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**Designing with Phase Change Materials for Satellite
Thermal Management**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Designing with Phase Change Materials for Satellite Thermal Management

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Statement of Originality

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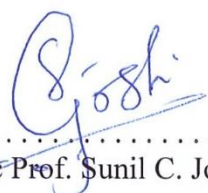

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- I prepared the manuscript drafts. The manuscript was revised by Mr Lai-Iskandar Samson, Dr Tan Dunlin, Mr Simonini Luca, Dr Dudon Jean-Paul, Dr Tsang Siu Hon, Assoc Prof Joshi Sunil Chandrakant and Assoc Prof Teo Hang Tong Edwin
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- Mrs. Fei Ni Leong performed the 3D-C Graphene foam synthesis.
- Dr Tay Roland Ying Jie conducted the Transmission Electron Microscopy (TEM) and assisted in the interpretation of TEM data.
- Dr Dudon Jean-Paul and Mr Simonini Luca assisted with the thermal conductivity testing of samples and subsequent analysis of thermal conductivity results.
- Sample preparation, other characterizations and experiments were done by me in NTU.
- Data analysis was done by me, with assistance from Mr Lai-Iskandar Samson, Dr Tan Dunlin and Dr Tsang Siu Hon.

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Abstract

Due to the harsh environments experienced in space, multiple equipment, and subsystems on board satellites such as electronics, batteries, sensors, and transceivers, require thermal management to stay in the optimal performance temperature. Failure of any equipment could spell doom to the satellite mission, leading to huge loss of investments. Therefore, the thermal management system (TMS) on-board satellites are crucial for mission success. Conventional satellites have a greater luxury of power, on-board volume, and mass to house heavy, bulky, and power hungry TMS. Small satellites, or smallsats, that are typically less than 200 kg, do not have such luxuries. With limited resources, TMS on smallsats needs to be power efficient, compact in size and lightweight. Therefore, power passive TMS, are favoured over active TMS. The state of the art smallsat passive TMS include multilayer insulation, sun shields, paint coating, thermal louvers, flexible thermal straps, passive heat pipes, deployable radiators, and thermal storage units (TSU). Out of the passive TMS, TSU powered by solid-liquid phase change material (PCM) is an attractive solution which can provide long term temperature damping. Solid-liquid PCMs release and absorb large amount of stored heat at a relatively constant temperature when they melt and freeze, respectively. This temperature regulatory nature potentially enables TSU to substitute both the heating and cooling TMS of an equipment, hence freeing up volume on board and decrease overall cost. PCM have also been extensively researched on for a variety of applications. In this thesis, PCM enhanced with high thermal conductivity three-dimensional graphene (3D-C) micro-skeletal and carbon fibre honeycomb (CH) was developed and tested as potential PCM-based TSU.

Paraffin PCM have application in space as early as 1970s on the apollo lunar rover. Paraffins are highly suitable for space application as they have low outgassing, high thermal cycling stability, high energy density and a variety of melting temperatures available for

application, and are non-toxic, non-corrosive, and compatible with metallic and carbon-based materials commonly used on satellites. However, the poor thermal conductivity of paraffins, which results in slow heat spread, large thermal gradient within PCM and often insufficient temperature damping in equipment have greatly restricted their potential application and development, on this otherwise a great solution. Researchers have studied metallic and carbon allotrope inclusions for thermal conductivity enhancement of a PCM. Carbon allotropes have the advantage over metallics with their lower density and hence displacing less PCM when infused. Therefore, in this thesis, highly porous 3D-C and structurally sturdy CH are infused with PCM to form PCM composites with improved performances. These PCM composites are studied extensively to develop them for space application.

Studies in literature have been conflicted whether percolating discrete fillers or three-dimensional scaffolds are the better solution to improve the thermal conductivity of PCM. Therefore, first and foremost in this thesis, a systematic study is conducted between 2 samples of paraffin PCM infused with, respectively, interconnected 3D-C and discrete graphene powder (GP) derived from 3D-C and in the same mass fraction, to determine the better solution with respect to smallsat application. It is observed that PCM sample infused with 3D-C (3DCPCM) has a significantly better shape stabilization over thermal cycling and a higher thermal conductivity improvement over neat PCM of 300% than PCM sample infused with GP (GPPCM), where thermal conductivity improvement over neat PCM was only 60%. The interconnected network 3D-C in 3DCPCM is found to spread the ullage that will otherwise have formed in the PCM sample, as observed in GPPCM and neat PCM samples. Hence interconnected 3D-C is shown to be superior to the discrete GP to improve the thermal conductivity of PCM. Subsequently, 3D-C of various densities ($12.5 - 74.7 \text{ mg/cm}^3$) are synthesized and infused in PCM to study the effects of 3D-C loading on thermal conductivity and latent heat of fusion of 3DCPCM. It is observed that the thermal

conductivity of 3DCPCM increases with 3D-C density. A model is formulated using experimental results and the theory proposed by Ashby to predict the thermal conductivity of 3DCPCM using the density of 3D-C.

To determine the suitability of the PCM composite with use-case heat inputs, a demonstrator test bench setup is built. The test bench can concurrently test up to 4 different PCM composites in identical packaging with the same heat load. Performance is analysed based on a series of figure of merits (FOMs). 4 identical packaging, respectively filled with 3DCPCM, CH+3D-C infused with PCM (CH3DCPCM), CH infused with PCM (CHPCM) and neat PCM were tested simultaneously, at 3 use-case heat loads of 20, 15 and 10 W. It was found that CH3DCPCM and 3DCPCM significantly outperformed the other samples, with CH3DCPCM performing 10 – 40% better than 3DCPCM based on the FOMs.

Finally, to qualify 3DCPCM and CH3DCPCM for space, both sample in packaging were tested in two space environment tests: launch vibration and extreme temperature thermal cycling. The vibration test is conducted in operation conditions with PCM in the liquid state during the test. The results show that both samples retain their pre-test performance, hence showing that 3D-C structure can retain its structural integrity in launch vibration conditions in a liquid medium. The results of the extreme temperature thermal cycling show CH3DCPCM has a lower performance degradation as compared to 3DCPCM. It is interesting to note that CH3DCPCM post-test performs better than 3DCPCM pre-test, indicating both the significantly better performance of CH3DCPCM over 3DCPCM and the high resistance to extreme temperature cycles of CH3DCPCM.

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List of Abbreviations

3D	Three-dimensional
3D-C	Three-dimensional Graphene
3DCPCM	3D-C infused PCM
3D-DF	Three-dimensional Diamond Foam
ASTM	American Society for Testing and Materials
C	Carbon
CAD	Computer-aided Design
CEG	Compressed Expanded Graphite
CH	Carbon fibre Honeycomb
CH3DCPCM	CH and 3D-C infused PCM
CHPCM	CH infused PCM
CNC	Computer Numerical Control
CNF	Carbon Nanofiber
CNT	Carbon Nanotube
CVD	Chemical Vapour Deposition
DI	Deionized
DSC	Differential Scanning Calorimetry
ECSS	European Cooperation for Space Standardization
FE	Finite Element
FFT	Fast Fourier Transform
FOM	Figure of Merit
GNF	Graphene Nanofibre
GNP	Graphene Nanoplatelet
GP	Graphene Powder
GPPCM	GP infused PCM
gRMS	Root-mean-square acceleration
GSFC	Goddard Space Flight Center

HDPE	High Density Polyethylene
HR-TEM	High Resolution TEM
ISO	International Organization for Standardization
ISS	International Space Station
LEO	Low Earth Orbit
MIL-STD	United States Military Standard
MLI	Multi-Layer Insulation
MMOD	Micrometeoroids and Orbital Debris
MTPS	Modified Transient Plane Source
MWCNT	Multi-Wall Carbon Nanotube
NASA	National Aeronautics and Space Administration
Ni-G	Graphene coated Nickel
PCM	Phase Change Material
PI	Polyimide
PMMA	Poly(methyl methacrylate)
PPI	Pore-per-inch
PSLV	Polar Satellite Launch Vehicle
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscope
SMC	Space and Missile Systems Centre Standard
SWCNT	Single-Wall Carbon Nanotube
TEM	Transmission Electron Microscopy
TIM	Thermal Interface Material
TMS	Thermal management system
TRL	Technology Readiness Level
TSU	Thermal Storage Unit
UV	Ultraviolet

1. Introduction

1.1 Background

Satellites have become essential in the daily lives of people, being widely used in applications such as communications, broadcasting, navigation and positioning, geostationary meteorology, remote sensing and earth observation, and space-based information systems [1]. Currently, there are more than 2000 operational satellites of multiple sizes in orbit, majority of which are for communication [2]. In recent years, many players have joined the space race and launched satellites in the smaller form factor, commonly known as smallsats, due to the low cost of development and new technologies [3]. This has led to a surge of smallsats being launched in the past 10 years, mostly to the low earth orbit (LEO), with increasing trends projected in the next 10 years.

Depending on the application, each type of satellites has its own sets of challenges to overcome. For instance, satellites are required to withstand the harsh space environment which include atomic oxygen (AO), vacuum, extreme temperature swings, plasma, solar ultraviolet (UV) radiation, charged particle (ionizing) radiation, and impacts from micrometeoroids and orbital debris (MMOD) [4]–[6]. Therefore, the exterior of the satellite and interior subsystems need to be built to survive these harsh space conditions. One of the challenges of satellites is the cyclical temperature fluctuations experienced as they orbit around Earth due to the cyclical period in eclipse and sunlight. For these reasons, satellites are costly in terms of capital and manpower to design, build, test and launch [1]. Once in orbit, they are impossible to repair when damaged. The malfunction of certain key subsystems may lead to the decommissioning of the entire satellite, hence losing huge assets and potential revenue. Common causes of failure in satellites have roots in unresolved thermal issues. The temperatures of subsystems could fluctuate beyond their operational or survival temperature, thus causing the satellite to malfunction or fail completely. Therefore, thermal management

for on-board equipment and subsystems is crucial to enhance their reliability and ensure the success of the satellite's mission.

TMS on-board satellites differ according to the size of the satellite. Large conventional satellites, such as the International space station (ISS), have large power generation capacity and large volumes on board to accommodate bulky, more power hungry TMS. Conversely, smallsats have a tighter power, mass, and volume restriction than the larger conventional satellites, hence the TMS of smallsats are more restrictive in power consumption, mass, and volume requirements. Hence, the ideal TMS for smallsats do not consume power, are compact in size and lightweight. There are two categories of TMS, active TMS such as heaters and thermoelectric coolers, which consumes power, and passive TMS such as TSU, multi-layer insulation (MLI) and radiators, which does not consumer power. Both active and passive TMS generally experience a decrease in efficiency when downsized from applications in conventional satellites to smallsats, hence driving research to develop new technologies to rectify these issues [7].

The power restrictions on smallsats dictates that passive TMS are favoured to free up power budget for the primary subsystems of the satellites. Certain bulky TMS such as radiators are less readily deployed due to the restricted volume on board smallsats. Hence researchers look to the development of compact and lightweight passive TMS to replace current applications of active and bulky passive TMS. One such component is the TSU, often interfaced directly with key subsystems and equipment. One potential material for passive TMS is PCM. PCM-based TSU utilizes the latent energy evolved during the relatively isothermal phase change of the material to dampen the temperature changes in the equipment of interest, hence the equipment can be maintained within the operational range of temperature. Solid-liquid PCM would melt and store latent heat energy during periods of high heat flux and would freeze and release this stored latent heat during periods of low heat flux,

while maintaining a relatively constant temperature. This property of PCM is well catered to the periodic temperature change during orbit and hence PCM could regulate the temperature of a subsystem throughout the orbit. The temperature experienced by the exterior of a satellite in LEO ranges from -170 to 123 °C [8]. Typically, a satellite uses large and bulky radiators to cool on-board subsystems during sun-facing period of the orbit and electrical heaters to heat up equipment during the cold eclipse. Utilizing PCM-based TSU would replace both systems, therefore freeing up on-board volume, mass, and the satellite power budget.

Other than space applications, PCM has seen applications in multiple fields on-the-ground, such as passive cooling in building, battery cooling system, solar energy systems and textile [9]–[22]. The typical size and heat load of a TSU can vary widely depending on applications. Across all applications, one major limitation for most PCMs is the low thermal conductivity (k), in the range of $0.1 - 0.3$ W/mK, which limits their speed of heat spread, thus a significant thermal gradient can exist within the PCM, especially at higher heat loads. In such cases, there may be lethargy in heat exchange between the PCM and equipment, thus significantly weakening the temperature damping effects of PCM. The implication in application will be weak temperature damping in high loads, less precise temperature control, and limitations to low thickness-to-surface-area ratio form factors to reduce thermal gradient. With limited available volume on board, PCM with such form factor may not reach the required performance specifications for application. The effective k of the PCM needs to be improved for more flexible designs of the PCM packaging form factor and a more efficient usage of the large latent heat reservoir of PCM. One solution many researchers used was high k metallic inclusions, such as fins, honeycomb structures and porous foams, designed into the PCM packaging to improve thermal transport [23]–[28]. However, such designs increase the overall mass of the TSU, which translates to additional cost in satellite applications. The metallic inclusions also displace potential PCM volume. These two factors significantly

decrease the energy density of the PCM and increase the overall mass of the PCM-based TMS, which are not favourable trade-offs for satellite application. Therefore, additives that are lightweight with high k would be ideal for thermal transport enhancement of PCM in smallsats applications.

Researchers have turned to lightweight carbon allotropes, such as carbon nanotubes (CNT), carbon nanofibres (CNF) as replacement to the metallic inclusions [29]–[40]. Out of the carbon allotrope fillers, there has been an increasing interest in porous 3D-C micro-skeletal [41], synthesized by template assisted chemical vapour deposition (CVD) [42]. The 3D-C synthesized has ultralow density, good stability, high porosity, high specific surface area and high k held together in an interconnected network of graphene [43]–[45]. These properties of 3D-C have generated research works in multiple fields and applications such as sensors [46]–[48], thermoacoustic [49], thermal interface material (TIM) [50], shape memory polymer [51] and energy conversion and storage applications in batteries, supercapacitor, batteries, fuel cells and solar cells [52]–[55]. 3D-C is also a suitable scaffold for k enhancement of PCM as the low density and high porosity ensures minimal displacement of PCM, thus minimally changing the mass and attractive properties of PCM, while uniformly improving the k of PCM [56]. The resultant 3DCPCM has high k , and very similar energy density measured in latent heat of fusion (H_f) as the original PCM due to the very high porosity of 3D-C scaffold. 3D-C is also surface compatible with paraffin, a space qualified alkane group organic PCM with a large variety of phase change temperatures, high thermal cycling stability, compatibility with space-grade Al containers and is low cost and widely availability. Therefore, 3DCPCM is a highly suitable material for applications in PCM based TSU in smallsats applications.

