EVALUATION OF THERMAL PERFORMANCE OF BIO-BASED PHASE CHANGE MATERIALS COMPOSITES USING CARBON NANOMATERIALS

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ABSTRACT

Phase change materials (PCMs) have been considered for the latent heat thermal energy storage (LHTES) in buildings. Bio-based PCMs are type of organic fatty acid ester PCMs and significantly less flammable than paraffins so it can be used safely. However, they have a low thermal conductivity which severely reduces their thermal performances. In this study, Bio-based PCMs were prepared by the stirring of carbon nanomaterials such as exfoliated graphite nanoplatelets (xGnP) and carbon nanotubes (CNT) in liquid Bio-based PCMs at different mass fractions (1.0, 3.0 and 5.0 wt%). The micro structures were characterized using scanning electron microscopy (SEM) and it showed well-dispersion of Bio-based PCMs composites. Fourier transform infrared spectroscopy (FT-IR) results showed no chemical interaction between Bio-based PCM and prepared carbon nanomaterials. The thermal conductivity of Bio-based PCMs composites were increased as increasing carbon nanomaterials loading contents. Differential scanning calorimetry (DSC) analysis results indicated that Bio-based PCM/xGnP composites maintained their large latent heat values and suitable phase change temperatures due to large surface area and well-dispersion of carbon nanomaterials. Therefore, Bio-based PCM composites can be considered as suitable candidates for latent heat thermal energy storage.

INTRODUCTION

The latent heat thermal energy storage (LHTES) technique is an efficient and reliable means of using phase change materials (PCMs) to store and release thermal energy, because of its large heat storage capacity, and the nearly isothermal phase change behavior of PCMs [1]. Many kinds of inorganic and organic PCMs and their mixtures have been investigated as LHTES materials [2-5]. Inorganic PCMs, such as salt hydrates, salts, metals and alloy, have a high heat of fusion, good thermal conductivity, and are cheap and non-flammable. However, their applications are limited, because they are corrosive to most metals, undergo supercooling, and undergo phase decomposition [6]. Organic PCMs can be classified into two major categories: paraffins and non-paraffinic materials. Paraffins have been widely used, due to their large latent heat and proper thermal characteristics, such as minimal supercooling, varied phase change temperature, low vapor pressure in the melt, good thermal and chemical stability, and self-nucleating behavior [7]. However, most of the paraffins have not been used as a single PCM, because of their high flammability, which hinders their use in applications. There has been a lot of effort to solve this problem in the US industry, for over 20 years [8, 9].

A rather new material class of organic-based PCM, here termed Bio-based PCMs, are significantly less flammable than paraffins, because they are encapsulated as discrete blocks, between two layers of heavy-duty plastic film. Fire retardant materials can also be added to paraffins to reduce their flammability, but this generates the expense of altering the thermophysical properties of the material [9]. Bio-based PCMs are a type of organic fatty acid ester PCMs made from underused and renewable feedstock, like vegetable oils. So they are cheaper than paraffins, and can be mass-produced. Therefore, it is effective to apply them to fields that need large application scope. They possess some superior properties, comparable to those of paraffins in PCM applications. They have good thermal stability for thousands of melting and freezing cycles, with no risk of oxidation, because they are fully hydrogenated. Also, they are capable of absorbing, storing, and releasing large amounts of latent heat, similar to conventional paraffins, and are equally amenable to microencapsulation. They are expected to undergo small volume changes, and have no supercooling during freezing.

They have melting congruency, and suitable melting points that are in a relatively low temperature range; and they can also be manufactured such that the melting point can be varied between -22.7 °C and 78.3 °C, which facilitates their use in various heat storage applications [8-10]. Due to these advantages, together with growing interest in the use of fats and oils for sustainable chemistry, the fatty acids derivatives have been evaluated as promising PCMs. Many researchers have focused on their thermal properties, for testing their suitability in heat storage applications, but only limited thermal data is now available in the literature [10-17].

