of lithium ion batteries. In his research work, authors opted myristyl alcohol as PCM and enhanced its performance with biochar derived from neem tree as supporting material, in addition the thermal conductivity of the composite increased by 3.91 times at a weight fraction of 24%. Bordoloi et al. [27] developed biochar using a) yellow oleander; b) water hyacinth and c) sugarcane bagasse to be used as supporting matrix to overcome the issue of low thermal conductance and issue of leakage in

commercialised organic PCM. Thermal conductivity of the composite increased from 0.126 W/m·K to 0.154 W/m·K with a mixture of biochar developed from all three sources of biomass owing to the heat conductance carbon networks of the dispersed biochar. Based on the literature studies discussed above and best of author's knowledge, a gap is identified in exploring the potential of green synthesised biochar of coconut shell to opt as nanomaterial. Whereas in the current research we perform carbonising in a control atmosphere ensuring pollution free synthesis technique. Furthermore, there is an utmost attraction towards synthesis of eco-friendly nanomaterials demonstrating effective thermo-physical characteristics to compete with the commercial nanomaterials.

Herein, we synthesise a new carbon-based nanoparticle by carbonization of coconut shell (CS) adopting a green synthesise technique for contemporaneously providing enhanced thermal conducting features and optical absorbance of organic PCM. Coconut (Scientific name: Cocos Nucifera) shell was opted as a precursor for carbon based nanoparticle developed owing to a) eco-friendly, low cost agro based solid waste; b) can be transferred into activated biochar through carbonization process with high carbon content; c) exhibit higher surface area to volume, with porous nature and thermal conductive [28]; d) can be readily procured as India accounts for 31.45% of world coconut production and leads globally according to data from Indian Trade Portal and Malaysia is ranked as the 12^{th} largest producer of coconut. Polyethylene glycol (PEG) operating at phase transition temperature of 35-38°C with 142 J/g of latent heat storage has been selected owing to their special feature of non-corrosiveness; no degree of supercooling; economical; chemically stable and best preferred for thermal regulation units. Nonetheless, the issue of low thermal conductivity and poor optical absorbance confines real time application of PEG in most of the thermal energy storage and thermal regulation implementations. Ultimately there is a need for energising nanoparticles with features of being sustainable, cheaper, non-reactive, non-toxic, non-polluting, highly stable, available in nature and easy to handle. Table 1 compares a few recent studies that used biochar-based nanoparticles to improve the heat transfer characteristics of PCM in comparison with the present research. To the best of the author's knowledge and the literature studies in table 1, there is a need for additional studies into the possibility of using green biochar made from coconut shells as a nanomaterial. Exploring the potential of coconut shell as nanoparticle via green synthesis technique to enhanced the thermo physical characteristics of organic PCMs and energy storage materials would be of great scientific benefit. Additionally, coconut shells are a naturally occurring agricultural resource that is used as a cooking fuel in rural areas despite being considered a waste product. CS nanoparticle are easy for mass production at low cost, and are significant for effective commercialisation. In contrast, the current study uses a synthesis process that ensures no pollution

by carbonising in a control atmosphere. In order to compete with commercial nanomaterials, there is also a strong pull towards the synthesis of eco-friendly nanomaterials with strong thermo-physical properties. Henceforth, in this research framework we develop PEG/CS nanocomposite PCM operating at phase transition temperature of 35-38 °C with different weight fraction (0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% & 1.3 wt%) of CS nanoparticle via two step method. Morphological behaviour, chemical stability of functional group, optical property (absorbance & transmissibility), energy storage potential (heating & cooling), thermal conductivity, degradation stability, reusable reliability and thermal performance of PEG/CS nanocomposite is experimentally tested and analysed. Thermal reliability of the developed nanocomposite PCM is evaluate for 500 number of thermal cycles. Results and findings ensure the potential of green synthesised carbon based CS nanoparticles in energising organic PCM. Influence of porous nature, non-uniform structure and 500-800 nm sized CS NP causing low interfacial thermal resistance for improved thermal network channels and pathways for extra heat transfer and phonon propagation are discussed. Conversely, PEG blends within the micro pores of CS nanoparticles and between lamellar structures for ensuring better energy storage is explained. Developed PEG/CS nanocomposite are less dense and economical for thermal regulation applications with more focus on sustainable future. Based on experimentally determined thermal characteristics the developed organic nanocomposite PCM is expected to contribute effectively for thermal regulation units with more focus on sustainability.

Table 1: Biochar nanoparticle for enhanced thermal features of phase change materials

Nano material	**PCM Ratio (%)**	**Thermal Conductivity (%)**	**Energy Storage (J/g)** ΔH_m	ΔH_c	**Reference**
Expanded Perlite	70.1	-38.78	-23.64	-22.13	[29]
Expanded Perlite/Carbon	66.4	82.12	-29.01	-26.70	
Diatomite	50	10.34	-39.01	-50.68	[30]
Diatomite/Expanded Graphite	47.5	68.96	-42.84	-52.15	
Diatomite/Expanded Graphite	45	131	-44.36	-54.28	
Expanded Vermiculite	66.1	-	-33.93	-33.90	[31]
Expanded Vermiculite/Silver nanowire	62.1	104	-37.87	-37.91	

Hybrid (Corn Straw + Graphene Oxide)	80	3.7	-34.1	-32.1	[24]
Graphene Nanosheets	95 90 85	1592 2592 4707	-8.5 -12.6 -16.8	-7.8 -14.1 -17.8	[32]
MWCNTs	99.5	37	+6.1	+3.1	[33]
Reduced Graphene Oxide	98	-	-4.67	-7.9	[34]
Coconut Shell Nanoparticle	99	114.58	+6.30	+2.46	This work

2.0 Materials and Methods

2.1 Materials

Energy storage material opted in the current research work is polyethylene glycol (PEG-1000) with a phase transition temperature of 35-38 °C, acquired from Millipore Sigma. PEG-1000 has a melting enthalpy of 146 J/g, density of 1.2 g/cm^3 with white colour appearance. Agro solid waste of coconut shell (CS) was acquired from Tamil Nadu, India which is used as the raw waste material for the green synthesis of CS nanoparticles. The green synthesise technique adopted for preparing the nanoparticle developed in the current research investigation is described in Section 2.2.

2.2 Synthesis of Coconut Shell Biochar based Nanomaterial

This section describes the green synthesis technique adopted to develop coconut shells into useful nanoparticles for effective energy storage materials. Figure 1a provides pictorial representation of techniques involved in green synthesis of nanomaterial from solid waste. To begin with, coconut shells are extracted from agro solid waste and smashed into smaller pieces of size 20-25 mm using mallet. We wash the coconut shell using deionized water to remove dust and sand particles to develop nanoparticles of better features. Followed by washing, the cleaned coconut shells are dried in vacuum over 125 °C for 12 hours. Furthermore, coconut shells are converted into biochar by the carbonisation process. Coconut shell is carbonised in a nitrogen atmosphere at a temperature of 1000 °C using a high temperature tube furnace ensuring pollution free technique. The carbonised coconut shell scraps are further processed using hand crushing and wet ball milling to reduce their particle size. Using hand crushing, the carbon scraps of coconut shells are reduced to 1.5-1.8 µm, tailed by wet ball milling for 24 hours at 500 rpm with dwell period of 05 minutes in between every 10 minutes of operation. Wet ball milling is carried out using 1 mm balls to particulate the carbon coconut shell

scraps with inclusion of water. The ball milled samples are dried in an oven at 200 °C to obtain the final nanoparticle.

