

## Article

# Effect of Graphene Nanoplatelet Size on the Thermal Properties of Bio-Based Phase-Change Materials for Thermal Energy Storage

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## Abstract

The rising environmental impact of building energy consumption has intensified the demand for sustainable energy solutions. Latent heat thermal energy storage (LHTES) using phase-change materials (PCMs) offers a highly effective approach to improve energy efficiency; however, the intrinsically low thermal conductivity of most PCMs limits their practical performance. This study explores the thermophysical properties of a commercially available bio-based PCM (CrodaTherm™ 60) enhanced with graphene nanoplatelets (GNPs) to improve heat transfer performance. Nano-enhanced PCMs (NePCMs) were prepared using a two-step process combining magnetic stirring and ultrasonication, incorporating GNPs at 2, 4, and 6 wt.%. Solid-phase density measurements of the NePCMs and viscosity measurements of the pure PCM were also conducted to support material characterisation. The results indicate distinct behaviours for the two nanoparticle sizes. At 6 wt.% nanoparticle loading, for 2 nm particles, the thermal conductivity increases by up to 13.9%, whereas for 6–8 nm particles, the enhancement is 148.9% of the pure PCM. Additionally, a reduction in latent heat is observed, with a proportional relationship to mass loading, as expected. These findings underscore the need for improved nanoparticle dispersion and formulation strategies to optimise both thermal performance and stability.

**Keywords:** phase-change materials; graphene nanoplatelets; thermal storage; bio-based phase-change material



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## 1. Introduction

Solar energy has gained significant attention in recent years as the global community faces escalating energy demands, resource depletion, and environmental challenges.

Thermal energy storage (TES) plays a critical role in maximising the utilisation of solar energy by mitigating the intermittency inherent to renewable sources. Among TES technologies, latent heat thermal energy storage (LHTES) has emerged as a highly promising solution due to its high energy density and nearly constant operating temperature during the phase-transition process [1]. Phase-change materials (PCMs) are widely employed in LHTES systems because of their favourable characteristics, including high energy storage capacity, chemical stability, environmental compatibility, and non-toxicity. Organic PCMs, particularly paraffin-based materials, currently dominate research and commercial implementation owing to these advantages [1–3]. However, their carbon footprint is often

overlooked, as most paraffin-based PCMs are derived from non-renewable petrochemical sources. Bio-based PCMs offer a sustainable alternative, exhibiting thermal properties similar to those of conventional PCMs while being derived from renewable resources. Research on bio-based PCMs has expanded rapidly in recent years [4,5], highlighting both their potential and their limitations [6]. Despite their environmental benefits, bio-based PCMs alike share a major performance limitation: low thermal conductivity. This restricts heat transfer during melting and solidification, thereby reducing the overall efficiency of LHTES systems.

Various enhancement strategies have been implemented to overcome this limitation and improve heat transfer, including encapsulation approaches that improve thermal stability and mitigate leakage [7,8], shape-stabilisation methods using carbon-based supports to retain structural integrity during phase transitions [9–11], fins designed to accelerate melting and discharging [12,13], metal foams that enhance heat transfer through high-porosity conductive pathways [14], and the incorporation of highly conductive additives that improve thermal conductivity and overall PCM performance [15–19]. Among these, adding high-conductivity particles is a widely adopted approach. These particles can be classified into three main categories: metal-based, such as silver (Ag); metal-oxide nanoparticles, such as aluminium oxide ( $\text{Al}_2\text{O}_3$ ) [20]; and carbon-based nanoparticles, including carbon nanotubes (CNTs) [21], multi-walled carbon nanotubes (MWCNTs), shown to enhance stability and conductivity in bio-based PCMs [12], and graphene nanoplatelets (GNPs), which improve both thermal conductivity and cycling performance [22–24].

Several comprehensive reviews have examined the enhancement of PCMs using highly conductive nanoparticles [25–28]. D'Oliveira et al. [25] provided an extensive overview of the thermophysical properties of nano-enhanced phase-change materials (NePCMs) in the temperature range of 20–70 °C, highlighting their potential for LHTES in residential applications. Their review showed that the enhancement of PCMs with conductive nanomaterials strongly depends on particle size, shape, and composition. However, significant discrepancies remain in the reported results, indicating the need for further investigation to fully understand nanoparticle–PCM interactions. Similarly, Hayat et al. [28] conducted a detailed review of the characteristics and potential applications of NePCMs, discussing the thermophysical behaviour of both unitary and hybrid systems. Their analysis identified major factors contributing to variations in thermal conductivity and energy storage capacity, noting that most existing research has focused on comparing different nanoparticles rather than on the influence of particle size, an area that still requires deeper exploration.

Ideal characteristics of NePCMs include high latent heat, high thermal conductivity, small volume change, rapid crystallisation, and low subcooling [3]. Graphene, with its exceptional thermal conductivity ranging between 3500–5000 W/(m·K) [28] and impressive mechanical strength, has shown great potential for enhancing the thermal properties of PCMs composites. He et al. [29] prepared multiple NePCMs based on myristic acid enhanced by different carbon-based nanoparticles, including graphene nanoplatelets (GNPs), multi-walled carbon nanotubes (MWCNTs) and nano-graphite (NG). The results concluded that the inclusion of the nanoparticles increased the thermal conductivity of the myristic acid, especially when using GNPs with a mass concentration of 3 wt.%, which increased the thermal conductivity by 176.26% when compared to the MWCNTs and NG, which increased the thermal conductivity by 47.30% and 44.01%, respectively, with the same mass fraction. An experimental study conducted by Tahan Latibari et al. [30] encapsulated CrodaTherm™ 60 with polyurea and an added mass fraction of 0.1 wt.% graphite nanoplatelets (multi-layered material) to enhance the thermal conductivity of the base material; the characterisation of the microencapsulated PCMs (MePCMs) showed that

samples containing 0.1 wt.% graphite nanoplatelets possessed a latent heat of 95.5 kJ/kg at a phase-transition temperature of 64 °C. The melting rate of the base PCM with the inclusion of the high-conductivity particles was increased.

Many studies have incorporated carbon-based nanomaterials into PCMs to improve thermal conductivity; however, the reported results vary widely due to differences in PCM chemistry, nanoparticle type, morphology, loading level, and preparation method. Such variability makes it difficult to identify the most suitable nanomaterial for a specific PCM system. This work addressed this challenge by providing a systematic assessment of bio-based NePCMs enhanced with graphene nanoplatelets (GNPs), with particular attention to the influence of nanoparticle morphology on the resulting thermophysical properties.

Existing research on graphene-enhanced PCMs rarely differentiates between GNP grades or reports key morphological parameters such as platelet thickness, aspect ratio, or specific surface area. As a result, the effects of GNP size and structural characteristics on the behaviour of organic PCMs remain unclear. No available study has directly compared two distinct GNP types within the same bio-based PCM matrix prepared without any dispersant or surfactant, a condition that allows the dispersion quality and network formation to depend solely on the inherent characteristics of the nanoparticles.

The present work fills this gap by examining how differences in GNP thickness ( $\approx 2$  nm versus 6–8 nm) and the associated variations in surface area influence thermal conductivity, latent heat, density, and viscosity. Isolating these effects in the absence of stabilising additives provides new insight into the fundamental mechanisms governing nanoparticle–PCM interactions and supports the development of rational design strategies for next-generation bio-based NePCMs.

## 2. Materials and Methods

### 2.1. Materials

The bio-based PCM used in this study was CrodaTherm™ 60 (Croda60), supplied by Croda International Plc (Snaith, UK), with a melting temperature of approximately 60 °C. Graphene nanoplatelets (GNPs) with two different thickness ranges were employed: GNP-1 (purity 99.5%, thickness  $\sim 2$  nm) and GNP-2 (purity 99.5%, thickness 6–8 nm), both purchased from Iolitec (Heilbronn, Germany). All conductive particles were used as received without any additional purification or surface treatment. The key thermophysical properties of Croda60 and the two GNP types are summarised in Tables 1 and 2. For all measured properties, both the mean value and the corresponding standard deviation are reported to reflect experimental variability.