1.2 Motivation

Paraffin has been favoured as a PCM due to its chemical and thermal stability, large H_f and wide variety of phase change temperatures [57], [58]. Researchers have typically used metal and carbon inclusions to improve its k [59]–[61]. While material studies on PCM infused with various carbon allotropes have shown to improve k , the degree of improvement varied greatly across multiple studies [28]–[39], largely due to the different methods of testing k , different filler loading, and different base PCM used across studies. Hence it is not clear which type of filler, largely grouped as interconnected scaffolds or discrete fillers, was more suitable to enhance PCM for space applications. Currently, no study has been conducted to prove the advantage of one filler over the other. Therefore, a systematic study between PCM infused with interconnected scaffold and discrete filler of the same material is required to clearly determine a better solution. There is also a lack of studies detailing the effect of loading density for CVD grown 3D-C on the k of 3DCPCM. A model to predict the bulk k for 3DCPCM based on the density of 3D-C is not available in literature. Therefore, a detailed study with sufficient 3DCPCM samples of various 3D-C loading needs to be conducted.

After the initial material study, PCM composites needs to be studied in packaging with use-case heat inputs to determine the thermal performance of the PCM in use-case conditions. Typically, a unique in-house setup would be built for each application to test PCM composite in packaging [37]. Finally, the suitable PCM composite in packaging needs to undergo space environment qualifications, such as launch vibration qualification, to ensure performance is retained after exposure to the space environment. There are currently no studies that document the thermal performance of 3DCPCM in packaging and no studies carried out on subjecting 3DCPCM in packaging to space qualification tests. Hence, it is paramount to study 3DCPCM in use-case packaging and conditions qualified for space environment to mature this technology.

1.3 Objectives and Scope

The primary objective of this thesis is to provide the space industry with a new efficient lightweight PCM-based TSU with fast response to heat loads and high energy storage density as innovative solutions for efficient passive TMS on board smallsats. This is achieved by combining the low density and high k of highly porous 3D-C with the high H_f and space environmental stability of paraffin PCM to achieve a PCM composite of high effective k , with minimal change to the positive properties of paraffin.

To facilitate the advancement of 3DCPCM for space application, the following studies were conducted.

- A systematic study between 2 samples of paraffin PCM infused with, respectively, interconnected 3D-C and discrete GP derived from 3D-C in the same mass fraction, were conducted. Samples were tested for their k and initial stage thermal cycling stability to clearly determine the better filler.
- 3D-Cs of various density were synthesized and infused with PCM to determine the optimal filler loading and derive a model to predict the k of 3DCPCM based on the density of 3D-C used.
- The thermal response to use-case heat loads of the PCM in packaging were studied to determine the suitability of the PCM composite in use-case scenarios. To facilitate comparison between different PCM composites, a demonstrator test bench setup was built that house and test different PCM composites in identical packaging with the same heat load concurrently. This setup can effectively determine the best PCM composite under each heat load input. Post analysis of the respective thermal response results was done to clearly show the degree of difference between each PCM composite.

- A finite element (FE) model of the PCM in packaging was created and verified with experimental results to allow parametric and predictive analysis to be conducted.
- A novel PCM composite, CH3DCPCM, was proposed and analysed with the test bench to address the potential issues with 3DCPCM in packaging with large thickness.
- Finally, both 3DCPCM and CH3DCPCM were tested in two space environment tests: launch vibration and extreme temperature thermal cycling, to determine the suitability of each sample in these two aspects of the space environment.

The scope of this thesis is limited to developing an efficient passive thermal solution, based on PCMs, for smallsats in LEO.

1.4 Organisation of Thesis

Chapter 1 describes the background, motivation, objectives, and scope of this thesis. In Chapter 2, the literature on smallsats and the orbiting environment is reported, followed by the current thermal management solutions employed in the satellites and the challenges of applying current solutions to smallsats. The potential benefits of a PCM based TMS is reported, followed by the literature on PCM, its current applications and limitations, and its design consideration for satellite applications. Chapter 3 details the experimental methods and setups for synthesis and characterization of 3D-C and various PCM composites studied in this thesis. Chapters 4 to 7 present the implementation of the research objective, which include the material study of 3DCPCM, introduction of PCM demonstrator test bench and the corresponding analysis methods, novel material CH3DCPCM introduction and analysis using PCM demonstrator test bench, and space environment qualification tests of the PCM composites in the PCM demonstrator packaging. Lastly, Chapter 8 provides a summary of the contributions in this thesis and recommendation for future studies.

2. Literature review

2.1 Space environment

The space environment differs greatly from that on earth. Satellites in space experience environmental threats such as vacuum, thermal cycling, extreme temperature swings, plasma, solar UV radiation, charged particle (ionizing) radiation, and impacts from MMOD [4]. In the LEO environment, there is an additional concern of single-oxygen atoms, AO, which has been documented to erode non-metallic materials [5], [6].

Therefore, the materials and equipment used in space must survive various environmental conditions in space, vibrations and heat spikes during launch and remain functional and reliable throughout its mission duration. Multiple standards such as those from the European Cooperation for Space Standardization (ECSS), United States military standard (MIL-STD), Space and Missile Systems Centre Standard (SMC) and the International Organization for Standardization (ISO) have documented strict qualification standards and test conditions to qualify that a material or an equipment is safe for space. Examples of such tests are sinusoidal vibration qualification test, random vibrational test and thermal vacuum and extreme temperature thermal cycling test.

2.2 Low Earth Orbit

The altitude and inclination of an orbit are important characteristics of an orbit and would determine the orbital period, and more specifically, eclipse and Sun facing time. Assuming a geocentric orbit, LEO is broadly defined as orbits within the range 200 – 2000 km in altitude, with an orbital period of less than 128 minutes [62]. The temperature experienced by the exterior of a satellite in LEO ranges from –170 to 123 °C [8].

2.3 Satellite types

Artificial satellites are man-made machines that are launched into space orbits to fulfil certain missions. Satellites can be categorized by their size, weight, and mission. Tubbal et al. [63] documented various classifications of satellites along with their mass, cost to build and power consumption. Conventional satellites typically have a mass of more than 1000 kg and have power consumption requirements of about 1000 W. The ISS and Hubble Space Telescope are examples of such conventional satellites. Satellites with a mass of less than 600 kg are typically classified as smallsats. Out of the smallsats, microsatellites and nanosatellites are categories of satellites with a typical wet launch mass of 10 – 100 kg and 1 – 10 kg, respectively. Microsatellites have the power consumption requirements in the range of 50 – 250 W, while nanosatellites have the power consumption requirements in the range of 10 – 100 W. A further subset of nanosatellites is the Cubesat. Cubesats use multiples of a standard volumetric size and dimension of 1 U, or $10 \times 10 \times 10 \text{ cm}^3$, with a mass of no more than 1.33 kg/U, as modular building blocks to standardize nanosatellite volume and dimensions. Nanosatellites/CubeSats have an average operational life expectancy of about 1 year [64]. Some examples of standard CubeSat sizes are shown in Figure 2.1.

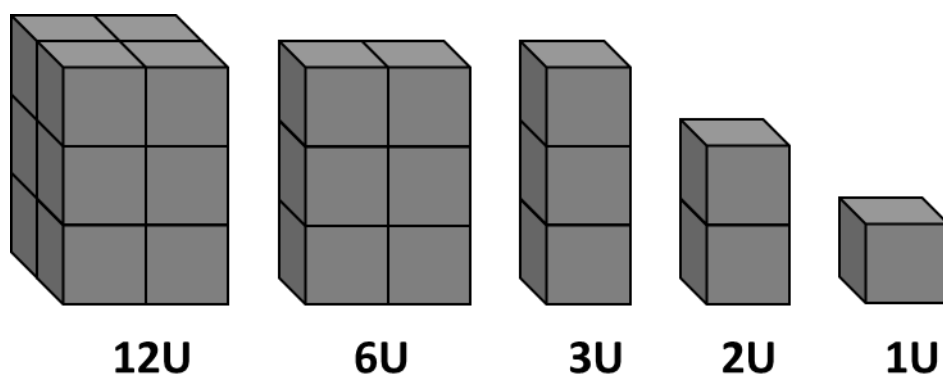


Figure 2.1 Examples of standard sizes for CubeSats.

The advantages of smallsats over conventional satellites include lower production costs, simplified project management procedures that allow a shorter production timeline, and a smaller form factor which allow smallsats to be deployed easier in swarms or constellations,

hence greatly increasing their mission potential. Smallsats also present a lower hurdle to research entities as compared to conventional satellites, therefore the capacity of space related research conducted would be enlarged. However, smallsats have some drawbacks in application. As a result of miniaturization, there would be a tighter mass, power, volumetric and dimensional restriction for smallsats as compared to conventional satellites. Smallsats have a smaller thermal inertia than conventional satellites, resulting in a faster temperature decay during eclipse. The smaller body of smallsats also means a smaller surface area to house solar panels for power generation. For instance, one of the state-of-the-art Cubesat technology for power generation is a set of 2×3 U spring-loaded V-shaped solar-array panels named eHaWK 27A-84FV manufactured by MMA Design which has a beginning of life peak power output of 84 W [65]. This peak power output is about 4% that of the Hubble Space Telescope which has an average power output of 2100W. Therefore, a significant redesign of crucial subsystems, including the TMS, would be required to ensure the functionality of the mission payload under the tighter restrictions of smallsats.

2.4 Satellite thermal management

Components within the satellite are required to be maintained within their operating temperature range to function optimally. Satellites in orbit often cycle through temperatures beyond the operating temperature range of these components, leading to potential malfunction of key components. Hence suitable TMS are crucial for the survival and optimal operation of a satellite. Some typical operating and survival temperatures of the various subsystems are shown in Table 2.1.

Table 2.1 Typical operating and survival temperatures of space subsystems [66]

Component/System	Operating Temperature (°C)	Survival Temperature (°C)
Digital electronics	0 – 50	-20 – 70
Analog electronics	0 – 50	-20 – 70
Batteries	10 – 20	0 – 35
Infrared detectors	-269 – -173	-269 – 35
Solid-state particle detectors	-35 – 0	-35 – 35
Momentum wheels	0 – 50	-20 – 70
Solar panels	-100 – 125	-100 – 125
S-band Transceiver	-40 – 85	–

There are two categories of TMS for satellites: active and passive. Active TMS draw power from the power storage of the satellite to manage the temperature of the satellite. Conversely, passive TMS do not require power from the satellite to operate. Passive thermal control methods are attractive to satellite designers because they are associated with low cost, low volume, light weight, low risk, and a proven reliability [7]. Table 2.2 summarizes the advantages and disadvantages of active and passive TMS.

Table 2.2 Advantages and disadvantages of active and passive TMS.

	Advantage	Disadvantage
Active TMS	Higher precision and control	- Requires activation - Consumes power - Higher probability of failure
Passive TMS	- No input power required - Smaller probability of failure - Low cost, volume, and weight	- Activation modes locked in during fabrication - Lesser precision

The choice of TMS depends largely on the mass category of the satellite. As mentioned previously, smallsats have limited power generation and storage capacities, and a smaller thermal inertia. Therefore, passive thermal control methods are especially attractive for smallsats of a lower mass category as they do not consume the precious and limited power resources on board.

The state-of-the-art thermal control systems for small satellites are presented in the following sections.

2.4.1 Active Thermal Management Systems

Active TMS rely on input power for operation. They are known to be more precise than passive systems and have been shown to be more effective [7]. National Aeronautics and Space Administration (NASA) documented three active systems for smallsats with a technology readiness level (TRL) of at least 6.

- 1) Electric heater,
- 2) Mini Cryocoolers,
- 3) Thermoelectric Coolers

Electrical resistance heaters are typically applied to battery packs in smallsats. They can be controlled by a temperature sensor to be activated during eclipse to maintain the temperature of the battery. The mini cryocoolers are mainly used for instruments or subsystems requiring cryogenic cooling, for example the infrared sensors.

2.4.2 Passive Thermal Management Systems

Passive TMS requires zero input power to regulate the temperature within a satellite, hence freeing up the power budget for other subsystems on the smallsats. NASA documented the current state of the art passive systems for small spacecraft, summarised in Table 2.3, most of which were a redesign of passive systems on conventional satellites.

Table 2.3 State of the art Passive Thermal Management Systems (TMS) for SmallSats [7]

Product	TRL in LEO environment
MLI Materials	9
Paint	9
Selective Surface and Metallised Tape Coatings	9
Thermal Gap Fillers and Conductive Gaskets	9
Sun Shields	4 – 7
Flexible Thermal Straps	7
Storage Units	7
Thermal Louvers	7
Thermal Switches	7 – 9
Deployable Radiators	6
Passive Heat Pipes	7

The technology of certain products, such as surface paint and metallised tape coatings, could be easily transferred to smallsats without much redesign or degradation in performance. However, most of the products face difficulty in miniaturizing and often suffer major efficiency degradation. One example is the MLI. MLI blankets are usually applied to the surface of a satellite. They act as a barricade to block external solar flux and reduce internal heat dissipation. MLI are made up of multiple layers of thin, metal-coated plastic film, with low k materials sandwiched in between layers to minimise thermal contact between layers. However, the performance of MLI drastically decreases when downsized or compressed, and it is difficult to avoid compression since smallsats needs to be loaded onto a tight-fitting deployers or launcher. Due to this, despite the high TRL, MLI do not performance as well on smallsats as compared to on conventional satellites [7].

Some systems required major redesign due to the power, mass, and volumetric restrictions on smaller satellites, for example thermal louvers and radiators, which dissipates heat to space through radiation. Typical louvers on spacecraft are associated with large dissipative surface area, large mass, and high input power, all of which are limited on smallsats. An example of a redesigned thermal louvers was the one produced by NASA Goddard Space Flight Center (GSFC) [7], [67] to include bimetallic springs to actuate the flaps, which increases heat dissipation, when the spacecraft temperature rises, and closes the flap when the spacecraft had cooled sufficiently.

Thermal straps and heat pipes assist in heat transportation from the subsystem of interest to heat sink, which is usually a radiator, and does not remove or heat up the subsystem. It requires application in tandem with a heat sink. The effectiveness of such systems depends largely on the effectiveness of the heat sink itself which, as mentioned above, are less efficient on a smaller satellite due to limited dissipative surface area.

TSU consisting of PCM is an upcoming passive TMS product for smallsats in LEO. Solid-liquid PCMs are substances that absorb thermal energy from the surrounding when it melts into liquid and releases thermal energy as it freezes back to solid. This occurs at a relatively constant temperature. PCMs have been extensively researched on for spacecraft application in the 1970s [68], [69]. PCMs were highly attractive for satellite TMS because the environmental temperature changes from sun-facing to eclipse during a period of orbit naturally resets the PCM for its next load. When the satellite is sun-facing, the solid PCM absorbs thermal energy from the component heated up by the solar flux and melts. When the satellite is in the cold eclipse, this stored thermal energy would be released back to the component as the PCM freezes. As such, a PCM based TSU acts as a temperature buffer for a component experiencing cyclical periods of high and low heat flux and required no additional power budget from the satellite. Figure 2.2 shows a temperature versus time curve simulation

of the final 5 out of 10 orbits of an external node in a 12U CubeSat orbiting in LEO, with and without a PCM that changes phase at 35 °C. The outcome was a more damped temperature fluctuation in the node with PCM as compared to without PCM, and temperature in the node with PCM became isothermal when temperature increased to the phase change temperature of the PCM. PCM TSU had wide variety of applications in heat sinks, spacecraft heat exchangers [70], thermal oscillation damping and thermal protection of thermally sensitive electronics. Typically, such PCM TSU were packaged in a hermetically sealed aluminium container and interfaced directly with the subsystem of interest on one surface. The current state-of-the-art solid-liquid PCM TSU was developed by Thermal Management Technologies and is at TRL 7. The company had developed a standard low-cost, low lead time CubeSat application pack, as well as a custom designed package, which had considerations for desired isothermal phase change temperatures, interfaces, latent energy storage, thermal stability, and heat removal methods. The first PCM TSU developed by Thermal Management Technologies was sent to LEO in 2018 [8]. The relevant literature on PCMs and their known design challenges would be documented in the subsequent section.

