INVESTIGATIONS ON A NOVEL COMPOSITE PHASE CHANGE MATERIAL COMPRISING PARAFFIN WAX AND CQDs FOR THERMAL CONDUCTIVITY ENHANCEMENT

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ABSTRACT

Thermal energy storage using Phase Change Materials (PCMs) has become crucial in combating the energy crisis and is leading to innovative approaches in energy storage management. As part of this study, novel composite PCMs were prepared by dispersing Carbon Quantum Dots (CQDs) with weight percentages of 1%, 5%, 10%, 15% and 20% in Paraffin Wax (PW). The study aims to investigate thermal conductivity enhancement of these composite PCMs and examine their applicability in thermal energy storage. Ultrasonication was utilized to prepare the composites. Scanning electron microscope (SEM) was employed to study surface morphology of microstructures of the PCMs. Thermal conductivity was determined using a Heat Flow Meter and results revealed a remarkable increase. Maximum enhancement ratio of 97.38% was obtained for the 20 wt.% composite PCM.

Key words: Paraffin Wax, Carbon Quantum Dots, Phase Change Material, Composite PCMs, Thermal Conductivity, energy storage

1. Introduction

The utilization of Phase Change Materials (PCMs) has garnered significant attention as a promising solution for energy conservation by storing excess energy as latent heat and bridging the gap between energy demand and supply [1]. PCMs possess a remarkable ability to store substantial amounts of energy and release it when undergoing a phase transition. Hence the primary and crucial characteristic of PCMs lies in
their capacity to effectively store thermal energy [2]. Nevertheless, limited thermal conductivity of PCMs hinders the realization of their full potential, as it impedes the heat transfer involved in the charging and discharging processes [3]. A logical solution to address this limitation is to introduce highly conductive materials, which can serve as thermal conductivity promoters, into the composition of PCMs to form a composite [4]. One of the techniques that significantly enhances the thermal conductivity of PCM is when nanometer-sized materials with high thermal conductivity, such as nanoparticles, nanofibers, nanotubes, and nanosheets, are dispersed within it [3]. While metals and metal oxides have indeed improved the thermal conductivity of PCMs, they also contribute to an increase in weight, leading to a decrease in overall heat storage density as well as thermal and chemical stability. In recent times, carbon-based fillers, including graphite, carbon nanotubes, carbon nanofibers and graphene, have been employed to improve the thermal conductivity of PCMs. This is primarily due to their exceptional thermal conductivity and low density [5].

Shi et al. conducted experiments on PCMs made of paraffin mixed with exfoliated graphite nanoplatelets (xGnP) and graphene. The findings demonstrated that the solid-phase thermal conductivity of paraffin/xGnP was 2.7 Wm$^{-1}$K$^{-1}$ and paraffin/graphene composites was and 0.5 Wm$^{-1}$K$^{-1}$ representing a substantial increase compared to the thermal conductivity of pure paraffin wax (0.25 Wm$^{-1}$K$^{-1}$) [6]. Wang et al. introduced multi-wall carbon nanotubes (MWCNTs) into paraffin as a dispersion. The findings indicated that the addition of 2 wt.% MWCNTs led to a significant improvement in thermal conductivity of paraffin by 35% in solid state and 45% in the liquid state [7]. In their study, Mohammad et al. utilized vacuum impregnation to create a PCM composite by combining paraffin with graphene oxide (GO) sheets. The outcome of their research demonstrated a remarkable enhancement in thermal conductivity, with the composite's value increasing from 0.305 Wm$^{-1}$K$^{-1}$ to 0.985 Wm$^{-1}$K$^{-1}$ [8]. Ali et al. conducted studies with paraffin wax, nanographene (NG) composite PCM and found that at 3 wt.% of nanographene, thermal conductivity increased by 146% and latent heat decreased by 3% [9].

Carbon-based materials, known for their high thermal conductivity, are extensively employed as dispersants. Consequently, the utilization of new carbon allotropes has witnessed a steady increase in recent years [3]. The exceptional characteristics of carbonic nanomaterials, including nanodiamonds, carbon nanotubes, fullerenes, graphene sheets, and fluorescent carbon nanoparticles or carbon quantum dots (CQDs), have sparked significant interest and led to extensive research. These materials possess remarkable properties, making them highly promising for a diverse range of technical applications [10].