**Table 1.** Thermophysical properties of the CrodaTherm™ 60 [31].

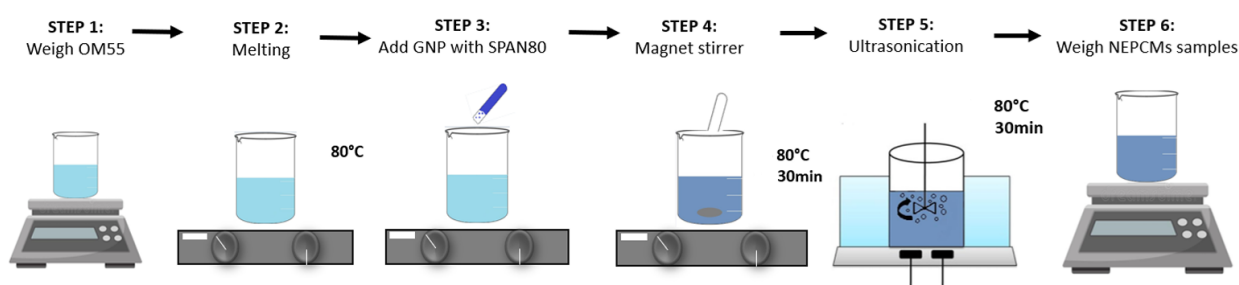
| Properties                                  | Notes                     | CrodaTherm™ 60 |
|---------------------------------------------|---------------------------|----------------|
| Latent heat of melting [kJ/kg]              | DSC scanning rate 1 K/min | 217            |
| Peak melting temperature [°C]               | DSC scanning rate 1 K/min | 60             |
| Latent heat of solidification [kJ/kg]       | DSC scanning rate 1 K/min | −212           |
| Peak solidification temperature [°C]        | DSC scanning rate 1 K/min | 58             |
| Density [solid] [kg/m <sup>3</sup> ]        | 55 °C                     | 922            |
| Density [liquid] [kg/m <sup>3</sup> ]       | 65 °C                     | 821            |
| Specific heat capacity [solid] [kJ/kg K]    |                           | 2.3            |
| Specific heat capacity [liquid] [kJ/(kg·K)] |                           | 1.4            |
| Thermal conductivity [solid] [W/(m·K)]      |                           | 0.29           |
| Thermal conductivity [liquid] [W/(m·K)]     |                           | 0.27           |
| Volume expansion 55 to 65 °C                |                           | 11.9%          |

**Table 2.** Properties of graphene nanoplatelets [32].

| Properties                                      | GNP-1 | GNP-2   |
|-------------------------------------------------|-------|---------|
| Thickness [nm]                                  | 2     | 6–8     |
| Specific Surface Area (SSA) [m <sup>2</sup> /g] | 750   | 120–150 |
| Purity [%]                                      | 99.5  | 99.5    |

## 2.2. Preparation Methods

The preparation of nano-enhanced PCMs (NePCMs) was carried out using a two-step method that provides better control over GNP properties and their interactions with the PCM, ensuring proper integration into the matrix (Figure 1). This technique has been widely reported in the literature [24,33–35], although its effectiveness depends on several factors, including PCM characteristics, nanoparticle type, and processing conditions (such as mixing intensity and duration).

**Figure 1.** Two-step method synthesis process for the preparation of the NePCMs through magnetic stirring and ultrasonication [24].

In the first step, 80 g of PCM in solid form was weighed and heated on a hot plate stirrer (IKA<sup>TM</sup> RCT, Staufen im Breisgau, Germany) at 80 °C until entirely melted. Once melted, graphene nanoplatelets (GNP-1 or GNP-2) were added at different mass fractions (2, 4, and 6 wt.%). The mixture was magnetically stirred at 800 rpm for 30 min at 80 °C. In the second step, the molten samples were ultrasonicated in an ultrasonic bath (BANDELIN “Sonorex digitec”, Berlin, Germany) for an additional 30 min at the same temperature to improve particle dispersion and break up clusters. No surfactants or nucleating agents were added, enabling investigation of the direct effects of GNP incorporation and size variation on NePCM performance.

## 2.3. Characterisation Methods

The morphology and thermal properties of the NePCMs were characterised using various equipment, as described herein.

### 2.3.1. Scanning Electron Microscopy (SEM)

The surface morphology and microstructure of GNP-1, GNP-2, the PCM, and the dispersion within the NePCMs were examined using scanning electron microscopy (SEM, TESCAN MIRA3, Brno, Czech Republic) at room temperature. For SEM imaging of GNP-1 and GNP-2, samples were prepared by dispersing the nanoplatelets in isopropyl alcohol (IPA) and subjecting the mixture to ultrasonication in a BANDELIN “Sonorex digitec” bath for 30 min to break up agglomerates. PCM and NePCM samples were coated with a 10 nm chromium layer using a Quorum Q150V sputter coater (Lewes, UK) to improve electrical conductivity. SEM images were captured at an accelerating voltage of 3.05 kV using a consistent magnification and field of view to enable comparative analysis of different NePCM

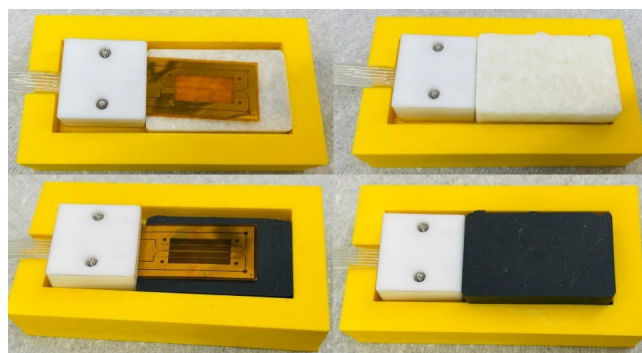
mass fractions. The lowest available voltage was selected to minimise potential sample damage during imaging, ensuring accurate and reliable morphological observations.

### 2.3.2. Differential Scanning Calorimetry (DSC)

Phase-change properties, including melting and solidification temperatures and latent heat capacity, were determined for the PCM and NePCMs using differential scanning calorimetry (DSC, Setaram 131, Caluire-et-Cuire, France) equipped with a nitrogen cooling system. Measurements were performed at constant heating and cooling rates of 2 K/min and 10 K/min over the temperature ranges 15–90 °C for the heating cycle and 90–15 °C for the cooling cycle under a continuous argon gas flow. Samples weighing between 7 and 9 mg were prepared on a precision balance ( $\pm 0.1$  mg), placed in 30  $\mu$ L aluminium crucibles at room temperature, and sealed with lids to ensure complete contact during analysis.

### 2.3.3. Thermal Conductivity (Transient Hot Bridge)

The thermal conductivities of the PCM and NePCMs were measured using a Linseis Transient Hot Bridge (THB, Bayern, Germany) 100 instrument with an accuracy of approximately 5%. The THB/B sensor, with a measurement range of 0.01–2 W/(m·K), was positioned between two solid block samples (50 mm  $\times$  25 mm, average thickness 8 mm), see Figure 2, and a weight of about 3 kg was applied to ensure good contact between the sample surfaces and the sensor. Before testing, a single-point calibration was performed using polymethyl methacrylate (PMMA), which has a reported thermal conductivity of 0.194 W/(m·K). Measurements were conducted at room temperature, with multiple readings taken for each sample; the reported values represent the average of these measurements along with their respective standard deviations. The heating current was set to 60 mA, the measurement time was set to 30 s, and a delay time of 10 times the measurement time was used to allow the sample to cool between measurements.



**Figure 2.** Pure PCM and NePCM samples in contact with THB/B sensor.

### 2.3.4. Viscosity Measurement

A Brookfield DV-E digital viscometer (Brookfield, MA, USA) equipped with a thermostat accessory that can heat the samples between 293 K to 573 K with temperature control of  $\pm 1$  K was used to measure the viscosity of Croda60. An SC4-18 spindle, designed to measure viscosities between 3 mPa·s and 10,000 mPa·s, was used with the DV-E digital viscometer. The measurement procedure consisted of the following steps: approximately 9 g of material was weighed and placed in the viscometer chamber, after which the temperature was increased up to the melting point of the substance. Once it melted, the spindle was submerged and carefully aligned. A 20 min thermal stabilisation period was allowed before commencing measurements. Viscosity data were collected from the melting temperature up to approximately 110 °C. At each temperature point, five consecutive viscosity measurements were recorded over a 15 min interval. To minimise uncertainties

associated with sample preparation, temperature equilibration, and spindle alignment, the complete measurement procedure was repeated on three samples, and the average values and standard deviations are reported here. The repeatability of the viscosity measurements was better than 2%. The calibration verification of the viscometer was previously reported in our earlier work [36].

### 2.3.5. Density (Archimedes' Principle)

The densities of the PCM and NePCMs were measured in a solid state using Archimedes principle; an Ohaus density determination kit and a balance (Fisherbrands, Liverpool, UK, with an uncertainty of 0.0001 g) were used. This method is described in BS EN 1183-1 [37]. The displacement liquid used was pure ethanol at 20 °C. All the samples were first measured in the air ( $m_{air}$ ) and subsequently measured immersed in ethanol ( $m_g$ ). Additionally, the ethanol and air temperatures were measured. Temperature changes can affect weighing and reduce the accuracy of density measurements. The solid density ( $\rho$ ) of all the samples was provided by the following equation:

$$\rho = \left( \frac{m_{air}}{m_{air} - m_g} \right) \cdot (\rho_E - \rho_A) + \rho_A \quad (1)$$

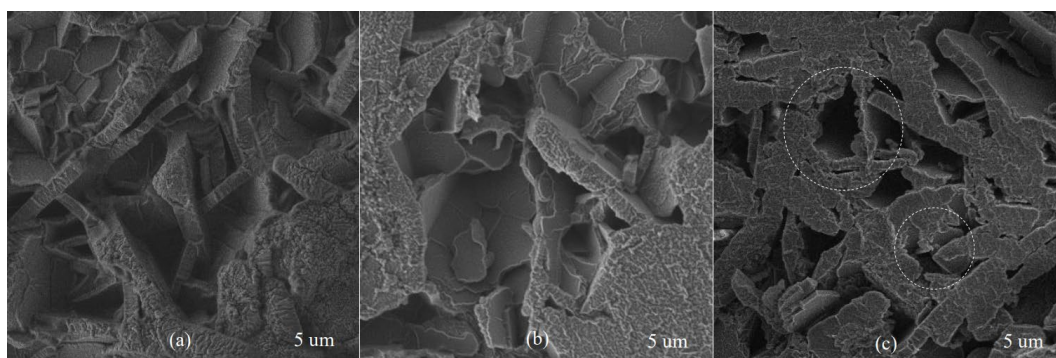
where  $\rho_E$  and  $\rho_{EA}$  are the densities, in kg/m<sup>3</sup>, of ethanol and air, respectively, at atmospheric pressure (0.1 MPa). The density was measured for at least three samples, and the average for each substance is reported.

