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2020

Li, W. H., Lai-Iskandar, S., Tan, D., Simonini, L., Dudon, J.-P., Leong, F. N., ... Teo, E. H. T. (2020). Thermal conductivity enhancement and shape stabilization of phase-change materials using three-dimensional graphene and graphene powder. *Energy & Fuels*, 34(2), 2435-2444. doi:10.1021/acs.energyfuels.9b03013

<https://hdl.handle.net/10356/137112>

<https://doi.org/10.1021/acs.energyfuels.9b03013>

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Thermal conductivity enhancement and shape-stabilization of phase change materials using three-dimensional graphene and graphene powder.

Wen Hao Li ^{†, ‡, §}, S. Lai-Iskandar ^{†, §, ⊥}, Dunlin Tan ^{†, ₹}, Luca Simonini ^{†, §, □}, Jean-Paul Dudon [□],

Fei Ni Leong [⊥], Roland Yingjie Tay [‡], Siu Hon Tsang [‡], Sunil C. Joshi [‡], and E Hang Tong Teo ^{⊥, *}

[†] Thales Solutions Asia Pte. Ltd., 21 Changi North Rise, Singapore 498788, Singapore

[‡] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[§] Smart small satellite systems Thales in NTU S4TIN, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[⊥] School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

[₹] CNRS-International NTU Thales Research Alliance CINTRA UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Singapore 637553, Singapore

[□] Thales Alenia Space (TAS), 5 allée des Gabians – B.P. 99, 06156 Cannes-la-Bocca, France

[‡] Temasek Laboratories@NTU, 50 Nanyang Avenue, Singapore 639798, Singapore

KEYWORDS

Phase change materials; Nanomaterial additives; Thermal energy storage; Three-dimensional graphene; Thermal conductivity enhancement; Interconnected scaffold

ABSTRACT

The porous interconnected structure of three-dimensional graphene (3DC) combines the excellent thermal conductivity of graphene with an interconnected architecture, thereby creating a thermal network within composites infused with 3DC. In this study, improvements in thermal conductivity, latent heat of fusion (H_f) and shape-stability of paraffin were compared between paraffin phase change materials (PCM) infused with 3DC and with discrete graphene flakes (GP) at the same filler loading to quantify the advantage of the interconnected structure. Paraffin infused with a 3DC of higher bulk density (3DC_H) was also compared to identify the effects of increasing filler density. Thermal conductivity of the PCM composites was measured using the hot-disk method and shape-stabilization was compared through thermal cycling in an environment chamber. We found that the interconnected architecture of 3DC improved the properties of the paraffin matrix in multiple ways. 3DC improved the solidification process for paraffin with heterogeneous nucleation, helped to retain the shape of the PCM composite over thermal cycling, reduced void formation within the PCM and induced a large increase in thermal conductivity at 7.4 times and 5.2 times that of neat paraffin for composites infused with 3DC_H and regular 3DC respectively, with only a small trade-off in H_f .

1. INTRODUCTION

Passive thermal management systems (TMS) using phase change materials (PCMs) has wide applications, such as PCM modules and PCM heat sinks used on space satellites, mobile electronic devices and buildings¹⁻⁸. PCM absorbs a large amount of latent heat (H_f) when it melts and releases the latent heat during the solidification phase. For small satellites, where the power and mass budget are very tight, passive (no power input required) TMS becomes an attractive solution. Furthermore, the periodic temperature fluctuation experienced by a satellite during orbit helps to reset the PCM for its next load. Paraffin wax based PCM is one candidate for passive TMS for space application due to its high energy density, chemical and thermal-cycling stability, non-corrosiveness, self-nucleating behaviour and low outgassing⁹⁻¹². However, paraffin has low intrinsic thermal conductivity which limits the speed of heat spread and hence the rate of charging and discharging of latent heat. To overcome this limitation, common strategies to enhance the thermal conductivity of PCM includes infusion of graphene or metallic fillers¹³⁻²². Paraffin also contracts 9 -14 % during solidification²³ which distorts its shape and hence requires additional design consideration in its packaging to include a ullage space and means to retain thermal contact with the container walls. Melt-induced pressure spike can occur within the packaging due to a combined effect of microgravity and paraffin density change in space. Therefore high melt pressures resulting in structural deformation often occur with PCM heat sinks undergoing cyclic operations^{5, 24}. Current solutions are based on including carbon graphite fibres to shape stabilize the liquid paraffin⁵. One other important requisite of a PCM composites for space application is its retention of the initial material properties after multiple phase change cycles that the PCM composites would experience during its mission lifetime¹².

Graphene allotropes have been widely studied as suitable high thermal conductivity fillers for PCM, largely due its surface compatibility with PCMs, its high intrinsic thermal conductivity (1000-6000 W/mK)²⁵, and a relatively low density as compared to metal fillers. Some forms of graphene fillers commonly applied to PCMs are discrete graphene fillers (GP) such as graphene nanoplatelets (GNP) and carbon nanotubes (CNT)²⁶⁻²⁸, and self-assembled porous three dimensional structures such as CNT sponge²⁹ and expanded graphite^{18, 30-31}. More recently, three-dimensional graphene (3DC)³², a porous graphene interconnected skeleton, synthesized using template assisted chemical vapour deposition (CVD)³³, has been studied as a scaffold for PCM¹⁵. 3DC synthesized using the CVD method differs from other self-assembled porous carbon-based structures mainly because 3DC is nearly defect-free at the surface of the graphene and consist of intrinsically interconnected graphene network with low junction resistance³⁴, therefore resulting in a smaller phonon scattering at the junctions and better thermal transport properties. Compared to 3D graphene synthesized by the self-assembled method, 3DC has a lower bulk density and higher open porosity^{15, 18-19}, therefore potentially displacing less of the PCM matrix and retaining the large H_f of the PCM composite, hence maximising the fill efficiency of the resulting PCM composite. However a known issue in the application of 3DC is its poor bulk mechanical strength and brittle plastic deformation³⁵. Due to these properties, the interconnected structure of the 3DC may be damaged during handling or the infusion process, therefore drastically reducing the thermal transport properties of the resulting PCM composite.