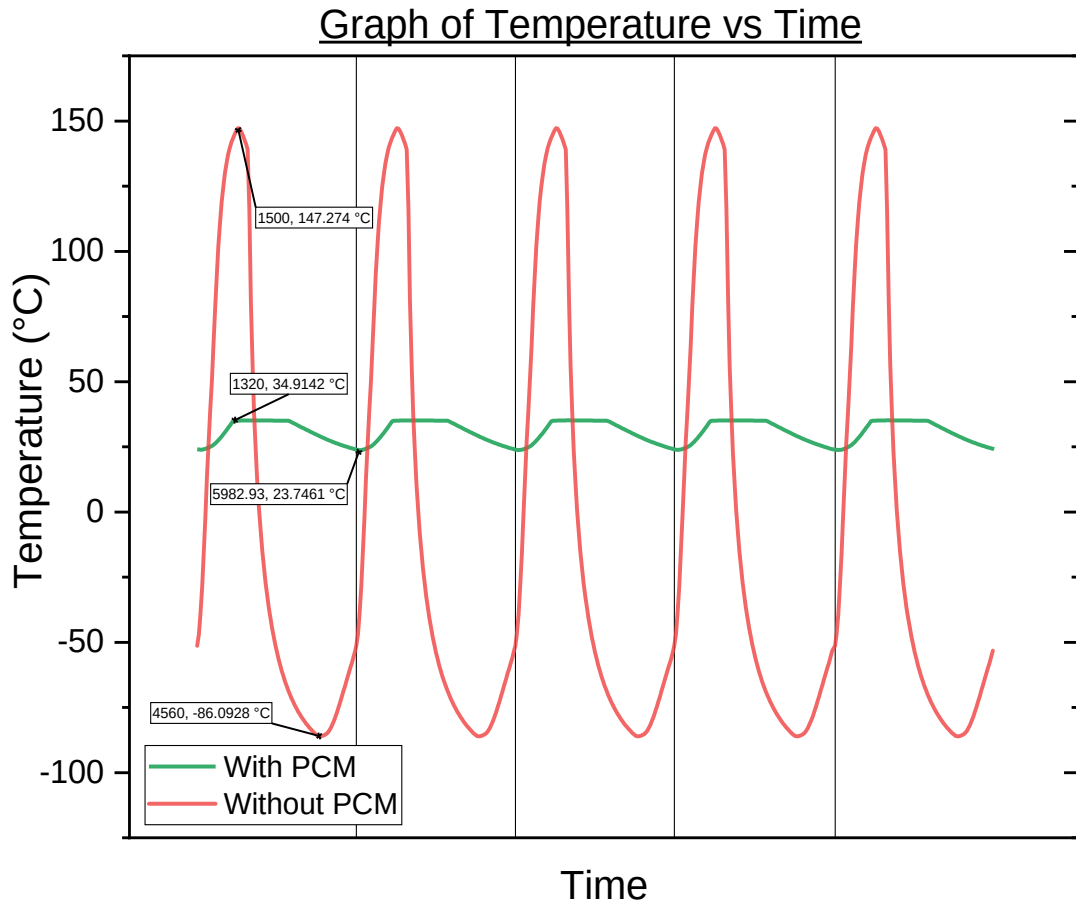


Figure 2.2 Simulated temperature vs time curve of an external node of a 12U Cubesat, with and without PCM that changes phase at 35 °C.

2.5 Phase Change Materials

PCMs are substances that absorb and release latent thermal energy during phase change at a relatively constant temperature. This phase change could be solid-to-solid, solid-to-liquid, solid-to-gas, or liquid-to-gas phase change. Due to the large volumetric and hence pressure changes involved for solid-to-gas or liquid-to-gas phase change, it was less feasible for application on spacecrafts and hence beyond the scope of this project. The phase change of interest would be solid-to-liquid phase change due to the smaller volumetric changes and large latent thermal energy of such phase change. A typical temperature-time graph of a PCM is shown in Figure 2.3

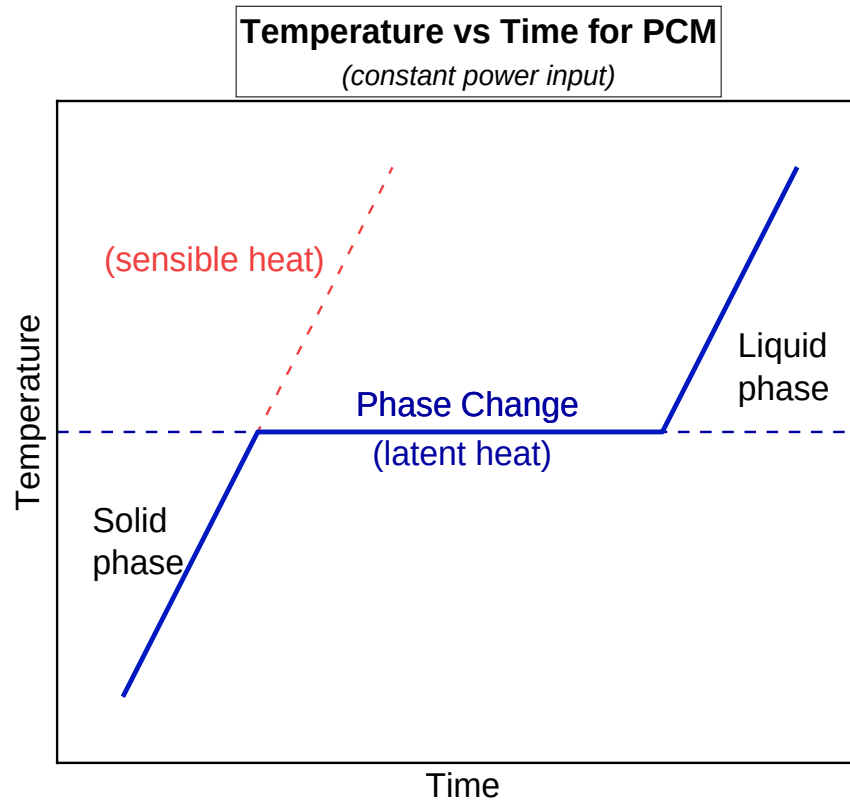


Figure 2.3 Typical Temperature vs time graph of a PCM under constant power source

There are 3 main classification of PCM with solid-liquid phase change available: organic, inorganic, and eutectic. A summary of the various classes of PCM is shown in Figure 2.4.

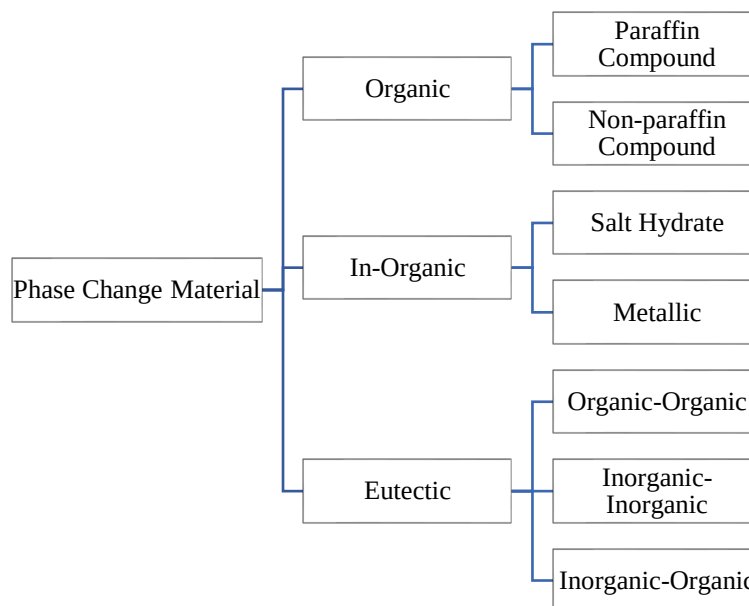


Figure 2.4 Classification of phase change material

2.5.1 Organic PCM

Organic PCM are further categorised as paraffins and non-paraffins. Advantages of organic PCM include thermal cycling stability, homogeneous nucleation without phase segregation and no supercooling.

2.5.1.1 Paraffin

Paraffin wax consists of a mixture of mostly straight chain alkane, also known as poly(ethylene), with the basic chemical formula of $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$. As the carbon chain length and hence the molecular mass of the paraffin increases, the intermolecular forces between the alkane molecules increase. Hence a larger amount of energy is required to overcome the intermolecular forces for melting to occur and the phase change would occur at a higher total energy level, and hence the melting temperature (T_{melt}) is higher. The T_{melt} of usable paraffin wax ranges from -40 to 150 °C, and the H_f ranges from 180 to 270 kJ/kg. A list of T_{melt} and H_f of paraffin wax with carbon chain length of 11 to 30 is recorded in Table 2.4. The T_{melt} of paraffin could be tuned further by mixing paraffin wax of various chain length [71], allowing paraffin to have a wide selection of temperature for various application. Paraffin wax also has the added advantage of high H_f , non-toxic, non-corrosive and compatibility with metal and carbon containers. The properties of paraffin also remain largely similar across the number of carbon chains [72].

The limitations of paraffin are its low k , broad T_{melt} , and incompatibility with some plastics [72]. The k was in the magnitude of ~ 0.2 W/mK, resulting in slow heat transfer rate and large temperature gradient within a block of paraffin wax. This phenomenon leads to localised heating, hence underutilizing the large H_f of paraffin. Phase change of paraffin wax occurs over a range as seen in Table 2.4, therefore the H_f would be released over a temperature range, further slowing down the energy storage/release process.

Despite the limitations, paraffin PCM heat sinks have been applied to space as early as the Apollo era, where the Lunar Rover Vehicle used 2 boxes of paraffin wax to absorb heat from battery and the drive control electronics [73]. PCM heat sink, using pentadecane, for heat exchanger had been studied and tested on the ISS as a novel concept for active thermal control system [74], [75].

Table 2.4 Phase transition temperature and latent heat of paraffin wax from carbon chain length of 11 to 30 [72].

Name	Chemical Formula	Molecular Weight (g/mol)	$T_{transition}$ (°C)	T_{melt} (°C)	$H_{f, transition}$ (kJ/kg)	$H_{f, melt}$ (kJ/kg)	$H_{f, total}$ (kJ/kg)
n-Undecane	C ₁₁ H ₂₄	156.314	-36.6	-25.6	43.9	141.3	185.2
n-Dodecane	C ₁₂ H ₂₆	170.341	-	-9.6	-	210.5	210.5
n-Tridecane	C ₁₃ H ₂₈	184.368	-18.2	-5.4	41.6	154.8	196.4
n-Tetradecane	C ₁₄ H ₃₀	198.395	-	5.9	-	229.9	229.9
n-Pentadecane	C ₁₅ H ₃₂	212.422	-2.3	10.0	43.2	163.7	206.9
n-Hexadecane	C ₁₆ H ₃₄	226.449	-	18.2	-	228.9	228.9
n-Heptadecane	C ₁₇ H ₃₆	240.476	11.1	22.0	45.5	168.3	213.8
n-Octadecane	C ₁₈ H ₃₈	254.504	-	28.2	-	243.5	243.5
n-Nonadecane	C ₁₉ H ₄₀	268.531	22.8	31.9	51.4	170.6	222
n-Eicosane	C ₂₀ H ₄₂	282.558	36.2	36.4	-	247.3	247.3
n-Heneicosane	C ₂₁ H ₄₄	296.585	32.5	40.2	52.2	160.8	213
n-Docosane	C ₂₂ H ₄₆	310.612	43.0	44.0	90.8	157.6	248.4
n-Tricosane	C ₂₃ H ₄₈	324.639	40.5	47.5	67.0	166.3	233.3
n-Tetrecosane	C ₂₄ H ₅₀	338.666	48.1	50.6	92.4	162.1	254.5
n-Pentacosane	C ₂₅ H ₅₂	352.693	47	53.5	73.9	178.4	252.3
n-Hexadosane	C ₂₆ H ₅₄	366.720	53.3	56.3	87.9	162.2	250.1
n-Heptacosane	C ₂₇ H ₅₆	380.747	53.0	58.8	76.0	158.7	234.7
n-Octacosane	C ₂₈ H ₅₈	394.774	58.0	61.4	89.8	163.7	253.5
n-Nonadosane	C ₂₉ H ₆₀	408.802	58.2	63.4	72.7	161.7	234.4
n-Triacontane	C ₃₀ H ₆₂	422.829	62.0	65.4	-	251.1	251.1

2.5.1.2 Non-Paraffin

Organic non-paraffin PCM are hydrocarbons with additional functional groups. Example of organic non-paraffin PCM are vegetable oil, esters, fatty acids, and alcohol. A variety of materials belong to this category and their properties vary widely. Abhat et al. [76], have studied and identified organic non-paraffin that is suitable for PCM. Amongst the choices, fatty acids have advantageous properties such as high H_f , reversible solid-liquid phase transition, no supercooling and non-flammability. Limitations of fatty acids include low k , corrosivity, and cost.

2.5.2 In-organic PCM

In-organic PCMs are further subcategorized into salt hydrate and metallic.

2.5.2.1 Salt Hydrates

Salt hydrates consist of a salt molecule integrally associated with water molecules. An example of salt hydrate is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Attractive attributes of salt hydrates include low cost, high specific heat capacity (c_p) and high H_f . However, salt hydrates display signs of supercooling and phase separation due to innate poor nucleation and have limited application temperature availability. Furthermore, the hydrated mass decreases over multiple cycles hence affecting its physical and thermal properties, thus salt hydrates have poor thermal cycling stability. Salt hydrates have a major disadvantageous property of incongruent melting which result in a certain amount of irreversible phase change process and also a decrease in H_f [9]. Salt hydrates are also corrosive to most metal containers.

2.5.2.2 Metallics

Metallic PCM consists of metals and metal alloys with low melting point. Metallics have the advantage of high k and high volume specific H . However, due to the high density of metal, metallics are heavy and have high weight penalties. The resultant weight specific H_f is

much lower compared to organic PCMs. For example, Gallium, a metallic PCM, has a H_f of 78 - 83 kJ/kg [77], which is less than 50% that of most organic PCM that range from 180 kJ/kg to 270 kJ/kg.

2.5.3 Eutectics

A eutectic compound is defined as a homogeneous solid mixture of two or more types of elements, and only forms at a specific composition ratio of each element such that the eutectic compound will changes phase homogeneously.