## 3. Results and Discussion

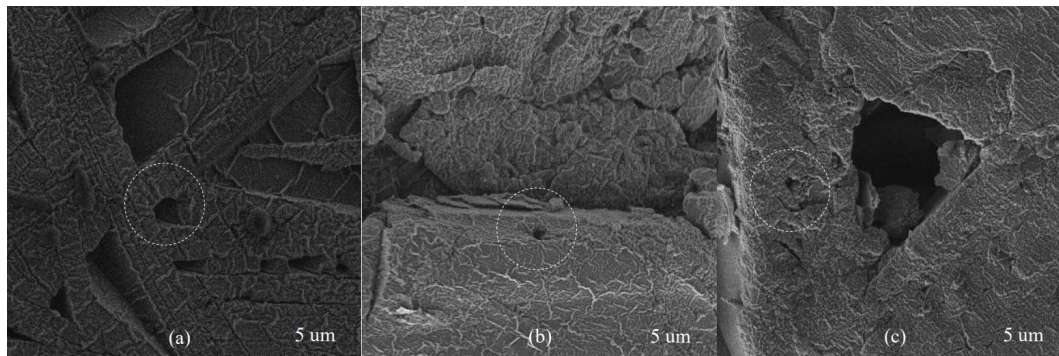
In this section, the experimental characterisation results for the thermophysical properties of the PCM and NePCMs are presented.

### 3.1. Microstructure Analysis Using SEM

The surface morphological characteristics and microstructures of the prepared NePCMs with GNP-1 and GNP-2 were examined by SEM. This investigation aimed to provide insights into the distribution and arrangement of the GNP-1 and GNP-2 within the PCM matrix. The analysis was conducted to establish a relationship between the NePCMs' morphology and their thermal properties, specifically focusing on latent heat and thermal conductivity. Figure 3 shows the characteristics of the NePCMs with 2, 4, and 6 wt.% of GNP-1. The SEM images show a rough, non-uniform surface with a few cracks highlighted. The same behaviour is observed, though less evident, in Figure 4, which shows the characteristics of the NePCMs with 2, 4, and 6 wt.% GNP-2.



**Figure 3.** SEM images of the PCM with (a) 2 wt.% GNP-1, (b) 4 wt.% GNP-1 and (c) 6 wt.% GNP-1 at a view field of 30 μm and SEM HV of 3.05 kV. The dashed circles mark selected porous areas.



**Figure 4.** SEM images of the PCM with (a) 2 wt.% GNP-2, (b) 4 wt.% GNP-2 and (c) 6 wt.% GNP-2 at a view field of 30  $\mu\text{m}$  and SEM HV of 3.05 kV. The dashed circles mark selected porous areas.

### 3.2. Latent Heat and Phase-Change Temperatures

The following thermal properties of the PCM and the NePCMs based on GNP-1 and GNP-2, including the onset melting temperature ( $T_{onset\_m}$ ), peak melting temperature ( $T_{peak\_m}$ ), onset solidification temperature ( $T_{onset\_s}$ ), peak solidification temperature ( $T_{peak\_s}$ ), melting latent heat ( $\Delta H_m$ ) and solidification enthalpy ( $\Delta H_s$ ), were obtained and processed using a heat-flux DSC. The samples were subjected to two heating/cooling rates: 2 K/min and 10 K/min. The detailed data obtained from the DCS measurements, the estimated latent heat capacity, and the reduction in latent heat capacity are presented in Tables 3 and 4. It is expected that the addition of GNPs to the PCM will reduce the latent heat capacity of the resulting NePCMs because the presence of solid nanoparticles decreases the mass fraction of active PCM undergoing phase transition. Since GNPs do not melt or crystallise, they do not contribute to the latent heat, and the theoretical enthalpy of the composite can therefore be estimated using a simple mass-balance relationship:

$$\Delta H_{c,nepcm} = \Delta H \cdot \varphi \quad (2)$$

**Table 3.** Variation in the latent heat capacity and phase-change temperature for both melting and solidification processes regarding loading content of GNP-1 and GNP-2 at 2 K/min.

| Samples | wt [%] | Melting                |                       |                         |                     |                             | Solidification         |                       |                         |                     | $\Delta T$ |
|---------|--------|------------------------|-----------------------|-------------------------|---------------------|-----------------------------|------------------------|-----------------------|-------------------------|---------------------|------------|
|         |        | $T_{onset\_m}$<br>[°C] | $T_{peak\_m}$<br>[°C] | $\Delta H_m$<br>[kJ/kg] | $\Delta H_m$<br>[%] | $\Delta H_{cal}$<br>[kJ/kg] | $T_{onset\_s}$<br>[°C] | $T_{peak\_s}$<br>[°C] | $\Delta H_s$<br>[kJ/kg] | $\Delta H_s$<br>[%] |            |
| Croda60 | -      | 57.2                   | 60.6                  | 208.64                  | -                   | -                           | 58.2                   | 55.7                  | 210.47                  | -                   | 4.9        |
|         | 2      | 57.5                   | 60.5                  | 190.49                  | 8.7                 | 204.4                       | 58.4                   | 56.4                  | 191.15                  | 9.1                 | 4.1        |
|         | 4      | 57.7                   | 60.1                  | 187.78                  | 10.0                | 200.2                       | 58.4                   | 56.9                  | 188.55                  | 10.4                | 3.2        |
|         | 6      | 58.1                   | 60.1                  | 184.20                  | 11.7                | 196.1                       | 58.2                   | 57.2                  | 183.29                  | 12.9                | 2.9        |
|         | 2      | 57.7                   | 60.1                  | 199.02                  | 4.6                 | 204.4                       | 55.2                   | 57.3                  | 199.31                  | 5.3                 | 4.4        |
|         | 4      | 57.4                   | 60.2                  | 192.05                  | 7.9                 | 200.2                       | 58.6                   | 56.1                  | 190.73                  | 9.3                 | 2.9        |
|         | 6      | 57.3                   | 60.6                  | 189.36                  | 9.2                 | 196.1                       | 58.5                   | 56.4                  | 189.75                  | 9.8                 | 4.5        |

$T_{onset\_m}$ : onset melting temperature,  $T_{peak\_m}$ : peak melting temperature,  $\Delta H_m$ : experimental latent heat of melting,  $\Delta H_{cal}$ : calculated latent heat of melting,  $T_{onset\_s}$ : onset solidifying temperature,  $T_{peak\_s}$ : peak solidifying temperature,  $\Delta H_s$ : experimental latent heat of solidifying,  $\Delta T$ : degree of supercooling.

Here,  $\Delta H_c$  is the theoretical value of the melting enthalpy of the NePCMs,  $\Delta H$  is the melting enthalpy of pure PCM, and  $\varphi$  is the weight fraction of PCM in the composite. This theoretical dilution effect provides a baseline expectation for the reduction in latent heat; however, experimental data frequently show a more pronounced reduction when

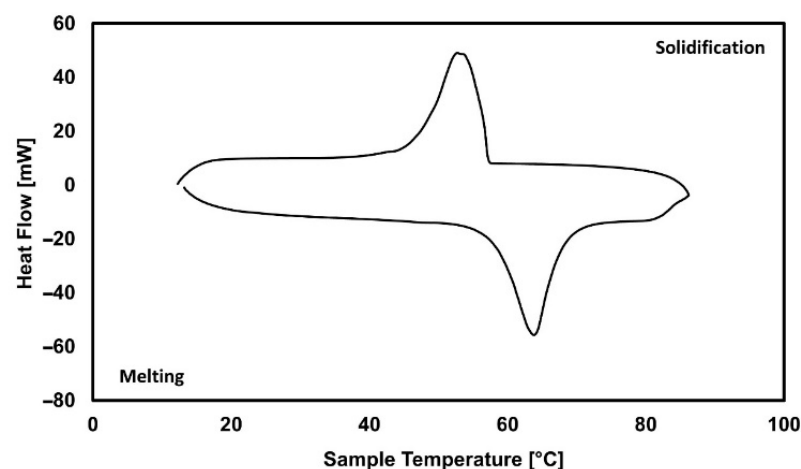
GNPs are incorporated into organic PCMs. Differential scanning calorimetry studies have demonstrated that latent heat decreases with increasing GNP loading, beyond what is predicted by simple mass dilution, indicating the presence of additional mechanisms.

