Hybridization of 2D Nanomaterials with Lauric Acid for Solar Thermal Energy Storage

Farrah Ezzah Ab Latif[1], Khairunnisa Mohd. Pa'ad[1,2], Tomoya Tsuji[1], and Norhuda Abdul Manaf[1,*]

[1]Department of Chemical and Environmental Engineering, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Kuala Lumpur, Malaysia

[2]Department of Applied Science, Muroran Institute of Technology, Muroran, Japan

Email: farah.ezzah@gmail.com (F.E.A.L.), khairunnisa.kl@utm.my (K.M.P.); t.tsuji@utm.my (T.T.); norhuda.kl@utm.my (N.A.M.)

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***Abstract*—Thermal Energy Storage (TES) using Phase Change Material (PCM) features an innovative technology for a clean and renewable energy transition. PCM is a sophisticated medium that can store huge volumes of latent heat for TES. This study demonstrates a facile synthesis of Lauric Acid (LA) based PCM hybridized with 2D nanomaterials which are Graphene Nanoplatelets (GNP) and MXene. The results showed that inclusion of GNP increases the thermal conductivity of PCM nanocomposites by 13% at a mass fraction of 1 and 3%. Differential scanning calorimeter results showed that the latent heat enthalpy reduced with the increment of GNP and MXene mass fraction, due to the reduction of LA per unit mass area. There are insignificant changes of melting temperature for LA/GNP compared to LA/MXene which is evident that addition of GNP is capable to maintain and stable the PCM temperature. Based on this study, PCM with mass fraction of 3% GNP (LA/GNP$_2$) exhibited the best candidate for TES application due to its trade-off between thermal conductivity and energy storage efficiency, if compared with LA hybridized with MXene (LA/Mxene).**

***Keywords*—phase change material, Mxene, graphene nanoplatelets, thermal energy storage**

I. Introduction

Renewable energy sources and energy efficiency are highly valued in today's energy politics. Both represent important efforts to slow down climate change and a chance for countries with few or no fossil energy resources to become less reliant on fossil fuels. Nevertheless, the intermittent availability of certain renewable energy sources hinders their widespread implementation. For example, wind power plants can only generate electricity when there is sufficient wind, while solar collectors or photovoltaic panels can only produce electricity when the sun is shining. Therefore, the development of feasible and efficient energy storage system is essential for energy conservation, mitigation of greenhouse gases and over-dependency on fossil fuels. In this case, Thermal Energy Storage (TES) emerged as a new game changer for solar energy by using Phase Change Materials (PCM) concept. PCMs are frequently used for thermal management and TES systems due to their excellent ability to maintain a nearly constant temperature as well as their high energy storage density. It has grown in popularity over the past few decades for several applications, including air conditioning, cooling, thermal protection, solar heating, and indoor thermal comfort.

Lauric Acid (LA) is a type of organic PCM that offers the benefits of high latent heat, good chemical, and thermal stability, and nearly no supercooling and nontoxic. Nevertheless, like other organic material, LA features poor thermal conductivity and limited light absorption capacity, which hinders its efficiency and performance as a TES. This limitation has led to a growing interest in 2D nanomaterial encapsulation into LA/fatty acid to improve its thermal conductivity as well as TES performance. This underpinned with the study conducted by [1] where, the addition/hybridization of supporting material can improve the thermal conductivity of the product and at the same time maintain the condition of the PCM during phase change.

Graphene-based materials are known as the most researchable 2D nanomaterial due to its exceptional characteristics such as high thermal conductivity large surface area, excellent mobility of charge carriers and large light absorption capacity [2, 3]. These characteristics demonstrate its capability for TES application [4, 5] if compared with other classical 2D nanomaterials. Benbrika *et al.* [6] studied the effect of Graphene Nanoparticles (GNP) on 1-tetradecanol. The study observed the effect of GNP at the mass fraction of 0.5, 1 and 3 wt%. The result showed that the heat transmission and solidification processes were improved by the addition of GNP. Where, the inclusion of GNP in the PCM has a notable effect on the energy storage capacity, as the stored energy decreases with the addition of GNP. It was found that incorporating a 3% injection of GNP resulted in a decrease of up to 14% in stored energy. Hence, it is of utmost importance to meticulously evaluate the amount of GNP added to the PCM to effectively enhance its overall performance.