To explore the size and elemental composition of the green synthesis CS nanoparticle, the developed nanoparticle is tested using particle sizer and Energy Dispersive X-Ray Analysis (EDX). Particle size indicates the size of the CS nanoparticle to be in the range of 500-800 nm. The synthesised nanoparticle comprised of 92% of carbon element as evaluated under EDX and also indicates the presence of other elements like O, K, Cl, Ca, Si, Na and Al as can be inferred from **(Supplementary S2-S3 and T2- Appendix III)**

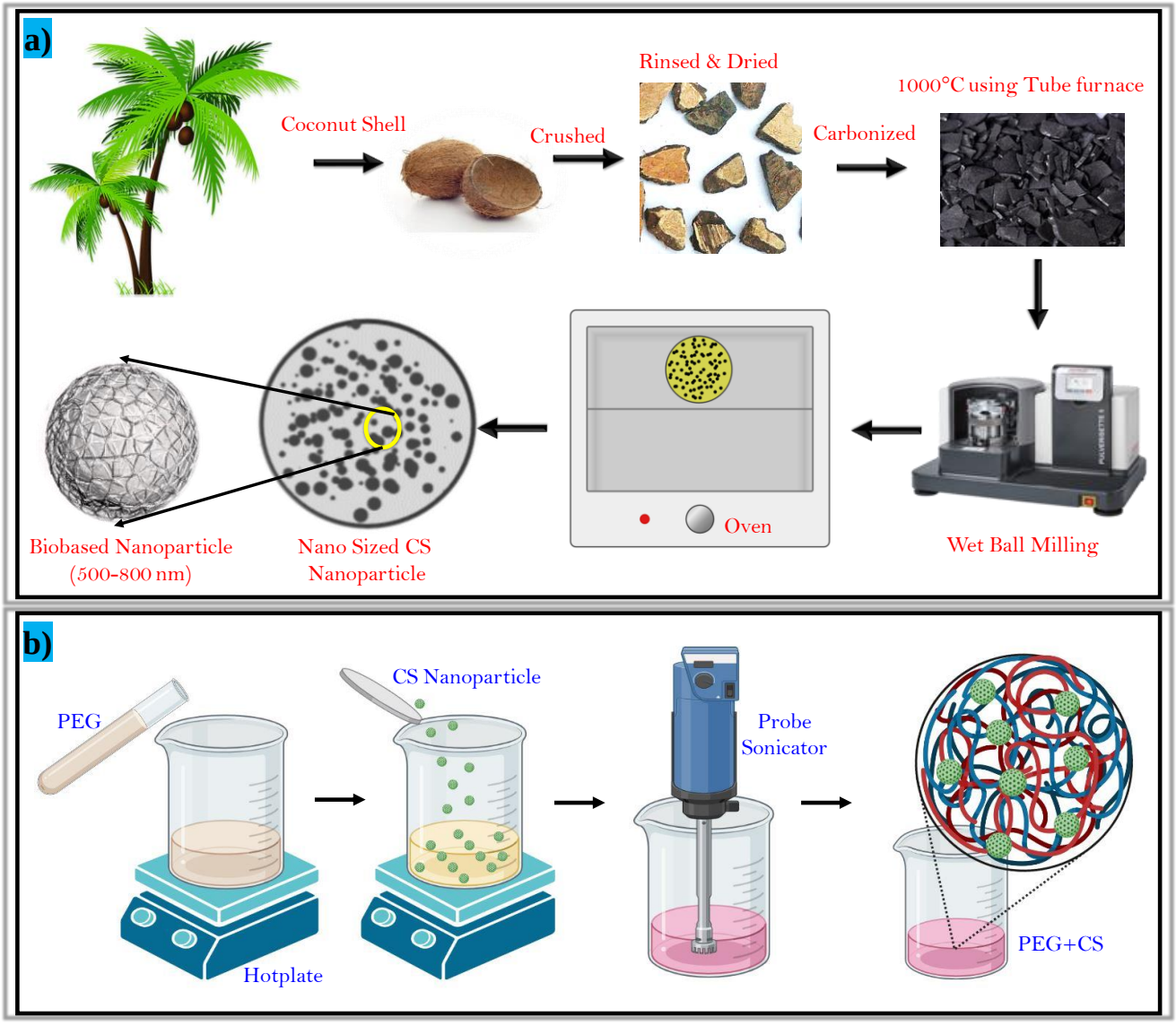


Figure 01: a) Green synthesis process of coconut shell into nanomaterial; b) Step by step development process of CS nanoparticle dispersed organic PCM.

2.3 Preparation of Coconut Shell Biochar/Polyethylene Glycol Composite

In the current experimental investigation, CS biochar nanoparticle synthesised as described in section 2.2 is dispersed with organic PCM PEG-1000 to develop the nanocomposite adopting a

two-step technique. Figure 1b illustrates the preparation technique of CS nanoparticle dispersed PEG-1000 nanocomposite. Initially, 20 g of PEG-1000 is weighed and melted in a beaker using a hot plate maintained at 65°C. Subsequently, we disperse 0.04 g (0.2%) of the green synthesised CS nanomaterial with PEG-1000 PCM melted to liquid state. The nanocomposite mix is now sonicated using a probe sonicator for 45 minutes and the nanocomposite is cooled down to obtain the required green synthesised CS biochar based nanoparticle dispersed PCM nanocomposite sample. The developed PEG+CS biochar nanoparticles are considered for further morphological, chemical, optical and thermal characterization evaluations. Likewise, to determine the optimum weight concentration of CS nanoparticles exhibiting the improved thermal feature, nanocomposite samples are developed with weight fraction of 0.3%, 0.5%, 0.7%, 1.0% and 1.3% CS nanomaterial.

2.4 Characterization Techniques and Instruments

To synthesise the nanoparticle, develop the nanocomposite, characterise the morphological behaviour, exhibit the thermo physical properties and to evaluate the thermal cycling ability of PEG-1000 with CS nanoparticle we opt for a few sensitive instruments. We use a high temperature tube furnace (Model: Gero 30-3000 °C, Carbolite) for carbonising the coconut shell into biochar in an eco-friendly manner. Planetary ball mill (Model Pulverisette 5, Fritsch, Germany) is used to reduce the green synthesised biochar into finer nanoparticles. Particle size of the synthesised CS nanoparticle using particle analyser by Anton Paar (Model: Litesizer 500). The FESEM instrument was fortified with an Energy Dispersive X-ray Spectroscopy (Oxford Instrument EDX) system, which was operated to determine the elemental compositions of the PCM composite samples. To analyse the chemical stability of the CS based nanocomposite PCM Fourier Transform Infrared Spectroscopy (FTIR) (Model: FTIR Spectrum TWO, Perkin Elmer) is used. Thermal conductivity is determined using TEMPOS with dual needle SH-3, at room temperature of 25 °C. Differential scanning calorimetry (DSC) (Model: DSC 3500 Sirius, NETZSCH) was used to analyse the melting temperature and latent heat properties of PCM composite. DSC melting and cooling curves were inspected between 05 °C and 55 °C under the N_2 atmosphere with a heating rate of 5 °C/min. A thermogravimetric analyzer (TGA) (Model: TGA 4000, Perkin Elmer) is used to conduct a thermal deterioration analysis on pure PCM and the composite PCM. The temperature for TGA is ramped up to 500 °C at a rate of 10 °C/min in an N_2 environment. A customized thermal cycling unit is used to accelerate the charging and discharging cycle of the developed nanocomposite. The uncertainty associated with the instruments are provided **(Supplementary T1- Appendix I)**. All curves were plotted in Origin software.