**Table 4.** Variation in the latent heat capacity and phase-change temperature for both melting and solidification processes regarding loading content of GNP-1 and GNP-2 at 10 K/min.

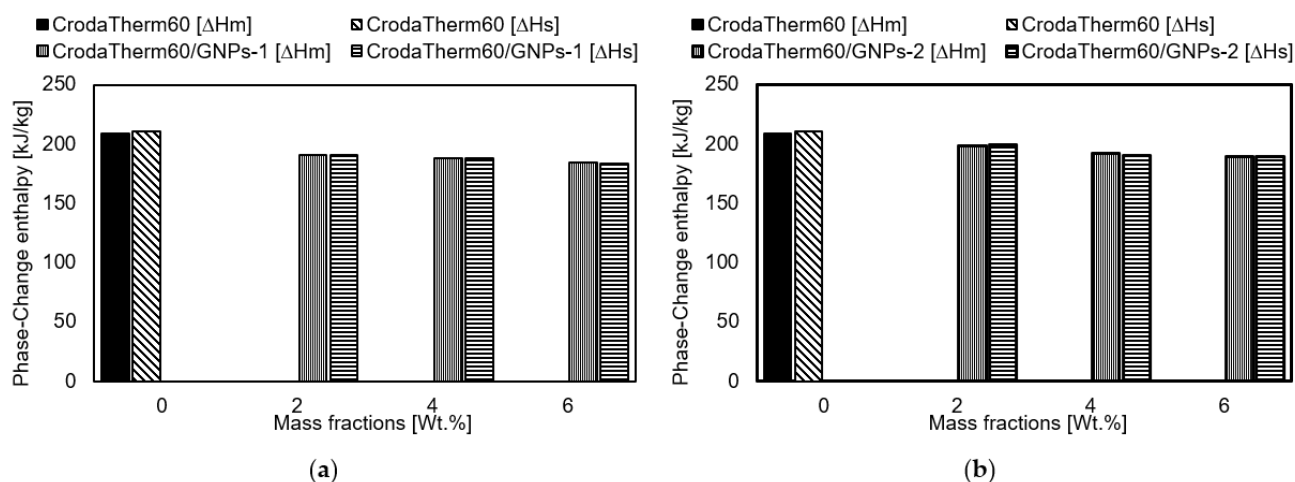
| Samples | wt [%] | Melting                |                       |                         |                     |                             | Solidification         |                       |                         |                     | $\Delta T$ |
|---------|--------|------------------------|-----------------------|-------------------------|---------------------|-----------------------------|------------------------|-----------------------|-------------------------|---------------------|------------|
|         |        | $T_{onset\_m}$<br>[°C] | $T_{peak\_m}$<br>[°C] | $\Delta H_m$<br>[kJ/kg] | $\Delta H_m$<br>[%] | $\Delta H_{cal}$<br>[kJ/kg] | $T_{onset\_s}$<br>[°C] | $T_{peak\_s}$<br>[°C] | $\Delta H_s$<br>[kJ/kg] | $\Delta H_s$<br>[%] |            |
| Croda60 | -      | 57.6                   | 60.6                  | 195.45                  | -                   |                             | 57.2                   | 53.43                 | 210.20                  |                     | 7.2        |
|         | 2      | 57.5                   | 60.5                  | 181.46                  | 13.0                | 191.54                      | 58.1                   | 55.25                 | 183.44                  | 12.8                | 5.3        |
|         | 4      | 56.9                   | 60.1                  | 184.99                  | 11.3                | 187.63                      | 58.2                   | 55.18                 | 187.01                  | 11.1                | 4.9        |
|         | 6      | 58.3                   | 60.1                  | 182.39                  | 12.5                | 183.72                      | 58.2                   | 56.19                 | 189.46                  | 9.9                 | 3.9        |
|         | 2      | 57.8                   | 60.1                  | 197.29                  | 5.4                 | 191.54                      | 58.2                   | 55.10                 | 195.87                  | 6.9                 | 5          |
|         | 4      | 57.8                   | 60.2                  | 179.95                  | 13.7                | 187.63                      | 58.2                   | 55.88                 | 189.29                  | 10.0                | 4.3        |
|         | 6      | 58.0                   | 60.6                  | 183.67                  | 11.9                | 183.72                      | 58.1                   | 53.88                 | 187.01                  | 11.1                | 6.7        |

$T_{onset\_m}$ : onset melting temperature,  $T_{peak\_m}$ : peak melting temperature,  $\Delta H_m$ : experimental latent heat of melting,  $\Delta H_{cal}$ : calculated latent heat of melting,  $T_{onset\_s}$ : onset solidifying temperature,  $T_{peak\_s}$ : peak solidifying temperature,  $\Delta H_s$ : experimental latent heat of solidifying,  $\Delta T$ : degree of supercooling.

Figure 5 shows the DSC curves of Croda60 during solidification and melting. Table 1 provides the thermophysical properties of the pure PCM matrix as provided by the supplier. The latent heat of fusion of the material was reported to be 215 kJ/kg, and the average measured value in this study was 208.64 kJ/kg, 2.95% lower than the reported value but still in good agreement. As seen in Figure 6, for the phase-change enthalpies of the PCM/GNP-1 and PCM/GNP-2 at heating/cooling rates of 2 K/min for the melting and solidification process, there are no significant differences between the solidification and melting latent heat measured from the DSC equipment, indicating that the material exhibits a reversible phase transition. This is a desirable characteristic in applications where efficient and predictable energy storage is essential, such as thermal energy storage systems [38]. The melting process of PCM starts at 57.2 °C, and the endothermic peak reaches the maximum point at 60.6 °C. Both endothermic and exothermic processes show a single peak, indicating that the material undergoes only one major transformation.

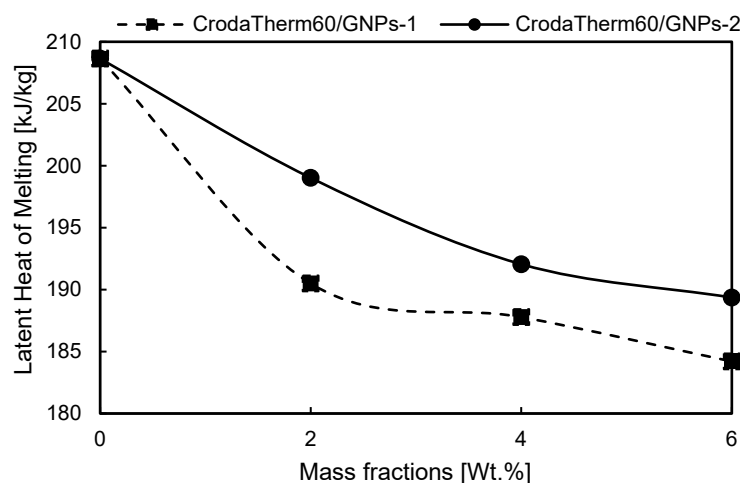


**Figure 5.** DSC curves of pure PCM.



**Figure 6.** Phase-change enthalpies of NePCMs at 2 K/min heating and cooling rate for melting and solidification: (a) with GNP-1 and (b) with GNP-2.

Figure 7 presents the variation in the latent heat of melting as a function of the mass fraction concentration (2, 4, and 6 wt. %) for the NePCMs prepared with GNP-1 (thickness ~2 nm) and GNP-2 (thickness 6–8 nm). The results clearly indicate that incorporating highly conductive particles into the PCM matrix leads to a noticeable reduction in latent heat. For NePCMs with GNP-1, the melting latent heat decreased by approximately 8.7%, 10%, and 11.7% for 2, 4, and 6 wt. % concentrations, respectively. Similarly, the corresponding reductions during solidification were 9.1%, 10.4%, and 12.9%. For the NePCMs with GNP-2, the reductions in the melting latent heat were 4.6%, 7.9%, and 9.2%, while the reductions in the solidification latent heat were 5.3%, 9.3%, and 9.8%, respectively. Overall, the NePCMs prepared with GNP-1 exhibited slightly greater reductions compared to those prepared with GNP-2.



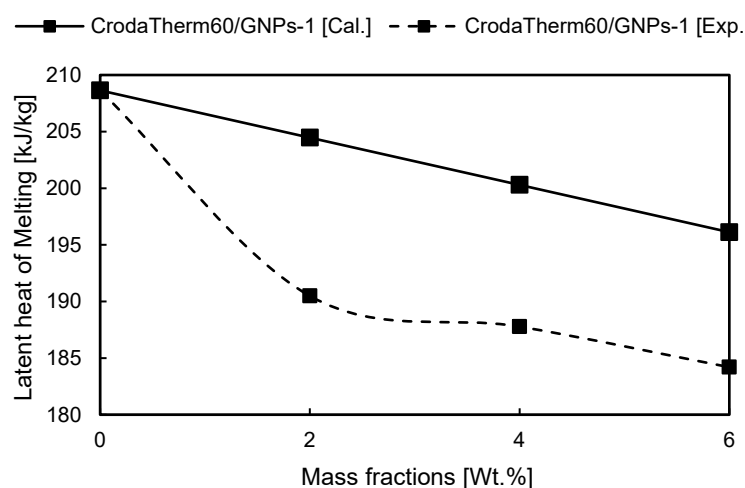
**Figure 7.** Latent heat of melting for NePCM-GNP-1 and NePCM-GNP-2 at 2 K/min heating/cooling rate.

