

Synthesis and Characterisation of Lauric Acid Phase Change Material with Graphite/Carbon Nanotubes for Thermal Energy Storage Application

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The advancement of renewable solar energy has led to the emergence of phase change materials (PCMs) as thermal energy storage. Besides acting as a heat storage material, PCM is able to absorb excess heat that enables the reduction of operating temperature of a solar system. Organic PCM (i.e. fatty acid) as a latent heat storage is capable of storing fourteen times more heat per volume unit than other sensible heat storage. This property became among the pulling factors for the researchers in incorporating PCM in their solar system. Nevertheless, commercial organic PCMs encounter several drawbacks for instance low energy conversion ability and the low thermal conductivity. Doping of reinforcement material such as graphene-based material/carbon nanotube is capable of improving the performance of fatty acid as PCM composite. In this work, lauric acid (LA) based PCM using graphite powder (G) and multi-walled carbon nanotubes (MWNT) as filler with mass concentrations of 7 wt% are prepared. Surface morphology and X-ray powder diffraction analysis show no new functional groups were produced after the composite synthesis. Energy storage efficiency, including melting/solidification temperatures and enthalpies, are measured using a differential scanning calorimeter (DSC). It is exhibited that the presence of the supporting material has considerable influence on the phase change temperature and enthalpies, at 38.22 °C and 169.34 J/g for LA-MWNT and 39.03 °C and 120.49 J/g for LA-G. The scanning electron microscope demonstrates that the LA-based PCM could be filled with the pores of graphite and MWNT. LA-MWNT based PCM composite exhibited excellent heat energy storage efficiency (at 89.0%) if compared with LA-G. This indicated that the LA-MWNT has huge potential to be a frontier material for thermal energy storage.

1. Introduction

The economic well-being and technological competitiveness of the country are significantly influenced by energy. A significant need for energy has resulted from rapid development. The expansion of resources and the expansion of the energy supply have not been able to keep up with the rising demands put forth by the expanding population, growing urbanization, and developing economy. It is crucial to develop effective and affordable energy storage systems in order to save energy, lessen reliance on fossil fuels, and minimize greenhouse gas emissions. Energy storage systems alleviate imbalances in supply and demand while also enhancing the performance and dependability of the energy system. When combined with renewable energy sources like solar energy, wind energy, waste heat recovery, biogas, etc., energy storage can significantly lower overall energy usage and conserve local conventional energy sources.

Thermal energy storage (TES) using phase change material (PCM) emerges as a new game changer for solar thermal technology. Sensible storage systems (SHS), which use single-phase heating and cooling to store energy, latent heat storage (LHS), which uses two-phase melting and solidification, and thermochemical heat storage, which uses reversible chemical reactions between reactive components, are examples of TES. Low temperature solar thermal applications frequently use SHS systems and require a big storage volume. While

LHS exhibited great storage density and isothermal phase shift of the latent heat which make it unique and preferable.

The application of PCM is able to bridge the gap between supply and demand and during off-peak and peak hours. High LHS exhibited in PCM possess unique criteria due to its capability to store high energy storage in small volume and charging and discharging heat at constant temperature. PCMs can be categorized into three, which are inorganic, organic and eutectic mixtures. Among them, organic PCM (i.e. fatty acid) features a superior performance such as high phase change enthalpy (Harish et al., 2015), non-toxicity (Liu et al., 2021) with broad range of melting temperature at minimal cost.

Lizcano-González et al. (2022) have synthesized fatty ester-based PCM from palm oil by-product. Other common organic PCM is lauric acid (LA) that can be extracted from vegetables oil to use as PCM (Feng et al., 2018). However, fatty acid based PCM has certain undesirable properties such as low energy conversion ability and low thermal conductivity (Li and Mu, 2019). This limitation leads to an extensive exploration on the impregnation/addition of nanocarbon-based material to enhance the performance of fatty acid as PCM composite in term of heat storage capacity and latent heat. Numerous researchers have used LA to create binary shape-stabilized composite PCM with excellent thermal properties for air conditioning, cold storage, and solar water heater. Liu et al. (2021) experimentally demonstrated that using LA-hybridized bentonite composite PCM which has better efficiency when compared with LA as PCM.