In spite of these desirable properties of Bio-based PCMs, they have a major drawback, that of low thermal conductivity, which severely reduces the rate of heat storage and extraction during the melting and solidification cycles. This can be a problem in some active applications like electronic devices and plastic injection molds [18]. To improve their thermal conductivity, carbon nanomaterials can be effective enhancements. In particular, exfoliated graphite nanoplatelets (xGnP), which were fabricated by an exfoliation process from natural graphite, have superior mechanical, electrical and thermal properties, due to their nanosize [19]. Also, carbon nanotubes (CNT) with smaller density show better stability and thermal properties in the organic matrix [20]. For these reasons, among numerous carbon nanomaterials, exfoliated graphite nanoplatelets (xGnP) and carbon nanotubes (CNT) were chosen for this study, and were employed with different loading contents, to obtain high thermal conductivity of Bio-based PCM. Investigations of their morphology and chemical compatibility, as well as their thermal properties, were carried out. The results can help us gain materials having high thermal performance.

EXPERIMENTAL

Materials

Organic fatty acid ester PCM with a melting temperature of 28.13 °C and latent heat capacity of 149.2 J/g were used directly as PCMs in this study, and were obtained from Korea C&S Corporation in South Korea. Details of the Bio-based PCMs are shown in Table 1.

Table 1 Properties of Bio-based PCM

Parameters	Bio-based PCM
Melting point (°C)	28.13
Boiling point (°C)	418
Latent heat (J/g)	149.20
Density (kg/m3)	860
Viscosity @ 30 °C (cp)	7
Thermal conductivity (W/mK)	0.2

Two types of carbon nanomaterials, xGnP and CNT were prepared. The graphite was obtained from Asbury Graphite Mills, Inc., NJ, USA, and xGnP were manufactured by applying a cost- and time-effective exfoliation process that was initially proposed by Drzal's group [19]. Hollow tube-shaped

CNT were purchased from EM-POWER Corporation in South Korea. In spite of the superior properties of CNT, their use has been confined to higher value-added business, due to their high cost burden for synthesis process. Meanwhile, applying graphite is a very cost effective way for high thermal conductivity, because xGnP are made of low-cost carbon materials like graphite.

Preparation of Bio-based PCM composites loading carbon nanomaterials

The samples were prepared by adding xGnP and CNT at different mass fractions into Bio-based PCMs, using a sonication process. Fig. 1 shows the scheme for the sample preparation route. The Bio-based PCMs were melted by heating at 60 °C. After melting process, the xGnP or CNT were mixed into the liquid PCM, with different mass fractions of 1.0, 3.0 and 5.0 wt%, to establish the relationship between the thermal properties of the Bio-based PCM composites and the mass fraction of xGnP and CNT. After stirring, the mixtures were ultrasonicated at an ultrasonic pulse velocity of 25 m/s for 20 min. Finally, the liquid mixtures were injected in the mold, and cooled. The seven types of Bio-based PCM composites are shown in Table 2.
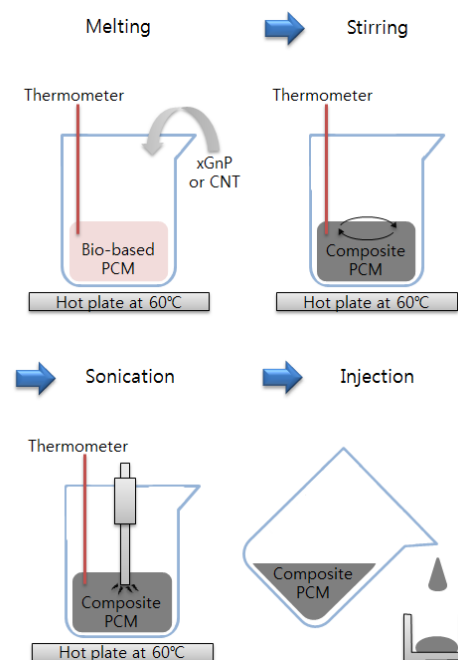

Figure 1 Scheme for the sample preparation route

Table 2 PCM composites with different mass fractions

No.	Sample
1	Bio-based PCM
2	Bio-based PCM/xGnP 1.0 wt%
3	Bio-based PCM/xGnP 3.0 wt%
4	Bio-based PCM/xGnP 5.0 wt%
5	Bio-based PCM/CNT 1.0 wt%
6	Bio-based PCM/CNT 3.0 wt%
7	Bio-based PCM/CNT 5.0 wt%

Characterization techniques

The morphology of the pure Bio-based PCM and Bio-based PCM composites at different loadings were observed by means of scanning electron microscopy (SEM, JEOL JSM-6360A) at room temperature. SEM images were obtained with an accelerating voltage of 12 kV, and working distance of 12 mm. The samples were coated with a gold coating of a few nanometers in thickness, to increase electrical conductivity. Fourier transform infrared spectroscopy (FT-IR, 300E Jasco) was used to confirm the change of chemical groups of composites at room temperature, by analyzing FT-IR spectra of the pure Bio-based PCM and Bio-based PCM composites. Using DSC instrument (DSC Q 1000, TA instrument, USA), the melting and heat storage behaviors of the pure Bio-based PCM and Bio-based PCM composites loading xGnP and CNT were examined. Experiments were conducted at a 5 °C /min heating rate, and a temperature range of 0–80 °C.