This theoretical dilution effect provides a baseline for interpreting enthalpy changes; however, experimental measurements frequently show a more pronounced reduction when GNPs are incorporated into organic PCMs. DSC analyses have reported declining latent heat values with increasing GNP loading, in many cases exceeding values predicted solely from mass dilution. It is important to note that DSC experiments typically use very small sample masses, which can increase measurement variability, particularly in nanocomposite systems where local agglomeration, uneven nanoparticle distribution, or partial phase

separation may occur. Such inhomogeneities can influence the effective crystallisation behaviour sampled during each measurement, thereby contributing additional scatter to the recorded enthalpy values [39].

Beyond these experimental limitations, several intrinsic material mechanisms further explain deviations from theoretical predictions. FTIR studies have shown that GNPs interact physically with organic PCMs without forming chemical bonds, indicating that adsorption of PCM molecules onto GNP surfaces can restrict molecular mobility and reduce the extent of crystallisation [39,40]. The 2D morphology and high surface area of GNPs also disrupt the lamellar packing typical of organic PCMs, altering nucleation, crystal growth, and solid–liquid transition behaviour. These structural disturbances intensify with higher GNP surface area and poorer dispersion quality, both of which are strongly dependent on nanoparticle morphology. Indeed, changes in melting and solidification behaviour have been shown to become more pronounced at higher concentrations or when dispersion is limited, leading to further reductions in latent heat beyond those predicted by dilution alone. NePCMs containing thinner, higher-surface-area nanoplatelets (such as GNP-1), which may exhibit greater degrees of agglomeration and higher dispersion, disrupt the lamellar packing typical of organic PCMs. These systems are expected to exhibit larger enthalpy reductions and greater measurement variability, particularly when prepared without dispersants, where direct PCM–GNP interactions and more localised inhomogeneities lead to greater structural disruption [39,40].

Supercooling is a natural phenomenon that keeps the PCM in its liquid phase below its solidification temperature; in the field of LHTES, it is considered a disadvantage because it prevents the release of latent heat from the material [39]. The degree of supercooling ( $\Delta T$ ) of NePCMs for the different GNPs is shown in Table 3. The peak melting temperature ( $T_{peak\_m}$ ) and solidification temperature ( $T_{peak\_s}$ ) of Croda60 were experimentally determined to be 60.6 °C and 55.7 °C, respectively. The theoretical latent heat was calculated using Equation (2); the values are shown in Table 3, and they can be observed in Figure 8. The results indicate that the experimentally measured latent melting heat for each NePCM is lower than the calculated value. The discrepancies in the calculated values may be due to the surface morphology, structure, size, and dispersion of the nanoparticles in Croda60 [40,41], as well as due to the accuracy and precision of the equipment used.



**Figure 8.** Comparison of the calculated and experimental latent heat of melting of Croda60/GNP-1.

### 3.3. Density

The density of nanoparticles plays a significant role in increasing the thermal conductivity of enhanced phase-change materials; a higher density makes the nanoparticles

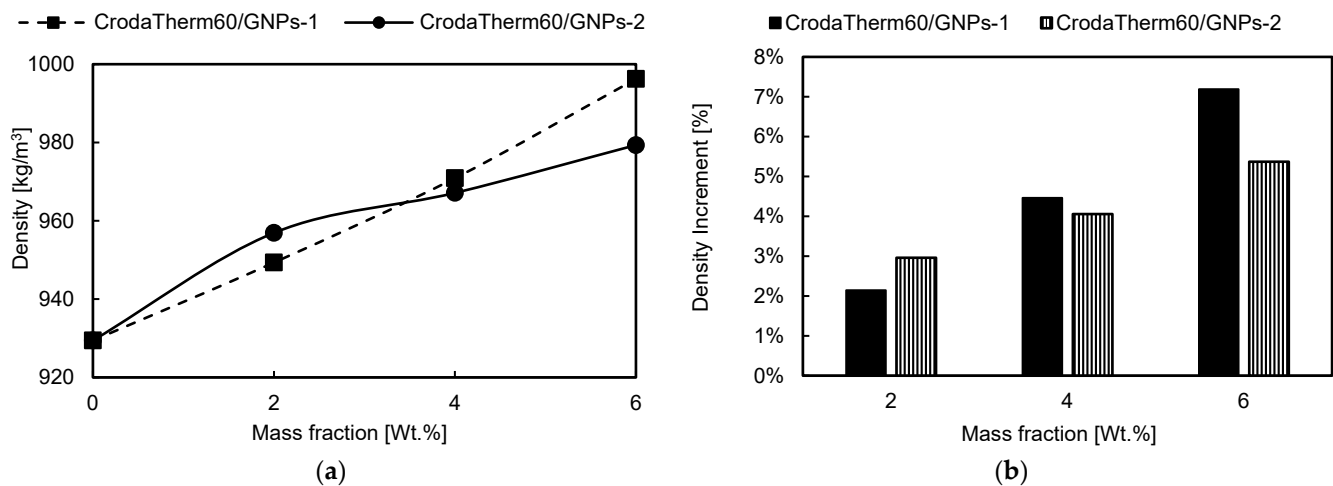
less porous, thereby reducing the chances of PCM absorption within their pores while maintaining latent heat [25]. Besides that, a high nanoparticle density causes sedimentation to the bottom, resulting in fewer nanoparticles exposed in the PCM. Table 5 shows the experimentally measured densities ( $\rho$ ) at different mass fractions for the enhanced phase-change materials with both GNP-1 and GNP-2 incorporated. The increase in density and standard deviation is also presented.

**Table 5.** Experimental densities ( $\rho$ ) of the different NePCMs at room temperature.

| PCM     | Nano  | wt. [%] | Temperature [°C] | Density (Solid) [kg/m <sup>3</sup> ] | Increment in Density [%] | Standard Deviation [kg/m <sup>3</sup> ] |
|---------|-------|---------|------------------|--------------------------------------|--------------------------|-----------------------------------------|
| Croda60 | -     | 0       | 24               | 929                                  | -                        | 1                                       |
|         |       | 2       | 23               | 949                                  | 2.14                     | 1                                       |
|         | GNP-1 | 4       | 23               | 971                                  | 4.46                     | 3                                       |
|         |       | 6       | 23               | 996                                  | 7.19                     | 1                                       |
|         | GNP-2 | 2       | 24               | 959                                  | 3.24                     | 4                                       |
|         |       | 4       | 23               | 967                                  | 4.06                     | 4                                       |
|         |       | 6       | 23               | 979                                  | 5.37                     | 7                                       |
|         |       |         |                  |                                      |                          |                                         |

The physical properties of the two highly conductive particles are presented in Table 2; however, the density of each particle was not available from the supplier list. Figure 9a shows the variation in density with the inclusion of the two different sizes of graphene nanoplatelets, denominated GNP-1 (thickness of 2 nm) and GNP-2 (thickness ranging between 6–8 nm), into the PCM matrix. From the results, the density increase was greater with the inclusion of GNP-1. Specifically, GNP-1 has a much higher specific surface area and a significantly thinner platelet morphology than GNP-2. These characteristics intensify van der Waals interactions between platelets and matrix, leading to higher interaction with the PCM matrix. Therefore, GNP-1 has a greater propensity to form compact structures with the PCM matrix, leading to densely packed PCMs and a more substantial rise in bulk density. This explanation is consistent with the findings of Santos et al. [42], who demonstrated that graphene/graphite nanoplatelets with higher surface area exhibit lower dispersion efficiency and stronger agglomeration, producing microstructures with higher effective density in polymer matrices. Similar behaviour has been reported for PCM systems. Vigneshwaran et al. [43] showed that increasing the GNP concentration in organic PCMs leads to agglomeration-driven densification of the composite, along with a reduction in latent heat due to restricted molecular mobility around aggregated GNP clusters. This supports our interpretation that the higher-surface-area GNP-1 forms more compact microstructures than the thicker GNP-2 and therefore produces a larger observed increase in density.

A limitation of this work is the absence of direct density measurements in the liquid state for the NePCM formulations. For engineering relevance, the liquid-phase density can be approximated from literature values for paraffin and fatty-acid PCMs in the relevant temperature range [36], which indicate a modest decrease in density upon melting and with increasing temperature. These estimates suggest the volumetric changes expected during TES operation; however, precise values for the current GNP-enhanced system should be confirmed experimentally. Future work will therefore include temperature-dependent density measurements in the liquid state for both the base PCM and the NePCMs.