2.5.4 PCM selection criteria for space

Extensive studies has been conducted by multiple institution and groups to identify ideal characteristics and potential candidates of PCM for various applications, including building passive thermal control, electronics devices, textiles and space TMS [7]–[20]. With space environment application, additional considerations for PCM selection were needed. The ECSS had identified the ideal characteristic of PCM for space thermal energy storage device, summarised in Table 2.5. The selection of PCM would vary for each specific satellite component requiring thermal management.

Table 2.5 Ideal characteristic of PCM for space application

Thermal properties	Physical properties	Chemical properties	Economic properties
• Appropriate T_{melt} for application • High H_f • High c_p • High k in both phases	• High density • Low volume change during phase transition • Low coefficient of expansion • No tendency to supercooling • Reversible solid-liquid transition • Low vapour pressure • High flash point • No outgassing	• Non-Toxic • Non-corrosive • Compatible with structural material • Identical chemical composition in solid and liquid phase • Thermal cycling stability	• Abundant • Low cost

In implementation, solid-liquid PCM types have 3 main design challenges. Firstly, the response time of PCM to external thermal changes is sluggish, hence improvement in the k of PCM would be required to hasten response time and fully utilize the latent energy of PCM.

Secondly, the solid-liquid transition creates the design challenge of containment in the liquid phase [74]. Furthermore, the volumetric changes during phase change from solid to liquid state should be accounted for to prevent mechanical failure of the container. Most paraffin wax exhibits a volume increase up to 15 – 20% during phase change to the liquid phase. Therefore, a sealed packaging that accounts for the volumetric changes would be required to hold the PCM in the liquid phase.

Lastly, the space application poses an additional set of challenges for PCM, as well as limits the solutions for the previous considerations. For instance, the vacuum in space would

require the PCM containment packaging to be made of space qualified materials that have high wettability with the PCM and be hermetically sealed. Furthermore, the PCM in its packaging will have to survive the launch conditions and be in the appropriate phase when the satellite is set into orbit.

All the design considerations must be considered in tandem for the successful implementation of a PCM thermal regulatory device in space. The design considerations are elaborated in the subsequent sections.

2.6 Thermal conductivity enhancement of PCM

Neat PCMs are handicapped by their low thermal conductivity ($k = 0.1 - 0.3 \text{ W/mK}$). Within a typical aluminium ($k = 200 \text{ W/mK}$) container, heat energy preferentially flows faster through the aluminium container and diffuses very slowly throughout the PCM volume from the walls of the container. The PCM at the walls of the container melts and superheats as heat energy is not drawn away fast enough. Fleischer [72] illustrates this effect using a PCM encased in a box as shown in Figure 2.5. The heat flux could bypass the PCM and be transferred through the sides of box which has a lower thermal resistance. The PCM device might therefore act as a thermal insulator instead of a thermal sink.

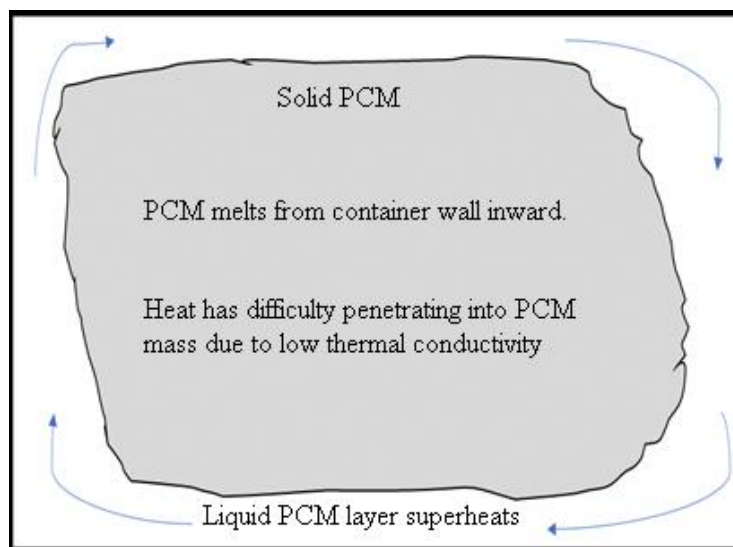


Figure 2.5 Melting process of PCM encased in a box.

Therefore, there are numerous studies in literature regarding k enhancement of PCM at the material level. The most common strategy is infusing PCM with high k additives, such as carbon nanoparticles and metal. These high k fillers will be the heat energy carriers to spread the heat throughout the PCM. However, such inclusions displace PCM volume, which lowers the storage energy in the same volume. The additives used are often of higher density than PCM, therefore increasing the final mass of the TMS. Lower storage energy and higher mass strains the already limited mass budget in smallsat applications. The ideal additive for smallsat application must sufficiently increase the k of the PCM with a small trade-off in storage energy capacity and mass.

Metals and carbon have high k and are mostly surface compatible with PCM, hence these materials have potential to achieve high k enhancement at low loadings in PCM composites. Other fillers such as ceramics materials serve purpose other than thermal conductivity enhancement, hence this report will focus on metallics and carbon materials.

At the nanoscale, heat conduction in carbon, a non-metallic material, is driven by phonons, which is an atomic lattice induced vibration [78]. The mean of heat transfer is liken to the longitudinal waves in a long stretch spring coil that sends energy packets from one end of the spring to the other. Hence a tighter crystalline structure will result in faster phonon travel and hence faster heat transport. The tight covalent sp^3 or sp^2 bonds in carbon allotropes allow phonons to move rapidly through these materials. However crystalline defects such as vacancies or polycrystalline boundary layer can scatter these phonons, hence lowering the heat transport properties of the filler. The intrinsic k of a carbon filler is affected by the mean free path of the phonons within the nanoparticle, meaning the average length a phonon can travel before being scattering by a crystalline defect. With a lower mean free path, there is a higher chance for phonon scattering, and hence a lower k , vice versa. Thus, for PCM

application, the k of PCM/nanoparticle composites would theoretically be highest when using nanoparticles with low internal scattering, which translate to low crystalline defects.

There are 2 main methods to infusing additive material found in literature, a) dispersion of discrete nanofillers and b) infusion with freestanding three-dimensional (3D) scaffolds. In the following sections, the research regarding additive inclusion of each approach is reported, with focus on metallic and carbon materials. The relative k enhancement, storages capacity and mass are listed and compared in the sections below.

2.6.1 Discrete nanofillers

Nanoscale metallic and carbon inclusion is a promising avenue for research. These nano-fillers have high surface area to volume ratios, high intrinsic k and can have a significant impact in the thermal properties of PCM at low loading levels. Multiple research has been conducted to determine the k improvement and effects on thermal storage of various nano-fillers [23], [29]–[36], [38], [39]. Nano-fillers include single-wall and multi-wall carbon nanotubes (SWCNT, MWCNT), graphene nanofibre (GNF), graphene nanoplatelet (GNP), copper and silver nanoparticles. The loading of the nano-fillers is usually reported either in weight fraction (wt.%) or volume fraction (vol.%). The nanoparticles PCM composites are prepared by intensive sonication in molten PCM to evenly disperse the nanoparticles, followed by solidification. The loading of nano-fillers ranged from 0.2 to 10 wt.% and 0.05 to 11.4 vol.%. The thermal storage defined by the H_f of each PCM composite is recorded if available. Elgafy et al. [29] infused carbon nanofibers (CNF) into paraffin wax at 1, 2, 3 and 4 wt.%. The k improvement measured using laser flash method is 1.35 times that of paraffin at 4 wt.% CNF. Some research groups performed surface treatment to the nanofillers before infusion to improve PCM-filler interface contact. Wang et al. [30] infused MWCNT treated with ball milling with paraffin wax at various loading from 0.2 to 2.0 wt.%. Wang et al. reported that k of PCM increased with increasing filler loading, to a maximum of 1.29 times

at 2.0 wt.% and the H_f of PCM composite decreased by the same fraction as the filler loading. Cui et al. [34] infused CNF and CNT into soy wax and paraffin at 1, 2, 5 and 10 wt.%. k of composite sample improved with increasing filler loading. A maximum k improvement of 1.4 times that of neat paraffin was measured at 10 wt.% loading. Cui et al. also reported an insignificant improvement in k when filler loading increased from 5 to 10 wt.%, where k increased only changed from 1.37 to 1.40 times that of paraffin. This suggest that k plateaus after a critical amount of nanofillers has been added. Another important parameter in composite with discrete filler is the percolation threshold, which indicated the lowest concentration of nanofillers required for the dispersed fillers to form an interconnected path within the PCM matrix. Warzoha et al. [38] dispersed GNP in paraffin at 0.05, 0.1, 0.2, 0.3 and 0.4 vol.% and observed optical micrographs of each sample as shown in Figure 2.6. Percolating network was achieved at 0.3 vol.% loading of GNF. PCM nanocomposites at 2.8, 5.8, 8.5 and 11.4 vol.% GNF was subsequently prepared, and the highest k was recorded at 11.4 vol.% with a 1.8 times improvement, with H_f dropping to 0.89 that of paraffin. Warzoha et al. also compared k increase of solid PCM and liquid PCM and concluded that GNF was more effective in improving k for solid PCM for all filler loadings, and k of liquid PCM remained like neat paraffin until 11.4 vol.%, suggesting that the nanofiber networks are not stable enough to remain physically attached when PCM is in the liquid state until a dense enough nanofiller concentration is achieved. Other than nanofiller concentration, the morphology of the nanofiller also significantly affects k improvement. Fan et al. [40] prepared paraffin-based PCM nanocomposites of 1 – 5 wt.% with various discrete carbon-based nanofillers including MWCNT, CNF and GNP. Among the nanofillers, the neat PCM relative k enhancement of nanocomposites with 5 wt.% planar GNP was significantly higher at 2.7 as compared to the wired-shape MWCNT and CNF, which had maximum relative k enhancement of 1.3 times, measured at the same loading and temperature. The more efficient relative enhancement of GNP was primary attributed to the planar geometry which lowers the

geometric contribution of phonon mismatch between filler and paraffin matrix interfaces, which leads to less significant phonon scattering. This means that heat energy can be transported from paraffin to filler with lesser loss due to the favourable planar surface morphology as compared to wired or cylindrical morphology.

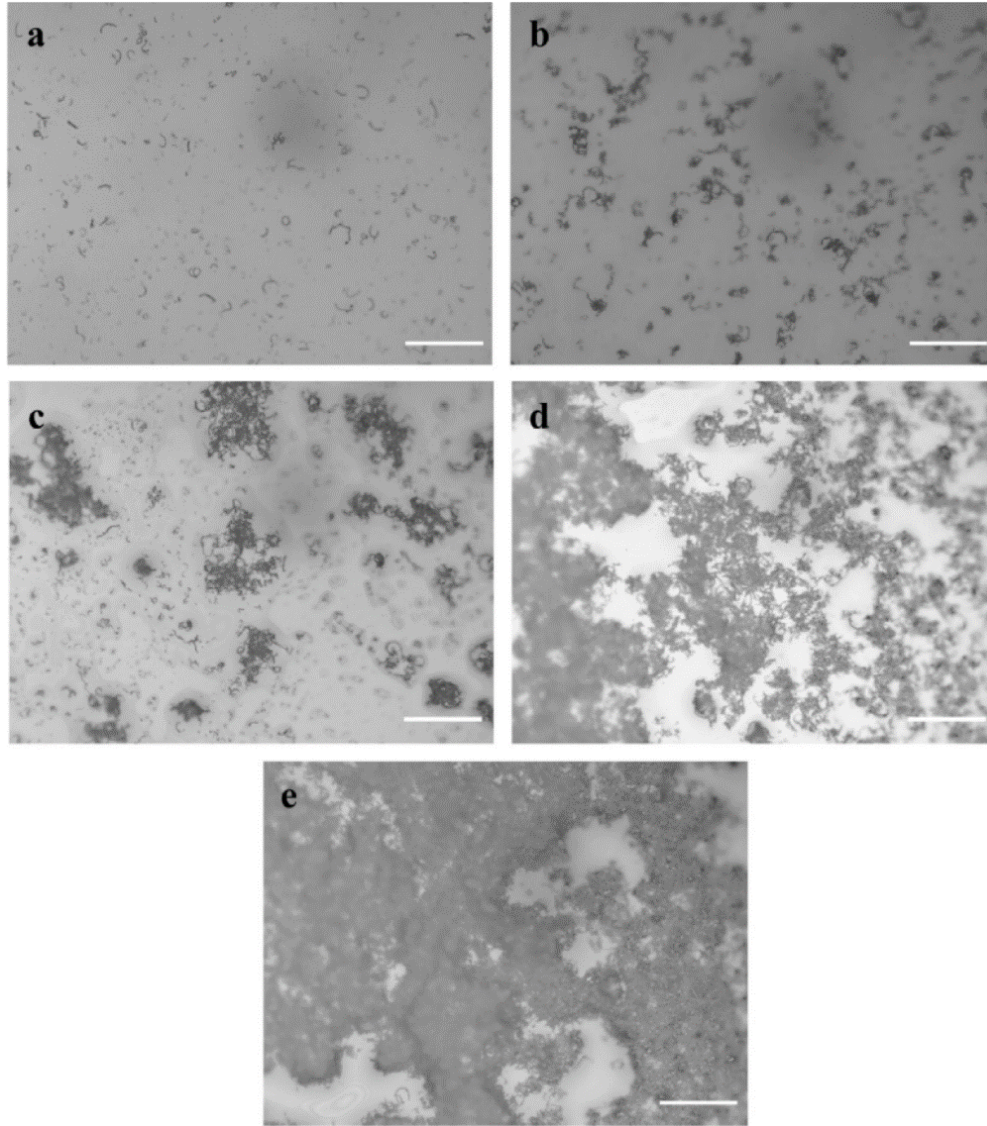


Figure 2.6 Optical micrographs of herringbone style GNF (HG NF) distribution in PCM at volume concentrations of (a) 0.05%, (b) 0.1%, (c) 0.2%, (d) 0.3%, (e) 0.4%. Scale bars are shown in white and are 100 μm . [38]

Despite the advantages, one major disadvantage of discrete nanofillers is the low cycling stability of the resultant PCM composite due to phase separation of particles and PCM over phase change [24], [79]. Intense sonication of liquid PCM was needed to evenly disperse the nanoparticles. However, when PCM melts into a liquid again, the discrete nanofiller

particles become free to move and tend to agglomerate due to Van de Waal's forces of attraction. Over a few cycles, the initial percolating network of nanofillers would be less well distributed than before, and the effective k of the PCM composite would be lowered. Some researchers have turned to free-standing interconnected high k scaffolds to ensure the percolating network remains intact over multiple thermal cycles. A summary of the k enhancement of PCM with discrete fillers is shown in Table 2.6

Table 2.6 Summary of k enhancement of PCM with discrete fillers

PCM type	Filler name	Fill fraction (wt.%)	Relative $k_{(\text{composite})}$	Relative H_f	Ref
Paraffin	CNF	1 – 4	1.07 – 1.35	NA	[29]
Paraffin	MWCNT	0.2 – 2.0	1.10 – 1.29	0.998 – 0.980	[30]
Paraffin	CNF	1 – 10	1.24 – 1.41	NA	
Soy wax	CNF	1 – 10	1.28 – 1.45	NA	[34]
	MWCNT	1 – 10	1.06 – 1.24	NA	
Paraffin	GNF	~ 8 – 28	1.2 – 1.8	0.93 – 0.89	[38]

2.6.2 Three-dimensional scaffolds

One advantage of using 3D scaffolds as fillers for PCM composite is the shape stability of the composite over phase change cycles. In applications where PCM needs to be sealed in a casing, the 3D scaffold helps retain the thermal contact with the packaging and ensures better heat transport to the PCM. The 3D scaffolds used to increase k of PCM can be largely categorized into metallic and carbon-based scaffolds.