The thermal conductivity improvement of PCM with 3DC and GP fillers (3DCPCM and GPPCM) have been achieved in different studies and thereafter compared across these studies^{15, 36-38}. It was found that the magnitude of enhancement varies widely from study to study. The methods to obtain the thermal conductivity of samples were also different across these studies, thereby

creating more potential errors in the results. Furthermore, there was no study to systematically compare the scale of improvement caused by the interconnected architecture of 3DC over discrete fillers such as GP.

In this study, we consolidated various experimental factors, such as filler ratio, type of PCM used and thermal conductivity measurement method, and conducted a systematic comparison study between 3DCPCM and GPPCM. The results of this study will enable a quantitative benchmarking of 3DC fillers with GP fillers in terms of thermal conductivity enhancement and its efficiency in maximizing the energy density of the PCM composite. The physical behaviour of 3DCPCM and GPPCM over initial thermal cycling was also studied to determine the shape-stability of each composite. In addition, this study introduces a scalable method to increase the bulk density of 3DC with little compromise to its quality.

2. EXPERIMENTAL METHODS

2.1 MATERIALS PREPARATION

The paraffin used in this study is RT35HC, from Rubitherm, with a melting temperature centred at 35 °C. This paraffin was used as a reference sample for the studies reported.

3DC was fabricated using Ni catalyst template-assisted CVD method³³. A Ni foam with 60 PPI and 95% porosity was used as template. 3DC of two different densities were fabricated by changing the number of growth runs and precursor deposition time. Low density 3DC, denoted as 3DC_L, was fabricated over a single growth run lasting 90 minutes, with a methane precursor flow rate of 70 sccm. 3DC of high density, denoted as 3DC_H, was fabricated by repeating the 90 minutes CVD growth run 5 times on the same Ni foam. Multiple CVD growth was expected to increase the graphene content in the Ni foam, since after each CVD run, the carbon atoms dissolved in Ni at elevated temperature would precipitate as graphene during rapid cooling of Ni³⁹ which does not

redissolve at elevated temperature. This allows new carbon atoms to diffuse into Ni during the next CVD run and precipitate onto the existing graphene present, hence increasing the graphene content. The Ni foams with graphene (Ni-G) was soaked in HCl acid maintained at 85 °C for 2 days to fully etch away the Ni, leaving free-standing 3DC. Then the 3DC foams were washed multiple times in deionised water and dried over a hotplate for 1 day. The 3DC_H and 3DC_L samples have a bulk density of 0.0747 g/cm³ and 0.0128 g/cm³ respectively, measured by using the mass of the entire sample divided by the cuboid volume enclosed by the Ni template.

3DCPCM composites were prepared by fully immersing 3DC foam in an aluminium mould filled with liquid paraffin wax and allowing the composite to solidify at room temperature. The resulting composite was released from the mould and the excess PCM was removed. The 3DCPCM samples were cut and sanded down to the desired dimension. The resulting filler loading of 3DCPCM prepared using 3DC_H and 3DC_L was 9 wt.%, denoted as 3DC_HPCM, and 1.5 wt.%, denoted as 3DC_LPCM, respectively. The 3DCPCM samples were observed to have retained the thickness of its respective 3DC foam.

Initially, a 3DC with an even lower bulk density of 0.0083 g/cm³ was fabricated, however the 3DC was observed to collapse to 70% of its original thickness after infusion with paraffin, which indicates a compromise to the 3DC structure. Hence, we determined that the bulk density of 3DC_L, at 0.0128 g/cm³, was close to the lower limits to produce 3DCPCM composites without structural damage during infusion.

GP was fabricated using a portion of 3DC_L sample. 3DC_L was grounded in an agate mortar pestle. The grounded GP was weighed and dispersed in acetone using an ultrasonic water bath (Elmasonic P30H), maintained at 50 °C, over 1 hour. A specific weight of liquid paraffin was added into the mixture such that the weight of GP makes up 1.5 wt.% of the combined weight of GP and PCM,

which is the same filler loading as the 3DC_LPCM samples. The mixture of graphene, acetone and PCM was further sonicated for 8 hours. The mixture was then poured into a beaker heated to 100 °C on a hotplate and stirred with a magnetic stirrer to evaporate the remaining acetone from the solution. The mixture of dispersed graphene powder and PCM was poured into an Al mould and left to solidify completely. The resulting sample was cut and sanded down to the desired dimensions. Figure 1 shows a schematic of the preparation process of GPPCM.

