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

by

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*Thermal energy storage using phase change materials (PCM) 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 PCM were prepared by dispersing carbon quantum dots (CQD) with weight percentages of 1%, 5%, 10%, 15%, and 20% in paraffin wax. The study aims to investigate thermal conductivity enhancement of these composite PCM and examine their applicability in thermal energy storage. Ultrasonication was utilized to prepare the composites. The SEM was employed to study surface morphology of micro-structures of the PCM. 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, composite PCM, thermal conductivity, energy storage, phase change materials*

## Introduction

The utilization of PCM 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]. The PCM 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 PCM lies in their capacity to effectively store thermal energy [2]. Nevertheless, limited thermal conductivity of PCM 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 PCM 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

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nanosheets, are dispersed within it [3]. While metals and metal oxides have indeed improved the thermal conductivity of PCM, 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 PCM. This is primarily due to their exceptional thermal conductivity and low density [5].

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

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 CQD, 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].

Xu *et al.* [11] made an unexpected discovery of a new type of carbon material, while attempting to produce single-walled carbon nanotubes which they identified as carbon nanoparticles. Sun *et al.* [12] introduced a laser ablation method for producing CQD 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 obtained from graphite powder used as a precursor. The CQD 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 the aforementioned traits, CQD 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 CQD 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 PCM. Incorporating CQD into PCM 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 CQD 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 CQD 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 CQD in the area of thermal energy storage for increasing thermal conductivity of PCM 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 PCM by incorporating CQD into paraffin wax. The CQD were skillfully dispersed within the paraffin wax matrix, with different weight percentages of 1%, 5%, 10%, 15%. and 20% encompassing low and high weight fractions.

The paraffin wax, 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 PCM thereby assessing their potential for application in thermal energy storage management.

## Materials and procedure

### *Materials*

The paraffin wax granules were obtained from Krokio Products Pvt. Ltd. Mumbai India. Melting point of paraffin wax is between 50-57 °C*. The CQD powder was procured from Metro composites laboratory, Chennai, India.

### *Fabrication of nanocomposite PCM*

The required quantity of CQD were dispersed into the melted paraffin wax and stirred for 30 minutes 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 PCM thus prepared were categorized according to the weight percentage of CQD added, as presented in tab. 1.

**Table 1. Labels of composite PCM**

| Sample | wt.% CQD | Labels of composite PCM |
|---|---|---|
| 1 | 1% | PWCQD-1 |
| 2 | 5% | PWCQD-5 |
| 3 | 10% | PWCQD-10 |
| 4 | 15% | PWCQD-15 |
| 5 | 20% | PWCQD-20 |

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

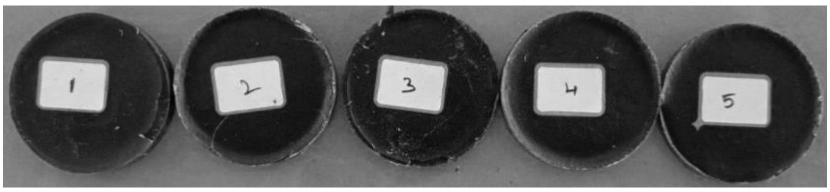


**Figure 1. Prepared Composite PCM**

* As specified by the manufactures

### *Scanning electron microscope*

The SEM images of paraffin wax and composites were taken by HITACHI S-3700N SEM with a provision of magnification from 5x-300000x. These images are useful in learning morphology including the micro-structures of the samples.

### *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. The 1-D 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 1-D 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 0.1-10 W/mK and accuracy is ±3%. The thickness of sample used for testing was 5 mm.

## Results and discussion

### *Morphology*

The SEM was employed to capture the morphology of the surface of the PCM. Figures 2-8 depict the SEM images of paraffin wax, CQD powder, and the composite PCM, showcasing their morphological characteristics.

