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Synthesis of Bio-Composite Phase Change Material Using Bioderived Graphitic Biochar for Enhanced Thermal Properties

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Abstract

Thermal energy storage (TES) systems with phase change materials have become a promising solution for sustainable energy storage. They promote sustainable energy by boosting the use of renewables, lowering emissions, and enhancing energy security. However, thermal energy storage using PCMs (phase change material) faces limitations due to low thermal conductivity and potential leakage. Here in this research, we aimed at the development of a bio-composite PCM from locally sourced bio-materials based on their readiness and availability for sustainable improvement of thermal properties. Paraffin wax was selected as the PCM candidate whereas graphitic biochar was synthesized from pyrolyzed water hyacinth and rose petals following low-temperature pyrolysis. The thermal conductivity of the novel composite was found 8.84 W/mK whereas in the purest form of paraffin wax, the thermal conductivity varies within 0.2-0.5 W/mK. These initial findings highlight a significant improvement in thermal conductivity which paves the way for further research to optimize bio-composite PCMs for efficient thermal energy storage applications.
Keywords: Bio-composite, Greenhouse gas emission reduction, Energy Security, Renewable energy storage

1. Introduction

Finding sustainable energy sources and solution to environmental pollution are the most daunting tasks the global scientific community is bestowed with. To satisfy the huge demand for energy and ensure that they don't add upon environmental crisis, utilization of renewable energy is a must. Solar thermal energy is quite ample, clean and sustainable but its intermittent nature hampers its use on a continuous basis. To overcome intermittency barriers, solar thermal energy must be stored so that its utilization comes in line with our preferences.

PCM in this case can be handy as a medium for storing solar thermal energy. Besides utilizing solar energy they can be used as industrial waste heat recovery system, in passive temperature control systems [1-3]

But traditional PCM performance is limited by lower thermal conductivity resulting in slow and uneven phase change process. This may result in the life reduction of the PCM container vessel and heat exchanger tubing plus their reduction of charging and discharging cycles they can go through while not deteriorating properties.

Besides this, PCM has another issue of form stability without which they can leak out of the container vessel or may also react with them.[4]

Recently scientists are greatly involved in development of specially engineered matrix material that can increase both form stability and thermal conductivity to improve stability and performance of the PCM. These filler matrices can be carbon-based biomaterials, metal-based materials or other synthetic materials. Addition of graphitic carbon-based biomaterials can be very handy in this manner as it would serve both waste management and make renewable energy more available. Furthermore, characterization of such graphitic biochar's prepared via pyrolysis confirm high carbon content and further processing of such materials like using ball milling can enhance many other filler properties like porosity, surface area, adsorption, carbon content and reduce particle size and impurity which will greatly improve both form stability and conductivity of PCM when incorporated as matrix material.[5] Fig. 1 depicts methods used by various literatures to increase the thermal conductivity of PCM.

EG (15%wt) and D-mannitol composite solves both issues of poor form stability and low thermal conductivity. It shows a thermal conductivity of 7.3 W/mK. which is 12 times higher than that of the original D-Mannitol conductivity of 0.6 W/mK. [6]