**Figure 9.** (a) Variation in density with the inclusion of graphene nanoplatelets into the PCM matrix and (b) density increments.

### 3.4. Thermal Conductivity

In thermal energy storage applications, the central role of PCM is to absorb and release thermal energy effectively, and this factor is highly dependent on the thermal conductivity of the PCM [41]. Table 6 summarises the variation in the solid thermal conductivity of the pure PCM and NePCMs at mass fractions of 2, 4, and 6 wt.% and the corresponding thermal conductivity enhancement rates. The solid thermal conductivity was taken between 19–25 °C, and the tests were repeated at least three times for each sample. The reported values are averages of multiple data points, and the corresponding standard deviations indicate the variability observed among the measurements.

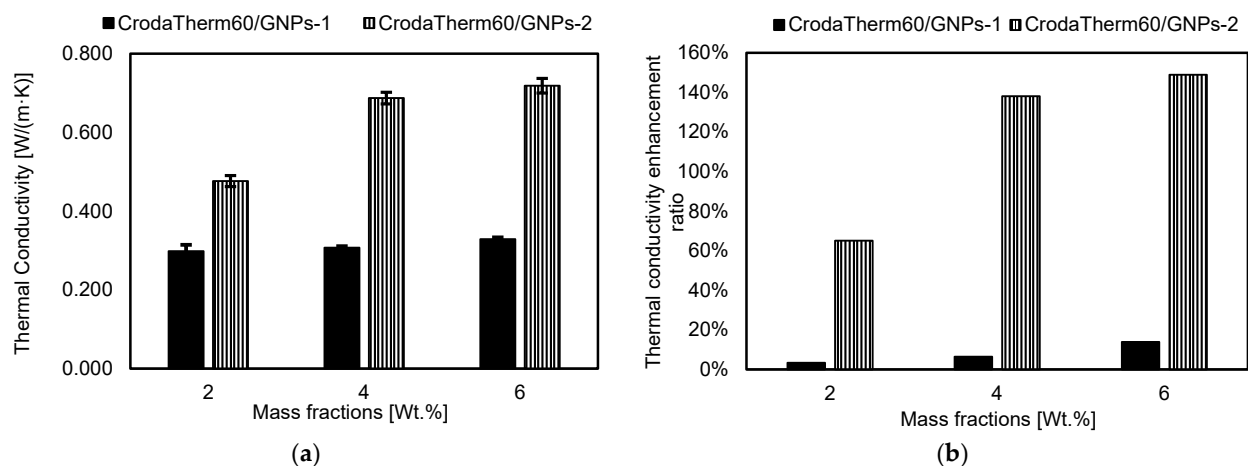
**Table 6.** Effect of the mass fraction of GNP-1 and GNP-2 on the thermal conductivity of the NePCMs.

| PCM     | Additive | wt. % | Temperature [°C] | Thermal Conductivity [W/(m·K)] | Thermal Conductivity Enhancement [%] | Standard Deviation [W/(m·K)] |
|---------|----------|-------|------------------|--------------------------------|--------------------------------------|------------------------------|
| Croda60 | -        | -     | 19.0             | 0.289                          | -                                    | 0.014                        |
|         | GNP-1    | 2     | 24.0             | 0.298                          | 3.4                                  | 0.016                        |
|         |          | 4     | 22.9             | 0.307                          | 6.4                                  | 0.004                        |
|         |          | 6     | 21.4             | 0.329                          | 13.9                                 | 0.005                        |
|         | GNP-2    | 2     | 19.0             | 0.476                          | 65.0                                 | 0.014                        |
|         |          | 4     | 19.9             | 0.687                          | 138.0                                | 0.015                        |
|         |          | 6     | 24.9             | 0.719                          | 148.9                                | 0.019                        |

Graphene nanoplatelets were selected for their high thermal conductivity (3500–5000 W/(m·K) [28]) and two-dimensional nature [41], which allows them to be porous at the nanoscale, thereby facilitating the incorporation of the PCM and increasing the melting and solidification rates. Two different graphene nanoplatelets were selected to investigate the effect of size on the thermal properties of the pure PCM. The main difference between the two GNPs incorporated into this study is their size and specific surface area (SSA), with GNP-1 having a thickness of 2 nm and an SSA of 750 m²/g, and GNP-2 having a thickness of 6–8 nm and an SSA of 120–150 m²/g. According to the literature, the specific surface area of nanoparticles plays a significant role in enhancing the thermal conductivity of NePCMs, as increased surface area creates more contact points between the base material

and the nanoparticles, thereby increasing heat transfer. Thus, in theory, a high surface area should enhance the PCM's thermal conductivity by creating a network of paths for phonon transfer [26].

Table 6 and Figure 10 present thermal conductivity measurements for the pure PCM and for the effect of different mass fractions (2, 4, and 6 wt.%) of GNP-1 and GNP-2 on the thermal conductivity of the storage material. The thermal conductivity measured for the pure PCM was  $0.289 \text{ W}/(\text{m}\cdot\text{K})$ , which closely matches the supplier-reported value of  $0.290 \text{ W}/(\text{m}\cdot\text{K})$ .



**Figure 10.** Thermal conductivity values (a) and thermal conductivity enhancement ratio (b) of NePCMs incorporated with different mass fractions of GNP-1 and GNP-2.

Regarding the NePCMs, the highest increase in thermal conductivity was recorded for the NePCMs based on PCM with GNP-2, with the results for mass fractions of 2, 4, and 6 wt.% being  $0.476$ ,  $0.687$ , and  $0.719 \text{ W}/\text{m}$ . These enhancements represent improvements of 65.03%, 138.05%, and 148.94%, respectively. However, unexpected behaviour was observed with the thermal conductivity enhancement when incorporating GNP-1. Due to its higher specific surface area, a much higher conductivity enhancement was theoretically expected; however, very low thermal conductivity enhancements were observed, with values of 3.39%, 6.42%, and 13.93% for mass fractions of 2, 4, and 6 wt.%, respectively.

The sharp increase in thermal conductivity observed for the GNP-2 composites can be attributed to the formation of a more efficient, thermally conductive network at higher loadings. Although no dispersant or surfactant was used, the thicker GNP-2 platelets (6–8 nm) may exhibit a lower tendency toward agglomeration than the thinner, high-surface-area GNP-1, enabling improved platelet–platelet contact and facilitating a percolation-like transition that markedly enhances heat conduction. Similar non-linear increases in thermal conductivity have been reported in GNP-enhanced PCMs prepared without surfactants, where network formation dominates the thermal response [25,44]. Moreover, recent microstructural studies confirm that thermal conductivity in GNP–PCM systems is governed primarily by filler connectivity and network topology rather than by filler type alone [45].

Thermal conductivity measurements were performed only in the solid state at approximately  $20\text{--}25^\circ\text{C}$ , which is substantially below the melting temperature of the bio-based PCM ( $\approx 60^\circ\text{C}$ ). As a result, the data presented here does not capture the behaviour of the nanocomposite in the near-melting or liquid state, where viscosity, molecular mobility, and the structure of the GNP network may differ from those in the solid phase. These factors may influence both the magnitude and the temperature dependence of the thermal conductivity enhancement during actual thermal energy storage operation. Future studies should therefore include temperature-dependent thermal conductivity measurements, particularly

in the phase-transition region and in the liquid state, to fully evaluate the performance of GNP-enhanced PCMs under realistic TES conditions.

A comparison with the literature values presented in Table 7 highlights the large variability in thermal conductivity enhancement reported for GNP-modified fatty-acid PCMs and provides a useful context for evaluating the Croda60–GNP composites. Reported thermal conductivities at loadings of 2–6 wt.% span a wide range, reflecting strong dependence on PCM chemistry, nanoplatelet characteristics, and dispersion approach. For instance, OM55 shows only a modest 14–17% improvement at 2–6 wt.% GNP-1 [24], whereas stearic acid exhibits substantially higher enhancements of 44%, 105%, and 158% at 2, 4, and 6 wt.% using 6–8 nm GNP-2 [46]. Even greater increases have been documented for myristic acid (+127% at 2 wt.%) and for eutectic palmitic–stearic acid when combined with PVP (+134% at 4 wt.% and +273% at 8 wt.%) [27,47]. As shown in Figure 11, the thermal conductivity enhancement obtained with GNP-2 aligns well with the values reported for systems using nanoplatelets of similar size, while the response observed for GNP-1 is consistent with results reported by authors employing comparable particle characteristics [48]. These comparisons reinforce that the thermal conductivity performance of GNP–PCM composites is governed by nanoplatelet morphology, specific surface area, and the degree of conductive network formation within the solid matrix. Deviations from ideal behaviour commonly could be attributed to incomplete dispersion or agglomeration, which hinder the development of continuous pathways and increase interfacial thermal resistance.