2.6.2.1 Metallics

High k metallics such as aluminium, copper and nickel, with k of 236, 401 and 94 W/mK, respectively [80], are commonly used as fillers for paraffin [24]–[27], [57]. Xiao et al.

[26] prepared paraffin/nickel foam and paraffin/copper foam composite PCMs. At 22.0 wt.% Ni and 25.7 wt.% Cu, the relative k were 3.2 and 16 times that of neat paraffin, respectively. The relative mass of the PCM composite was 1.25 and 1.31, and relative H_f was 0.76 and 0.714 respectively for 22.0 wt% Ni and 25.7 wt% Cu, which is slightly lower than the weight loading of paraffin of each sample. In another study, Xiao et al. [28] prepared paraffin/nickel foam and paraffin/copper foam composite PCMs using foams of different porosity. The highest relative k for paraffin/nickel was 6.6 recorded at the lowest porosity of Ni foam used (90.61%). The highest relative k for paraffin/copper was 45.2 recorded at a porosity of 88.89%. Xiao et al. concluded that for metal foams, the effective k of the composite was primarily due to how much of the metal is present in the composite, which is expected as the metal used had a much higher k than paraffin. Copper was also more effective at improving the effective k of paraffin composites than nickel due to the higher k of copper. Researchers have also attempted to use a combination of metallics with graphene and diamond coating to further enhance k . Hussain et al. [24] compared k of paraffin composites infused with nickel foam and nickel foam coated with graphene (Ni-G) synthesized using CVD. Compared to neat paraffin, relative k of Ni/paraffin was 6.3, relative mass was 1.17 and relative H_f was 0.84. For Ni-G/paraffin, relative k was 24.2, relative mass was 1.36 and relative H_f was 0.69 compared to neat paraffin. The coating of graphene significantly improved the relative k , at a cost of additional mass and larger reduction in H_f . Zhang et. al. [57] prepared paraffin/3D-diamond on copper substrate foam (3D-DF) composite PCM. 3D-DF was synthesized by template-directed CVD on Cr-modified Cu foam. At a loading factor of 35.9 wt%, relative k of the PCM composite was 26.8 times that of neat PCM. Relative H_f was 0.648 and relative mass was approximately 1.6. The magnitude of H_f and mass trade-off was like Ni-G. In conclusion, the common trend for PCM composite with metallic scaffold was a high relative k of up to 16 times, however the trade-offs are a significant mass increase and low relative H_f .

2.6.2.2 Carbon scaffold

An alternate 3D scaffold that has been used to enhance k in PCM are carbon-based scaffolds and they have been studied by multiple groups [32], [39], [56], [79], [81]–[84]. They can be widely categorized as graphite foams and the less dense 3D-C. Graphite foams, like metallic foams, increases the surface area of high thermal conductivity in contact with the PCM, resulting in a more even melting and freezing, and thus a smoother heat absorption and rejection process. Graphite foams are commonly made from compressed expanded graphite (CEG) [85], by hydrothermal reaction of graphene oxide prepared by the modified Hummers' method [86], [87] or by foaming of mesophase pitch at high temperature and pressure and subsequent graphitization at 2800 °C [88]. Graphite foams prepared using such methods have good mechanical properties, are chemically inert and have irregular pores sizes with an open porosity of 96% [39], [89], and anisotropic k properties, with a much higher relative k in the radial direction, perpendicular to the direction of compression [81], [82]. The common method of composite preparation is liquid PCM impregnation into graphite foams in ambient or vacuum conditions. Impregnation ratio (α) is calculated by dividing the volume fraction of the paraffin by the open porosity (ε) of the scaffold foam, as shown in equation (2.1).

$$\alpha = \frac{vol\%_p}{\varepsilon} \quad (2.1)$$

Warzoha et. al [39] reported that vacuum impregnation can improve α to nearly 100% of the open porosity of the graphite foam, as compared to an average α of 61% under ambient conditions.

With CEG foams, the apparent density of the graphite scaffold can be tune-able. Wu et al. [81] prepared stearic acid and CEG composites with packing density of 700, 800, 900, 1000 kg/m³ and CEG of 15, 20, 25, 30 wt.%. The composite with 25 wt.% CEG and packing density of 900 kg/m³ was concluded to be the optimal configuration, with a relative k of 129

in the radial plane and 4 in the axial plane, and relative H_f of 0.75. Py et al. [82] prepared PCM composites with CEG and hexadecane, a type of paraffin wax, with 5 – 35 wt% of CEG. Relative k was reported to be 20.8 – 416.7 in the radial plane and 16.7 - 41.7 in the axial plane. The anisotropy was associated with the different alignment of the graphite crystal basal planes, which k could vary from 10 (x-axis) to 2000 (a-axis) W/mK. This irregularity makes it more difficult to predict the effective thermal conductivity of PCM/graphite foam composites. Overall, PCM composites with graphite foams helps achieve shape-stabilization, a higher relative k than PCM composites with copper foam, at a similar trade-off of relative H_f .

3D-C is a novel graphene-based micro-skeletal scaffold synthesized through template assisted CVD. Chen et al. [42], the first research team to publish on CVD growth of 3D-C, documented the procedure of synthesis. Ni foam was used as template. During the CVD, graphene precipitates onto the surfaces of the Ni foam template/catalyst, forming a few-layers-graphene coating, or Ni-G. A protective coating of poly(methyl methacrylate) (PMMA) is used before etching the Ni template in hot hydrochloric acid. Acetone is subsequently used to dissolve PMMA, resulting in free-standing 3D-C. This interconnected network of graphene occurs below the percolation threshold of discrete graphene filler, hence a more reliable method to ensure a thermal network exists within the PCM composite. The 3D-C synthesized has an ultralow density of $\sim 5 \text{ mg/cm}^3$, a high porosity of $\sim 99.7\%$ and very high specific surface area of up to $850 \text{ m}^2/\text{g}$. These properties are ideal as PCM scaffold for applications that require very low mass, and high PCM latent energy density, such as smallsat. However, 3D-C have been reported to be brittle [44], hence increasing the difficulty of handling and infusion process. Therefore, methods to reinforcement 3D-C may be required before infusion with paraffin.

Thermal properties of paraffin wax infused with 3D-C have been studied [32], [56], [84]. Ji et al. [56] prepared 3D-C/paraffin composites at 2.4 wt.% and reported a relative k of

8.2 and insignificant changes in H_f . This 3D-C has a lower porosity (99.2%) and hence higher apparent density as compared to that reported for Chen et al. [42]. Ji et al. also annealed a sample of 3D-C at 3000 °C for 1 hour in inert argon environment. The annealed 3D-C filled 3.6 wt.% of the corresponding 3D-C/paraffin composite and has a relative k of 18.0 and relative H_f of 0.98. The results show that 3D-C is a promising reinforcement to produce PCM composites with negligible change to paraffin mass and H_f . The trade-off will be a smaller relative k as compared to graphite foam and some metal foam, and higher difficulty in handling due to brittleness. The positive characteristics perfectly fulfil the criteria for smallsat application. A summary of the k enhancement of PCM with 3D scaffolds is shown in Table 2.7.

Table 2.7 Summary of k enhancement of PCM with 3D scaffolds

PCM type	Filler name	Fill fraction	Relative $k_{(\text{composite})}$	Relative H_f	Ref
Metallics					
Paraffin	Ni foam	~10 vol.%	6.3	0.84	[24]
	Ni-G foam	~10 vol.%	24.2	0.69	
Paraffin	Ni foam	19 – 22 wt.%	3.2 – 4.2	0.78 – 0.76	[26]
	Cu foam	25.7 wt.%	16.1	0.73 – 0.70	
Paraffin	Cu foam	NA	14.2 – 45.2	NA	[28]
	Ni Foam		3.5 – 6.6		
Paraffin	Cu foam	41 wt.%	10.2	0.67	[57]
	3D-DF	41 wt%	26.8	0.65	
Carbon scaffold					
Paraffin	UGF (annealed)	3.6 wt.%	18	0.982	[56]
	UGF	2.4 wt%	8.2	1.008	
Erythritol	UGF	1.8 wt.%	2.6	0.985	
Paraffin	Graphite foam	22 wt.%	10.8	0.78	[83]
Paraffin	Carbon foam	9.2 wt.%	3.4	0.87	[84]

2.7 Containment of PCM

To implement solid-liquid PCM in application, containment in terms of packaging is required to hold the PCM in its liquid state to not contaminate the system. There are three main types of containment, macro-encapsulation, micro-encapsulation and form stabilized PCM [72]. The common goal of these systems is to completely contain the liquid PCM in a shell or capsule. One main challenge is the PCM volume change during melting. This results in an empty space within the container while the material is in the solid phase, referred to as ullage space, and has been reported by NASA in early 1977 [68] and observed by various researcher [36], [79], [90]. This ullage space will lead to a decrease in thermal contact of the container with the PCM and within the PCM itself. Therefore, additional design to the container is required to maintain the k of the PCM system.

Micro-encapsulated PCM have been studied as a slurry mixture with water and silicon oil as a coolant in a heat exchanger for spacecraft thermal systems [91]. This process allows PCM to remain in the powdered solid form within the micro-encapsulation after melting. However, the k of PCM remains low, and would remain at low heat transfer efficiency in passive TMS applications.

Macro-encapsulation was used in previous space applications of paraffin TMS [73]–[75], [92]. PCM, with additives in some applications, were hermetically sealed in containers to ensure zero outgassing and leakage of PCM. In the application of PCM heat sink [74], PCM was sealed in aluminium containers, forming the heat sink, and pipes for the coolant were built around the PCM heat sink for heat exchange. Macro-encapsulation is the ideal method of encapsulation for space application since it allows for the hermetic sealing of PCM.

A rigid porous skeletal wettable by the PCM would commonly be infused with PCM for form-stabilization. The skeletal act as the supporting scaffold and liquid PCM would be added for infusion. In some combinations, the combination of atmospheric pressure and

capillary forces of the porous skeletal was sufficient to contain the PCM, even in the liquid state. A combination of sufficiently high frictional force between the skeletal walls and viscous liquid PCM and small pore size were the key factors that determine the containment effect. Such form stabilized PCM can eliminate the ullage created by PCM during solidification. Yang et al. [93] reported on PCM infused with cellulose and graphene aerogel as form-stabilized PCM composite. The PCM used did not leak in the liquid state. The study attributed this phenomenon to the capillary forces of the cellulose/graphene aerogel skeletal. Zeng et al. [94] investigated a eutectic mixture of erythritol and mannitol as PCM infused with 1 – 5 wt.% of exfoliated graphite as form-stable PCM thermal energy storage. Sari [95] fabricated form-stabilized paraffin with high density polyethylene (HDPE) of various fill fractions as solid-liquid PCM for thermal energy storage. Sari also reported that the H_f of the final composite changes according to the paraffin fill fraction, i.e., the PCM composite with 50 wt.% paraffin will have about 50% of the H_f as neat 100 wt.% paraffin. Hence the trade-off for form-stabilization would be the mass of PCM displaced by the rigid porous skeletal. Zhang et al. [96] reported a similar finding with paraffin/HDPE/expanded graphite infused with intumescent flame retardant, where the PCM composites with 60 wt.% paraffin has less than 60% of the original H_f of paraffin. This method of encapsulation removes the need of a casing, hence reducing the mass of the PCM TSU. However, the holding forces will be weaker in the vacuum space environment resulting in possible unwanted leaks. This compromise deems this encapsulation method on its own unusable for space application.

2.8 Conclusions

PCM TSU as passive TMS is an attractive thermal solution for smallsats as PCM TSUs have high energy density, small form factor, relatively less bulky and lightweight, and do not consume power. The temperature cycles experienced during orbit could naturally reset the PCM for the next thermal load. Out of the available PCMs, organic paraffin PCMs are

highly suitable for space application as they have low outgassing, high thermal cycling stability, high H_f and a variety of T_{melt} available for application, and are non-toxic, non-corrosive and compatible with metallic and carbon-based materials commonly used on satellites. These properties ensure high performance and low degradation of PCM functionality throughout the 1-year service lifetime of a CubeSat. However, to successfully implement PCM TSU in smallsats, the k of paraffin needs to be improved, and the packaging of the PCM require considerations for the phase change volumetric difference and hermetic sealing. The ideal k enhancement method would be one that sufficiently improves k , at minimal expense of mass and volumetric specific H_f , which translate to low mass and volumetric loading of the additive into paraffin. The additive and packaging material should be surface compatible with paraffin to optimise heat transfer.

In this thesis, paraffin wax was selected as the base material of research and 3D-C micro-skeletal was identified as a suitable additive to paraffin for k enhancement and form-stabilization. Aluminium Al6061 was selected as the container material for PCM macro-encapsulation. Thermal analysis was conducted on PCM composites in packaging with use-case parameters to obtain realistic PCM TSU performance results in application. The composite of 3D-C and paraffin wax has not been studied in context of space environment applications; hence the results will be a novelty.

3. Experimental Methods

Throughout this thesis, 3D-C micro-skeletal was used as the primary scaffold material for k enhancement and shape-stabilization of PCM for smallsat application. Different apparent densities in two groups of 3D-C (5 and 10 mm thick) were first studied to realise the minimum density of each group of 3D-C to remain un-compromised after infusion with PCM. Subsequently, a systematic study was conducted between 3D-C and GP derived from 3D-C to determine the better filler for PCM in smallsat application. Thereafter, the impact of different filler fraction of 3D-C was studied on 1 cm thick 3D-C variant to obtain the optimal range of 3D-C fraction in the 3DCPCM. Synthesis of 3D-C embedded in CH as an alternate scaffold reinforcement for PCM composite is described in Chapter 6. The minimum apparent densities of 3D-C to synergize with CH was obtained from that study.

A paraffin PCM with high H_f and favourable working phase change temperature was selected from supplier, Rubitherm, as the base PCM matrix. The selected PCM, named RT35HC [97], has a T_{melt} of 34 – 36 °C, H_f of 240 (± 7.5 %) kJ/kg and expansion of 12% during melting.

The experimental methods to synthesize 3D-C micro-skeletal, discrete GP, 3DCPCM, GPPCM and CH3DCPCM, along with their standard characterization are described in this Chapter.