Figure 1. Schematic of the preparation of GPPCM. a-c) 3DC foam was grounded to GP and added to acetone solution for initial sonication. d) PCM was added into the mixture and mixture was further sonicated for 8 hours. e) Mixture is stirred in a beaker at 100°C to evaporate the acetone. f) PCM with suspended GP was poured into an Al mold to solidify fully at room temperature. Sample was extracted and sanded to obtain g) GPPCM.

2.2 CHARACTERIZATION

The morphologies of 3DC_H, 3DC_L and GP was characterised with a JEOL JSM IT100 scanning electron microscope (SEM). Raman spectroscopy was observed using a WITec UHTS 300 Raman Spectrometer at an excitation wavelength of 532nm. Transmission electron microscopy (TEM) was used to characterise the lattice structure and the crystalline structure of exfoliated flakes of graphene on the 3DC_H and 3DC_L samples. Differential scanning calorimeter (DSC) measurements was done on NETZSCH STA 449 F3 differential calorimeter. Samples were sealed in standard aluminium pans and heated with a heating rate of 10 K min⁻¹. Thermal conductivity measurement was

conducted on Hot Disk TPS 3500, according to ISO 22007-2. Thermal cycling was conducted in Thermotron SE300-6-6 environmental temperature test chamber. The physical characteristics of the samples before and after the thermal cycling and the post-experiment cross-section of each sample was recorded with a camera.

3. RESULTS AND DISCUSSION

3.1 MORPHOLOGY

Figure 2 shows the morphology of 3DC and GP captured using SEM. The SEM image in Figure 2a-d shows both 3DC_H and 3DC_L consist of open pores and continuous interconnected structure. The open pores would allow liquid PCM to flow freely throughout the 3DC network during infusion resulting in a higher fill fraction as compared to a scaffold with some closed pores. The cross-section of fractured 3DC struts in Figure 2b and d show the struts are hollow and have a distinct inner and outer layer. The reason for two macro layers of strut walls can be inferred from the original process to manufacture the Ni foam via CVD on a porous polyurethane (PU) template⁴⁰ followed by sintering to remove the PU. This process produces Ni scaffold with hollow Ni struts. Subsequently, during the CVD synthesis of 3DC, the carbon atoms dissolved in Ni would have been deposited and precipitated⁴¹ on both the inner and outer surface of the hollow Ni strut, thus the distinct inner and outer macro layer of graphene. Figure 3 shows a schematic of the synthesis process of 3DC from PU. During subsequent CVD runs, this mechanism allows further dissolution and precipitation of carbon atoms in Ni, hence making it a viable method to perpetually increase the graphene content in 3DC. Comparing Figure 2b and d, the strut walls of 3DC_H is significantly thicker, measuring 6 – 10 μm , as compared to the strut walls of 3DC_L, which measures 1 – 2 μm . This is an indication that 3DC_H has a higher deposition of graphene than 3DC_L. The SEM image of GP, Figure 2e, shows distinctly separated flakes of graphene less than 200 μm in diameter.

Figure 2. SEM image of (a-b) 3DCL and (c-d) 3DCH, showing interconnected struts and open pores, (e) GP, showing distinctly separated flakes.

Figure 3. Strut cross-section schematic of the synthesis process of 3DC from polyurethane (PU). (a) PU, (b) PU coated with Ni after CVD, (c) Ni shell remains after PU is removed via sintering, (d) Graphene coats Ni on both inner and outer surface after CVD. (e) 3DC strut with distinct outer and inner layer after removal of Ni via acid etching.

Figure 4a shows the Raman spectra for 3DC_H, 3DC_L, and GP. A small D peak at 1350 cm⁻¹ is observed for GP, indicating the presence of crystal defects⁴²⁻⁴³. The D peak for both 3DC_H and 3DC_L was much less observable, indicating minor crystalline defects. The crystal defects in GP were likely to be caused by ultrasonication during the fabrication process of GP which accentuated the minor crystalline defects in 3DC_L. The intensity ratio of G (1580 cm⁻¹) peak and 2D (2690 cm⁻¹) peak for all 3 samples are consistent with multi-layer graphene. The results indicate that samples of 3DC_H and 3DC_L consist of high quality graphene.

Figure 4b-e shows TEM images for samples of 3DC_H and 3DC_L. The graphene flakes that were derived from 3DC_H were, in general, thicker than that from 3DC_L as observed by the darker contrast in their bright-field images (Figure 4b and d). The selected area electron diffraction (SAED) on both samples (inset of Figure 4b and 4d) shows 6 diffracted spots which confirms the hexagonal lattice structure. Figure 4c and e shows the high-resolution images taken at the edge of the flake. The interlayer spacing for both samples are measured to be about 0.35 nm, which is consistent with that of multi-layer graphene. From the TEM image, the thickness of the 3DC_L flake is ~24 nm. However, for the 3DC_H flake, it is too thick to be measured by high resolution imaging. Using the weight ratio difference between the 3DC_H and 3DC_L, the thickness of the 3DC_H is ~140 nm. Both the Raman and TEM characterization results indicate that apart from the difference in thickness, the crystallinity in both 3DC_H and 3DC_L are identical. The results also verify that multiple CVD growths will produce 3DC samples with high quality graphene.

Figure 4. (a) Raman spectroscopy of 3DC_H, 3DC_L, and GP, (b) & (d) Image of exfoliated graphene flakes and inset shows the selected area electron diffraction (SAED) of 3DC_H (b) and 3DC_L (d). SAED of both samples confirms the hexagonal lattice structure of the flakes. (c) & (e) Interlayer spacing of the flakes taken from the edge of the flake from sample shows consistency with multilayer graphene.