Zheng (2017) prepared three different types of fatty acids (capric acid, LA and stearic acid) with the addition of expanded perlite. A eutectic composite of LA-stearic acid exhibited high latent heat enthalpy compared to other eutectic composites. The Scanning Electron Microscopy (SEM) pattern shows that the pores of expanded perlite filled with PCM featured the capability for thermal energy storage. Chinnasamy and Appukuttan (2019) has studied the thermal properties of LA/myristyl alcohol as a novel binary eutectic PCM for indoor thermal comfort. One endothermic peak was observed during melting and two endothermic peaks are observed during freezing with corresponding latent heats at 151.5 and 151.6 J/g. The decomposition of the eutectic mixture occurs at 165 °C. Therefore, the prepared eutectic PCM is thermally stable over a wide range of operating temperatures. Yang et al. (2019) have successfully prepared a porous carbonized woods (PCWs) with LA as composite phase change materials (CPCMs). For LA/PCWs, their peak positions were almost the same as LA, indicating that LA was well encapsulated in PCWs and no chemical change occurred. SEM images of the LA/PCWs has indicated that the physical adsorption of LA on the walls was not strong, and the compatibility with LA was weak. Liang et al. (2018) synthesised LA and graphene oxide (GO) composite PCM via vacuum assisted impregnation method. The as synthesised LA/GO featured identical size distribution in the PCM composite which evident an intact shape stability, enhance thermal and electrical conductivities. Harish et al. (2015) prepared a graphene nano-based PCM using LA and exfoliated multilayer graphene nanoplatelets (MLG) using simple ultrasonic sonication. There were no noticeable changes of the enthalpy for LA PCM and LA-MLG due to incomplete chemical reaction between the PCM and the MLG. Their study indicated that that the maximum thermal conductivity was in sync with the increment of graphene nanoplatelets. Yang et al. (2020) prepared LA/expanded graphite (EG) composite based PCM for photo-to-thermal conversion. The SEM result shows that LA was homogeneously distributed in EG which gave merit to the phase transition. It was found that the increment of EG mass fraction did not provides significant impact to the enhancement of latent heat enthalpy. Feng et al. (2018) infiltrated LA into the multiwall carbon nanotubes (MWNT) via vacuum-based infiltration-purification subjected to different LA volumes. They observed that melting point and latent heat of LA confined in MWNTs are lower than the pure LA which at 54.8 % of LA filling ratio, the as synthesized PCM composite has the highest thermal storage efficiency at 56.9 %. Qian et al. (2015) evaluated heat storage efficiency of polyethylene glycols (PEGs)-Ag nanoparticles (AgNPs) diatomite PCM subjected to different PEG mass ratio. It was indicated that the PEG-AgNPs PCM featured high efficiency compared to pure PEG with 1 % difference. Mitran et al. (2015) prepared LA impregnated with mesoporous silica as shape stabilized PCM via impregnation method. It was observed that the heat storage efficiency was proportional to the LA weight fraction. Whereas, at high LA weight fraction, the efficiency is increased. The SEM pattern showed the as synthesized LA with mesoporous silica exhibited partial pore filling and reduced nanoconfined phase enthalpy with hexagonal ordered pore.

Based on the existing studies, only scarce works highlighted on the quantification of heat energy storage efficiency especially for PCM composites. Whereas existing work only highlighted the storage efficiency via qualitative analysis, such as SEM and leakage study. Besides that, two different formulations that can be used to calculate storage efficiency has contributed to the discrepancy on the finding thus jeopardizes the research outcomes. Due to that, Zahir et al. (2022) conducted a study to investigate the acceptable equations to be adopted. They found that the equation proposed by Mitran et al. (2015) is more sensible and acceptable to evaluate the storage efficiency compared to other related studies.