3.1 Raw Materials and Synthesis methods

3.1.1 Growth of 3D-C

The 3D-C was synthesized using CVD method using Ni foam template as raw material based on the method used by Chen et al. [42]. The mechanism of CVD of graphene on Ni is a 3-step process; viz., 1) decomposition of methane (CH_4) precursor in the presence of Ni catalyst, 2) dissolving of carbon (C) atoms into the 1000 °C, C-soluble Ni substrate. 3)

Precipitation of C atoms as Ni substrate cools and C solubility decreases [98]. Hence the deposition of graphene onto the Ni foam could be increased in by extending the period of deposition. Furthermore, since the precipitated graphene does not readily re-dissolve in Ni again at high temperature, repeated runs of CVD process allow further dissolution of carbon atoms and precipitation of graphene onto the existing graphene deposits on the Ni foam. Using these methods, the graphene content on the Ni foam can be perpetually increased.

Two batches of Ni foam supplied from Latech Scientific Supply [99] were used as templates. One batch was 5 mm thick with 110 pore per inch (PPI) with an average apparent density of 0.147 g/cm^3 and the other batch was 10 mm thick with 60 PPI with an average apparent density of 0.420 g/cm^3 . The average values were calculated over 10 sample. The 10 mm thick Ni foam had a 10-sample average porosity of 95.3 %, and the 5 mm thick Ni foam had a 10-sample average porosity of 98.3%. Ni foam samples were cut to a standard 40 mm by 150 mm blocks and weighed in preparation for CVD.

One block of Ni foam was placed in a 2-inch inner diameter quartz glass tube and heated up to $1000 \text{ }^\circ\text{C}$ in a CVD furnace at a rate of $20 \text{ }^\circ\text{C/min}$ under an environment of Hydrogen (H_2) and Argon (Ar) gas as shown in Figure 3.1. The Ni foam was annealed at $1000 \text{ }^\circ\text{C}$ for 30 mins before the precursor gas, CH_4 , was channelled into the quartz tube to begin the carbon deposition. After the deposition period, the furnace was rapidly cooled in air to allow the carbon in the Ni foam to precipitate as graphene. The Ni-G foam was removed after the quartz tube has cooled to room temperature. The precursor deposition time can be adjusted to achieve different mass of graphene coating; a longer deposition time will lead to a high mass of graphene coating. Ni-G was weighed again, and the mass gain was recorded as the amount of graphene deposition.

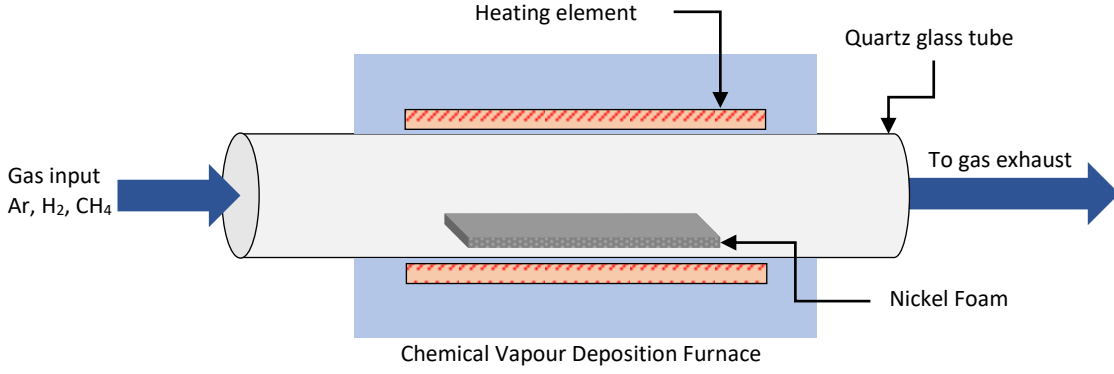


Figure 3.1 Schematic of CVD growth process of 3D-C

Ni-G was placed in 4 parts of 1 mol/dm³ hydrochloric acid (HCl) diluted with 6 parts of water for 30 hours at a reflux of 80 °C to fully etch the Ni substrate to obtain freestanding 3D-C. The 3D-C without the Ni substrate was washed multiple times in deionised water and dried in an oven at 70 °C for 12 hours. The 3D-C was weighed and was compared to the graphene deposition weight. If the 3D-C weight were more than 5% larger than graphene deposition weight, it was indicative that some Ni remain on the 3D-C and hence would need a longer etching period. In such cases, the 3D-C would be placed in HCl again for a further 6 hours or more before washing, drying, and weighing again. This method differs from that of Chen et al. [42], as the Ni-G was not coated with a protective layer of PMMA before etching in HCl. PMMA is difficult to remove completely and residues remain after the removal process, which will interfere with the thermal contact of 3D-C with paraffin and potentially affect the effective k of the composite. The graphene deposit on Ni-G needs to be of a critical apparent density before HCl etching to reduce damages to 3D-C during etching,

The apparent density and porosity of 3D-C is calculated indirectly based on measured values. The density (ρ) of 3D-C was calculated by dividing the mass (m) of freestanding 3D-C by the volume encompassed by the 3D-C micro-skeletal ($V_{(3D-C)}$), which was calculated by taking the product of the length (L), width (W) and thickness (t) of the 3D-C sample, as shown in equations (3.1) and (3.2).

$$V_{(3D-C)} = [L \times W \times t]_{(3D-C)} \quad (3.1)$$

$$\rho_{(3D-C)} = \left[\frac{m}{V} \right]_{(3D-C)} \quad (3.2)$$

The porosity (ϕ) of 3D-C was calculated using the theoretical density of pyrolytic graphite [100], $\rho_{(graphite)}$, as shown in equation (3.3).

$$\phi_{(3D-C)} = 1 - \frac{\rho_{(3D-C)}}{\rho_{(graphite)}} \quad (3.3)$$

3.1.2 Carbon Honeycomb

Space qualified CH was sourced from Ultracor Inc., product code UCF-126-3/8-2.0 [101]. The construction materials of CH were pitch fabric and cyanate. The cell size chosen was 3/8" or 9.525 mm, and wall thickness was approximately 0.1 mm. The nominal density of the CH is 32 mg/cm³ according to the datasheet. Sheet size and thickness of the CH can be customised. The CH has zero coefficient of thermal expansion (CTE) and a through-thickness k of 2.88 W/mK measured in Nitrogen, according to the datasheet provided by the supplier. Figure 3.2 (b) show a 45 mm * 45 mm * 10 mm thick CH sample with the mentioned properties. The holes on the CH cell walls were a property requirement for space as they allow air within the honeycomb core to escape to prevent pressure build up within cells. The holes also allow PCM to flow freely between honeycomb cells, thus maintaining the open cell property of the overall CH + 3D-C scaffold.

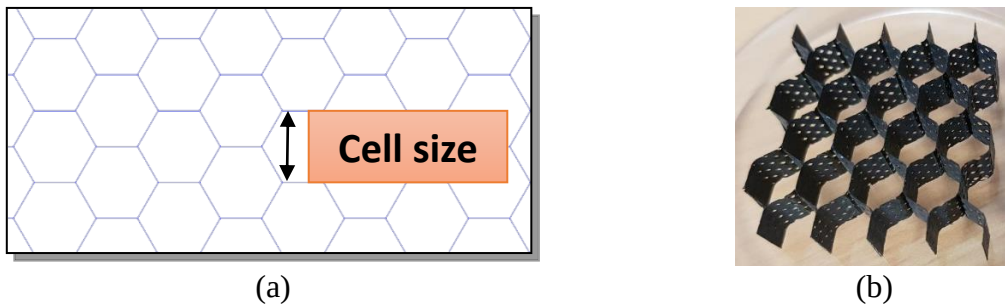


Figure 3.2 (a) Definition of cell size of a honeycomb cell. (b) Carbon honeycomb of dimensions 45mm * 45 mm * 10 mm thick.

3.2 Fabrication of PCM composites

3.2.1 Fabrication of 3DCPCM

The PCM used in this section is RT35HC. 3D-C was infused with PCM using the immersion method. Solid PCM pieces were placed in an aluminium (Al) mould and heated up on a hot plate at 70 °C until PCM was fully liquid. 3D-C sample was cut to size, weighed, and fully immersed in the PCM. Liquid paraffin was observed to wet the surface of 3D-C well and wick through the open pores of the 3D-C entirely, hence no additional agitation was required.

The Al mould was taken off the hot plate and the sample was slowly cooled at room conditions. Slow cooling allows nucleation to first occur on the graphene surfaces due to heterogeneous nucleation, thus ensuring thermal contact between the scaffold and paraffin. The excess PCM was removed and the 3DCPCM sample was weighed. A schematic of the 3DCPCM infusion process is shown in Figure 3.3. Neat paraffin samples were fabricated using the same method without adding 3D-C.

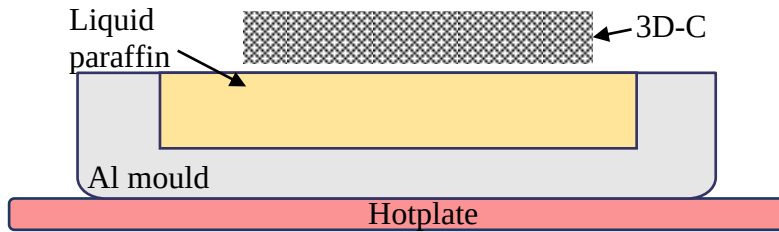


Figure 3.3 Schematic of infusion of 3D-C into PCM.

The graphene loading (φ) according to mass fraction of 3D-C for 3DCPCM was calculated by dividing the mass of the 3D-C ($m_{(3D-C)}$) by the final mass of the sample ($m_{(3DCPCM)}$) cut to the same dimensions as the 3D-C infused, as shown in equation (3.4). $\varphi_{(3DCPCM)}$ was found to be 1.5 wt.%.

$$\varphi = \frac{m_{(3D-C)}}{m_{(3DCPCM)}} \quad (3.4)$$

3.2.2 Fabrication of discrete GP and GPPCM

Discrete GP was fabricated using a portion of the 3D-C sample. 3D-C was ground in an agate mortar pestle. The ground GP was weighed and dispersed in acetone using an ultrasonic water bath (Elmasonic P30H), maintained at 50 °C, over 1 h. A specific mass of liquid paraffin was added into the mixture such that the mass fraction GP was the same graphene loading as in the 3DCPCM samples. The mixture of graphene, acetone, and PCM was further sonicated for 8 h. 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 GP 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. A schematic of the preparation process of GPPCM is shown in Figure 3.4.

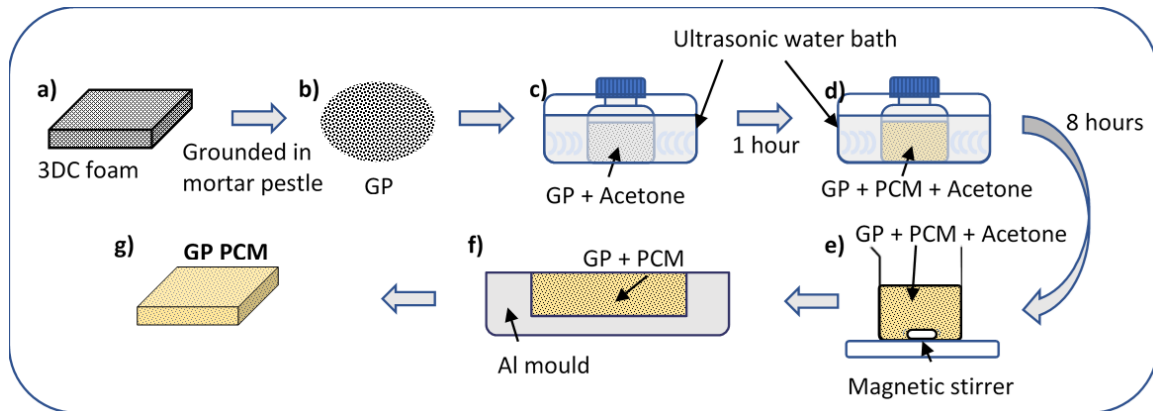


Figure 3.4: Schematic of the preparation of GPPCM. (a-c) 3D-C micro-skeletal was grounded to GP and sonicated in acetone solution. (d) PCM was added into the mixture and was further sonicated for 8 hours. (e) Mixture is stirred in a beaker at 100°C to evaporate the acetone. (f) PCM with suspended GP was poured into an Al mould to solidify fully at room temperature. Sample was extracted and sanded to obtain g) GPPCM.

3.2.3 Fabrication of CH3DCPCM

3.2.3.1 Carbon honeycomb core + 3D-C

CH would first be physically merged with 3D-C to form CH+3D-C scaffold. 3D-C needed to stay free-standing and be physically in contact with the inner walls of CH for CH+3D-C scaffold to be viable, hence a 3D-C of a higher density and rigidity would be favoured. CH with a cell size of 3/8 inches and dimensions of 45 mm * 45 mm * 10 mm thick

was placed on top of a 3D-C sample that was cut to a slightly larger length and width, as shown in Figure 3.5. The CH was lightly tapped to allow the CH cell walls to slice through the 3D-C in the required regions while retaining the structural integrity of the 3D-C in the rest of the sample. This method was advantageous because a successful CH+3D-C scaffold fabricated from this method would have CH cell walls hugging the 3D-C in the cell within, thus ensuring thermal contact on every interface of CH and 3D-C. The CH+3D-C scaffold was held with a pair of tweezers and the CH region was tapped a few times with a spatula to test the CH/3D-C interfacing and ensure that the 3D-C does not fall out.



Figure 3.5 CH was placed on top of 3D-C sample in preparation to be merged.

3.2.3.2 CH + 3D-C + PCM

The CH+3D-C scaffolds fabricated was prepared to be infused with PCM using the immersion method described in section 3.2.1, with RT35HC as PCM. After the PCM has solidified, the excess PCM was cut away, leaving the completed CH3DCPCM. Figure 3.6 shows the ideal merged CH/3D-C scaffold and CH3DCPCM at the corresponding viewing angles. The height of the CH should be flush with the 3D-C both before and after infusion, as seen in Figure 3.6 (a) & (b). This would indicate that the sample had retained its shape after infusion, and therefore 3D-C structure was not compromise both after merger with CH and after infusion with PCM. In such a case, shape stability property of 3DCPCM would have been preserved after addition of CH.

