Improved heat recovery from paraffin-based phase change materials due to the presence of percolating graphene networks

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A B S T R A C T

Presently, engineers are unable to fully utilize the high thermal energy storage capacities of paraffin-based phase change materials (PCMs) in electronics cooling and waste heat recovery applications due to their inherently low thermal conductivities, which result in slow melting and solidification rates. In order to increase the paraffin's thermal conductivity, several groups have implanted nanoparticles within PCMs. Despite remarkable improvements in their thermal conductivities, however, it is expected that less thermal energy can be harvested during the nanocomposite PCM's solidification period due to the removal of some PCM mass in favor of the nanoparticles. In this study, a heat exchanger system is used to extract thermal energy that has been stored within paraffin nanocomposites embedded in a thermal containment unit (TCU). We find that the amount of thermal energy that can be harnessed from MWCNT, Al or TiO$_2$ nanocomposite PCMs (at 20 v.% concentrations) is approximately 15–17% lower than the amount that can be extracted from the base paraffin during its period of solidification, as expected. However, the amount of thermal energy that can be harnessed from paraffin in the presence of graphene nanoparticle networks (15 nm thickness, 15 μm diameter, at 20 v.%) is found to be nearly 11% greater than for the base paraffin. Based on these results, it is posited that the paraffin's alkane molecules are beginning to align across the face of the graphene nanoparticles, resulting in a more crystalline paraffin structure at the graphene–paraffin interface and a higher absolute phase change enthalpy. Consequently, it is expected that this work will open up new avenues of research for the creation of advanced nanocomposite PCMs with exceptionally high thermal conductivities and thermal energy storage capacities.

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1. Introduction

Paraffin-based phase change thermal energy storage materials (PCMs) are expected to play a critical role in thermal abatement in portable electronic devices [1] and in the development of sustainable solar energy conversion systems [2–4], building and vehicle thermal management systems [5,6] and passive heat switch materials for smart grid applications [7,8]. This is primarily due to the large phase change enthalpy exhibited by paraffins (>200 kJ/kg), which is an intrinsic material property that is governed by the energy necessary to break apart the bond structures between neighboring atoms within the paraffin. However, the performance of paraffin-based PCMs in the aforementioned applications is inhibited by their low thermal conductivities (on the order of 0.1 W/m K [9,10]). In the case of an application with unconstrained volume (as is the case in many solar–thermal

energy conversion systems), faster melt and solidification rates correspond with a greater utilization of the PCM volume. As a result, more thermal energy is stored per unit time. Thus, it is critical that the thermal conductivity of the PCM be improved in order to increase the amount of thermal energy that can be stored and harnessed during solid–liquid phase transitions.

Several types of nanoparticles have become intriguing candidates as filler materials to enhance the thermal conductivity of PCMs. Among those with the most promise are carbon nanotubes (CNTs), graphene and multi-layer graphene, which have intrinsic thermal conductivities measured to be within the range of 1000–6000 W/m K [11,12]. These high thermal conductivities are primarily the result of the strong sp^2 bonds formed between neighboring carbon atoms. A comprehensive survey of the thermal enhancement of paraffins due to the presence of various carbon-based nanoparticles is given in Table 1.

Table 1 reveals that the thermal conductivity enhancement of paraffin due to the presence of carbon-based nanoparticles varies widely from study to study. However, there is reasonable

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Nomenclature

α	thermal diffusivity	*Subscripts*	
d	diameter of cold plate channel	c	characteristic
Δh	absolute phase change enthalpy	f	fluid
Δp	thermal penetration depth	m	melt
ΔT	outlet and inlet cold plate temperature difference	ma	melt absolute
E	energy	mf	melt final
η	thermal conductivity enhancement	mi	melt initial
k	thermal conductivity	nc	nanocomposite
$\dot{m}$	cold plate channel mass flow rate	np	nanoparticle
Nu	Nusselt number	PCM	phase change material
φ	volume fraction	s	solidification
Q	heat shed into cold plate	sa	solidification absolute
r	TPS sensor radius	sf	solidification final
ρ	density	si	solidification initial
t	time		
T	temperature		

agreement that when the paraffin is in its solid phase, extremely high thermal conductivity enhancements are achievable (up to two orders of magnitude higher than the base paraffin [6]) due to the presence of carbon-based nanoparticles, particularly when graphene and multilayer graphene are used.