**Table 7.** Comparison of thermal conductivity enhancement in fatty-acid PCMs with GNPs at room temperature.

| PCM                | GNP + Additive                  | wt. % | Thermal Conductivity [W/(m·K)] | Thermal Conductivity Enhancement [%] |
|--------------------|---------------------------------|-------|--------------------------------|--------------------------------------|
| Lauric Acid [23]   | -                               | 0     | 0.215                          |                                      |
|                    | 5–10 nm                         | 2.65  | 0.489                          | 127%                                 |
| Myristic Acid [27] | 3–10 nm                         | 0     | 0.2186                         |                                      |
|                    |                                 | 1     | 0.4405                         | 102%                                 |
|                    |                                 | 2     | 0.4963                         | 127%                                 |
|                    |                                 | 3     | 0.6039                         | 176%                                 |
| Stearic Acid [46]  | 6–8 nm<br>150 m <sup>2</sup> /g | 0     | 0.275                          |                                      |
|                    |                                 | 2     | 0.396                          | 44%                                  |
|                    |                                 | 4     | 0.565                          | 105%                                 |
|                    |                                 | 6     | 0.710                          | 158%                                 |
| OM21 [43]          | 300 m <sup>2</sup> /g           | 0     | 0.150                          |                                      |
|                    |                                 | 0.1   | 0.164                          | 9%                                   |
|                    |                                 | 0.3   | 0.167                          | 11%                                  |
|                    |                                 | 0.5   | 0.176                          | 17%                                  |
| OM30 [43]          | 300 m <sup>2</sup> /g           | 0     | 0.275                          |                                      |
|                    |                                 | 0.1   | 0.289                          | 5%                                   |
|                    |                                 | 0.3   | 0.337                          | 23%                                  |
|                    |                                 | 0.5   | 0.351                          | 28%                                  |
| OM35 [43]          | 300 m <sup>2</sup> /g           | 0     | 0.195                          |                                      |
|                    |                                 | 0.1   | 0.262                          | 34%                                  |
|                    |                                 | 0.3   | 0.214                          | 10%                                  |
|                    |                                 | 0.5   | 0.229                          | 17%                                  |

Table 7. Cont.

| PCM                                 | GNP + Additive                | wt. % | Thermal Conductivity [W/(m·K)] | Thermal Conductivity Enhancement [%] |
|-------------------------------------|-------------------------------|-------|--------------------------------|--------------------------------------|
| OM35 [48]                           | 6–10 nm + SDS                 | 0     | 0.22                           |                                      |
|                                     |                               | 0.2 * | 0.25                           | 14%                                  |
|                                     |                               | 0.4 * | 0.27                           | 23%                                  |
|                                     |                               | 0.7 * | 0.30                           | 36%                                  |
|                                     |                               | 0.9 * | 0.35                           | 59%                                  |
|                                     |                               | 1.0 * | 0.39                           | 77%                                  |
| OM46 [43]                           | 300 m <sup>2</sup> /g         | 0     | 0.251                          |                                      |
|                                     |                               | 0.1   | 0.272                          | 8%                                   |
|                                     |                               | 0.3   | 0.291                          | 16%                                  |
|                                     |                               | 0.5   | 0.306                          | 22%                                  |
| OM55 [24]                           | 2 nm<br>750 m <sup>2</sup> /g | 0     | 0.222                          |                                      |
|                                     |                               | 2     | 0.252                          | 14%                                  |
|                                     |                               | 4     | 0.256                          | 15%                                  |
|                                     |                               | 6     | 0.259                          | 17%                                  |
| Eutectic Palmitic–Stearic Acid [47] | 4–20 nm + PVP                 | 0     | 0.263                          |                                      |
|                                     |                               | 1     | 0.343                          | 30%                                  |
|                                     |                               | 2     | 0.435                          | 65%                                  |
|                                     |                               | 4     | 0.615                          | 134%                                 |
|                                     |                               | 8     | 0.981                          | 273%                                 |

\* The reported vol.% values were converted to wt.% using the respective solid densities.

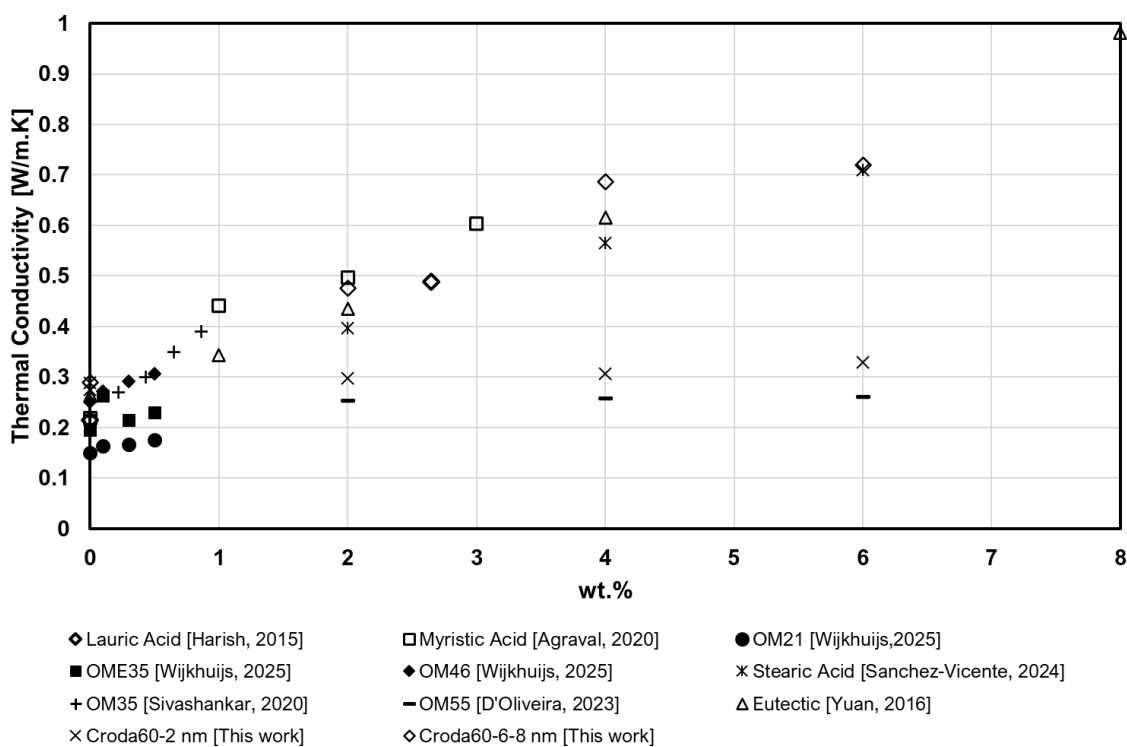


Figure 11. Thermal conductivity comparison at room temperature for GNP–fatty-acid PCM systems reported in the literature [23,24,27,45–48].

### 3.5. Viscosity

Viscosity is a crucial property in fluid dynamics and plays a significant role in the behaviour of PCMs. In the context of PCMs, viscosity affects their thermal performance and stability, and it is essential for the design of efficient thermal energy storage systems. This property is often not studied by many of the research papers presented in the literature. Table 8 and Figure 11 show the viscosity of Croda60 from 65 °C to 110 °C at 0.1 MPa. As shown in Figure 7, the viscosities of Croda60 decreased with increasing temperature, as expected. Comparing the viscosity of Croda60 with the viscosities of stearic acid, OM65 and paraffin, RT64HC, published in our previous paper [36], the viscosity of Croda60 is between the viscosity of stearic acid and the paraffin, as shown in Figure 11. According to our knowledge, viscosity data for Croda60 have never been published.

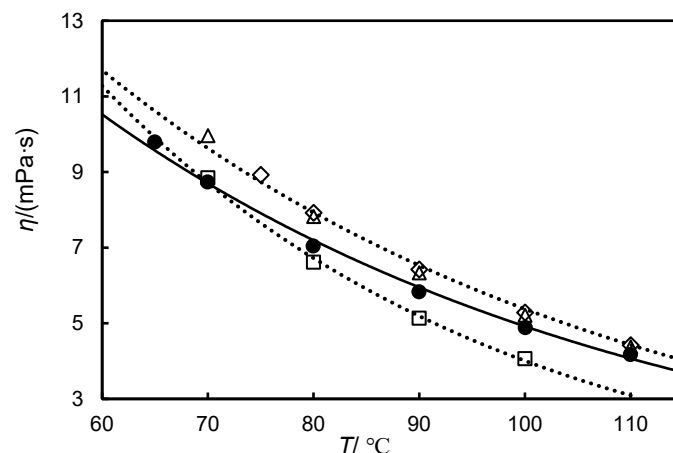
**Table 8.** Experimental viscosities (mPa·s) for Croda60.

| PCM     | Temperature [°C] | Viscosity [mPa·s] | Standard Deviation [mPa·s] |
|---------|------------------|-------------------|----------------------------|
| Croda60 | 65               | 9.79              | 0.02                       |
|         | 70               | 8.73              | 0.03                       |
|         | 80               | 7.04              | 0.03                       |
|         | 90               | 5.83              | 0.06                       |
|         | 100              | 4.88              | 0.01                       |
|         | 110              | 4.17              | 0.02                       |

The viscosity of Croda60 was fitted with the Andrade equation [49]. The equation is as follows:

$$\eta = A e^{\left(\frac{b}{T}\right)} \quad (3)$$

where  $\eta$  represents viscosity,  $T$  is temperature in degrees Celsius,  $A$  is the pre-exponential factor corresponding to viscosity at infinite temperature, and  $b$  is the activation energy parameter associated with the energy barrier for molecular motion. The correlation is shown in Figure 12. The adjusting parameters, along with the AAD and  $R^2$  values, are presented in Table 9. These AAD values are comparable to the experimental uncertainty, indicating that the equation accurately represents the data.