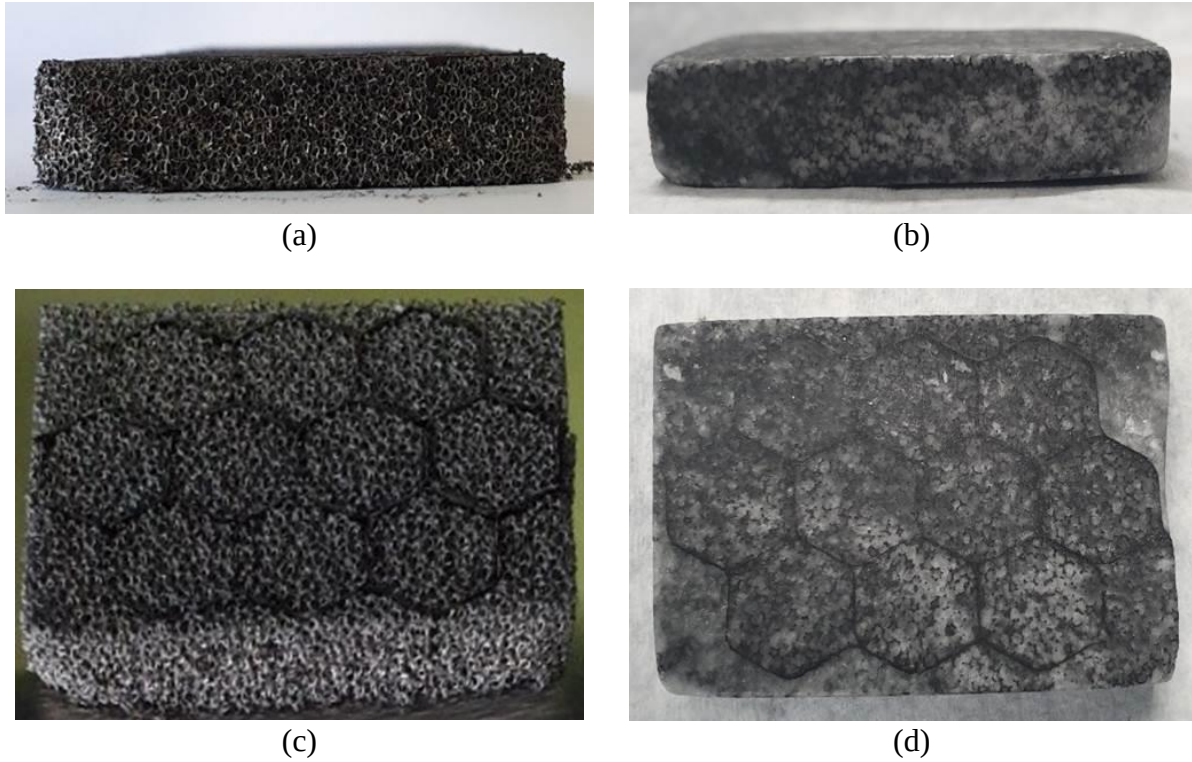


Figure 3.6 (a)&(c) Side and top view, respectively, of sample prior to infusion. CH+3D-C/10/2.0. (b)&(d) Side and top view, respectively, of sample after infusion. CH+3DCP/20.1.

3.3 Material Characterisation Methods

The material properties of 3D-C such as porosity, morphology and crystalline structure of the graphene are crucial indicators of the quality and hence potential k enhancement of the 3D-C for the PCM composite. Therefore, the 3D-C needs to be characterized before infusion into PCM. After infusion, the composite characteristic k and H_f needs to be obtained. In this section, the various characterization techniques are listed and explained in detail.

3.3.1 3D-C morphology and chemical structure

The morphologies of 3D-C were characterised with a JEOL JSM IT100 scanning electron microscope (SEM).

Raman spectroscopy was observed using WITec UHTS 300 Raman Spectrometer at an excitation wavelength of 532 nm to characterize the crystalline structure of graphene in 3D-C.

Transmission electron microscopy (TEM) was used to characterise the lattice structure and the crystalline structure of exfoliated flakes of graphene on the 3D-C sample. TEM was done by an external vendor. The 3D-C sample was first sonicated to exfoliate graphene interlayers in preparation for TEM.

3.3.2 Thermal conductivity measurements

Literature provides multiple measurement methods for bulk thermal conductivity measurement [102]. The methods can be broadly categorised into the slower steady-state methods, and transient methods, such as hot-wire method, laser flash diffusivity method and transient plane source method. Each method is limited by sample type and measurable k range with acceptable error. In general, it is highly challenging to measure the bulk thermal conductivity within a 5% error. Understanding the fundamentals and procedures of the selected testing technique is hence crucial to understand where the potential error sources arise. Measuring PCM composites has the added challenge of ensuring the sample does not change phase throughout the measurement. With an appreciation of error sources, certain random errors could then be eliminated or reduced, for example thermal contact resistance between the sample surface and the tester. Other sources of error such as losses to convection and radiation could be accounted for in calculation. Measurement standards such as the American Society for Testing and Materials (ASTM), and ISO were studied and followed closely such that the results could be better compared across measurements. Customised in-house measurement devices were built to cater to specific sample sizes and k range of PCM composites. The methods used and the calculations involved is documented in the following section.

3.3.2.1 Lee's disc method

The solid-state k of PCM composites can be obtained using the steady state Lee's disc method as per ASTM C177. This method is suitable for samples with thickness above 0.5 cm and $k < 2$ W/mK. Sachithanadam et al. [103] used a similar set-up to obtain the k of silica aerogel. This set-up consists of 3 copper plates of dimensions 7.5 cm * 4.5 cm * 0.3 cm and a silicon heater plate of dimensions 7.5 cm * 4.5 cm * 0.1 cm. Samples are required to be shaped into blocks with 7.5 cm * 4.5 cm surfaces and a thickness above 0.5 cm. An adjustable DC power supply is used to power the silicon heater. The temperature of each component, T_1 , T_2 , T_3 and T_{ambient} , was measured using k-type thermocouples and recorded with a data logger. A schematic of the set-up is shown in Figure 3.7. The measurements were conducted in a Thermotron SE-300 enclosed chamber to maintain a consistent ambient temperature and humidity of the setup.

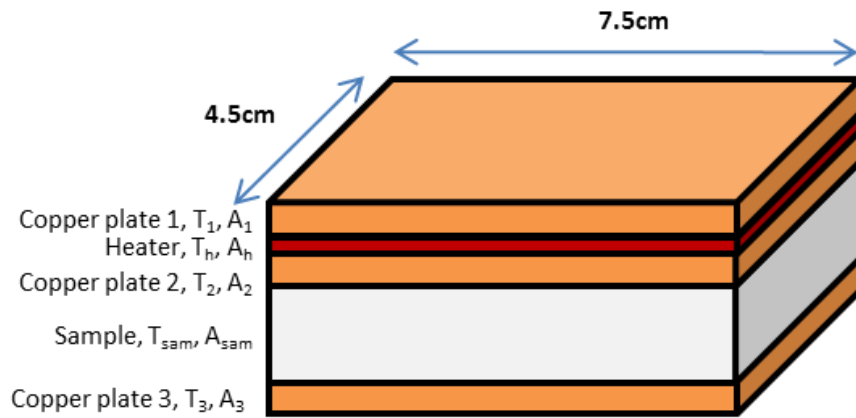


Figure 3.7 Schematic of thermal conductivity measurement using Lee's Disc method.

The steady state temperatures of each component were recorded. Steady state could be assumed after constant power has been applied to the heater for 2 hours, or the temperature variation picked up by the thermal couple is 0.1 °C or less for the past 10 mins. A typical temperature measurement is shown in Figure 3.8.

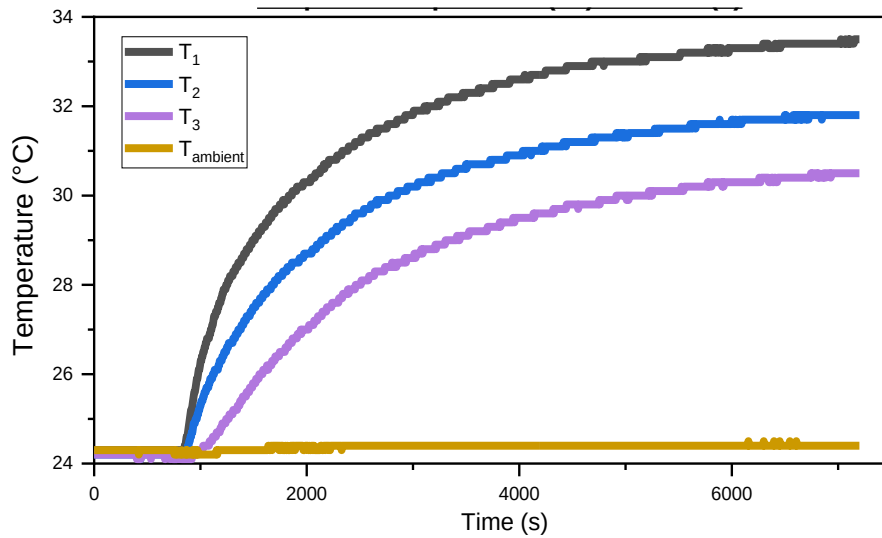


Figure 3.8 Typical temperature profile of 3DCPCM under power loading of 0.976W.

The PCM cannot enter the phase change to the liquid state during measurement as there was no containment for the liquid PCM in this set-up. Hence for the RT35HC PCM used, the temperature of the samples should not increase beyond 34 °C. The power rating of 0.976 W was found to be sufficient to reach the steady state just below 34 °C for 10 mm thick 3DCPCM samples. The image of the actual set-up with the 3DCPCM sample is shown in Figure 3.9



Figure 3.9 Actual set-up of the Lee's disc method with a sample of 3DCPCM.

The k of the sample could be derived using equation (3.5), where $\dot{Q}$ is the rate of heat flow into the sample measured in the unit W, $k_{(sam)}$ is the thermal conductivity of the sample measured in W/mK, and $((T_2 - T_3)/t_{(sam)})$ is the temperature gradient across the sample of cross section (A_{cs}).

$$\dot{Q}_{(sam)} = (kA_{cs})_{(sam)}(T_2 - T_3)/t_{(sam)} \quad (3.5)$$

However, heat loss through the surfaces of the setup by convection and emission must be accounted for. At steady state equilibrium condition, the rate of heat loss to the surrounding will be equivalent to the rate of heat generation in the heater, assuming temperature is uniform across the surfaces and edges of the individual part. The equation becomes,

$$VI = e_1\{A_1(T_1 - T_s) + A_2(T_2 - T_s) + A_3(T_3 - T_s) + A_h(T_h - T_s)\} + e_2A_{(sam)}(T_4 - T_s) \quad (3.6)$$

Where e_1 , e_2 represents the heat loss per unit area of Cu and PCM sample respectively with the units W/m^2K , T_s represents ambient temperature, VI is power supplied by heater and represents the heat generation in the heater.

Unknown heat loss constants e_1 and e_2 in equation (3.6) can be related to reduce the number of unknowns. For a body of uniform composition, its thermal mass, or heat capacity can be approximated to be equivalent to the product of the mass and specific heat capacity, $m \times c_p$. Therefore, the equivalent thermal mass of paraffin composite sample in terms of copper, for similar cross-sectional area, A_{cs} , can be represented as follows.

$$t_{Cu(eq)}(\rho \times c_p)_{Cu} = t_{(sam)}(\rho \times c_p)_{(sam)} \quad (3.7)$$

$$\frac{e_2}{e_1} = \frac{A_1}{A_2} = \frac{A_{Cu(eq)}}{A_{(sam)}} = \frac{Pt_{Cu(eq)}}{Pt_{(sam)}} = \frac{t_{Cu(eq)}}{t_{(sam)}} = \frac{(\rho \times c_p)_{(sam)}}{(\rho \times c_p)_{Cu}} \quad (3.8)$$

Where $t_{Cu(eq)}$ represents the equivalent thickness of the sample if it was made of Cu, P represents the perimeter of the cross-sectional area, which is constant for the Lee's Disc method, and ρ represents the density of the material. Since $A_1 = A_3$ and $A_h = \frac{1}{3}A_2$, combining equation (3.6) and (3.8) gives,

$$e_1 = \frac{VI}{A_1(T_1 + T_3 - 2T_S) + A_2\left(T_2 + \frac{1}{3}T_h - \frac{4}{3}T_S\right) + Pt_{Cu(eq)}(T_4 - T_S)} \quad (3.9)$$

The numerical value of e_1 can be found. Since the amount of heat flowing across the sample is equivalent to the heat emitted from Cu plate 3,

$$\dot{Q}_{(sam)} = e_1 A_3 (T_3 - T_S) \quad (3.10)$$

Substituting equation (3.10) into equation (3.5), an equation for $k_{(sam)}$ was obtained.

$$k_{(sam)} = \frac{t_{(sam)} e_1 A_3 (T_3 - T_S)}{(A_{cs})_{(sam)} (T_2 - T_3)} \quad (3.11)$$

The value of $k_{(sam)}$ can thus be found from the experimental data.

The Lee's disc set-up was calibrated using a reference material of known conductivity. Furthermore, when used to measure the k of neat PCM RT35HC, the result of $k_{(sam)} = 0.25$ W/mK agrees with the values reported in the data sheet provided.

The Lee's disc method was meant to be an in-house set-up to measure low k samples. It was not recommended to use this method to accurately measure samples with k values of more than 2 W/mK. After performing error analysis using equation (3.11), it was calculated that for a sample with $k = 2.5$ W/mK, using the inputs used in the experiment, power input = 1 W and sample dimensions of 7.5 cm * 4.5 cm * 1.0 cm, an error of ± 0.1 °C in $(T_2 - T_3)$ would swing the $k_{(sam)}$ result by $\pm \sim 0.5$ W/m, which would be a 20% uncertainty. For samples with $k = 0.25$ W/mK, the same error in $(T_2 - T_3)$ results in ± 0.017 W/mK or a 6.8% uncertainty. The uncertainty exponentially increases at higher k values. Since the resolution for each thermocouple is ± 0.05 °C and 2 thermocouples are required to obtain T_2 and T_3 , the resulting uncertainty at $k_{(sam)} > 2.0$ W/mK would be too large to get measurement accurately. This uncertainty excludes random errors and other systematic errors. Since the prevalent uncertainties were higher than the resolution of hardware recording the measurements,

another set-up that has a lower uncertainty at high thermal conductivity levels will be required if 3DCPCM samples had $k > 2.0$ W/mK.

3.3.2.2 Transient plane source method

Another method found suitable to obtain k of 3DCPCM samples was the commercial measurement device, C-Therm TCi modular system with a modified transient plane source (MTPS) sensor [104]. The machine operates in compliance with ASTM Standard D7984-16.

The MTPS sensor is a single-sided, interfacial heat reflectance sensor with an integrated spiral heating element. During measurement, the samples was placed onto the sensor fixture directly. Deionized (DI) water was used as a TIM to reduce the thermal contact resistance. A momentary known current was applied to the heating element, which resulted in a temperature rise at the interface between the sensor and the sample. This induced a change in the potential difference of the sensor element. The rate of increase in the sensor potential difference was used to directly determine the k of the sample according to factory calibration. A steeper potential difference increase per unit time is indicative of a faster rate of temperature increase and in extension, results in a lower k of the sample. Typical measurement takes 1-3 seconds. Measurements by MTPS method was conducted by an external vendor, Thermal Analysis Labs.

3.3.3 Latent heat of fusion measurements

The H_f of the PCM and its composites were measured using differential scanning calorimetry (DSC). DSC measures the temperatures changes of a small pan of sample (~10mg) against an empty reference pan in an environment of a known gas (Nitrogen or Helium), and heated/cooled with a known heat/cool rate. A schematic of the DSC set-up is shown in Figure 3.10.