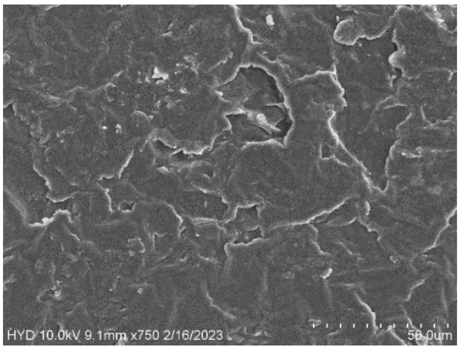


**Figure 2. Paraffin wax**

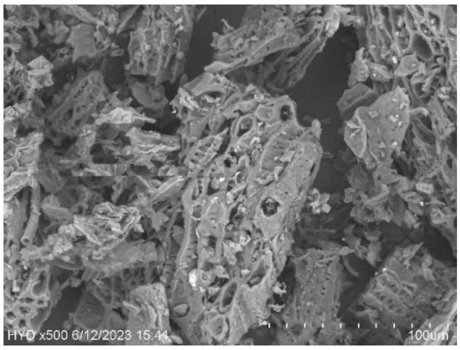


**Figure 3. The CQD powder**

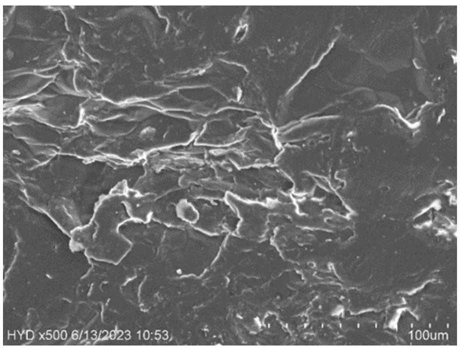


**Figure 4. The PWCQD-1**

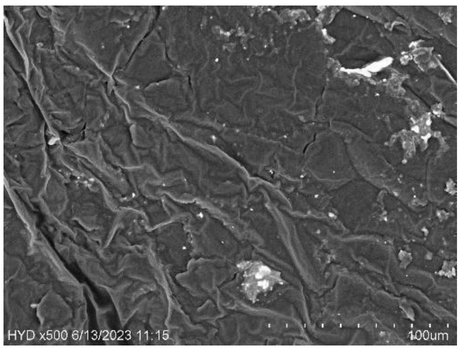


**Figure 5. The PWCQD-5**

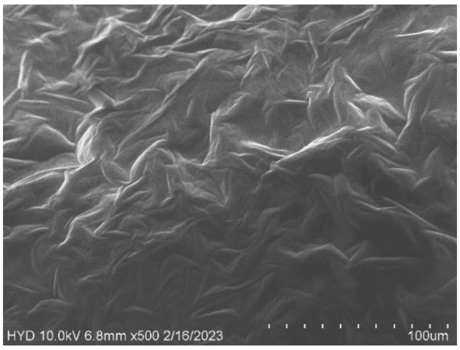


**Figure 6. The PWCQD-10**

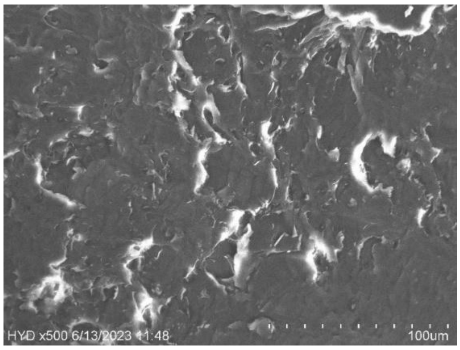


**Figure 7. The PWCQD-15**

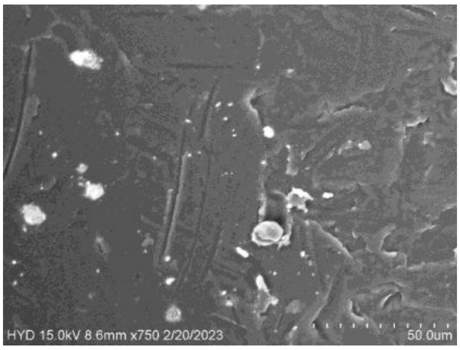


**Figure 8. The PWCQD-2**

Figure 2 showcases the SEM image of paraffin wax 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 paraffin wax, enabling a thorough examination of its characteristics.

In fig. 3, the SEM image of CQD powder at 500x 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 4-8 offer a comprehensive view of the SEM images depicting the composite PCM. These images vividly showcase the successful incorporation of CQD within the paraffin wax matrix, clearly demonstrating their presence in the composite. Additionally, the fluorescence nature of CQD is prominently exhibited in most of the images, highlighting their unique properties and further supporting their effective incorporation into the composite PCM.

Due to the high intensity of the electron beam used in SEM imaging, higher magnification was avoided for paraffin wax, CQD powder and composite PCM 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 previously were obtained at a suitable magnification level that balanced the need for clear visualization while preserving sample integrity.

### *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 PCM utilized in latent heat thermal energy storage systems (LHTESS). The PCM 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

[*] 750x

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 paraffin wax and composites was done by heat flow meter.