3.2 THERMAL CYCLING CHARACTERISTICS

The aim of this experiment was to study the physical characteristics of 3DCPCM and GPPCM over a few thermal cycles, in order to compare shape stabilizing effects of interconnected and discrete fillers. In this experiment, 3DC_LPCM, GPPCM and neat paraffin samples were used for comparison.

9.65 ± 0.01 g of each sample were prepared and placed in similar glass trays with a thermocouple attached to the inner walls. The samples were thermally cycled through their melting points over nine complete phase change cycles. A schematic of the set-up is shown in Figure 5a. The environmental test chamber was first cooled and held at 0 °C for 20 minutes. After which the chamber was rapidly heated from 0 °C to 70 °C over 5 minutes and held for 20 minutes until the samples of 3DC_LPCM, GPPCM and neat paraffin has fully melted. The chamber was then rapidly cooled to 0 °C over 5 minutes and held for 20 minutes to ensure that all samples had fully solidified. Figure 5a shows a schematic of the test set-up. Given the similar mass and exposed surface area, the sample with the highest thermal conductivity would reach the steady state temperature at the fastest rate. Since 20 minutes may not be sufficient for samples to reach steady state temperature, the sample with highest conductivity will attain the highest and lowest temperatures per cycle.

3.2.1 TEMPERATURE PROFILE

The temperature profiles of each sample for all nine cycles were recorded in Figure S1. Figure 5b shows the temperature profile of the first and last cycle of all three samples and of the thermal chamber. There is a smaller decrease in gradient at the inflection point for 3DC_LPCM and GPPCM as compared to paraffin wax. At the points of peak temperature, it was consistent that 3DC_LPCM

has the highest peak temperature, followed by GPPCM and then paraffin wax. A similar trend is observed at the points of trough temperature, where 3DC_LPCM consistently hit the lowest temperature, followed by GPPCM and then paraffin wax. This is indicative that 3DC_LPCM and GPPCM has a faster response with the temperature change and hence a higher thermal conductivity than neat paraffin. In the first cycle, the temperature profile of GPPCM followed closely to that of 3DC_LPCM. The largest difference between the temperature profiles of 3DC_LPCM and GPPCM was 2.4 °C on heating and 1.2 °C on cooling, with an average temperature difference of only 0.94 °C. However, for the last 3 cycles, some fluctuations in temperature was observed after the GPPCM was heated beyond its melting temperature. In addition, the temperature profile of GPPCM also deviated further from 3DC_LPCM, with the largest temperature difference of 5.6 °C on heating and 3.4 °C on cooling, with an average temperature difference of 2.0 °C. The temperature fluctuations in paraffin sample was attributed to the irregular melting of paraffin wax. We observed that paraffin sample was a melting solid block surrounded by liquid paraffin during the period of temperature fluctuations. Due to the low thermal conductivity of paraffin wax, there will be a large temperature gradient within the paraffin sample, which could result in convection currents within the sample. The presence of convection currents could mix the cooler melting paraffin at the solid-liquid front with the warmer surrounding liquid paraffin, which would be recorded as temperature fluctuation. This explanation is substantiated by the fact that there is no temperature fluctuation when the paraffin is solidifying, since convection does not occur in solids. Air bubbles were also observed to escape the melting solid paraffin during this period, which cause the solid paraffin to move randomly. This movement would also cause mixing of the paraffin resulting in temperature fluctuation.

The small temperature fluctuations in last three cycles of GPPCM is attributed to the phase separation of GP fillers with PCM, thereby causing the melting process of GPPCM to become more

similar to the paraffin sample. For 3DC_LPCM, the porous 3DC network would have hindered the convection currents, thus resulting in a smooth temperature rise. Furthermore, the high bulk thermal conductivity of 3DC_LPCM would ensure a smaller thermal gradient within the sample and hence a more uniform melting.

3.2.2 PHYSICAL BEHAVIOUR OVER PHASE CHANGE

To investigate the physical behaviours over phase change, the physical shape of the samples was compared before and after nine phase change cycles. The cross-section of each sample was also examined after the experiment.

During the solidification procedure in the test, we made observations on the neat paraffin sample that would be a concern for PCM containment. Solidification first occurred on walls of the sample tray and a decrease in the liquid level was observed. Subsequently, nucleation occurred at the top surface of the paraffin. After solidification is complete, there was a noticeable decrease in thickness

of the sample from the container walls towards the centre was noted, forming a depressed top surface as seen in Figure 6a. The cross-sectional view of the paraffin sample, Figure 6a, revealed a single large void at the core. The sample measures 10.2 mm at its largest thickness at its circumference, and only 7.3 mm at the smallest thickness. The depressed top surface and large void formation would be a concern during the material preparation process as this phenomenon creates a gap between the container walls and PCM, therefore increasing the thermal boundary conditions within the system and decreasing the response time of the TMS. The reason for the depressed top is attributed to the combined effect of the reduction in density of paraffin sample during solidification, which is a material property of paraffin wax, working in tandem with the solidification process of the paraffin sample in the glass tray. A schematic of the cross-sectional view of paraffin solidification process in the glass tray is shown in Figure 6e. RT35HC contracts by 14 % in volume during solidification⁴⁴. As the paraffin sample was cooled below its melting temperature, nucleation first occurred on the walls of the glass tray in contact with the paraffin due to the lower energy barrier for nucleation. At this solidification stage, the total volume of paraffin decreased and hence the drop in the liquid paraffin level. The top surface of the paraffin sample exposed to air started to nucleate probably due to the increase in cooling by convection of cold surround air. While the top solid layer of paraffin is thin, the reduction in volume of paraffin was compensated by the thin top layer collapsing and decreasing in height. However, when a thick enough top solid layer is formed, the outer solid shell of the paraffin sample becomes fixed, sealing the liquid core in the solid shell with the depressed top surface. The large void was formed when the liquid core had solidified and shrunk within the sealed solid shell without a mean to compensate for the decrease in volume. In application, the depressed top surface phenomenon of paraffin would reduce the effective contact area with its container, and hence slow the rate of heat transfer when PCM is in the solid state. This depressed