The thermal conductivity of the pure Bio-based PCM and Bio-based PCM composites with different loadings were measured by TCi thermal conductivity analyzer (C-Therm Technologies Ltd) at room temperature, 20 °C. The TCi can measure the thermal conductivity of small samples, through the Modified Transient Plane Source (MTPS) method. The TCi consists of a sensor, power control device, and computer software. A spiral-type heating source is located at the center of the sensor, and heat is generated at the center. The heat that has been generated enters the material through the sensor, during which a voltage decrease occurs rapidly at the heating source, and the thermal conductivity is calculated through the voltage decrease data [21]. This method showed high accuracy in existing paper [21]. The results are the average of five measurements, for each carbon nanomaterials loading and the coefficient of those correlation (R^2) is 0.99.
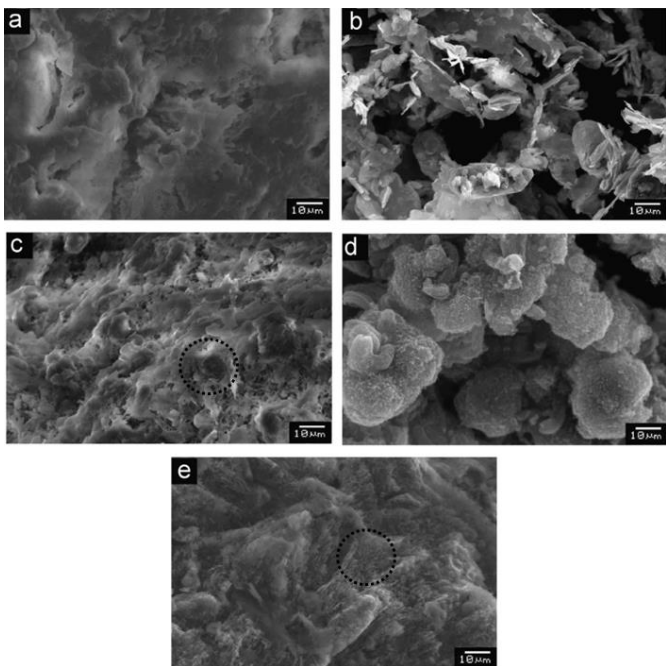

Figure 2 Scanning electron microphotographs (x 1,000) of (a) Bio-based PCM, (b) xGnP, (c) Bio-based PCM/xGnP 5 wt%, (d) CNT, and (e) Bio-based PCM/CNT 5 wt%.

RESULTS AND DISCUSSION

Characterization of Bio-based PCM composites

The morphology of Bio-based PCM and Bio-based PCM composites were studied by scanning electron microscopy observations. SEM images of the pure Bio-based PCM, xGnP, Bio-based PCM/xGnP 5.0 wt%, CNT and Bio-based PCM/CNT 5.0 wt% are shown in Fig. 2. In Fig. 2 (a), Bio-based PCM has a smooth surface with various sizes of particles, unlike other fatty acid esters-based PCM [22]. This is because it consists of various fatty acids, like palm oils, soybean oils and coconut oils. Fig. 2 (b) shows individual graphite nanoplatelets, of thickness <10 nm and average diameter 15 mm [23]. The nanosize of xGnP enables Bio-based PCM/xGnP composites to disperse well, despite their high loading contents, as observed in Fig. 2 (c). The original structure of xGnP was transformed by sonication process, and it looks like xGnP slightly covered the PCM surface. It is observed from Fig. 2 (d) that CNT has a net-like surface, and this is shown as well in Fig. 2 (e). CNT has large volume compared to the mass, but the dispersion of the CNT is uniform.