In 2004, Xu et al. made an unexpected discovery of a new type of carbon material, while attempting to produce single-walled carbon nanotubes (CNTs) which they identified as carbon nanoparticles (CNPs) [11]. In 2006, Sun et al. introduced a laser ablation method for producing CQDs with significantly improved fluorescence emission. They achieved this enhancement through surface passivation and gave the name "carbon quantum dots" to describe the fluorescent carbon nanoparticles (CNPs) obtained from graphite powder used as a precursor [12]. Carbon quantum dots (CQDs) were developed as a potential alternative to semiconductor quantum dots as they exhibit low toxicity, biocompatibility, affordability, and chemical inertness, while still offering similar fluorescence properties, making them an attractive choice for various applications [10]. In addition to the above traits, CQDs are also known to possess outstanding optoelectronic properties, simple synthesis methods, convenient surface functionalization, substantial specific surface area
which has sparked significant interest in research [13]. These remarkable characteristics of CQDs have great potential for a broad spectrum of applications.

Among the various carbon materials like carbon tubes or carbon fibers, graphene and porous carbon network, carbon dots stand out due to their inherent fluorescence characteristics, making them ideal candidates for the development of fluorescent functional composite phase change materials (PCMs). Incorporating CQDs into PCMs offers several significant benefits as they exhibit exceptional thermal conductivity properties owing to their distinctive nanoscale structure and large surface area, facilitating heat transfer to occur efficiently inside the composite PCM. The dispersion of CQDs through the entire matrix of the PCM leads to a substantial improvement in thermal conductivity, thereby enhancing the material’s capacity for storing and releasing energy [14].

Although CQDs are being extensively researched and used in diverse areas such as biomedical applications, photocatalysis, nanomedicine, material science, synthetic chemistry, supercapacitors, batteries, etc., [10,13] utilization of CQDs in the area of thermal energy storage for increasing thermal conductivity of PCMs has not been considered so far as per the authors’ knowledge. The pioneering aspect of this innovative research lies in the creation of novel composite PCMs by incorporating CQDs into PW. The CQDs were skillfully dispersed within the PW matrix, with different weight percentages of 1%, 5%, 10%, 15% and 20% encompassing low and high weight fractions.

PW, an organic material makes excellent choice as a PCM as it possesses distinct characteristics including chemical stability, non-toxicity, widest range of melting temperatures and flawless thermal stability, providing flexibility in its applications [15,16]. This study aims to investigate thermal conductivity enhancement of the prepared composite PCMs thereby assessing their potential for application in thermal energy storage management.

2. Materials and Procedure

2.1. Materials

PW granules were obtained from Krokio Products Pvt. Ltd. Mumbai India. Melting point of PW is between 50-57 °C. Carbon Quantum Dots (CQDs) powder was procured from Metro composites laboratory, Chennai, India.

2.2. Fabrication of nanocomposite PCMs

The required quantity of CQDs were dispersed into the melted PW and stirred for 30 min using ultrasonicator operating at 40 kHz and 120 W. The bath temperature was maintained at 80 °C for effective dispersion. The mixture simultaneously experiences heating and vibration. This technique aids in preventing the aggregation of nanoparticles and ensures their stability. The fine admixture was then poured into the silicon molds and allowed to solidify at room temperature. The samples were checked for any visual surface defects and then further investigation was undertaken on those samples free from surface defects.

The composite PCMs thus prepared were categorized according to the weight percentage of CQDs added, as presented in tab. 1.
Table 1. Labels of Composite PCMs

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% CQD</th>
<th>Labels of Composite PCMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1%</td>
<td>PWCQD-1</td>
</tr>
<tr>
<td>2</td>
<td>5%</td>
<td>PWCQD-5</td>
</tr>
<tr>
<td>3</td>
<td>10%</td>
<td>PWCQD-10</td>
</tr>
<tr>
<td>4</td>
<td>15%</td>
<td>PWCQD-15</td>
</tr>
<tr>
<td>5</td>
<td>20%</td>
<td>PWCQD-20</td>
</tr>
</tbody>
</table>

Photos of composite PCMs prepared by the above method are shown in fig. 1. Numbers on the sample composite PCMs refer to the sample number given in tab. 1.

![Figure 1. Prepared Composite PCMs](image)

2.2.1. Scanning Electron Microscope (SEM)

The scanning electron microscopy images of PW and composites were taken by HITACHI S-3700N SEM with a provision of magnification from 5x to 300,000x. These images are useful in learning morphology including the microstructures of the samples.

2.2.2. Thermal Conductivity

Thermal conductivity was determined by FOX 50 Heat Flow Meter supplied by TA instruments. The specimen was positioned amidst two parallel plates that are controlled by temperature. The two plates are kept at constant temperatures, with a difference between their respective temperature levels. One-dimensional steady-state heat transfer and Fourier's law of heat conduction were used to take measurements and to calculate thermal conductivity values. The measurements were conducted in a steady-state one-dimensional heat transfer scenario, and thermal conductivity was determined using Fourier's law of conduction for heat transfer. The temperature range of the instrument is -10-110 °C, testing range is 0.1 to 10 Wm⁻¹K⁻¹ and accuracy is ±3%. The thickness of sample used for testing was 5 mm.