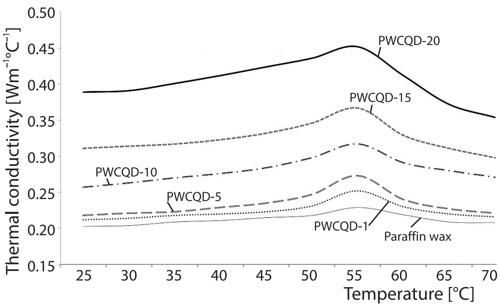


**Figure 9. Thermal conductivity variation with temperature of paraffin wax and composites**

### *Thermal conductivity vs. temperature*

Variation of thermal conductivity with temperature has a crucial role to play in designing and improving the performance of LHTESS. The study places substantial attention understanding how changes in thermal conductivity with respect to temperature can enhance the performance of LHTESS. Thermal conductivity changes with temperature of paraffin wax 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 phonon-s 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 paraffin wax 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 liquid convection, the motion of phonon-s 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 paraffin wax 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]:

$$\psi = \left(\frac{k_c - k_p}{k_p}\right) \times 100 \tag{1}$$

**Table 2. Thermal conductivity and enhancement ratios of paraffin wax and composite PCM**

| Material | Thermal conductivity, $k$ [Wm$^{-1}$°C$^{-1}$] | Enhancement ratio, $\psi$ [%] |
|---|---|---|
| Paraffin wax | 0.229 | 0 |
| PWCQD-1 | 0.252 ±0.015 | 10.04 |
| PWCQD-5 | 0.273 ±0.015 | 19.21 |
| PWCQD-10 | 0.317 ±0.015 | 38.43 |
| PWCQD-15 | 0.367 ±0.015 | 60.26 |
| PWCQD-20 | 0.452 ±0.015 | 97.38 |

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

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

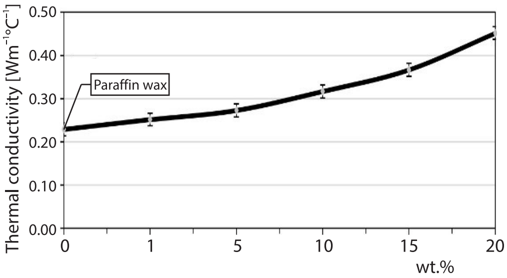


**Figure 10. Thermal conductivity increments with increase in weight percentages of CQD**

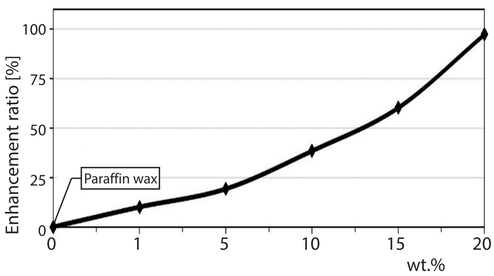


**Figure 11. Thermal conductivity enhancement ratio for different weight percentages of CQD**

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. The paraffin wax predominantly banks on the phonon-phonon-thermal transport mechanism since metals and conducting polymers are characterized by prominent electron transport [16].

In non-metallic PCM, 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 non-metallic PCM. Phonon-s, 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 PCM. 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 phonon-s can freely and randomly transmit without encountering any obstacles. Thermal conductivity of carbon-based composite PCM 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 PCM [14].

The findings of this study provide compelling evidence of a significant rise in thermal conductivity for the composites with doping of CQD in comparison to the reference material, paraffin wax. 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 PCM as an effective and efficient heat transfer material.

## Conclusions

- The variation of thermal conductivity with temperature is linear.
- Thermal conductivity of composite PCM increases from room temperature and reaches maximum value at 55 °C (phase change temperature)
- Thermal conductivity of composites decreases as the phase changes from solid to liquid.
- Thermal conductivity increases significantly with weight percentage of CQD.
- Maximum thermal conductivity of 0.452 ±0.015 is obtained for 20 wt.% composite PCM
- The enhancement ratio of thermal conductivity for 20 wt.% composite PCM is remarkable with 97.38%.
- The results signify that composite PCM prepared with CQD have a great potential in storing and releasing thermal energy.
- This study clearly demonstrates that PCM incorporated with CQD have a promising future in the field of thermal energy storage applications.

## Future scope

In addition the current investigation, there is a critical necessity and potential for further exploration of these composite PCM in thermal management studies. Conducting differential scanning calorimetry and thermogravimetric analysis tests are critical for the analysis of latent heat storage capacity and thermal stability of these composite PCM. Such comprehensive assessments would provide valuable insights into their suitability and applicability for thermal energy storage applications.

## Nomenclature

$k$ – thermal conductivity, $[\mathrm{Wm^{-1}{}^{\circ}C^{-1}}]$

*Greek symbol*

$\psi$ – enhancement ratio, [%]

*Subscripts*

c – composite PCM
p – paraffin wax

*Acronyms*

CQD – carbon quantum dots
LHTESS – latent heat thermal energy storage systems
MWCNT – multi-wall carbon nanotubes
PWCQD – parafin wax carbon quantum dots
xGnp – exfoliated graphene nanoplatelets

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