3.0 Results and Discussion

The current research work is focused on synthesising of eco-friendly nanoparticles in a greener way to enhance the chemical, thermal and optical features of organic PCM. This section illustrates and scientifically discusses the special features of coconut shell nanoparticles for energising the polyethylene glycol PCM. Morphological behaviours, chemical stability, energy storage potential, thermal conductivity, optical absorbance and transmittance of electromagnetic spectrum and thermal stability of CS nanoparticle dispersed composite PCMs are discussed below.

3.1 Microstructure and morphological visuals

To understand the microstructure, morphology and interaction of the synthesised CS nanoparticle, polyethylene glycol PCM and the nanocomposite of CS nanoparticle and phase change materials, SEM are presented in Figure 2. To begin with, the morphological and microstructure of the green synthesised CS nanoparticle is presented. The CS nanoparticle used in the current research to enhance the thermal feature of PEG-1000 PCM is green synthesised using agro waste of coconut shell. Figure 2a on a microscopic level displays the three dimensional multiple layered hollow structure (contributing to higher specific surface area) portraying a honeycomb shape, with numerous porous holes. The characteristic of high porosity and greater specific surface area of CS nanoparticles may facilitate in sustaining organic PEG PCM and safeguard resistance to leakage in molten state when included in higher proportion (20%) owing to better surface tension and capillary action (A form stable nanocomposite with PEG+CS-20% is evaluated for form stability in **Supplementary S1, Appendix II**). Owing to higher surface area compared to the volume, CS nanoparticles exhibit the ability to adsorb higher capacity of liquid molecules during phase transition of organic PCM, and supports stable PCM operating at lower temperature [35]. Figure 2b, represents the sticky nature with wavy surface of PEG-1000 organic PCM belonging to the family of alkane with long chains of polymer. Morphological visuals of CS dispersed PEG-1000 nanocomposite samples are presented in Figure 2c. We observe a uniform dispersion of CS nanoparticles over the PEG matrix, without any agglomeration and clustering. PEG blends within the micro pores of CS nanoparticles and between lamellar structures and ensures better energy storage to occur. The uniformly distributed CS nanoparticle establishes thermal hotspots within the PEG matrix and contributes in enhancing the heat transfer rate. Additionally the elemental analysis of PEG and PEG-BNP nanocomposites samples are presented in the supplementary document for further exploration **(Supplementary S4-S7 and T3-T4, Appendix III)**.

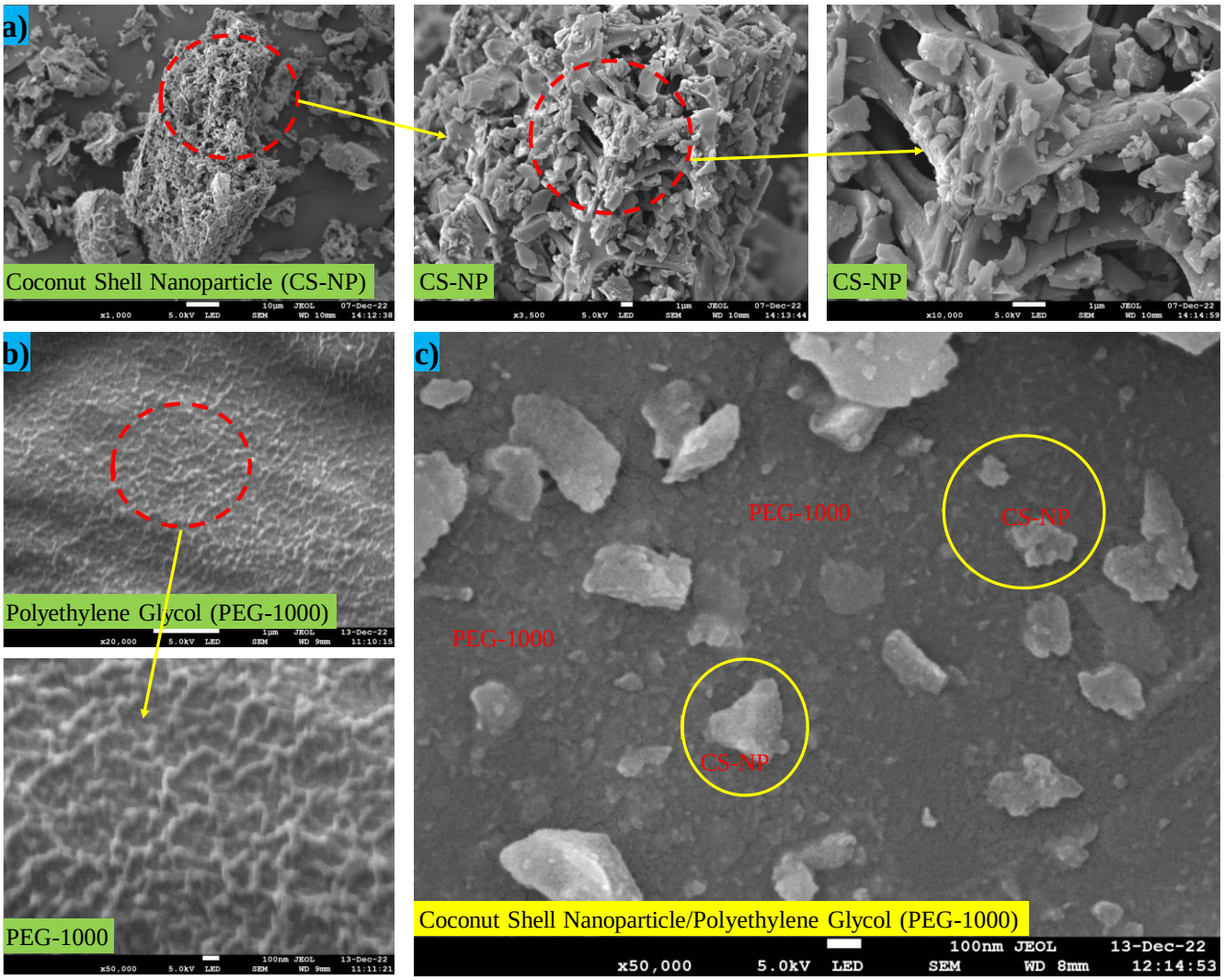


Figure 2: Microstructure of a) Coconut shell biochar; b) PEG-1000 and c) Coconut shell biochar dispersed PEG-1000 PCM.

3.2 Chemical stability evaluation using FTIR

The chemical stability and compatibility between PEG-1000 PCM and the green synthesised CS nanoparticle was experimentally investigated using the FTIR spectrometer, and the spectral peaks corresponding to each wavenumber are presented in Figure 3. Spectral peaks of PEG-1000, CS nanoparticle and nanocomposite samples of CS nanoparticle dispersed PEG-1000 are investigated. In pure PEG-1000 PCM the absorption bands occurred at 842 cm^{-1}, 949 cm^{-1}, 1105 cm^{-1}, 1239 cm^{-1}, 1280 cm^{-1}, 1341 cm^{-1}, 2880 cm^{-1} and 3450 cm^{-1}. The sharp spectral peak at wavenumber 842 cm^{-1} attributes to the peak of internal-CH_2 group [36]. C-H bond vibration and C-O-C of ether is indicated at wavenumber 949 cm^{-1} [37] and 1105 cm^{-1} [38] respectively. And the small sharp peaks between 1230-1350 cm^{-1} attributes to C-H scissor & bending vibration [39]. Absorption spectral peak at 2880 cm^{-1} attributes to C-H stretching vibration [40] and the wider peak around wavenumber 3448 cm^{-1} indicates the O–H stretching [39].