3. Results and Discussion

3.1. Morphology

Scanning Electron Microscope (SEM) was employed to capture the morphology of the surface of the PCMs. Figures 2 to 8 depict the SEM images of PW, CQD powder, and the composite PCMs, showcasing their morphological characteristics.
Figure 2 showcases the SEM image of PW obtained at a magnification of 50x. The use of low vacuum mode allowed for clear visualization of the material's layered structure. The image provides an effective understanding of the morphology of PW, enabling a thorough examination of its characteristics.
In fig. 3, the SEM image of CQD powder at 100x magnification can be viewed. This image offers valuable insights into the morphology and distribution of the CQD powder, enabling a better understanding of its characteristics, structure and potential applications. Most of the powder is in cluster form.

Figures 4 to 8 offer a comprehensive view of the SEM images depicting the composite PCMs. These images vividly showcase the successful incorporation of CQDs within the PW matrix, clearly demonstrating their presence in the composite. Additionally, the fluorescence nature of CQDs is prominently exhibited in most of the images, highlighting their unique properties and further supporting their effective incorporation into the composite PCMs.

Due to the high intensity of the electron beam used in SEM imaging, higher magnification was avoided for PW, CQD powder and composite PCMs to prevent the risk of material melting before capturing the images. The electron beam's intense energy can lead to undesired effects on certain materials, and in this case, it was crucial to ensure that the samples remain intact during the imaging process. Therefore, the SEM images presented above were obtained at a suitable magnification level that balanced the need for clear visualization while preserving sample integrity.

### 3.2. Thermal Conductivity

Thermal conductivity is an intrinsic property of a material that governs the rate at which heat is transmitted across it. This property influences the heat conduction capacity of a substance. The assessment of thermal conductivity plays a crucial role in evaluating the efficacy of PCMs utilized in latent heat thermal energy storage systems (LHTESS). PCMs are engineered for storing and releasing substantial amounts of energy during their transition between solid and liquid states. Greater thermal conductivity signifies the ability of PCM to transmit heat with increased efficiency, thereby enhancing its effectiveness in the storage and release of thermal energy. This data is essential for evaluating whether a PCM is appropriate for specific thermal energy storage applications. Thermal conductivity measurement for PW and composites was done by Heat Flow Meter.

#### 3.2.1. Thermal conductivity Vs Temperature:

Variation of thermal conductivity with temperature has a crucial role to play in designing and improving the performance of latent heat thermal energy storage systems (LHTESS). The study places substantial attention to understanding how changes in thermal conductivity with respect to temperature can enhance the performance of LHTESS. Thermal conductivity changes with temperature of PW and composites can be observed in fig. 9.
The findings indicate that thermal conductivity changes linearly with temperature ranging from room temperature (25 °C) to phase-change temperature (55 °C). It may be noted that thermal conductivity increased significantly in the solid state and reached its peak at 55 °C and then decreased in the liquid state. Thermal conductivity of PCM is mainly influenced by its matrix. It is determined by the collective movements of phonons over extensive distances in a flawless crystal structure and the alignment of molecules within the PCM matrix. As temperature increases, the molecular vibrations within the well-structured solid matrix of PCM are accelerated leading to increment in thermal conductivity. Beyond 55 °C, thermal conductivity declines as the PW changes its state from solid to liquid. In the liquid state, the presence of temperature gradients leads to density variations, creating buoyant forces that can induce convection within the bulk liquid PCM. In addition to liquid convection, the motion of phonons in the liquid state is hindered by viscous forces. This results in a decrease in thermal conductivity within the liquid phase [3].

Thermal conductivity values of PW and composites at 55 °C with enhancement ratios have been listed in tab. 2. Enhancement ratio ($\psi$) of composites were calculated using eq. (1) [17]. The Nomenclature section elucidates the meanings of the different parameters involved in eq. (1)

$$\psi = \left[(k_c - k_p)/k_p\right] \times 100$$

(1)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity [Wm$^{-1}$˚C$^{-1}$]</th>
<th>Enhancement Ratio $\psi$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW</td>
<td>0.229</td>
<td>0</td>
</tr>
<tr>
<td>PWCQD-1</td>
<td>0.252 ± 0.015</td>
<td>10.04</td>
</tr>
<tr>
<td>PWCQD-5</td>
<td>0.273 ± 0.015</td>
<td>19.21</td>
</tr>
<tr>
<td>PWCQD-10</td>
<td>0.317 ± 0.015</td>
<td>38.43</td>
</tr>
<tr>
<td>Material</td>
<td>Thermal Conductivity [Wm⁻¹°C⁻¹]</td>
<td>Enhancement Ratio ψ (%)</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>PWCQD-15</td>
<td>0.367 ± 0.015</td>
<td>60.26</td>
</tr>
<tr>
<td>PWCQD-20</td>
<td>0.452 ± 0.015</td>
<td>97.38</td>
</tr>
</tbody>
</table>