MXene is a new class of two-dimensional materials with the general formula of Mn+1XnTX, where M stands for transition metal that is titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, scandium, and many more, X stands for a non-metal such as carbon or nitrogen, and TX stands for the surface termination groups for example −OH, =O, and F, giving them superior electrical conductivity and large specific surface area [7]. Fan *et al.* [8] conducted a study where they synthesized a composite PCM consisting of Polyethylene Glycol (PEG) doped with MXene for efficient thermal management. The PEG/MXene composite exhibited excellent shape stabilization without any leakage, even as the temperature and MXene composition increased. Similar results were observed in [9]. Furthermore, various MXene-based PCMs have been successfully synthesized, including the polyurethane/MXene composite [10] and phosphorus-modified stearyl alcohol/MXene [11]. These PCM composites have shown notable enhancements in terms of photothermal conversion efficiency, phase change enthalpy, and mechanical properties. Based on the existing works, there were no comparative

analyses have been done on the GNP and MXene in combination with LA. Thus, the present paper evaluates the potential of those 2D nanomaterials for TES applications by considering thermal enhancement and heat storage efficiency.

II. Experimental Procedure

A. Materials and Method

The PCM used in this work is LA (Brand: Chemiz, purity 99%). While, GNP (Brand: US Nano, purity 95%, < 8 nm) and MXene multilayer nanoflake (Brand: Nanoshell LLC, purity 99.9%, < 100 nm) were used as the 2D nano-additive.

B. Synthesis of LA/GNP and LA/MXene Based PCMs

In this present work, the method described by Krishna *et al.* [12] and Zhang *et al.* [1] was modified. The preparation of the LA/GNP composite involved placing a certain weight of LA in a beaker, which was then placed in a water bath at 60 °C for 30 minutes to melt the PCM. Subsequently, different mass ratios of GNP were added into the molten LA subjected to the intensive sonication for 90 min, 50 °C at 50% amplification. The LA/GNP composite was dried in oven and cooled down to the ambient temperature. A similar approach was applied for the synthesis of LA/MXene composite as illustrated in Fig. 1. To evaluate the performance of the proposed PCMs and to provide a convincing comparative analysis, various mass fractions of 2D nanomaterial additives were prepared as shown in Table 1. These mass fractions were determined by referring to previous studies, such as [13] for GNP and [14] for MXene.

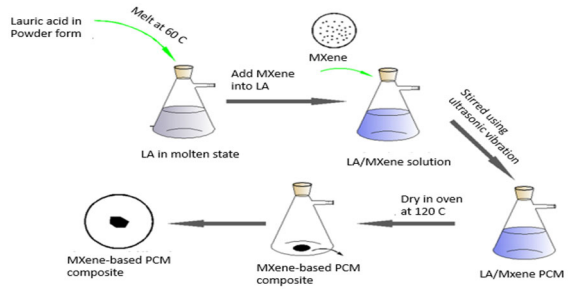

Fig. 1. Experimental set up for facile synthesis of LA/2D nanomaterial composite PCMs.

Table 1. The formulation of LA/2D nanomaterials

Sample	Mass fraction of 2D nanomaterials
LA	
LA/GNP_1	1.00%
LA/GNP_2	3.00%
LA/GNP_3	5.00%
$LA/MXene_1$	0.50%
$LA/MXene_2$	0.75%
$LA/MXene_3$	1.00%

A. Characterization Analysis

The microstructure and intra-structures of as synthesized LA/GNP and LA/MXene are elicited by using FESEM (Joel JSM 7800f). For thermal energy storage performance, PCM's heat of fusion and melting temperature was evaluated using differential scanning calorimeter, DSC (Star System, Mettler Toledo) and conducted from 30 °C to 1000 °C at the rate 10 °C/min under the nitrogen environment. Thermal conductivity of both nanocomposite PCMs were conducted using Transient Hot Bridge (THB-100, Linseies).

III. Result and Discusison

A. Morphology and Microstructure

Fig. 2 shows the FESEM micrograph of GNP and LA/GNP composites. It can be observed that GNP has a layered and flat structure. The same observation was found in [15, 16]. While the morphology of LA/GNP presents a spherical structure on the surface of GNP as depicted in Fig. 2(b). It shows that the flat and layered structure is exhibited on the LA/GNP morphology structure, which demonstrated that the GNP is successfully integrated into the LA.

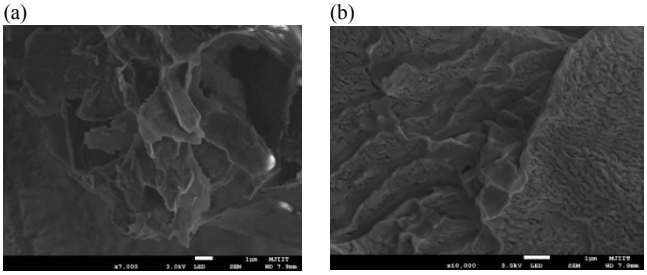

Fig. 2. FESEM images of (a) GNP, (b) LA/GNP.