Given that both biochar and activated carbon are amorphous carbons with substantial porosity, there is no real difference between them structurally. Even activated carbon made from biomass can be classified as a specific kind of activated biochar. However, unlike activated carbon, biochar usually has abundant surface functional groups (C−O, C=O, COOH, and OH, etc.), which being highly modifiable act as a platform for the synthesis of various functionalized carbon materials [41]. However, the currently synthesized coconut shell biochar nanomaterial is not modified based on functionalization elements and are developed without any further chemical processing. Subsequently the surface functional groups C−O, C=O, COOH becomes inactive as the developed biochar material has been synthesized using tube furnace at very high temperature of 1000 °C. During this process, the functional groups are least active and becomes inert on investigation under FTIR in the finger and functional group regions. The above inference is supported by the research work presented by Elnour et al. [42] where biochar nanoparticles were developed via pyrolysis at different temperature (300 °C, 400 °C, 500 °C, 600 °C and 700 °C), and disappearance of peaks are noticed. Likewise, investigating CS nanoparticles under FTIR denotes no spectral spikes, indicating the inactiveness of CS nanoparticles under the infrared spectrum. The nanocomposites of PEG with different weight concentration of CS nanoparticles, replicates the absorption spectral peaks as available in pure PEG-1000 PCM. Other than peak shifts, no spectral peaks seemed, thereby ensuring the interaction between PEG and CS nanoparticles to be only physical and no chemical reaction occurring between confirming the thermal stability. Subsequently XRD analysis of nanomaterial, PCM and nanocomposites are provided in **(Supplementary S8).**

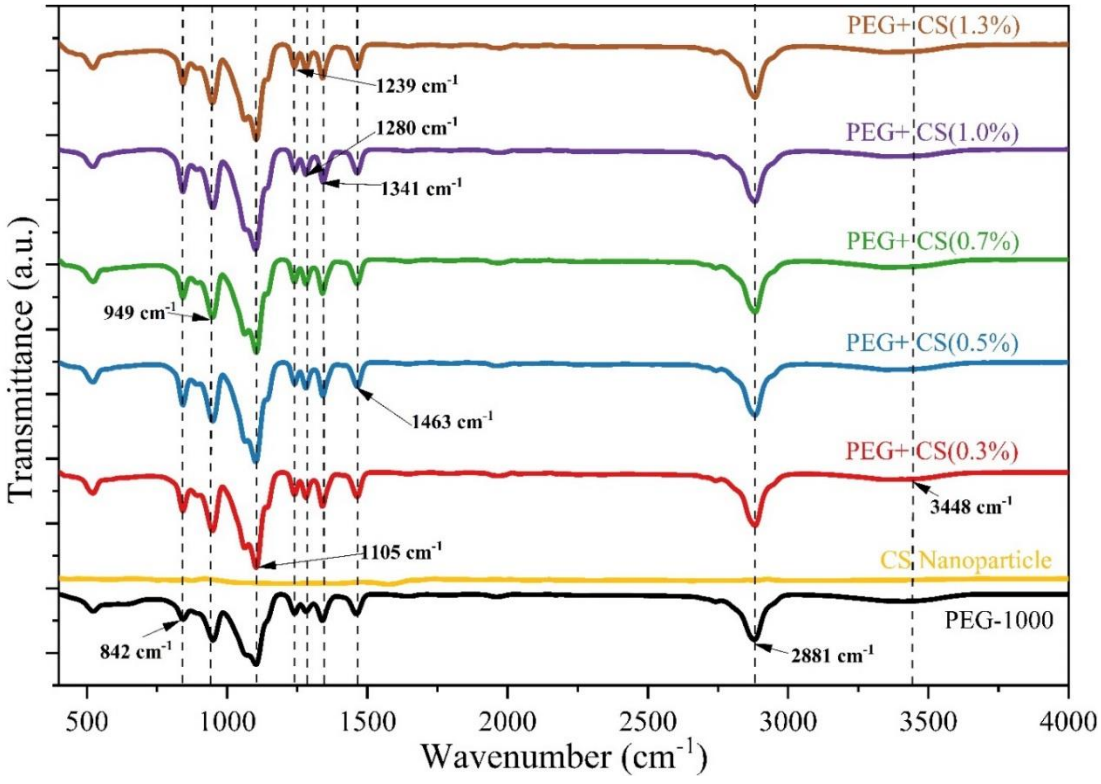


Figure 3: Function group and chemical stability analysis of base PCM and its nanocomposite with CS nanoparticle.

3.3 Optical absorbance and transmittance analysis

In this section, the optical properties like absorption and transmittance of PEG-1000 PCM and its nanocomposite with CS nanoparticle on incidence of photon within the electromagnetic radiation spectrum is investigated. Figure 4a & 4b illustrates the optical absorption and optical transmittance spectrum curve of PEG-1000 and the nanocomposite of CS nanoparticle dispersed PCM at different weight fraction. A beam of light rays is passed on PCM nanocomposite samples to understand the atoms and molecules absorbance potential exciting themselves from lower orbitals to higher orbitals. Phase change materials are thermal energy storage materials acting as thermal batteries. Meanwhile, the predominant source of eco-friendly thermal energy source is solar, radiating thermal energy in the form of electromagnetic waves. Henceforth, it is vital to evaluate and understand the optical properties of PCM for efficient development and integration of PCM with advanced technologies. From Figure 4a, the optical electromagnetic ray absorbance of PEG-1000 is inferred to be 0.43 owing to the opaque nature of organic material, and transparent texture of polyethylene glycol. Meanwhile with different weight concentrations of CS nanoparticles, there is an increasing trend. A CS nanoparticle with weight fraction of 0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% and 1.3 wt% exhibits an optical absorbance of 0.77, 0.83, 0.87, 0.92 and 0.94 respectively. A maximum increment in optical absorbance of about 118.6% is observed in the developed nanocomposite PCM with 1.3 wt% of CS nanoparticle. Increase in optical absorption of electromagnetic rays by PEG-1000 on dispersion of CS nanoparticles can be attributed to the following reasons; a) inclusion of CS nanoparticle reduces the band gap of the organic PCM molecules and improves n-electrons, π-electrons or combination of n-electrons & π-electrons to absorb the incidence radiation to excite the electrons more actively to the higher orbitals [43]; b) likewise the dark texture of CS nanoparticle, on uniform dispersion within the matrix of PCM contributes for better absorbance [8]. In addition the porous frame like structure of the CS nanoparticle, supports multiple reflection within the nanocomposite to better retrain the incident rays [44].