Enhancement of thermal conductivity of composite PCMs with increase in weight percentages of CQDs at 55 °C is clearly seen in fig. 10. The graph shows an upward trend of thermal conductivity as weight percentages of CQDs increase.

![Figure 10. Thermal conductivity increments with increase in weight percentages of CQDs](image)

Figure 11 demonstrates the thermal conductivity enhancement ratio of composite PCMs at 55 °C with respect to different weight percentages of composite PCMs. The graph reveals a linear variation of enhancement ratio.

![Figure 11. Thermal conductivity enhancement ratio for different weight percentages of CQDs](image)

In the realm of materials, acquiring a comprehension of thermal heat transport is critical for gaining insights into how materials transfer and store thermal energy. To effectively evaluate the thermal conductivity and overall effectiveness of materials in thermal energy storage applications, it is crucial to have a comprehensive understanding of the mechanisms governing thermal heat transport. Two primary mechanisms come into play: electron transport and phonon transport. Electron transport takes precedence in metals and conducting polymers, whereas phonon transport serves as the primary mode in insulators and semiconductors. PW predominantly banks on the phonon-phonon thermal transport mechanism since metals and conducting polymers are characterized by prominent electron transport [16].

In nonmetallic phase change materials (PCMs), the primary mechanism of thermal transfer is through lattice vibrations. Phonons, being the quanta of lattice vibrations, originate from these vibrations and
serve as the predominant thermal carriers at the microscopic level in nonmetallic PCMs. Phonons, the fundamental units of lattice vibrations in materials, play a crucial role as the driving force responsible for efficient heat transfer through thermal conduction in PCMs. Phonon transmission involves two counteracting mechanisms in terms of heat conduction: phonon diffusion and phonon scattering. Greater phonon diffusion leads to higher thermal conductivity, as these factors are directly related. In theory, the achievement of ideal thermal conductivity becomes possible when phonons can freely and randomly transmit without encountering any obstacles. Thermal conductivity of carbon-based composite PCMs also prominently relies on factors such as the graphitization degree and structural regularity of the carbon materials, as well as the types and loading contents of the PCMs.[14]

The findings of this study provide compelling evidence of a significant rise in thermal conductivity for the composites with doping of CQDs in comparison to the reference material (PW). Notably, 20 wt% CQD composite PCM exhibited the most remarkable improvement in thermal conductivity, reaching an impressive enhancement ratio of 94.32%. This substantial increase in thermal conductivity showcases the potential of the CQD composite PCMs as an effective and efficient heat transfer material.

4. Conclusions

1. The variation of thermal conductivity with temperature is linear.

2. Thermal conductivity of composite PCMs increases from room temperature and reaches maximum value at 55 °C (phase change temperature)

3. Thermal conductivity of composites decreases as the phase changes from solid to liquid.

4. Thermal conductivity increases significantly with weight percentage of CQDs.

5. Maximum thermal conductivity of 0.452 ± 0.015 is obtained for 20 wt.% composite PCM

6. The enhancement ratio of thermal conductivity for 20 wt.% composite PCM is remarkable with 97.38%.

7. The results signify that composite PCMs prepared with CQDs have a great potential in storing and releasing thermal energy.

8. This study clearly demonstrates that PCMs incorporated with CQDs have a promising future in the field of thermal energy storage applications.

5. Future Scope

In addition to the current investigation, there is a critical necessity and potential for further exploration of these composite PCMs in thermal management studies. Conducting Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) tests are critical for the analysis of latent heat storage capacity and thermal stability of these composite PCMs. Such comprehensive assessments would provide valuable insights into their suitability and applicability for thermal energy storage applications.
Nomenclature

°C     degree centigrade
k     thermal conductivity, [Wm⁻¹°C⁻¹]
wt.%     weight percent

Greek Symbol

ψ     thermal conductivity enhancement ratio, [%]

Subscripts

c     Composite PCM
p     Paraffin Wax

Acronyms

PW     Paraffin Wax
SEM     Scanning Electron Microscope
CQDs     Carbon Quantum Dots
PWCQD     PWCQD

References


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