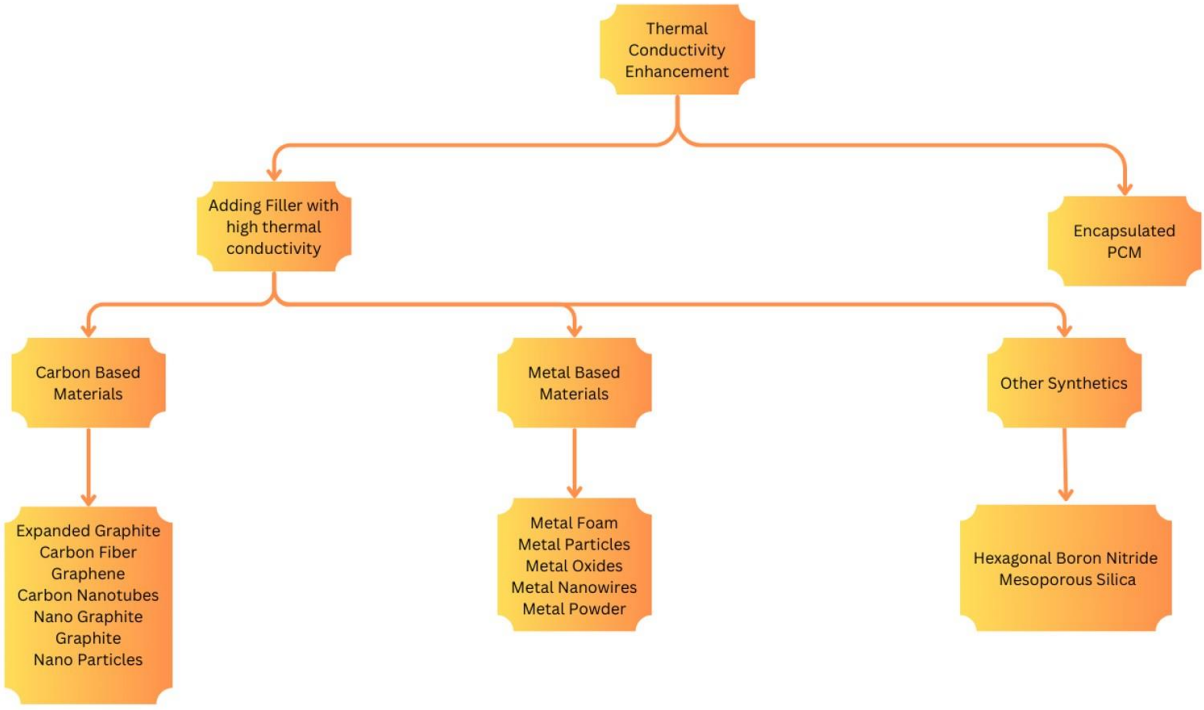


Fig. 1: Thermal conductivity enhancement approaches [7]

Eutectic mixture of Palmitic acid and Capric acid with 5% wt (most optimal weight percentage) of Expanded graphite as filler matrix shows varied values of thermal conductivity while melting and freezing it also showed 25.2% and 53.7% increase in the baseline thermal conductivity of 0.119 and 0.19 W/m.K during freezing and melting states respectively. [8]

While incorporating conducting carbon-based material carbon nanotubes can be also considered. Along with having high thermal conductivity carbon nano tubes also have bigger surface area to volume ratio and small density which helps to achieve form stability. [9]

In another experiment, Na_2CO_3 and MgO were used as compound PCM sample with increasing percentage of multiwalled carbon nano tube (MWCNTs). Thermal property analyzer showed that thermal conductivity increased with increasing mass percentile of carbon nano tube. In numbers it was illustrated as 0.5wt% of MWCNTs could increase thermal conductivity up to 69% compared with plane non-filler PCM samples. [10]

Another crucial and important finding was that, if a combination of various morphologies of carbon materials were used on a single or compound PCM then something remarkable could be achieved. For example, instead of paraffin diatomite mixture paraffin, diatomite and multiwall carbon nano tubes can drastically increase thermal conductivity by 42.45% [11]

In studies with carbon fiber, it has been also obtained that geometry of SCFs (short carbon fiber) can positively impact on thermal conductivity [12]

According to many experimental results incorporations of both carbon fiber and expanded graphite has synergistic effect and Small specific surface area is also more effective on thermal conductivity [13-14]

Graphene being highly conductive material can also be incorporated with PCM to enhance thermal conductivity. It was found that only 2% wt of graphene can increase thermal conductivity by 58.6% and exfoliated graphene can increase it to 41.4% with same weight percentage. [15]

There are also several studies on preparing a composite using biochar as they can also increase conductivity and form stability preventing PCM leakage. A study shows 43.76% increase in thermal conductivity of Palmitic acid PCM that used pinecone biochar in a 6:4 mass ratio (palmitic acid: pinecone biochar). [16] Although biochar PCM composites are studied but combining different biochar materials and then forming a composite with PCM is not a very experimented and documented topic. Biochar being very unique shows high thermal conductivity along with interesting microstructural and morphological characteristics. They can be easily produced by low temperature pyrolysis (300°-500°C). Physical properties and composition of produced biochar is dependent on contact with oxidants, pyrolysis duration, temperature, source of biomass etc. Low temperature pyrolysis can

confirm required physical and chemical properties with high carbon content and produce graphitic biochar that ensures very good thermal conductivity which will make it suitable for polymer reinforcement, energy storage, energy conversion, water purification (could become a good adsorbent material), making novel composites and flue gas treatment.[17-20]

This study discusses the preparation of a novel composite material incorporating water hyacinth and rose biochar with paraffin wax PCM. Biochar was prepared via low temperature pyrolysis (550°C) in a fixed bed reactor. This work also analyses thermal conductivity test results and justifies the mixture mass ratio combination to address the lower thermal conductivity of paraffin wax PCM.

2. Materials and methods

2.1 Materials.

For the PCM sample, organic paraffin wax PCM was selected having a phase transition temperature of 50–59° C and a latent heat of 210 kJ/kg [21]

As for the raw materials for production of graphitic carbon-based biochar, water hyacinth (*Eichhornia crassipes*) an aquatic weed plant, was harvested from the nearest river bank area of the Padma River. Rose (*Rosa rubiginosa*) petals were collected from RUET campus, Rajshahi, Bangladesh.