**Figure 12.** Experimental viscosities versus the temperature at 0.1 MPa for ●, Croda60 in this work, and for □, RT64HC, ◇, stearic acid, and △, OM65 from Costa et al. [36]. The solid line represents the fitting of Equation (3) with the parameters of Table 8. The dotted line is to guide the eye.

**Table 9.** Parameters A and b of Equation (3) along with the absolute average deviation (AAD) and R<sup>2</sup> values of the fitting for the viscosities of Croda60.

| PCM     | A<br>[mPas] | b<br>[°C] | AAD<br>[mPa·s] | R <sup>2</sup> |
|---------|-------------|-----------|----------------|----------------|
| Croda60 | 1.27        | 134.73    | 0.021          | 0.9933         |

It is important to note that all nanocomposite samples in this study were prepared without any dispersant or surfactant. As a result, the dispersion quality depended solely on the intrinsic particle morphology and the mechanical mixing steps employed, including an ultrasonic step. This might have two main implications for the observed thermal behaviour. First, the absence of surfactants could mean that agglomeration effects are more strongly governed by the surface area and thickness of the GNPs, which helps explain the contrast between GNP 1 and GNP 2: the thinner, high-surface-area GNP 1 tended to form compact aggregates, reducing network connectivity, whereas the thicker GNP 2 platelets could form more efficient conductive paths even without stabilisation. However, thinner GNP-1 platelets could also result in greater dispersion and greater disruption of the material structure, with reduced network formation between particles, leading to lower enthalpy and thermal conductivity. Second, the significant rise in thermal conductivity at higher GNP 2 loadings demonstrates that a continuous or near-percolated network can still be established without chemical stabilisers, consistent with previous reports of GNP-enhanced PCMs, where large conductivity jumps were observed in physically mixed systems without surfactants [25,44]. This might confirm that the enhancement mechanism in our materials is predominantly governed by particle morphology and network formation rather than by agglomeration-induced dispersion effects. GNP-2, with thicker particles, is able to form conductive pathways between particles in contact, resulting in higher thermal conductivity with less distortion in the packing structure. It should be noted that this paper focuses on establishing the fundamental relationships between GNP thickness, surface area, and thermophysical properties; systematic characterisation of GNP agglomeration was not included in the present work. Future studies could incorporate systematic measurements of agglomeration at selected GNP loadings to better elucidate the role of particle clustering in the thermophysical properties of thermal energy storage materials.

It is important to note that the stability of the nanocomposite PCM was not assessed in the present study. No measurements were performed to evaluate thermal cycling durability, sedimentation or phase separation behaviour, or possible changes in the GNP network structure under repeated melting and solidification. These factors are essential for determining the practical reliability of NePCMs in thermal energy storage systems, where materials may undergo thousands of charge–discharge cycles. As the focus of this work was specifically on understanding the effect of GNP morphology on the thermophysical properties of a single bio-based PCM, stability evaluation falls beyond the experimental scope at this stage. This represents a limitation of the study, and future work should include systematic thermal cycling tests, sedimentation analysis, and microstructural characterisation to fully validate the long-term performance of GNP-enhanced bio-based PCMs.

A further limitation of this study is that viscosity was measured only for the pure PCM, and no rheological data were obtained for the NePCM formulations containing graphene nanoplatelets. Viscosity can change significantly with nanoparticle loading, particularly in nanocomposite PCMs, where particle–particle interactions and microstructural rearrangements influence flow behaviour. In our previous work, we investigated the viscosity behaviour of stearic acid with GNP concentrations ranging from 2 to 6 wt.% [50]. The results showed that viscosity increased with GNP addition and decreased with temperature, reaching up to four–five times that of the base PCM. GNPs also influenced the rheological behaviour: stearic acid mixed with 6–8 nm GNPs exhibited non-Newtonian

behaviour at concentrations above 2 wt.%, while fluids with concentrations below 2 wt.% remained Newtonian. The rheological behaviour of the viscosity for Croda60 with GNPs is expected to be like stearic acid. Further viscosity measurements for the NePCMs could give us knowledge to fully assess their pumpability and suitability for dynamic TES systems. Future work should include systematic viscosity measurements for selected GNP loadings to better evaluate the operational performance of these nanocomposites under realistic thermal energy storage conditions.

#### 4. Conclusions

This experimental study investigated the thermal behaviour of a commercially available bio-based PCM enhanced with graphene nanoplatelets (GNPs) of two different size distributions. The influence of nanoparticle size, dispersion quality, and mass concentration on key thermal properties was systematically evaluated. The main conclusions are as follows:

- Differential scanning calorimetry (DSC) results showed variations in melting temperature and latent heat with the addition of GNPs. However, the standard deviation in the DSC measurements was relatively high, leading to partial overlap in the latent heat values across samples. As a result, the impact of GNP concentration on latent heat cannot be conclusively established, and any observed reductions should be interpreted with caution. The greatest reduction in latent heat (11.7%) occurred for the PCM with 6 wt.% GNP-1.
- Clear differences were observed between the two GNP types. GNP-1 ( $\approx 2$  nm thickness, high surface area) offered only modest thermal improvements, likely due to the lack of effective conductive pathways. In contrast, GNP-2 (6–8 nm thickness) produced a more efficient network structure, demonstrating that platelet thickness, aspect ratio, and network connectivity have a more decisive influence on heat transfer than surface area alone.
- The most significant improvement occurred in the sample containing 6 wt.% GNP-2, where the thermal conductivity increased from  $0.289 \text{ W}/(\text{m}\cdot\text{K})$  to  $0.708 \text{ W}/(\text{m}\cdot\text{K})$ , an enhancement of approximately 149%. This non-linear increase is consistent with the establishment of a more continuous conductive network and reflects a percolation-like behaviour typical of carbon-based thermal additives when sufficient connectivity is achieved, even without surfactants. Thermal conductivity measurements were performed only in the solid state at  $20\text{--}25^\circ\text{C}$ , substantially below the PCM's melting temperature, and future work should therefore include temperature-dependent measurements near and above the phase-transition region to fully assess NePCM performance under realistic operating conditions.
- NePCMs incorporating GNP-2 showed marked gains in thermal conductivity and retained latent heat values within acceptable limits. Although this reflects clear potential at the material level, comprehensive stability testing and additional validation are necessary prior to assessing their suitability for practical deployment.
- The addition of GNPs resulted in an increase in solid density, reflecting the higher density of the carbon nanostructures with the matrix. Viscosity decreased with temperature and remained within ranges reported for similar PCMs. The addition of GNPs (2–6 wt.%) is expected to increase the viscosity of Croda60 and modify its rheological behaviour. Therefore, a comprehensive rheological analysis is required before evaluating its suitability for practical pumping or heat transfer applications.
- It should also be noted that the long-term stability of the nanocomposite PCM, including thermal cycling durability and potential sedimentation, was not assessed in this study, and future work should address these aspects to fully determine its suitability for practical thermal energy storage applications.

Overall, this study demonstrates that incorporating appropriately selected graphene nanoplatelets without dispersants can significantly enhance the thermal performance of bio-based PCMs at the material level. These findings provide insight into the role of platelet morphology and network formation in determining thermophysical behaviour and serve as a foundation for the future design and optimisation of next-generation bio-based nanocomposite PCMs, with practical applicability contingent upon further rheological, stability, and system-scale evaluation.

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**Data Availability Statement:** The data supporting the findings of this study are available from the corresponding author upon reasonable request. No publicly archived datasets were generated or analysed in this work.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

|               |                                                   |
|---------------|---------------------------------------------------|
| Greek Symbols |                                                   |
| $\alpha$      | Thermal diffusivity ( $\text{m}^2\text{s}^{-1}$ ) |
| $\rho$        | Density ( $\text{kg}/\text{m}^3$ )                |
| Abbreviations |                                                   |
| DSC           | Differential Scanning Calorimeter                 |
| GNP           | Graphene Nanoplatelet                             |
| LHTES         | Latent Heat Thermal Energy Storage                |
| MePCMs        | Microencapsulated Phase-Change Materials          |
| MWCNTs        | Multi-Walled Carbon Nanotubes                     |
| NePCMs        | Nano-Enhanced Phase-Change Materials              |
| PCMs          | Phase-Change Materials                            |
| PMMA          | Polymethyl Methacrylate                           |
| PVP           | Polyvinyl Pyrrolidone                             |
| SDS           | Sodium Deoxycholate                               |
| SEM           | Scanning Electron Microscope                      |
| TES           | Thermal Energy Storage                            |

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