Similarly, the transmissibility of PEG-1000 and its nanocomposite with CS nanoparticle is calculated by comparing the spectral curves with the extra-terrestrial spectrum data [45]. On evaluation, PEG-1000 PCM exhibits an optical transmittance of 37.7%. Meanwhile, the transmissibility of the developed nanocomposite of PEG with CS nanoparticles at weight fraction of 0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% and 1.3 wt% is calculated to be 16.3%, 14.4%, 12.9%, 11.5% and 11.2% respectively. As the experiment is conducted within a closed environment, the reflection is negligible and the predominant phenomena of the incidence radiation is either absorption or

transmittance. As absorption and transmittance of electromagnetic rays are inversely proportional, increase in absorbance leads to decrease in transmissible nature of organic PEG. This optical absorbance property of the developed nanocomposite PCM sample is an excellent candidate for integration of PCM with solar thermal systems.

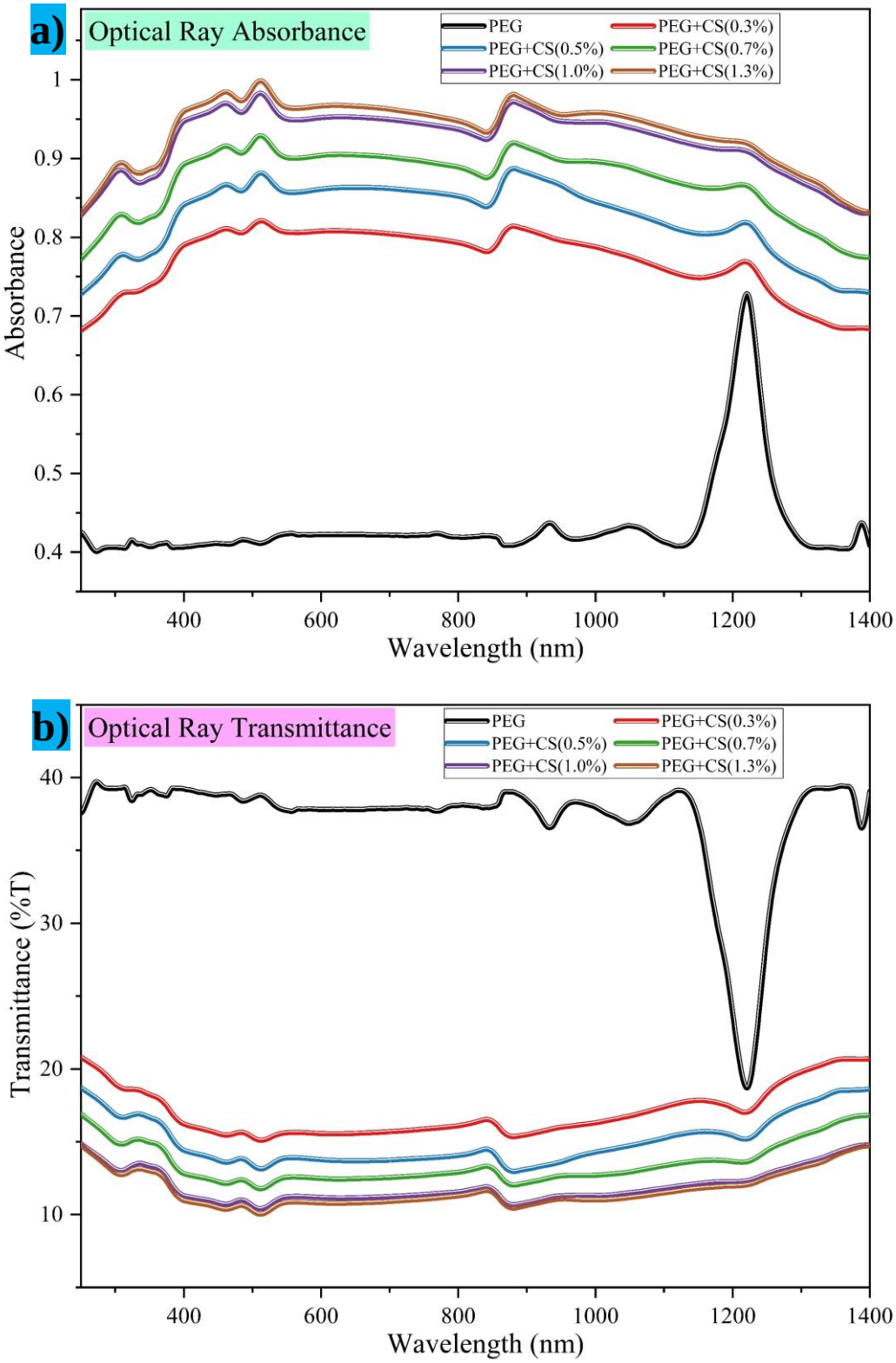


Figure 04: a) Optical Absorbance and b) Optical Transmittance of green synthesised coconut shell nanoparticle dispersed PEG-1000 nanocomposites

3.4 Thermal conductivity

Amidst the thermal features like, energy storage potential and thermal stability, thermal conductivity is a critical factor influencing the heat transfer rate or thermal response rate of energy storage materials. Thermal conductivity of PCM and its nanocomposite with CS nanoparticles are displayed in Figure 5a. In solid state, the thermal conductivity of PEG-1000 is measured to be 0.240 W/m·K signifying the low thermal energy charging/discharging efficiency. Nonetheless, developed nanocomposite samples of PEG with CS nanoparticle at weight fraction of 0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% and 1.3 wt% depicts thermal conductivity of 0.330 W/m·K, 0.378 W/m·K, 0.443 W/m·K, 0.515 W/m·K and 0.438 W/m·K respectively. Thermal conductivity of PEG is increased 2.14 times using the green synthesised CS nanoparticle through a two-step process. The direct instigation behind this thermal conductivity increment are; a) uninterrupted three-dimensional network & porous structure established better contact area with PEG, causing low interfacial thermal resistance for improved thermal network channels and pathways for extra heat transfer and phonon propagation in PEG+CS nano composite samples [46]; b) uniform dispersion of high conducting CS nanoparticle develops thermal networks within the matrix of organic PCM for improved heat transfer. In addition, the green synthesised CS nanoparticle consists of 92% of carbon element as inferred from elemental analysis depicting the thermal conductivity of the CS nanoparticle to be in the range of 116-160 W/m·K [47]. CS nanoparticle, creates numerous thermal hotspots among the matrix of PEG-1000 and contributes towards better thermal networks for effective energy transfer rate of the developed nano composite [48].

In contrast it is observed that at higher concentration of 1.3 wt% CS nanoparticles with PEG organic PCM, significant drop in thermal conductivity of the nanocomposite is noted, which is worthy of discussion. At higher concentration the following phenomena occurs a) the cohesive force of attraction between the CS nanoparticle tends to increase causing formation of clusters, this clusters slowly bulge to become dense molecule and due to agglomeration settles down on repeated phase transition and disrupts the uniform distribution for proper thermal channel [49] and b) the mean free path for intermolecular diffusion is restricted due to increase in density of the composite PCM. Additionally, to compare the thermal feature like thermal conductivity and energy storage of PEG/CS nanocomposite with other porous carbon-based three dimensional nanoparticles in existing literatures are consolidate in Table 1, which demonstrates the superior thermal properties of the developed nanocomposite in justification to the novelty of the current research.