2.2 Synthesis of water hyacinth and rose petal biochar.

Initially, the freshly collected water hyacinth samples were cleansed appropriately with water and cut into small pieces. These samples were then left for air drying for 24 hours. Once air dried, samples were washed several times with ethanol and de-ionized water for the removal of dust and debris.

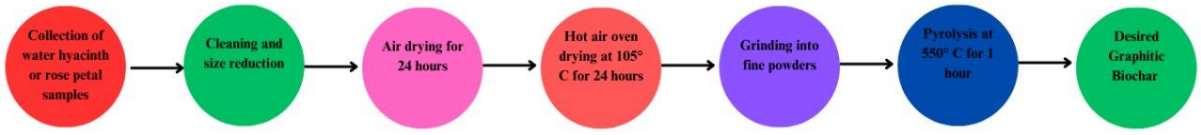


Fig. 2: Flow diagram of graphitic biochar production

After that, these dried water hyacinth fine powders had to undergo hot air oven drying at 105° C for 24 hours for the proper removal of moisture. After the completion of drying, multiple attempts of size reduction by means of hand grinder as well as electrical fine grinder machine were conducted for obtaining fine powders. For the final step of obtaining graphitic carbon-based biochar, low temperature pyrolysis of the sample at 550° C for 1 hour was carried out in presence of a constant supply of nitrogen gas for securing an inert condition within the reactor core of a fixed bed pyrolysis reactor. Eventually, freshly prepared graphitic carbon-based biochar from water hyacinth was obtained. Complete biochar development method is summarized in fig. 2

2.3 PCM biochar impregnation.

For integrating the bio-derived graphitic biochar within the paraffin wax PCM sample, direct impregnation method was adopted. Prior to that, both the graphitic biochar (freshly prepared rose biochar and water hyacinth biochar) was sieved to a specific size. Then in a sterilized beaker, 9 gm PCM paraffin wax was taken along with 1 gm each from rose derived biochar and water hyacinth biochar. This combination of materials was based on a quantitative ratio of (81.81: 9.09: 9.09) percentages of paraffin wax, rose biochar and water hyacinth biochar subsequently. Once proper amount of these materials was poured within the beaker, the beaker was heated in hot air oven for 1 hour at 100° C. During the heating process, upon reaching the melting point temperature the PCM melts, allowing the graphitic carbon-based biochar particles to penetrate within the PCM. The beaker was taken out of the oven at several interval where the sample had to undergo simultaneous stirring and heating by means of a hot plate magnetic stirrer apparatus. High speed (300-400 rpm, 5 hours, 60°C) mixing of the sample by the rotational movement of the hot plate stirrer's magnetic capsule promotes uniform distribution of the graphitic biochar within the paraffin wax PCM. Finally, a novel composite graphitic biochar enriched PCM sample was prepared. The total process of graphitic biochar production of this study is summarized with the help of fig. 3

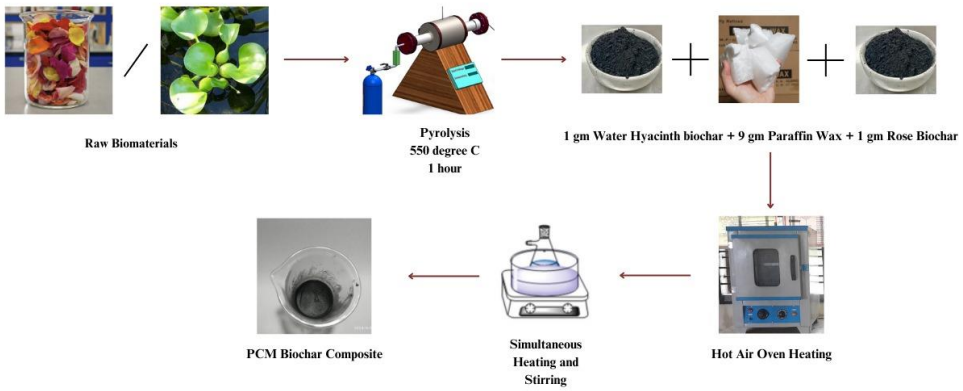
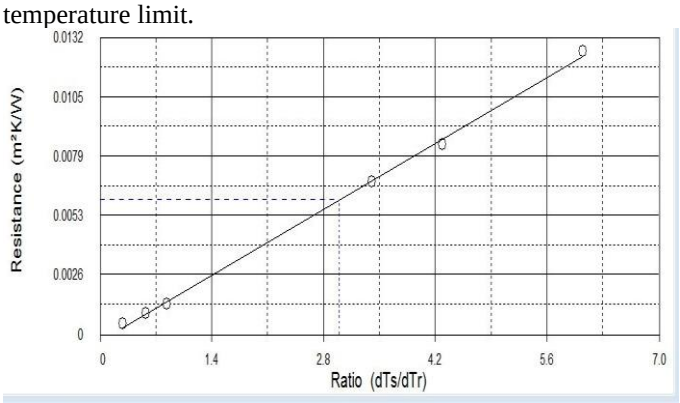