top was also present in GPPCM sample after the 9 cycles but was not present in the 3DC_LPCM sample.

GPPCM had the most noticeable physical difference amongst the samples. Initially, the GP was well distributed within the GPPCM as shown in Figure 6c. After thermal cycling, a distinct phase separation of fillers and PCM could be observed in GPPCM. The graphene particles have settled at the base of the sample, leaving a distinct white paraffin layer at the top of the sample, as seen in Figure 6d. The settling of the GP at the base of the sample suggests that the GP is denser than the paraffin wax, and thus sinking due to density difference. The phase separation would have occurred when GPPCM is in the liquid state, where the GP particles could freely move. The suspended GP agglomerate due to Van der Waal's forces of attraction between GP particles, and the denser GP particles settle due to gravity. For space applications, it could be argued that there is no gravity experienced in space, however all systems will have to be tested terrestrially over multiple cycles before employment for space, therefore the effects of thermal cycling on the ground is still relevant. During the terrestrial testing, the GP would have settled and change the properties of GPPCM already and therefore GPPCM is unreliable for space applications.

The 3DC_LPCM sample was cut at multiple points to reveal the cross-sections. Small voids were observed at random pores of 3DC_LPCM as shown in Figure 6b. The voids are expected to form after rapid thermal cycling as a result of the change in density of paraffin wax over phase change. During the cooling of the samples, nucleation was first observed on the struts of the 3DC. This shows that the 3DC skeleton provided multiple low energy barrier surfaces for paraffin to nucleate heterogeneously. The interconnected open pores in 3DC allow liquid paraffin to flow freely to compensate the decrease in volume during solidification. This happens until the paraffin in most of the pores is fully solidified, effectively enclosing the remaining liquid paraffin within the

corresponding pores. Voids form when this remaining paraffin solidifies and contracts within the closed pores. A schematic of paraffin solidification at the pores of 3DC to depict this phenomenon is shown in Figure 6f. Unlike neat paraffin, the voids in 3DC_LPCM are delocalised and dispersed, and hence the mechanical strength and high bulk thermal conductivity of the sample would be retained even after multiple phase change cycles. This interaction shows surface compatibility of 3DC with the paraffin, and that 3DC stabilizes the shape of the PCM, hence 3DC infused PCM will retain thermal contact with its container. Such shape stabilizing characteristics would also delocalise the high melt pressures experienced during application, hence reducing the structural deformation on the PCM container. This makes 3DC inclusion a potential solution for operating PCM in microgravity environments such as applications in space. Although there would be vacuum in the space environment, current space applications require PCM to be hermetically sealed in its packaging to prevent leakage that could contaminate other subsystems. Therefore the current results would be relevant for space PCM packaging sealed at atmospheric pressure. For space qualification, vacuum thermal cycling with PCM in its final packaging should be conducted in future studies.

The 3DC_LPCM sample pieces were subsequently melted to reveal that the 3DC remained free standing in its pre-infusion shape after the thermal cycling. This is indicative of that, at the bulk density of 0.0128 g/cm³, 3DC structure could withstand the stresses experienced during infusion and multiple phase change cycles and remain intact and interconnected.

3.3 THERMAL CONDUCTIVITY MEASUREMENT

Thermal conductivity measurements of the samples are shown in Table 1. The thermal conductivity of paraffin was measured 0.31 W/mK, in agreement with the commercial datasheet⁴⁴. Thermal conductivity of 3DC_LPCM was measured to be 1.61 W/mK, which is more than 5 times that of neat paraffin. On the other hand, the thermal conductivity of GPPCM was measured to be 0.40 W/mK at the same filler loading as 3DC_LPCM, only about 1.3 times that of neat paraffin. This significant difference in thermal conductivity measurement at the same filler loading confirms that the interconnected struts of 3DC provide a reliable thermal network and significantly improve the efficiency of thermal conductivity improvement as compared to discrete fillers of similar quality and filler ratio. Thermal conductivity of 3DC_HPCM was measured to be 2.30 W/mK, about 7.4 times that of neat paraffin and a significant further improvement over 3DC_LPCM. The further improvement in thermal conductivity indicated that the thicker strut walls in 3DC_H contributes to improvement in thermal conductivity of its composite. This results show that the thermal conductivity of the 3DCPCM composites can be further improved by increasing the bulk density of the 3DC scaffold used.