Present work evaluates heat energy storage efficiency of proposed PCM composite on top of the regular thermal energy storage analysis to address the gap in the existing research portfolio. This is because the efficacy of

solar heat is crucial in determining the capability of PCM to store heat and to measure the PCM activity (via heat storage efficiency). Whereas existing research only focused on the thermal (Qian et al., 2018) and stability performance (Imran Hussain et al., 2019). This finally can be served as an additional performance benchmark for effective solar thermal energy storage applications.

2. Materials and method

2.1 Sample preparation

In this work, LA with melting temperature of 44 °C is used as a PCM, at enthalpy rate of 180 J/g. Two different types of carbon-based materials were purchased from Sigma Aldrich Inc as an additive as shown in Table 1. These two carbon-based materials are selected due to their capability to enhance the thermal conductivity of pure PCM (Fan et al., 2013). Initially, LA is heated at constant temperature at 70 °C on the hot plate using a magnetic stirrer at 200 rpm for 10 min. The LA-PCM composite is prepared by adding 7 % weight concentration of graphite (G) into molten LA under rigorous stirring for another 30 min. The sample (LA-G) undergoes ultrasonic vibration for 1 h to facilitate a homogeneous dispersion. The sample is then dried in the oven at 120 °C for 2 h. Finally, the nano-enhanced LA composite sample is cooled to the ambient temperature. A similar procedure is applied for MWNT to obtain LA-MWNT based PCM composite as illustrated in Figure 1.

Table 1: Types of carbon-based materials with the properties

Material	Size
Graphite powder (G)	< 20 μm
Multi-walled carbon nanotubes (MWNT)	< 5 μm

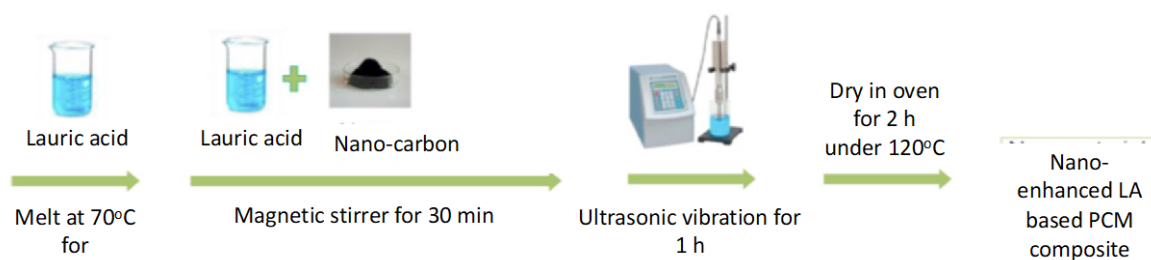


Figure 1: Schematic diagram of the synthesis of nano-enhance LA based PCM composite

2.2 Characterization analysis

SEM was used to determine the surface morphologies of LA-G and LA-MWNT to understand the effect of adding carbon-based material. An X-ray Diffractometer (XRD) is performed using $\text{CuK}\alpha$ at 40 mA and 45 kV with scanning angle is 10 to 80°. Thermal energy storage properties of LA-G and LA-MWNT based PCM composites were conducted using DSC Mettler Toledo. The flow rate of N_2 was set at 30 mL/min, and DSC curves were recorded from 30 to 100 °C with the scanning rate of 10 °C/min. Approximately 12 mg of each sample was prepared in an aluminum pan for the DSC study.