Fig. 3: PCM biochar impregnation

2.4 Thermal conductivity test. Based on the novel PCM biochar composite that was developed, thermal conductivity test of the sample was conducted. For the proper and valid result from the QuickLine-10 Conductivity Tester, the sample was prepared in dimension accordingly to a dimensional thickness 5.2540 cm (2.07 inch). The test was initiated with calibrated segment setpoint temperature of 5.22 °C whereas the stack temperature of the composite was maintained 23.64 °C. The calibration factor was kept at 2.0930e-003 with 3.3177e-004 m²K/W interfacial resistance. A reference DVM reading of 1.2510 at 26.31 °C was obtained where functioning sensors from the upper, lower and heat sink regions provided readings 1.6420 at 26.31 °C, 1.6390 at 26.52 °C, and 1.6380 at 26.59 °C subsequently. The temperature gradient was measured as in for delta T/reference of 3.00 °C, corresponding with delta T sample at -0.21 °C, delta T reference at -0.07 °C, and delta T stack at -0.28 °C. The mean temperature of the sample was found to be 26.42 °C. Eventually, the resulted thermal resistance of the composite PCM sample was obtained 5.95e-003 m²K/W with a value of 8.84 W/mK for the thermal conductivity.

3. Result and analysis

The following graph of fig. 4 illustrates the existing relationship between the thermal resistance of the composite PCM with changes in relative temperature (dTs/dTr) drop across the sample. Here x-axis represents the relative temperature drop (dTs/dTr) whereas the y-axis represents the thermal resistance (Rs). The analysis initiates with the existence of a linear relationship between the temperature differences ratio (dTs/dTr) and thermal resistance (Rs). This linearity proposes the thermal conductivity of the PCM composite to exist constantly throughout the temperature limit.



Here,
dTs/dTr = (Tu - T1) / (Tl - T1)
and
Ts = Tu - T1 and Tr = Tl - T1
Tu: Temperature of the upper plate.
Tl: Temperature of the lower plate.
T1: Temperature at the interface between the PCM sample and the lower plate

Fig. 4: Thermal resistance vs changes in relative temperature graph

The total interface resistance (Rint) was obtained to be 0.0063 m²K/W between the PCM sample and the surface plates. For obtaining the thermal conductivity, the slope was calculated as it is the reciprocal of thermal conductivity. This slope is known as the thermal resistance (Rs). This is carried out by choosing two random points on the curve and calculating the rise over run. The dTs/dTr was found to be 3.00, obtained from the values dTs = -0.21 °C and dTr = -0.07 °C. The value of the thermal resistance was obtained as Rs = 5.95e-003 m²K/W. Afterward, by graph plotting of the point (3.00, 5.95e-003) and sketching a line across this very point and the y-intercept, the linearity of the relationship was reinforced allowing the calculation of thermal conductivity using the slope since $\lambda = 1 / \text{slope}$. It is compulsory to use consistent units throughout the analysis procedures to establish proper accuracy of the experimental setup since the experimental findings and results are accurate only when fall

within the immediate vicinity of the tested temperature range. Eventually, the thermal resistance of the novel bio composite PCM sample was obtained as 5.95e-003 m²K/W, which results in a thermal conductivity of 8.84 W/mK.

4. Conclusion

In this work, preparation of a novel bio composite PCM has been discussed where water hyacinth and rose petal biochar were used as filler matrix. Simple direct impregnation method of forming the composite was found satisfactory as thermal conductivity of the paraffin wax increased from 0.5 W/m.K to 8.8 W/m.K. This experimental study doesn't include many other characterization tests which is a major drawback because chemical properties before and after composite preparation was not analyzed via FTIR hence there remains uncertainty regarding chemical interaction between filler matrix and PCM. Furthermore, pore size distribution of the composite and its crystalline structure could not be obtained as XRD was not performed. So, its form stability during phase transition is also not confirmed. Crystallization temperature, its thermal degradation behavior could not be studied due to lack of DSC test. Apart from this, this research proves incorporating graphitic biochar into paraffin wax PCM can effectively enhance thermal conductivity which is a major thermal property of this PCM, achieving a notable value of 8.84 W/mK. This improvement highlights the principal drawbacks of traditional PCMs such as their less thermal conductivity and leakage tendency. These findings emphasize the prospect of bio-composite PCMs as they contribute to the optimization of energy storage efficiency as well as ensure sustainable energy solutions by promoting renewable resources with less to no greenhouse gas emissions.

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