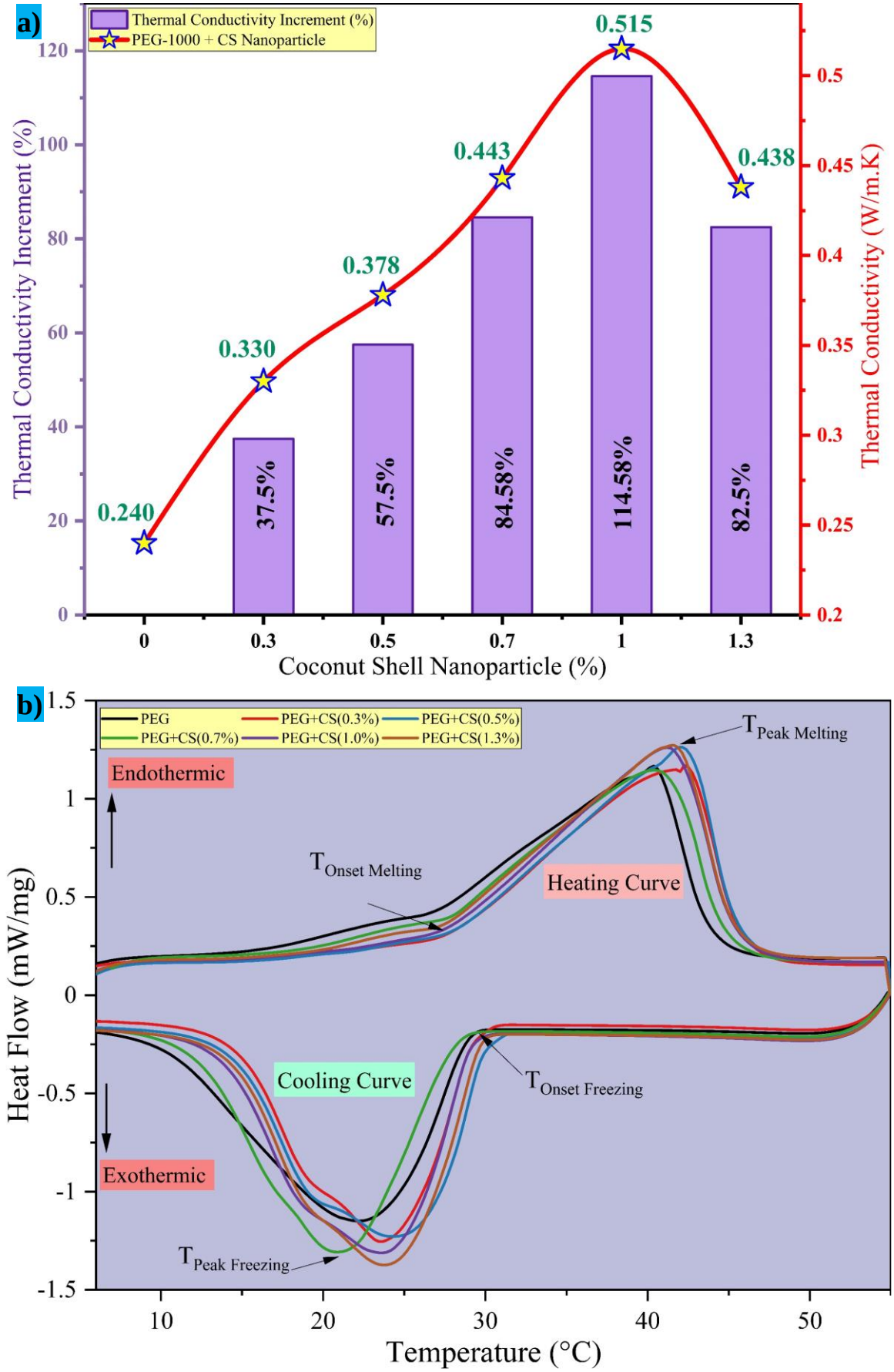


Figure 05: Thermo physical properties a) thermal conductivity increment of PEG-1000 PCM at different weight fraction of CS nanoparticle; b) Heating and Cooling Curve of nanocomposite PCM to analysis the heat storage enthalpy

3.5 Energy storage ability

Phase change thermal properties like melting ($\Delta \boldsymbol{H_m}$) and cooling ($\Delta \boldsymbol{H_c}$) enthalpy, phase transition temperature (T_m) of the developed CS nanoparticle dispersed nanocomposite PCMs, were studied using DSC instrument. The heat flow curves of PEG-1000 and PEG+CS nanoparticles at different weight fraction during phase transition process are depicted in Figure 5b. Enthalpy of the developed CS biochar based nanocomposite PCM during heating at weight fraction of 0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% and 1.3 wt% are 143.5 J/g, 148.2 J/g, 149.2 J/g, 150.1 J/g and 153.1 J/g respectively whereas for base PEG-1000 PCM the heating enthalpy is only 141.2 J/g. Whereas during freezing process, nanocomposite PCMs with 0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% and 1.3 wt% weight fraction of CS nanomaterial exhibit crystallization enthalpy of 138.9 J/g, 139.5 J/g, 140.7 J/g, 141.4 J/g and 146.3 J/g respectively whereas for base PEG-1000 PCM the crystallization enthalpy is only 138 J/g. The DSC heat flow curve contains a single peak in both endothermic and exothermic processes indicating the solid liquid phase transition. There is small drift in the melting temperature of PEG with increased weight fraction of CS nanoparticles in the direction of higher temperature compared to pure PEG. Likewise, the crystallisation temperature of the nanocomposite samples shows an advance in freezing. The change in phase transition temperature of the nanocomposite can be ascribed due to the porous structure nanoparticle effectively bonding the PCM and shifts the temperature slightly.

Furthermore, by analysing the area under the melting and cooling curve the phase transition is calculated. Apparently, the PCM pure PEG-1000 is an exceptional candidate for storing thermal energy owing to its latent heat of 142 J/g with phase transition temperature of 35-40 °C. Likewise PEG+CS nanocomposite exhibit a potential for cyclic heat storage/release ability at the same temperature range. On evaluation it is observed that the dispersed CS nanoparticles shows an increasing trend in melting enthalpy of the developed nanocomposite sample, which can be attributed due to a) the presence of C-H bond in the PEG+CS nanocomposite and higher number of domain electrons on the surface of nanoparticle affects and the intermolecular bonding between the interface of PEG and CS nanoparticle. The intermolecular force of attraction increases as PEG gets embedded within the porous gaps of CS nanoparticles and ensures stability [9]. With low concentration of CS nanoparticle, the strong intermolecular attraction is predominant and the melting enthalpy increases. Whereas at higher concentration of nanoparticles the replacement of energy storage PCM is maximum, and the increment occurring with intermolecular force of attraction becomes negligible results in lower melting enthalpy.

3.6 Thermal degradation evaluation

Thermogravimetric analysis (TGA) is used to evaluate the thermal stability and thermal degradation of PEG and its nanocomposites with CS nanoparticles. All the samples were heated to 500 °C at the rate of 10 °C/min under N_2 atmospheres using the TGA instrument to express better understanding of their thermal stability and thermal degradation nature. TGA and DTG thermal curves of PEG and PEG+CS nanocomposites are shown in Figure 6. It can be inferred from the TGA curve that PEG and its nanocomposite undergo a single step degradation. Until 215 °C, the developed nanocomposite samples exhibit extreme thermal stability and weight loss is negligible, whereas on further increase in temperature, PEG and its nanocomposites starts to degrade with infinitesimal variation in temperature. PEG decompose about 94% between the temperature ranges of 220-400 °C as the long chain polymer in PEG breaks down into monomer during heating at higher temperature, and the decomposition occurs [43]. The degradation of PEG reaches maximum weight percentage at 405 °C and the degradation process is completed at 440 °C. Moreover, the initial decomposition of PEG+CS(1.0%) occurs at higher temperature than pure PEG, ensuring that PEG+CS(1.0) sample exhibit outstanding thermal stability. Conversely, PEG+CS(1.0%) display early decomposition ahead of pure PEG, which is owing to the micro-composite formation between CS nanoparticle and PCM due to breakdown of molecules at higher temperature [50].