3. Results and discussion

3.1 Surface morphology of LA-G and LA-MWNT

Figures 2(a) and (b) show the surface morphology of LA-G and LA-MWNT. It can be observed that the LA-G has a stacking of sheet structure and deposits on the surface as shown in Figure 2(a). The stacking of sheet structure manifested graphite structure (Imran Hussain et al., 2019) with the presence of irregular pores whereas the deposition was due to blending with LA. This morphology can inhibit the leakage of LA composite and subsequently provide as a good candidate for thermal storage application. The commercial MWNT has a diameter within 20 to 30 nm (Janudin et al., 2017). Based on surface morphology analysis of LA-MWNT, there was increment in diameter of MWNT from 7 up to 40 nm as depicted in Figure 2(b). This was due to the attachment of acidic functional group of LA to MWNT, as illustrated by the smooth surfaces with cylindrical shape. The SEM result shows that the mixed composite of LA-MWNT had led to unclear interfaces between

MWNT and LA composite. This morphology features the capability of MWNT to retain the overall shape of PCM composite with well-dispersed in the LA. A similar shape was obtained in the study conducted by Fan et al. (2013). Figure 3 illustrates the XRD patterns of LA-G and LA-MWNT. It is a technique to study the exact structure of samples based on the characteristic manner of X-rays diffracted by the crystals. The XRD pattern of LA-G (Figure 3(a)) shows the presence of graphite diffraction peak at 2θ value of 26.22° while LA exhibited three strong diffraction peaks at $2\theta = 16.37^\circ$, 21.57° and 24.17° and the corresponding lattice distances are 5.4140, 4.1216 and 3.6826 (Feng et al., 2018). Visually, the diffraction peaks of LA and G simultaneously exist in the diffraction patterns of the LA-G, and only part of the intensity is weakened with no new diffraction peak appearing. The XRD pattern of LA for LA-MWNT (Figure 3(b)) shows three strong diffraction peaks at $2\theta = 16.17^\circ$, 21.54° and 23.95° and the corresponding lattice distances are 5.4799, 4.1261 and 3.7150. Two peaks corresponding to the hexagonal graphite structure of MWNT appeared at 26.67° and 43.78° . It was showed that no changes on the peak position of pure LA and MWNT which reveals that the limited space in MWNT does not affect the crystal structure of LA. Both XRD analyses demonstrate that the inclusion of G and MWNT does not affect the crystal structure of LA.