3.4 LATENT HEAT OF FUSION

The H_f measurement of the samples are shown in Table 1. The H_f of paraffin wax was measured to be 226.8 kJ/kg, which is similar to that reported in the datasheet⁴⁴. There was negligible changes in H_f after the infusion of fillers in both GPPCM and 3DC_LPCM. A 7% drop in H_f was measured in 3DC_HPCM. The absolute H_f per unit mass of paraffin wax have been calculated in previous works^{16, 20, 29} where carbon based fillers such as carbon nanotubes and discrete graphene was used as fillers. The absolute H_f of paraffin in these works were observed to have exceed that of neat paraffin at low loadings. Such phenomenon was attributed to the C-H $\cdots\pi$ bond interactions²⁹. In this study, the

absolute H_f was calculated to be 104%, 104% and 102% that of neat paraffin for GPPCM, 3DC_LPCM and 3DC_HPCM samples respectively. However these results fall within the uncertainty of the H_f measurements, hence the improvement is too small to conclusively show the interactions between graphene and paraffin. The small difference in the H_f of GPPCM and 3DC_LPCM is a confirmation that the two samples have identical graphene filler loading.

The combined results of thermal conductivity and H_f of the samples show that at low loading, the inclusion of 3DC scaffold increase the thermal conductivity of the composite by more than 5-folds, while having negligible changes in its energy density as shown by the H_f measurements. Furthermore, the thermal conductivity of 3DCPCM composite can be further increased by infusing 3DC scaffold with a higher bulk density, thereby making the thermal conductivity of 3DCPCM composite to be tuneable. The trade-off would be a minor reduction in H_f , at a similar magnitude as compared to the filler loading.

Table 1. Thermal conductivity and latent heat of fusion (H_f) measurements of the samples.

Sample	Filler loading	Thermal		Latent Heat			
		conductivity, κ (W/mK)	$\frac{\kappa}{\kappa_{paraffin}}$	of Fusion, H_f (kJ/kg)	$\frac{H_f}{H_{f,paraffin}}$	$H_{f,absolute}$ (kJ/kg)	$\frac{H_{f,absolute}}{H_{f,paraffin}}$
Paraffin	0.0	0.31 [$\pm$ 0.02]	1.0	226.8	1.00	226.8	1.00
GPPCM	1.5 wt.%	0.40 [$\pm$ 0.02]	1.3	232.2	1.02	235.7	1.04
3DC _L PCM	1.5 wt.%	1.61 [$\pm$ 0.08]	5.2	232.3	1.02	235.8	1.04
3DC _H PCM	9 wt.%	2.30 [$\pm$ 0.12]	7.4	210.1	0.93	230.9	1.02

4. CONCLUSIONS

High quality 3DC scaffolds was synthesized using templated assisted CVD growth. The precursor deposition time and number of growth cycles was increased to produce 3DC foam of a higher bulk

density and with similarly high graphene quality. The thermal response and shape-stability effects over multiple phase change, as well as thermal conductivity and H_f of paraffin PCM composites infused with 3DC and GP were compared. The 3DC scaffold retains the shape of PCM composite through multiple phase changes, therefore helps retain thermal contact and reduce melt pressures within the PCM container, making it a potential solution for operating the PCM in microgravity environments. In sharp contrast, the thermal properties of GPPCM changed after a few melt freeze cycles due to the settling of GP, therefore the thermal performance and physical behaviours, such as void formation, of GPPCM became similar to that of neat paraffin wax, hence making GPPCM less reliable than 3DCPCM for applications that requires thermal cycling. Furthermore, the interconnected structure of 3DC makes use of the high intrinsic thermal conductivity of graphene more efficiently as compared to GP of identical quality and filler loading, as shown by the larger thermal conductivity improvement of 5.2 times of neat paraffin in 3DC_LPCM as compared to 1.3 times in GPPCM. These results indicate that 3DC is a superior substitute to GP filler variations. The thermal conductivity of PCM composite further increased significantly to 7.4 times of neat paraffin when 3DC_H of a higher bulk density was infused. The H_f increased by 2% for GPPCM and 3DC_LPCM, and only decreased 7% for 3DC_HPCM. This shows that the thermal conductivity of 3DCPCM composites can be tuneable by infusing 3DC of a different bulk density, with a minor trade off in H_f . A scalable method to increase the bulk density of 3DC was introduced by simply repeating the growth process on the same Ni template to increase the graphene deposition. Such a method was shown to increase the number of layers of graphene on the 3DC strut walls, and retain crystallinity of the graphene in 3DC.

ASSOCIATED CONTENT

Supporting Information

Temperature profile of all thermal cycles.

ACKNOWLEDGEMENTS

This research is funded by Thales Alenia Space S.A., Thales Alenia Space S.p.A and Thales Solutions Asia Pte Ltd, under the Economic Development Board, Industrial Postgraduate Programme, with Nanyang Technological University, Singapore.