Fig. 3(a) reveals a distinct microstructure characterized by a densely packed layer or accordion-like structure, indicating the presence of MXene within the sample [17]. However, the configuration of this structure is not easily noticeable on the LA/MXene morphology due to the interaction between both materials. Where, the observed porosity suggests incomplete filling or weak interfacial bonding between LA and MXene. This scenario might contribute to the complex structure of MXene which caused the interface was not completely penetrated by the molten LA during the synthesis process [18].

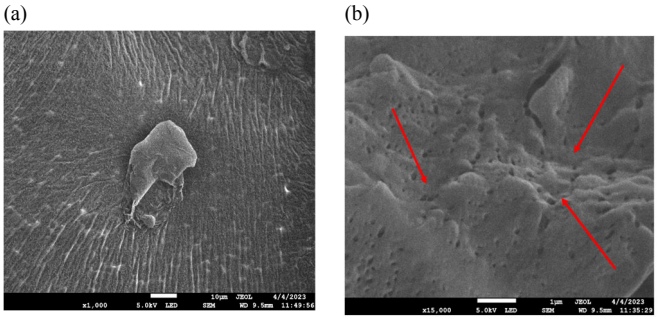

Fig. 3. FESEM images of (a) multilayer flake of MXene (b) LA/MXene.

A. Energy Storage Performance Analysis

The information extracted from the DSC analysis is tabulated in Table 2. It can be seen there is contradictory trend between the LA/GNP and LA/MXene in term of the phase change enthalpy and temperature which evident the hybridization of 2D nanomaterials may provide different impact to the PCM/LA. For all PCM composites, the addition of 1% of GNP (LA/GNP_1) and 0.5% of MXene ($LA/Mxene_1$) has led to the increment of latent heat enthalpy (melting and solidification) at averages of 4%. On the contrary, as GNP continues to increase from 3% to 5%, latent heat of melting and solidification of PCM nanocomposite decreased. This is possibly due to the reduction of LA per unit mass in the PCM composite [15]. Furthermore, as the PCM composites undergoes the transition from a liquid to a solid state during the solidification process, GNP remains in its solid state and absorbs heat from the PCM. Consequently, the

incorporation/addition of GNP leads to a decrease in the latent heat of solidification [19]. Taking this into account, it explained the decreasing trend of latent heat in the LA/GNP. Essentially, there are no significant changes on the phase change temperature of LA and LA/$GNP_{1/2/3}$ as illustrated in Fig. 4 (trend-line). This highlights that GNP as a thermally conductive additive and able to improve and maintain a stable phase change temperature.

Table 2. The phase change properties of LA/2D nanomaterials

Samples	Melting		Solidification	
	T_m (℃)	ΔH_m (J/g)	T_f (℃)	ΔH_f (J/g)
LA	46.11	180.00	39.96	171.75
LA/GNP_1	45.45	176.04	40.08	177.17
LA/GNP_2	45.95	166.67	39.83	166.23
LA/GNP_3	46.06	133.94	40.27	136.49
LA/$MXene_1$	45.43	174.42	40.27	176.63
LA/$MXene_2$	44.21	124.23	41.11	125.23
LA/$MXene_3$	45.56	153.50	40.55	155.48

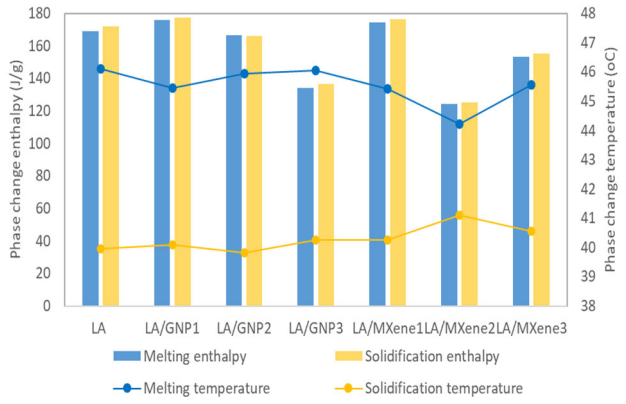

Fig. 4. (a) Phase change temperature and (b) Phase change enthalpy of LA and 2D nanomaterial based PCM.

The latent heat enthalpy (melting) for LA/MXene shows inconsistencies but exhibited a decreasing trend with increasing MXene loading. This behavior can be attributed to the interaction between MXene and the LA, which can affect the energy required for phase transitions. Where, MXene may enhance or hinder the movement of PCM/LA molecules during the phase change process, which then leads to the changes in enthalpy [20]. With the addition of MXene to pure LA, a slight decrease in the melting point was observed. This slight reduction in the melting temperature can be attributed to the beneficial effect of MXene in facilitating the phase transition, making the melting temperature of the LA/MXene composite lower than that of pure LA [21]. In contrast, the solidification temperatures exhibited an opposite trend. As the loading of MXene increased, the solidification temperature also increased. This phenomenon can be attributed to the interface interaction between the high surface energy atoms of pure LA and the high surface area of MXene nanomaterials [22].