FT-IR spectrum of the Bio-based PCM, Bio-based PCM/xGnP 5.0 wt% and Bio-based PCM/CNT 5.0 wt% are shown in Fig. 3. Bio-based PCMs are made from underused feedstock such as soybean oils, coconut oils and palm oils, etc. which are composed of fatty acids. Fatty acids such as α-linolenic acid are an organic compound found in many common vegetable oils and its molecular formula is $C_{18}H_{30}O_2$ [24]. In spectra of Bio-based PCM, there are two strong absorption bands arising from the –CH_3 and –CH_2 group of the esters, usually found in the 2916 cm-1 and 2848-2849 cm-1 regions, respectively. The peaks at 1739 cm-1 and 1171 cm-1 represent the stretching vibration of C=O and C-O groups, respectively. The spectra of Bio-based PCM/xGnP 5.0 wt% and Bio-based PCM/CNT 5.0 wt% are the same as that of the pure Bio-based PCM. This result indicates that there is no chemical reaction between esters and carbon nanomaterials.
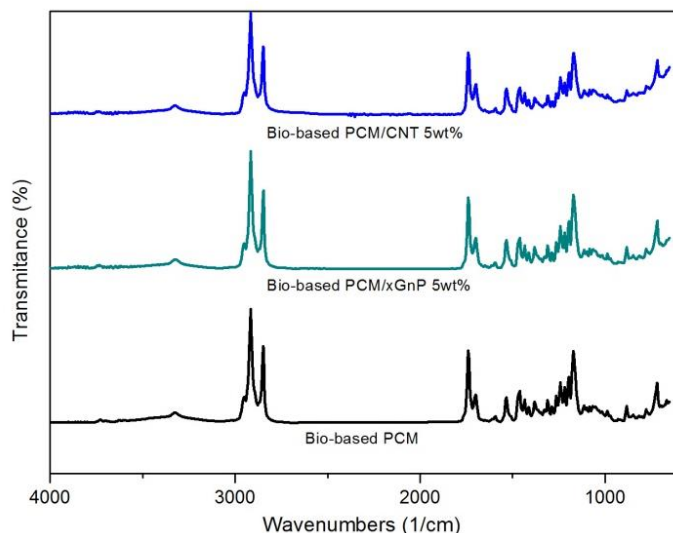

Figure 3 FT-IR spectra of Bio-based PCM, Bio-based PCM/xGnP 5 wt% and Bio-based PCM/CNT 5 wt%

Thermal conductivity of Bio-based PCM composites

The thermal conductivity of Bio-based PCM and Bio-based PCM composites are shown in Fig. 4. It can be found that the thermal conductivities of Bio-based PCM composites were remarkably improved compared to that of pure Bio-based PCM, with increasing loading contents of xGnP and CNT. Thermal conductivity will increase continuously with higher additive quantity of carbon nanomaterials, but no more than 5.0 wt% carbon nanomaterials were added, because they have a very low weight density. In table 3, the thermal conductivity of Bio-based PCM/xGnP composites with a mass fraction of 1.0, 3.0 and 5.0 wt% increased by 78 %, 297% and 336 %, respectively, and that of the Bio-based PCM/xGnP 5.0 wt% was found to be 0.671 W/mK. This result is comparable to Joen's report [23]. The thermal conductivity of conventional paraffin wax is 0.356 W/mK. The thermal conductivity of paraffin wax/xGnP 5.0 wt% showed 0.616 W/mK in this report. Bio-based PCM can exhibit higher thermal conductivity performance, compared to paraffin, by containing xGnP. The thermal conductivity of Bio-based PCM/CNT composites with a mass fraction of 1.0, 3.0 and 5.0 wt% increased by 166 %, 218 % and 248 %, respectively, and that of the Bio-based PCM/ CNT 5.0 wt% was found to be 0.536 W/mK.
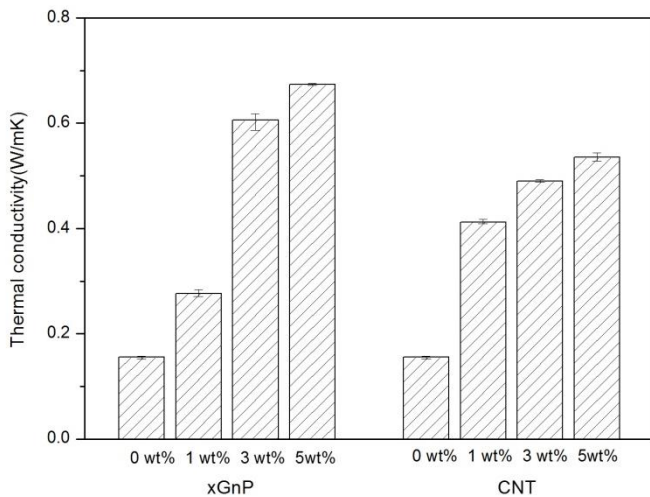

Figure 4 Thermal conductivity of Bio-based PCM and Bio-based PCM composites loaded with xGnP and CNT.