REFERENCES

1. Alexander Chin, R. C., Lori Brooks, Ryan Nugent, Dr. Jorgi Puig-Suari, Standardization Promotes Flexibility: A Review of CubeSats' Success. In *6th Responsive Space Conference*, AIAA, Ed. Los Angeles, CA, 2008.
2. Akeiber, H.; Nejat, P.; Majid, M. Z. A.; Wahid, M. A.; Jomehzadeh, F.; Zeynali Famileh, I.; Calautit, J. K.; Hughes, B. R.; Zaki, S. A., A review on phase change material (PCM) for sustainable passive cooling in building envelopes. *Renewable & Sustainable Energy Reviews* **2016**, *60*, 1470-1497.
3. Tomizawa, Y.; Sasaki, K.; Kuroda, A.; Takeda, R.; Kaito, Y., Experimental and numerical study on phase change material (PCM) for thermal management of mobile devices. *Applied Thermal Engineering* **2016**, *98*, 320-329.
4. Choi, M. K. In *Paraffin Phase Change Material for Maintaining Temperature Stability of IceCube Type of CubeSats in LEO*, 13th International Energy Conversion Engineering Conference, 27-29 July 2015, Reston, VA, USA, AIAA - American Institute of Aeronautics and Astronautics: Reston, VA, USA, 2015; p 22 pp.
5. Quinn, G.; Stieber, J.; Sheth, R.; Ahlstrom, T., Phase Change Material Heat Sink for an ISS Flight Experiment. In *45th International Conference on Environmental Systems*, Bellevue, Washington, 2015.
6. Fokaides, P. A.; Kylili, A.; Kalogirou, S. A., Phase change materials (PCMs) integrated into transparent building elements: a review. *Materials for Renewable and Sustainable Energy* **2015**, *4* (2), 6.
7. Boushon, K. E. Thermal analysis and control of small satellites in low Earth orbit. Missouri University of Science and Technology, Missouri University of Science and Technology, 2018.
8. Collette, J. P.; Rochus, P.; Peyrou-Lauga, R.; Pin, O.; Nutal, N.; Larnicol, M.; Crahay, J. In *Phase Change Material Device for Spacecraft Thermal Control*, 62nd International Astronautical Congress 2011, IAC 2011, October 3, 2011 - October 7, 2011, Cape Town, South africa, International Astronautical Federation, IAF: Cape Town, South africa, 2011; pp 6020-6031.
9. Ferrer, G.; Solé, A.; Barreneche, C.; Martorell, I.; Cabeza, L. F., Review on the methodology used in thermal stability characterization of phase change materials. *Renewable and Sustainable Energy Reviews* **2015**, *50*, 665-685.
10. Nazir, H.; Batool, M.; Bolivar Osorio, F. J.; Isaza-Ruiz, M.; Xu, X.; Vignarooban, K.; Phelan, P.; Inamuddin; Kannan, A. M., Recent developments in phase change materials for energy storage applications: A review. *International Journal of Heat and Mass Transfer* **2019**, *129*, 491-523.

11. Allahbakhsh, A.; Arjmand, M., Graphene-based Phase Change Composites for Energy Harvesting and Storage: State of the Art and Future Prospects. *Carbon* **2019**.
12. Hale, D. V.; Hoover, M. J.; Oneill, M. J. *Phase-change materials handbook*; NASA-CR-61363, LMSC/HREC-D225138; NASA Technical Reports Server, 1971.
13. Babaei, H.; Koblinski, P.; Khodadadi, J. M., Improvement in thermal conductivity of paraffin by adding high aspect-ratio carbon-based nano-fillers. *Physics Letters A* **2013**, 377 (19–20), 1358-1361.
14. Fang, X.; Fan, L.-W.; Ding, Q.; Yao, X.-L.; Wu, Y.-Y.; Hou, J.-F.; Wang, X.; Yu, Z.-T.; Cheng, G.-H.; Hu, Y.-C., Thermal energy storage performance of paraffin-based composite phase change materials filled with hexagonal boron nitride nanosheets. *Energy Conversion and Management* **2014**, 80, 103-109.
15. Ji, H.; Sellan, D. P.; Pettes, M. T.; Kong, X.; Ji, J.; Shi, L.; Ruoff, R. S., Enhanced thermal conductivity of phase change materials with ultrathin-graphite foams for thermal energy storage. *Energy & Environmental Science* **2014**, 7 (3), 1185-1192.
16. Warzoha, R. J.; Fleischer, A. S., Improved heat recovery from paraffin-based phase change materials due to the presence of percolating graphene networks. *International Journal of Heat and Mass Transfer* **2014**, 79, 314-323.
17. Xiao, X.; Zhang, P.; Li, M., Effective thermal conductivity of open-cell metal foams impregnated with pure paraffin for latent heat storage. *International Journal of Thermal Sciences* **2014**, 81, 94-105.
18. Guo, X.; Zhang, S.; Cao, J., An energy-efficient composite by using expanded graphite stabilized paraffin as phase change material. *Composites Part A: Applied Science and Manufacturing* **2018**, 107, 83-93.
19. Zhang, D.; Chen, M.; Wu, S.; Riara, M.; Wan, J.; Li, Y., Thermal and rheological performance of asphalt binders modified with expanded graphite/polyethylene glycol composite phase change material (EP-CPCM). *Construction and Building Materials* **2019**, 194, 83-91.
20. Wang, J.; Jia, X.; Atinafu, D. G.; Wang, M.; Wang, G.; Lu, Y., Synthesis of “graphene-like” mesoporous carbons for shape-stabilized phase change materials with high loading capacity and improved latent heat. *Journal of Materials Chemistry A* **2017**, 5 (46), 24321-24328.
21. Zhao, W.; France, D. M.; Yu, W.; Kim, T.; Singh, D., Phase change material with graphite foam for applications in high-temperature latent heat storage systems of concentrated solar power plants. *Renewable Energy* **2014**, 69, 134-146.
22. Ramakrishnan, S.; Wang, X.; Sanjayan, J.; Wilson, J., Heat Transfer Performance Enhancement of Paraffin/Expanded Perlite Phase Change Composites with Graphene Nanoplatelets. *Energy Procedia* **2017**, 105, 4866-4871.
23. I. Chemical, Crystallographical and Physical Properties of Liquid Paraffins and Paraffin Waxes. In *Developments in Petroleum Science*, Freund, M.; Csikós, R.; Keszthelyi, S.; Mózes, G. Y., Eds. Elsevier: 1982; Vol. 14, pp 13-140.
24. Gregory Quinn, E. H., Ryan Stephan *Phase Change Material Trade Study: a Comparison between Wax and Water for Manned Spacecraft*.
25. Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E. P.; Nika, D. L.; Balandin, A. A.; Bao, W.; Miao, F.; Lau, C. N., Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. *Applied Physics Letters* **2008**, 92 (15), 151911.
26. Shi, J.-N.; Ger, M.-D.; Liu, Y.-M.; Fan, Y.-C.; Wen, N.-T.; Lin, C.-K.; Pu, N.-W., Improving the thermal conductivity and shape-stabilization of phase change materials using nanographite additives. *Carbon* **2013**, 51, 365-372.