Eqs. (1)–(2) [23, 24] are utilized to determine the latent heat storage efficiency (λ) and relative latent heat efficiency (η) of the 2D PCM nanocomposites. These calculations serve the purpose of establishing a straightforward comparison and quantifying the thermal energy storage capability of the PCMs, as delineated in Tables 3. It can be seen LA/GNP_1 possess the highest λ follows by LA/$MXene_1$ that implies the phase change latent heat loss is smaller or negligible. Based on the result from λ and η LA/GNP_1, LA/GNP_2 and LA/$MXene_1$ exhibited high heat storage efficiency which reflect high energy storage capacity in practical application.

$$\lambda = \frac{\Delta H_{m\_2D\_PCM}}{\omega_{PCM} \times (\Delta H_{m\_PCM})} \quad (1)$$

$$\eta = \frac{\Delta H_{m\_2D\_PCM}}{\Delta H_{m\_PCM}} \quad (2)$$

where, ω_{PCM} is the mass fraction of the PCM in the composites.

Table 3. The performance of LA/2D nanomaterials

Samples	λ (%)	η (%)	Thermal conductivity (W/(mK))
LA			0.23
LA/GNP_1	98.8%	97.8%	0.23
LA/GNP_2	95.5%	92.6%	0.26
LA/GNP_3	78.3%	74.4%	0.26
LA/$MXene_1$	97.4%	96.9%	0.23
LA/$MXene_2$	69.5%	69.0%	0.24
LA/$MXene_3$	86.1%	85.3%	0.24

C *Thermal Conductivity Analysis*

Thermal conductivity played a vital role in determining the performance of 2D PCM composites as it directly influenced the rate at which thermal energy was stored and released. It is obvious that as the mass fraction of GNP and MXene increases, the thermal conductivity also increases as shown in Table 3. High addition of GNP and MXene mass fraction led to the minimal thermal conductivity enhancement between 0.1–0.3 point. Therefore, it can be concluded that LA/$GNP_{2/3}$ demonstrate the best thermal conductivity performance compared to other PCM composites. Interestingly, there is no significant changes of thermal conductivity for LA/GNP_1 and LA/$MXene_1$ if compared with the pure LA, which is stagnant at 0.23 W/mK. This can be explained from the molecular perspective where transition of GNP/MXene nanoparticles from a fully dispersed state to a compact aggregated state, resulting in a decrease in nanoparticle densities [25]. This transition has adversely affected the molecular-level interaction between LA and GNP/MXene, subsequently impacting the efficiency of heat transfer. The mismatch between GNP/MXene and LA led to interfacial thermal resistance, which further degraded the thermal current [26]. These phenomena collectively contributed to the insignificant changes in thermal conductivity observed in the LA/GNP_1 and LA/$MXene_1$.

Table 4. Comparison of thermal conductivity with literature values

PCM	Thermal conductivity (W/(mK))	Ref.
LA/$GNP_{2/3}$	0.26	Present work
n-heptadecane/polystyrene	0.17	[27]
LA/polystyrene	0.18	[28]
Parrafin/gypsum-matrix	0.24	[29]
Poly(melamine-formaldehyde)/ Graphene oxide	0.19	[30]
LA/GNP	0.138	[13]

Table 4 compares the thermal conductivity of LA/$GNP_{2/3}$ with previous studies. The thermal conductivity found in the present work is higher than the maximum recorded thermal conductivity of the previous work. This indicated that GNP is

a good additive to enhance the heat transfer of the PCM if compared with Mxene. This can be attributed to its large specific surface, high thermal conductivity, and homogenous dispersion of GNP in LA at mass fraction of 3 and 5 wt%.

IV. Conclusion

LA based PCM composites hybridized with 2D nanomaterial (GNP and Mxene) were prepared. Thermal conductivity of the 2D PCM nanocomposite was found to increase gradually with increasing the mass fraction of GNP and Mxene, except at LA/GNP_1 and LA/$Mxene_1$. A reasonable thermal conductivity enhancement of ~13% was measured in this work at a GNP of 3 and 5 wt%. The energy storage performance was also compared between LA, LA/GNP and LA/MXene at various wt%. The calculation showed that LA/$GNP_{1/2}$ demonstrated high percentage of heat storage efficiency and relative latent heat efficiency. DSC results show insignificant change in melting temperature for LA/GNP compared to LA/Mxene. LA/GNP_2 was identified as the best candidate to use as a PCM for TES application based on the preliminary result obtained in this study.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Farrah Ezzah Ab Latif conducted the research, analyzed the data and wrote the paper, Khairunnisa Mohd. Pa'ad, Tomoya Tsuji and Norhuda Abdul Manaf analyzed the data, review the paper; all authors had approved the final version.

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