Table 3 Thermal conductivity and rate of increase of Bio-based PCM composites.

Sample	Mass fraction (wt%)	Δ T (°C)	Thermal conductivity (W/mK)	Rate of Increase (%)
Bio-based PCM	-	0.99	0.154	-
Bio-based PCM/xGnP	1	0.91	0.274	78
	3	0.74	0.612	297
	5	0.72	0.670	336
Bio-based PCM/CNT	1	0.82	0.410	166
	3	0.78	0.490	218
	5	0.76	0.536	248

Thermal energy storage performance of Bio-based PCM composites

Fig. 5 shows DSC graphs of Bio-based PCM and Bio-based PCM composites. DSC data, such as melting temperature, freezing temperature and latent heat, are presented in Table 4. The latent heat of the PCMs is obtained as the total area under the peaks of the solid-liquid transitions of the PCMs in the composite, by numerical integration.
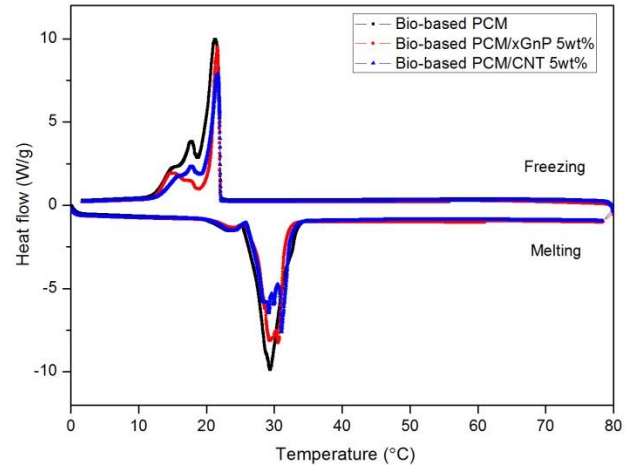

Figure 5 DSC graph of Bio-based PCM and Bio-based PCM composites

Table 4 DSC data of Bio-based PCM and Bio-based PCM composites.

Sample	Mass fraction (wt%)	Melting		Freezing	
		T (°C)	Latent heat (J/g)	T (°C)	Latent heat (J/g)
Bio-based PCM	-	29.4	146.7	21.3	133.1
Bio-based PCM/xGnP	1	31.2	146.6	21.1	130.7
	3	30.6	144.5	21.6	127.7
	5	29.6	143.5	21.7	124.3
Bio-based PCM/CNT	1	29.2	133.4	21.7	125.1
	3	31.1	132.4	21.5	124.5
	5	31.6	130.1	17.0	121.0

It can be seen that the latent heat of the Bio-based PCM/xGnP composites nearly approaches that of the pure Bio-based PCM. There is no significant difference of the latent heat between pure PCM and Bio-based PCM/xGnP composites, because xGnP, which has high surface area and nanoparticle size, is well dispersed in PCM. However, in the case of the Bio-based PCM/CNT composites, the latent heat was quite decreased by adding CNT. Similarly, there have been a lot of previous results that the latent heat of the composites was decreased by carbon nanomaterials, and this was explained as being because the three-dimensional net structure confines heat movement in the PCM composites [25-27]. However, in comparison of thermal energy storage characteristics of the