27. Yavari, F.; Fard, H. R.; Pashayi, K.; Rafiee, M. A.; Zamiri, A.; Yu, Z.; Ozisik, R.; Borca-Tasciuc, T.; Koratkar, N., Enhanced Thermal Conductivity in a Nanostructured Phase Change Composite due to Low Concentration Graphene Additives. *The Journal of Physical Chemistry C* **2011**, *115* (17), 8753-8758.
28. Chen, J.; Walther, J. H.; Koumoutsakos, P., Covalently Bonded Graphene–Carbon Nanotube Hybrid for High-Performance Thermal Interfaces. *Advanced Functional Materials* **2015**, *25* (48), 7539-7545.
29. Chen, L.; Zou, R.; Xia, W.; Liu, Z.; Shang, Y.; Zhu, J.; Wang, Y.; Lin, J.; Xia, D.; Cao, A., Electro- and Photodriven Phase Change Composites Based on Wax-Infiltrated Carbon Nanotube Sponges. *ACS Nano* **2012**, *6* (12), 10884-10892.
30. Zhang, P.; Hu, Y.; Song, L.; Ni, J.; Xing, W.; Wang, J., Effect of expanded graphite on properties of high-density polyethylene/paraffin composite with intumescent flame retardant as a shape-stabilized phase change material. *Solar Energy Materials and Solar Cells* **2010**, *94* (2), 360-365.
31. Canseco, V.; Anguy, Y.; Roa, J. J.; Palomo, E., Structural and mechanical characterization of graphite foam/phase change material composites. *Carbon* **2014**, *74*, 266-281.
32. Pettes, M. T.; Ji, H.; Ruoff, R. S.; Shi, L., Thermal Transport in Three-Dimensional Foam Architectures of Few-Layer Graphene and Ultrathin Graphite. *Nano Letters* **2012**, *12* (6), 2959-2964.
33. Chen, Z.; Ren, W.; Gao, L.; Liu, B.; Pei, S.; Cheng, H.-M., Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nat Mater* **2011**, *10* (6), 424-428.
34. Guan, L.-Z.; Zhao, L.; Wan, Y.-J.; Tang, L.-C., Three-dimensional graphene-based polymer nanocomposites: preparation, properties and applications. *Nanoscale* **2018**, *10* (31), 14788-14811.
35. Nieto, A.; Boesl, B.; Agarwal, A., Multi-scale intrinsic deformation mechanisms of 3D graphene foam. *Carbon* **2015**, *85*, 299-308.
36. Ibrahim, N. I.; Al-Sulaiman, F. A.; Rahman, S.; Yilbas, B. S.; Sahin, A. Z., Heat transfer enhancement of phase change materials for thermal energy storage applications: A critical review. *Renewable and Sustainable Energy Reviews* **2017**, *74* (Supplement C), 26-50.
37. Khan, Z.; Khan, Z.; Ghafoor, A., A review of performance enhancement of PCM based latent heat storage system within the context of materials, thermal stability and compatibility. *Energy Conversion and Management* **2016**, *115*, 132-158.
38. Liu, L.; Su, D.; Tang, Y.; Fang, G., Thermal conductivity enhancement of phase change materials for thermal energy storage: A review. *Renewable and Sustainable Energy Reviews* **2016**, *62*, 305-317.
39. Li, X.; Cai, W.; Colombo, L.; Ruoff, R. S., Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling. *Nano Letters* **2009**, *9* (12), 4268-4272.
40. Paserin, V.; Marcuson, S.; Shu, J.; Wilkinson, D., *The chemical vapor deposition technique for Inco nickel foam production-manufacturing benefits and potential applications*. 2003.
41. Seah, C.-M.; Chai, S.-P.; Mohamed, A. R., Mechanisms of graphene growth by chemical vapour deposition on transition metals. *Carbon* **2014**, *70*, 1-21.
42. Ferrari, A. C., Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects. *Solid State Communications* **2007**, *143* (1), 47-57.
43. Tuinstra, F.; Koenig, J. L., Raman Spectrum of Graphite. *The Journal of Chemical Physics* **1970**, *53* (3), 1126-1130.
44. GmbH, R. T. Data sheet - RT35HC. https://www.rubitherm.eu/media/products/datasheets/Techdata_-RT35HC_EN_06082018.PDF.