Differential thermogravimetric (DTG) curve of PEG and its nanocomposite with CS nanoparticle in Figure 6b depicts the derivative weight loss, which reflects the concentration of nanoparticles in the developed composite. Owing to high purity PEG undergoes maximum weight loss during decomposition, whereas other composites lose lower percentage of weight compared to pure PEG. The shift in final degradation temperature of the nanocomposite samples can be better interpreted from the DTG curve. However, the working temperature for the developed nano composite is usually below 55 °C as its phase transition temperature is 38 °C, which is far lower than the degradation temperature of the tested samples, and is preferred for thermal regulation systems. More information on the TGA analysis of the developed nanocomposite can be inferred from visuals presented **(Supplementary S9-S14 and Appendix V)**

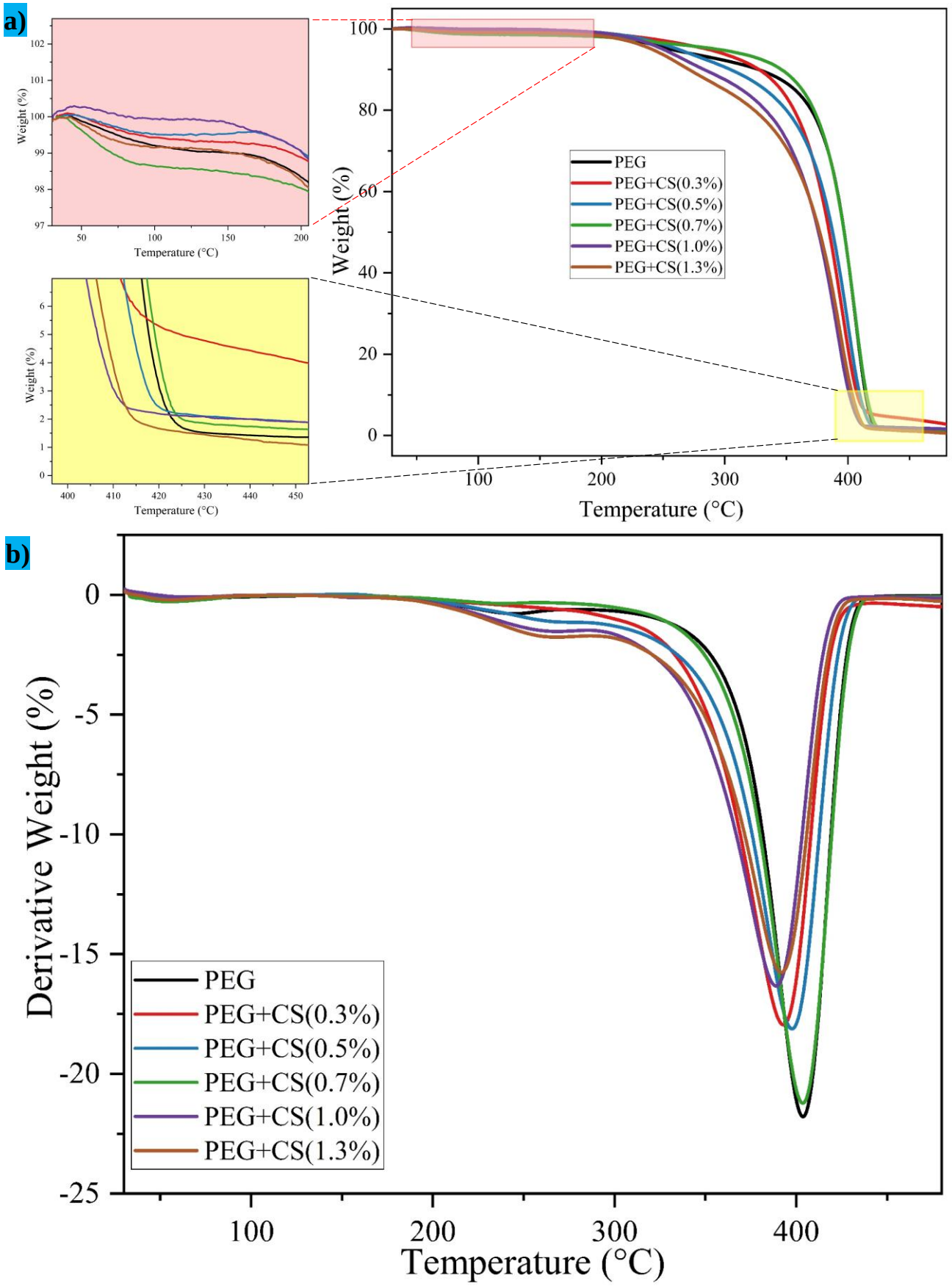


Figure 06: a) Thermal degradation curve and b) differential thermogravimetric (DTG) curve of PEG-1000 and its nanocomposites with CS nanoparticles.

3.7 Thermal cycling potential

Thermal stability and reusability potential of the developed nanocomposite PCMs is a crucial feature, which restricts their integration with real time thermal systems. Herein, we investigate the thermal stability of PEG/CS nanocomposite PCM with 1.0 wt% of CS nanoparticles for 500 numbers of charging and discharging thermal cycles. Figure 7 consolidates the chemical stability evaluation by FTIR spectrum, energy storage heat flow curves and thermogravimetric curve of PEG and PEG/CS nanocomposite PCM before and after 500 cycles.