prepared composites with other fatty acid esters-based composite PCMs reported in literature, Bio-based PCM composites with carbon nanomaterials still showed high latent heat storage performance [22]. When CNT 1 wt% was blended into Bio-based PCM, the thermal conductivity of the composite PCM increased to a maximum of about 166 %, while the latent heat decreased only to a maximum of about 10 %.
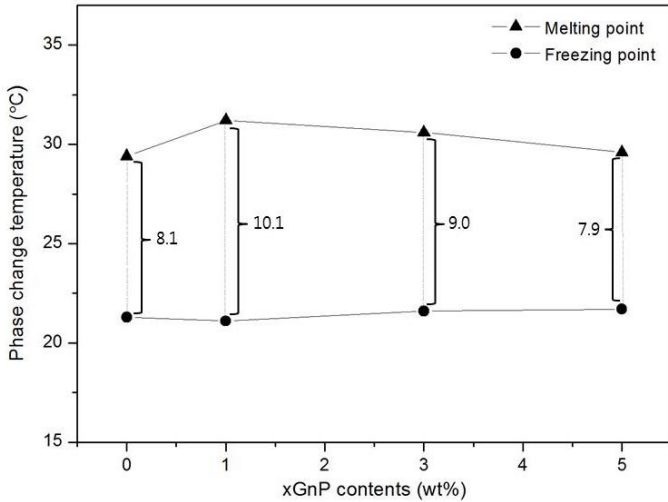

Figure 6 The phase change temperature and degree of supercooling of Bio-based PCM/xGnP composites
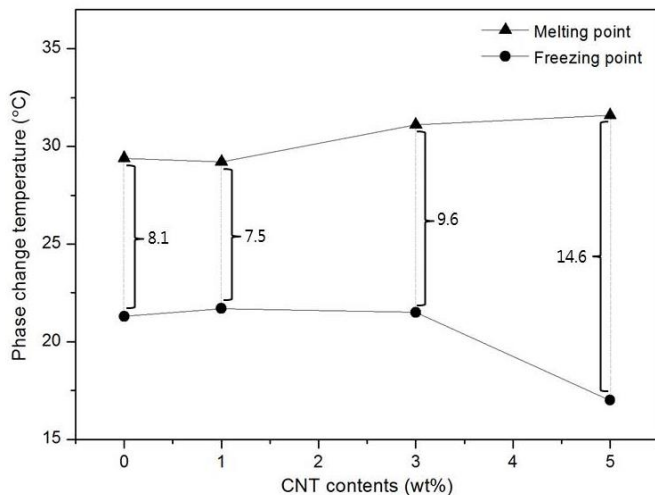

Figure 7 The phase change temperature and degree of supercooling of Bio-based PCM/CNT composites

Figs. 6 and 7 show the phase change temperature of the Bio-based PCM composites and degree of supercooling, expressed by the difference between melting temperature and freezing temperature obtained from DSC curves. As can be seen in Fig. 6, with the increase of xGnP content, the melting points of Bio-based PCM/xGnP composites were gradually decreased, but the freezing points were increased. Therefore, the degree of supercooling is slightly decreased by xGnP contents. According to the previous study, supercooling of more

than a few degrees will interfere with proper heat extraction from the store, and 5–10 ℃ supercooling can prevent it entirely [28]. In reference to the research of Lei Zhang about graphite nanoplatelets [25], the degree of supercooling is expected to minimize significantly with high loading contents, due to large aspect ratios and specific surface areas of xGnP. In contrast, Bio-based PCM/CNT composites had the opposite tendency, which cause an increased degree of supercooling, to a great extent. Therefore, Bio-based PCM with high CNT loading contents, more than 5 wt%, is not suitable for thermal energy storage.

CONCLUSION

Bio-based PCM Composites loaded with xGnP and CNT were prepared for high thermal conductivity, using a sonication process. From the cryogenically fractured surface of the composite PCMs, xGnP and CNT were well dispersed into Bio-based PCMs. There was no chemical reaction between esters and carbon nanomaterials. As the carbon nanomaterials loading contents were increased, thermal conductivity was highly increased. In particular, Bio-based PCM/xGnP 5.0 wt% showed the greatest increase of thermal conductivity, by 336 %. In the case of Bio-based PCM/CNT composites, they show a high increase of 166 %, in spite of their low loading contents 1.0 wt%. The latent heat of Bio-based PCM/xGnP composites showed almost the same as the pure Bio-based PCM, due to good dispersion of xGnP, with a high surface area and nanoparticle size. Those of the Bio-based PCM/CNT composites were slightly decreased but they are still affordable values. The degree of supercooling is increased to a great extent, so they have to be used carefully with a low weight percent of CNT under 10 wt%, to avoid thermal disadvantages. Furthermore, in order to utilize PCMs in buildings, they need to be prevented from instability in liquid state by using shape-stabilization, micro-encapsulation and incorporation techniques. The studied Bio-based PCM composites are equally amenable to micro-encapsulation as described in existing papers [24].

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