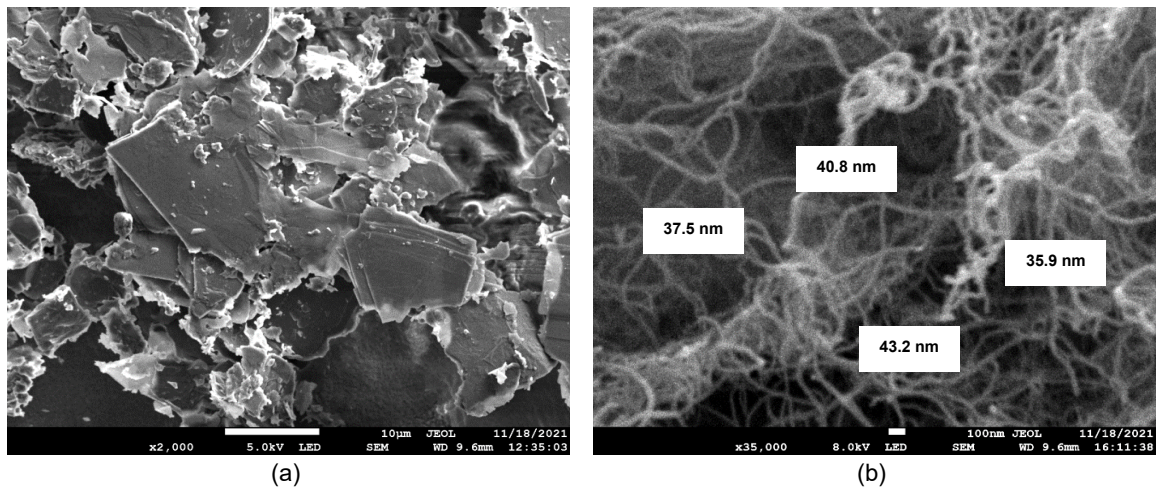


Figure 2: SEM images for (a) LA-G and (b) LA-MWNT

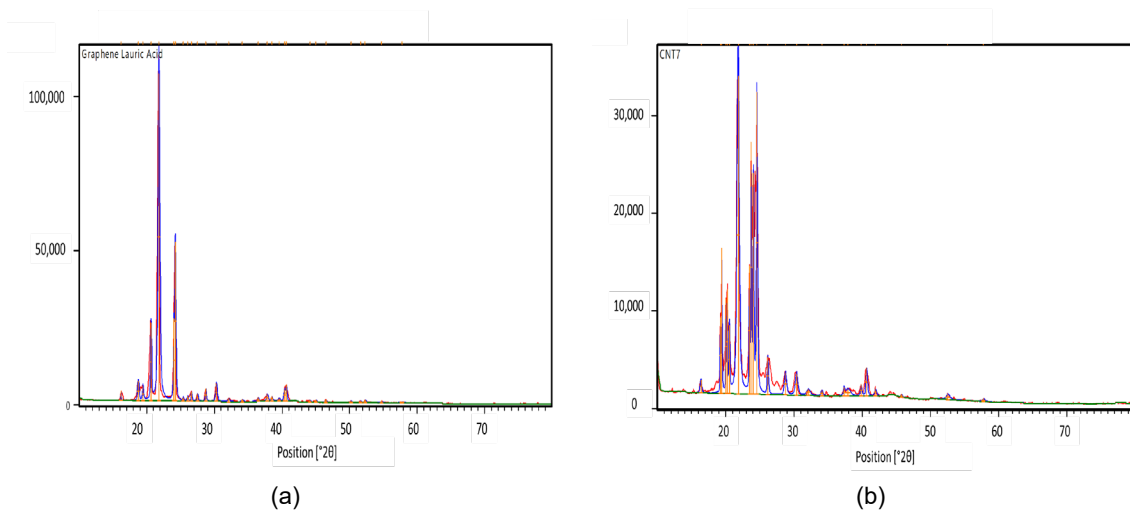


Figure 3: XRD analysis of (a) LA-G and (b) LA-MWNT

3.2 Characterization of thermal performance

One of the significant criteria for PCM in the application of solar thermal energy storage is its phase transition temperature and latent heat which can be obtained from DSC analysis, as illustrated in Figure 4 and quantified in Table 2. The inclusion of G and MWNT has caused decrement of phase change enthalpy for melting and

solidification (LA enthalpy = 180 J/g) as tabulated in Table 2. These results are corroborated with (Fan et al., 2013) work when they considered inclusion of carbon based material into the PCM. The changes of both latent heats (phase change enthalpy) evident the existence of chemical reaction between LA and G/MWNT via absorption of LA onto the surface pore of G/MWNT. The addition of G and WMNT have raised the solidification temperature (44 °C for pure LA) for both PCM composites. Similar finding was observed in Fan (2018). This phenomenon indicates that infusion of carbon-based material (G and MWNT) into PCM would be beneficial to the phase transition and suitable for regions with higher temperature during summer (Zheng et al., 2017). The solidification temperature of LA-MWNT is higher as compared to the solidification temperature of LA-G. This scenario may be due to the availability of lower melting temperature phase in LA-MWNT, as shown in Figure 4. LA-MWNT based PCM possess good thermal performance compared to LA-G in term of the latent heat of melting and solidification at 149.06 J/g and 169.34 J/g.

To compare the performance and activity of both PCM composites in storing the thermal energy, heat storage efficiency (γ) is evaluated using Eq(1) (Mitran et al., 2015):

$$\gamma = \left(\frac{H_{m,PCM}}{X_{PCM} \times H_{m,LA}} \right) \times 100\% \quad (1)$$

Where X_{PCM} represent the LA weight fraction in PCM, $H_{m,PCM}$ and $H_{m,LA}$ are the total heat of fusion of PCM and LA. As tabulated in Table 2, the heat energy storage efficiency for LA-G is 72.6 % while thermal energy storage efficiency for LA-MWNT is 89.0 %. Based on the aforementioned analysis, LA-MWNT composite exhibits enhance latent heat and heat storage efficiency if compared to LA-G.