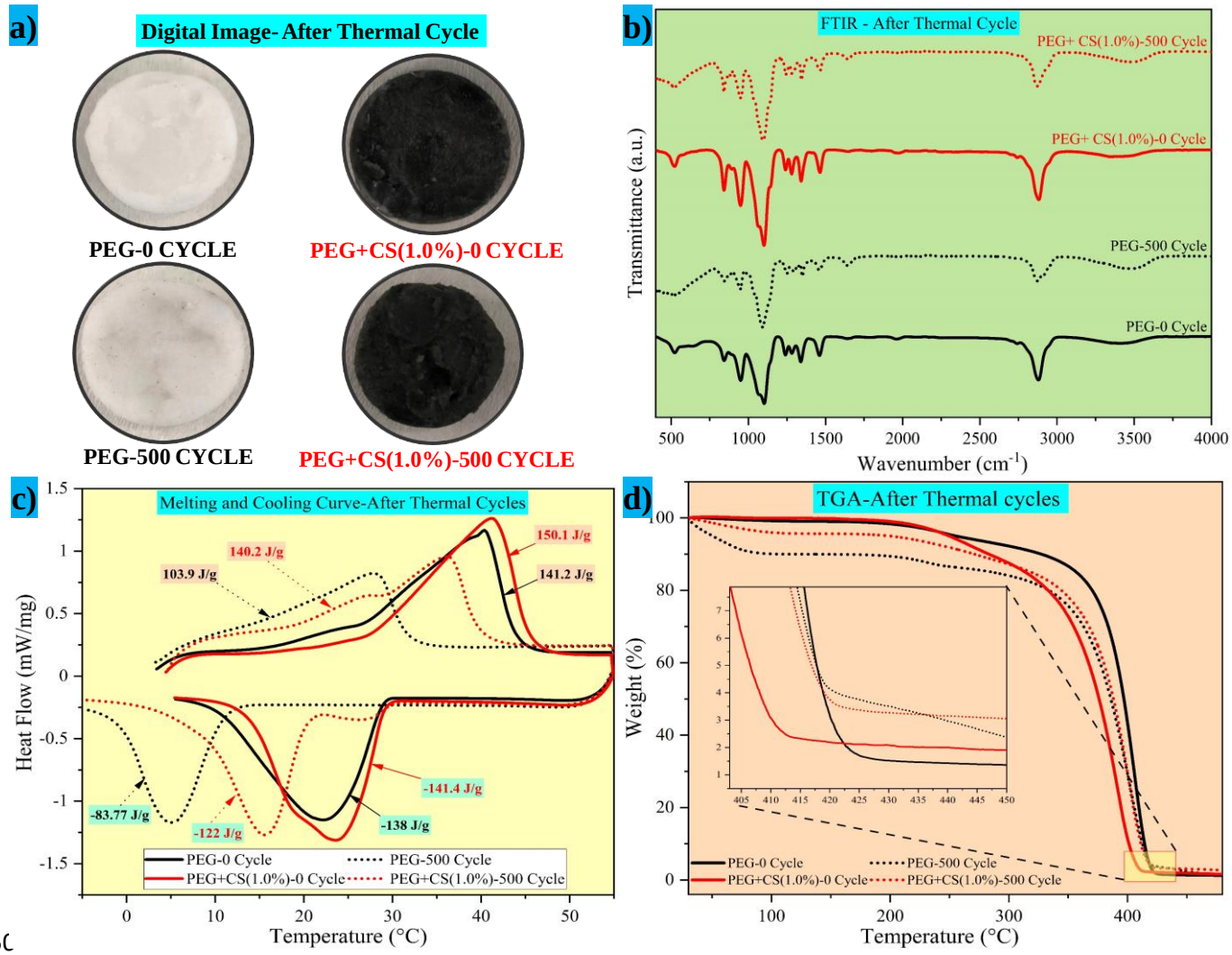


Figure 07: Evaluation of PEG and PEG/CS nanocomposite before and after 500 thermal cycles a) Digital image; b) Chemical stability using FTIR; c) Energy storage potential and d) Thermal degradation curve.

The digital view of PEG after 500 thermal cycles indicates change in texture and formation of carbon content with repeated thermal cycle, whereas PEG/CS nanocomposite does not exhibit much variation in texture. However, there is a change in the solidity of PEG and PEG/CS nanocomposite, which is a representation of weaker bonding of long chain polymers. Minor variation in FTIR spectrum can be noticed in Figure 7b, on comparison of PEG and PEG/CS samples before

and after thermal cycle, in regard to the intensity of the peak. Variation in intensity of peak is expected as this is a common phenomenon owing to accelerated thermal cycle, whereas the peaks are in correspondence to the same wavenumber before and after 500 thermal cycle. Conversely, no new peaks are observed ensuring that no chemical reaction and thermal degradation has occurred with repeated usage of PCM. Besides Figure 7c illustrates the heat flow curves of PEG and PEG/CS nanocomposite with single peak ensuring the solid-liquid phase transition. As can be inferred from above figure, the peak melting temperature of the PEG PCM is predominantly varied establishing a instability during phase transition as its exposed higher temperature at a faster rate, and ageing of PEG PCM occurs. Whereas with nanocomposite PEG+1.0CS, proper dispersion of CS nanoparticles retains and absorbs much of heat supplied, and restricts breakage of intermolecular bonding between PEG molecules and well facilitates CS nanoparticles binds stronger with PEG as they retain PCM within their porous honeycomb structure and reduce the drop in melting temperature of PEG+CS nanocomposite considerably. The variation in peak transition temperature of PEG/CS(1.0%) is far within the margin of error providing extended operation of PCM for energy storage. Likewise, with repeated thermal cycling's, the intermolecular force of attraction and the binding between the PEG-PEG molecules and PEG-CS molecules disrupts and lowers the energy storage ability [28]. Furthermore, influence of impurity is also a factor to be considered causing reduction in energy storage potential of the samples. Nonetheless, in real time application, the PCM are expected to encapsulate within closed environment (preventing impurity), as well the operation temperature is within permissible limit and the charging and discharging occurs at slow rate. In regard to the energy storage potential (ΔH_m) and (ΔH_c) of PEG declines by 26.4% and 39.3% respectively after 500 thermal cycles, whereas (ΔH_m) and (ΔH_c) of PEG/CS(1.0%) shows a variation by 6.6% and 13.7% after 500 number of thermal cycles. The heat flow results proves the ability of PEG/CS nanoparticles to be opted for repeated usage within a drop in latent heat. During repeated thermal cycles, the bonding between the long chain polymers weakens resulting in lower intermolecular force of attraction reducing the energy storage enthalpy. Thermal conductivity of the developed nanocomposite PCM after thermal cycling displays 0.501 W/m·K The drop in thermal conductivity of the sample after 500 thermal cycles is owing to thermal cycling effect, where the developed nanocomposite undergoes repeated energy storage and discharge. As we have conducted accelerated thermal cycling of 500 thermal cycles, during the process inclusion of any impurities in the environment is also more likely to impact the thermal conductivity. Another significant property evaluated to ensure the ability of PCM for practical application is the thermal stability, which is generally characterised using the thermogravimetric curve indicated in Figure 7d. Both PEG and PEG/CS nanocomposite undergo one step thermal degradation before and after thermal cycling. It

can be inferred from the TGA curve, that PEG undergoes weight loss up to 10% within the temperature range of 30-100°C, whereas PEG/CS nanocomposite depicts better thermal stability with 3-4% weight loss. Nonetheless, the maximum degradation temperature of pure PEG and its nanocomposite with CS nanoparticles is increased after thermal cycling, which can be ascribed due to the repeated heating and cooling. Thermal stability of PEG/CS(1.0%) nanocomposite exhibits closely similar chemical and thermal stability before and after thermal cycling ensuring their potential to be used in energy storage systems.

4.0 Conclusion

Novel three dimensional highly porous carbon based coconut shell nanoparticles are successfully synthesised through green approach to be incorporated with PEG based PCMs adopting two step methods to enhance the thermo physical features. CS nanoparticles with porous frame like structure, supports multiple reflection of the incident electromagnetic waves within the PCM matrix and increases the optical absorbance from 0.43 to 0.94 contributing to about 118.6%. Subsequently, the increase in optical absorbance reduces the transmittance of electromagnetic waves from 37.7% to 11.2%. PEG/CS nanocomposite PCM, specifically with weight fraction 1.0% possessed 3D thermal conducting network resulting in thermal conductivity enhancement by 114.5% (from 0.24 W/m·K to 0.515 W/m·K). Conversely, they also demonstrate an increase in energy storage potential of 150.2 J/g compared to 141.2 J/g of PEG during heating and exhibits 141.4 J/g compared to 138 J/g of PEG during freezing. More importantly, the developed nanocomposite maintains the thermal feature even after 500 thermal cycles, ensuring their charging and discharging potential for reusability. Possessing, excellent chemical stability, optical absorbance, thermal feature like thermal response, energy storage and thermal stability brands the developed CS nanoparticle dispersed PEG/CS nano composite PCMs to be envisaged in low temperature waste heat recovery, thermoregulation comfort in buildings, electronic cooling system, and so on.

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