While most of the literature has focused on enhancing the thermal conductivity of paraffin-based PCMs, the amount of thermal energy that can be stored during the phase change is also based on their phase change enthalpies. Generally, the insertion of nanoparticles into a PCM reduces its apparent phase change enthalpy due to the displacement of some PCM mass [15,17–24]. For instance, Xiang and Drzal [15] find that the apparent phase change enthalpy of paraffin is reduced by roughly 7.4% in the presence of graphene nanoplatelets at an 8 wt.% loading level. Considering the error associated with the use of differential scanning calorimetry (DSC), the resulting decrease should be expected based on the mass displacement of PCM. However, in order to evaluate the effect of the nanoparticles on the thermal energy storage capacity of the PCM itself, one must measure the absolute phase change enthalpy (absolute phase change enthalpy = apparent phase change enthalpy ÷ PCM mass fraction) [24]. In this case, most studies find that the absolute phase change enthalpy of paraffin-based PCM's either: (1) does not change in the presence of nanoparticles or (2) is reduced in the presence of nanoparticles due to an increase in the disorder of neighboring alkane chains. Conversely, a handful of recent studies [24–26] suggest that the alkane molecules begin to align across the carbon atoms in carbon-based nanoparticles, resulting in a more crystalline structure at the nanoparticle–PCM interface and therefore an increase in the thermal energy storage

capacity of the PCM. These striking results are contrasted against the apparent phase change enthalpies that remain unaltered or reduced in Fig. 1 [22,27,28,24,29,30].

In Fig. 1, the ratio of the absolute phase change enthalpy for nanocomposite paraffin PCMs to the phase change enthalpy for the base paraffin PCMs used in various studies (denoted by ε) is given as a function of the volume fraction of embedded nanoparticles. A value of ε = 1 corresponds to the case when the nanoparticles have no effect on the absolute phase change enthalpy of the surrounding PCM. Even when normalized against the PCM mass, most results suggest that ε is below 1 and decreases as a function of increasing volume fraction of nanoparticles. This implies that the PCM structure at the interface is more amorphous than the base PCM. Conversely, some available data suggest that the absolute phase change enthalpy of a PCM increases in the presence of carbon-based nanoparticles (and, in particular, graphene-based nanoparticles), which implies that the PCM structure at the interface is more crystalline than the surrounding bulk PCM [31].

While increases in the absolute phase change enthalpy of graphene-based nanocomposite PCMs are observed in the literature [27,28,24], we have been able to find no studies that examine the effect of this increase on the amount of thermal energy that can be stored and recovered from a PCM in application. Moreover, it is unclear whether the absolute phase change enthalpy of a PCM can be increased enough to overcome a reduction in overall PCM volume due to the presence of nanoparticles. Thus, in this study we determine the effect of implanting a high volume fraction of graphene nanoparticles (20 v.%) on the absolute phase change enthalpy of a paraffin PCM (determined by differential scanning calorimetry,

Table 1
Literature survey of the thermal conductivity enhancement for paraffins achieved through the implantation of carbon-based nanoparticles.

Nanoparticle type	Nanoparticle thickness/diameter (nm)	Nanoparticle length (µm)	Concentration[b]	Thermal Conductivity Enhancement, η (%)[a]	Reference
MLG	35	~10	10 wt.%	640	[13]
MWCNT[c]	8–15	0.5–2	4 wt.%	19	[14]
MWCNT[c]	<10	5–15	4 wt.%	8	[14]
CNF[c]	150–200	10–30	4 wt.%	20	[14]
MLG[c]	4–20	5–10	4 wt.%	93	[14]
MLG	10	15	5 v.%	1,101	[15]
CNF	2–100	20	11.4 v.%	80	[9]
CNF[c]	2–100	20	11.4 v.%	30	[9]
MLG	8	0.5	20 wt.%	20,900	[6]
MLG	0.6–1.1	0.5–3	5 v.%	80	[16]

[a] ($\eta = k - k_m/K_m$), where k_m is the thermal conductivity of the base paraffin.
[b] wt.% = weight fraction, v.% = volume fraction.
[c] Represents a case when nanoparticles are embedded within a paraffin that is above the melt point (i.e. in its liquid phase).