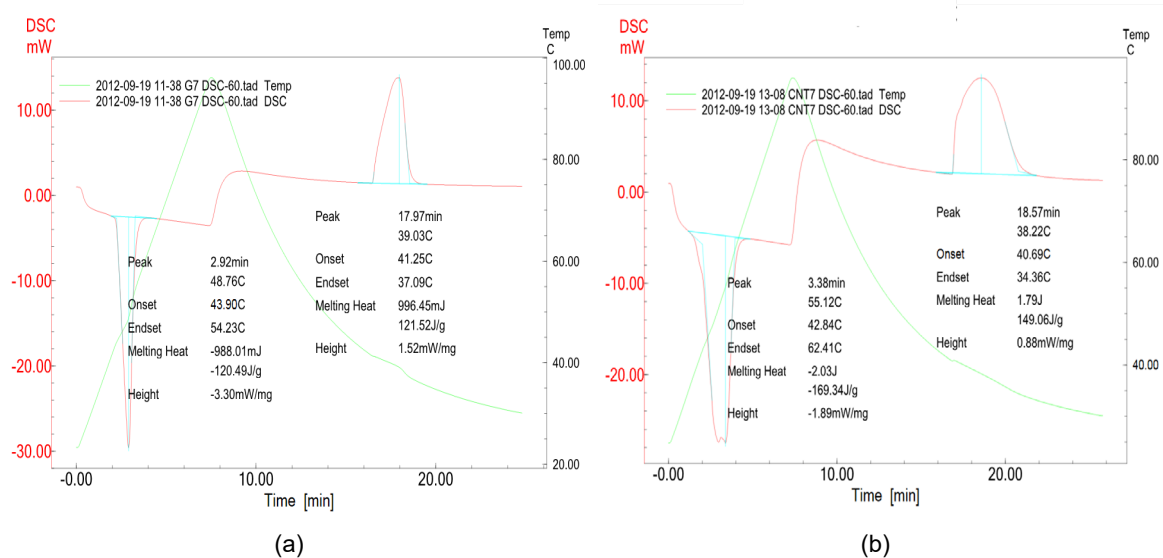


Figure 4: DSC curves of the (a) LA-G and (b) LA-MWNT. The upper and lower bundles of curves represent the heating the cooling processes

Table 2: DSC and heat storage efficiency of LA-G and LA-MWNT

PCM composite	Melting		Solidifying		γ (%)
	Temperature (°C)	Latent heat (J/g)	Temperature (°C)	Latent heat (J/g)	
LA-G	39.03	121.52	48.76	120.49	72.6
LA-MWNT	38.22	149.06	55.12	169.34	89.0

4. Conclusions

In this paper, the LA is selected as a base-PCM with the addition of carbon-based material as a supporting material which are G and MWNT. A 7 % of mass concentration of G and MWNT were added into the LA under the sonification process. The LA-G and LA-MWNT based PCM composites are analysed and tested via SEM, EDX and DSC methods. The SEM illustrates that the LA could be filled with the pores of G and MWNT. LA-MWNT based PCM exhibits outstanding thermal performance compared to LA-G in term of the latent heat of

melting and solidification at 149.06 J/g and 169.34 J/g. Heat storage efficiency result is consistent with the thermal performance at 72.5% for LA-G and 89.0% for LA-MWNT. The changes of phase transition temperature as well as latent heat shows there were chemical reaction occurred during the synthesis process. While no impurities exhibited in the XRD analysis with strong peaks exhibited for LA and G/MWNT in both PCM composites. A preliminary result of this present work is able to provide insight on the potential LA-G composite as thermal energy storage from the perspective of heat storage efficiency. Further research can focus on the thermal storage efficiency and thermal conductivity measurement to address the shorthand assessment of this work.

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