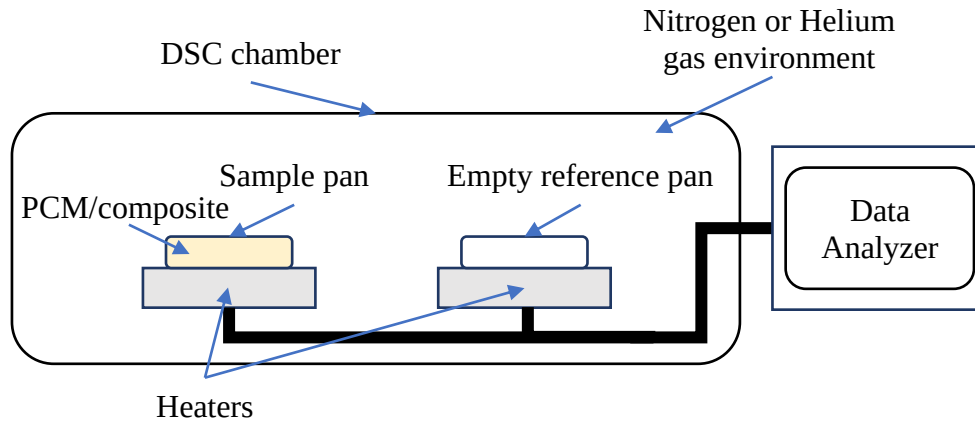


Figure 3.10 Schematic of a Differential Scanning Calorimeter

The heat flow obtained can be plotted as a function of time or temperature. The c_p and the H_f can be obtained from the graph of heat flow against temperature. TA Instruments DSC 2920 was used to carry out the measurements, and an integrated data analyser was used to program the heat cycles and extract the H_f from the results. Standard Al sample pans and lids provided by TA Instruments were used. A 5.00 – 10.00 mg sample was measured and loaded onto the Al pan. The lid was fitted on and the pan was crimped to contain the PCM. For samples using RT35HC as PCM matrix, a constant ramp rate of 5 °C/min was used. The sample was initially cooled to 0 °C, then heated to 70 °C and cooled back to 0 °C, and that would mark one cycle of measurement. A one-minute stabilization time was programmed at 0 °C and 70 °C to allow the sample to equilibrate at that temperature before the next stage. An alternative method for H_f measurement which considers PCM in use-case packaging is discussed in section 6.3.3.2.

4. Enhanced Phase Change Material: 3DCPCM

The objective of the material studies is to develop PCM composite with higher relative k at a minimal trade-off of relative H_f and mass. In Chapter 1, the advantages and disadvantages of each k enhancement method were listed and compared. The solution that was highly appropriate for smallsat application was infusion of high k 3D-C micro-skeletal with paraffin PCM as it provides a significant improvement in k with the smallest mass and H_f penalty. The synthesis process of 3D-C, infusion techniques with paraffin, characterization of samples were studied and improved such that the resultant samples better fitted the application criteria.

4.1 Sample Fabrication

4.1.1 Minimum apparent density of 3D-C

Two batches of Ni foam template were used in this fabrication, one with 10 mm thickness and 60 PPI, and the other with 5 mm thickness and 110 PPI. Samples of 3D-C was synthesized from both batches of Ni foam template according to the experimental methods described in section 3.1.1, with samples differing in CH₄ deposition at 1.0, 1.5 and 2.0 hours, to determine the critical apparent density of 3D-C and the trend of deposition time with 3D-C apparent density.

4.1.1.1 Results and Discussion

The results of deposition time and the corresponding apparent density of 3D-C is tabulated in Table 4.1. The sample naming convention for 3D-C sample is “3D-C/ (thickness) / (total deposition time)”.

Table 4.1 Total deposition time (h) and 3D-C density (g/cm^3) and porosity of various 3D-C samples. Values with * are calculated based on the graphene deposition.

Sample name	Ni foam thickness (mm)	Total deposition time (h)	$\rho_{(3D-C)}$ (mg/cm^3)	$\phi_{(3D-C)}$
3D-C/5/1.0	5	1.0	4.5*	0.998
3D-C/5/1.5	5	1.5	8.3	0.996
3D-C/5/2.0	5	2.0	16.3	0.993
3D-C/10/1.0	10	1.0	9.7	0.996
3D-C/10/1.5	10	1.5	12.8	0.994
3D-C/10/2.0	10	2.0	20.7	0.991
3D-C/10/4.5	10	4.5	42.6	0.982
3D-C/10/6.5	10	6.5	63.8	0.972
3D-C/10/7.5	10	7.5	74.7	0.967

The deposition rate per unit time was slightly higher for 10 mm thick foams. This was attributed to the lower porosity and hence higher Ni content in the 10 mm thick foams, thus allowing a larger amount of C to be dissolved.

3D-C/5/1.0 was the only sample to partially disintegrate during the HCl etching step, therefore the 3D-C density was calculated based on the graphene deposition mass. Hence the critical 3D-C apparent density would be between 4.5 and 8.9 mg/cm^3 for 5 mm thick foam and below 9.7 mg/cm^3 for 10 mm thick foam. This means that in future synthesis processes, a similar batch of 5 mm and 10 mm thick 3D-C can be synthesized using the method of HCl etching without PMMA if the graphene deposition exceeds 8.3 and 9.7 mg/cm^3 , respectively. The critical density of 3D-C should be characterized again for every batch of Ni foam with different porosity, PPI and strut thickness, for methods of synthesis using HCl etching without PMMA.

Each freestanding 3D-C sample could be shaped into simple cuboid blocks as well as circular samples using laboratory blade and aluminium cutting moulds, as shown in Figure 4.1 (b) and (c), in preparation for infusion with paraffin.

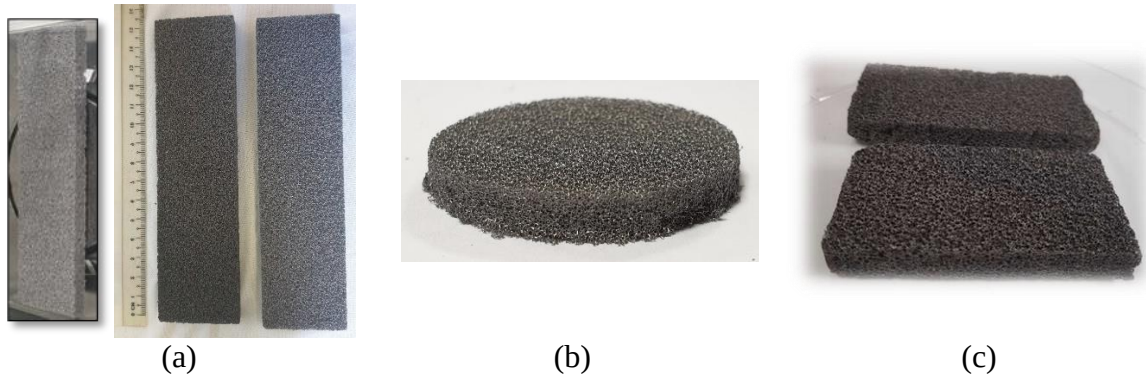


Figure 4.1 (a) 10 mm thick Ni foam (left), Ni-G (centre) and free-standing 3D-C (right). (b) 5 mm thick 3D-C cut into circular samples of radius 33 mm. (c) 10 mm thick 3D-C cut into cuboid blocks

4.1.2 Fabrication of 3DCPCM

The samples of 3D-C synthesized as described in section 4.1.1, were infused with PCM, according to the methods described in section 3.1.2.

4.1.2.1 Results and Discussion

Figure 4.2 (a) and (b) shows neat paraffin samples and 10 mm thick 3DCPCM samples after infusion. 3DCPCM sample prepared using 3D-C/1.5/5 was found to have a 30 % thickness reduction after infusion, which indicate that the 3D-C had collapsed during the process of infusion, as shown in Figure 4.2 (c). The structural integrity of the 3D-C and hence the thermal network would have been compromised. 3DCPCM prepared using the rest of the 3D-C samples was observed to have the same thickness as the 3D-C micro-skeletal, which indicates that the structure of 3DC withstood the infusion process. Hence the minimum apparent 3D-C density to produce a free-standing 3D-C was found to be 9.7 mg/cm^3 for the 10 mm thick sample and 16.3 mg/cm^3 for the 5 mm thick sample.

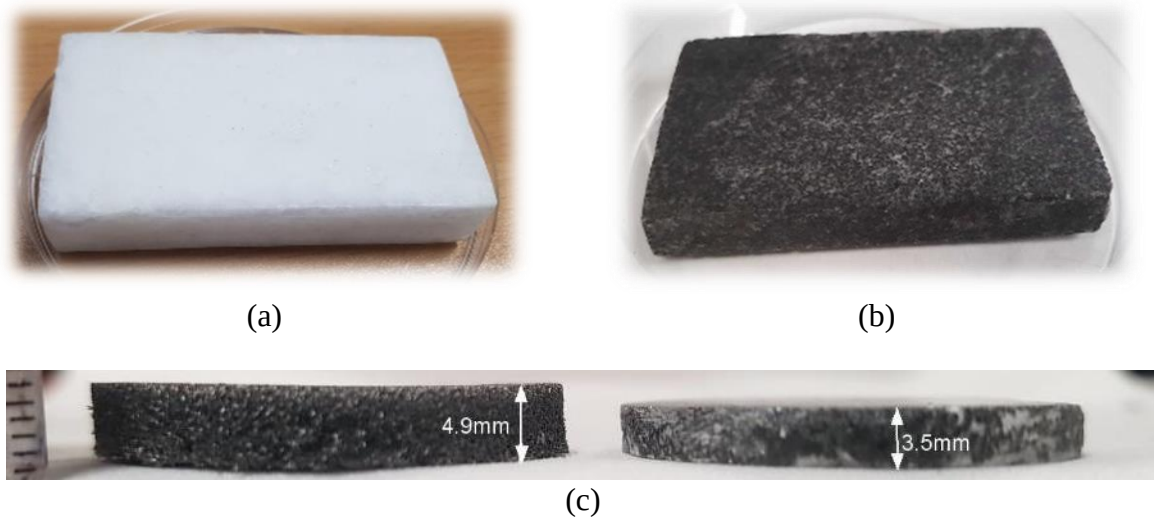


Figure 4.2 (a) Neat paraffin wax, (b) 3DCPCM after infusion with 10 mm 3D-C. (c)(left) 3D-C measuring a thickness of 4.9 mm, (right) 3DCPCM measuring 3.5 mm after infusion, a thickness reduction of about 30%

A 3DCPCM sample infused using 3D-C/10/10 was melted on a folded Al foil boat placed on a hot plate as shown in Figure 4.3. After the paraffin has completely melted, the 3D-C remained free-standing in its pre-infusion shape and dimensions. This is indicative of that, at the apparent density of 9.7 mg/cm^3 , 3D-C structure could withstand the stresses experienced during infusion and remain intact and interconnected.

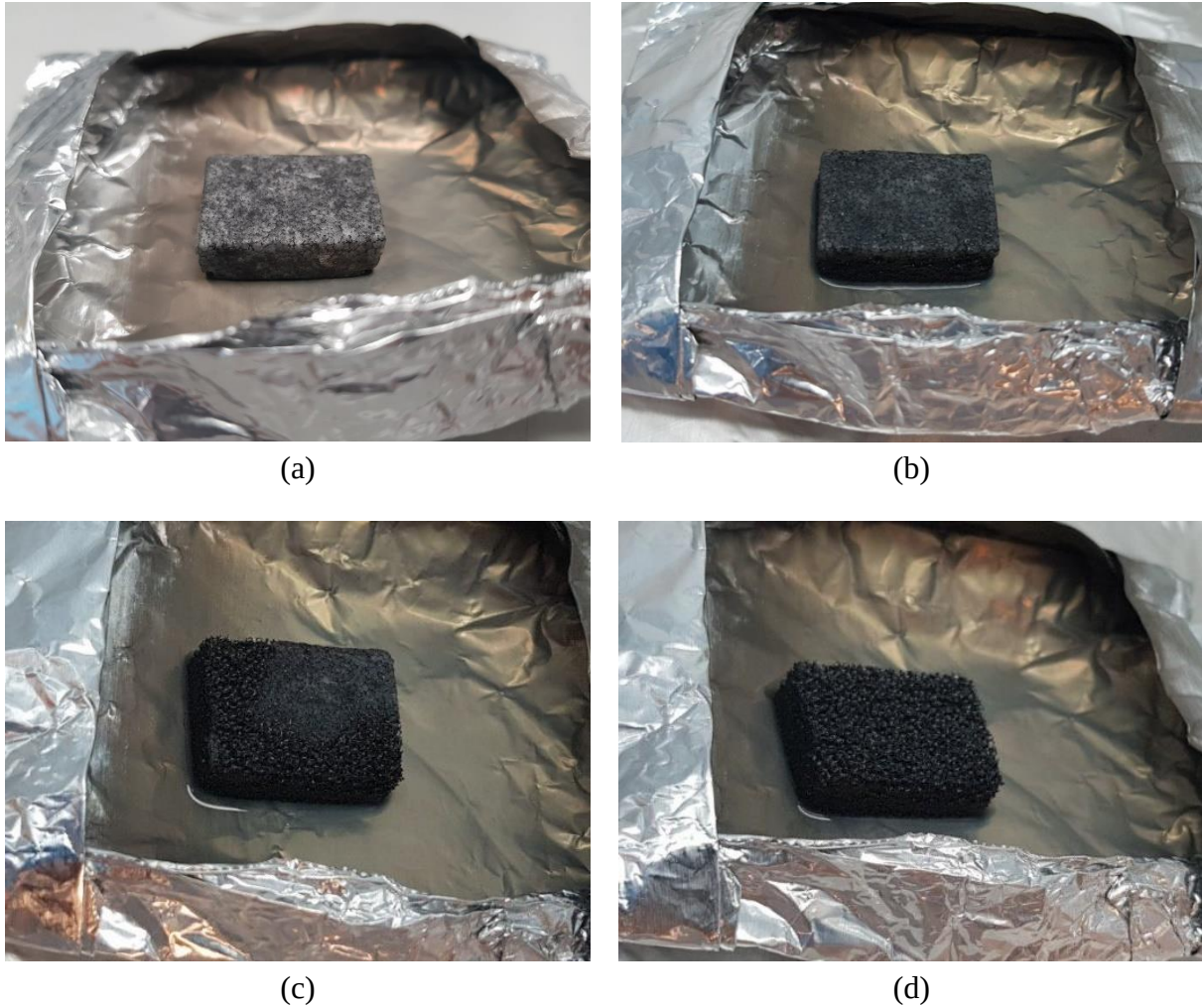


Figure 4.3 3DCPCM with 3D-C/10/10 at 0.0097 g/cm^3 melted in folded aluminium foil boat placed on a hot plate. (a) Initial 3DCPCM sample. (b-c) hotplate was turned on and the melting of the paraffin was documented at various stage of melting. (d) Paraffin has completely melted revealing the free-standing 3D-C retain its shape and dimensions pre-infusion.

4.2 Systematic study of 3DCPCM and GPPCM

As mentioned in the section 2.6, there have been multiple studies documenting the improvement in thermal properties of PCM, such as k and H_f , when carbon based discrete fillers or interconnect scaffolds were incorporated with the PCM. There was a need to identify the benefits and trade-offs of discrete fillers and interconnected scaffolds to determine the better group for space application. However, it was challenging to compare results over different studies as there were different measurement standards, sample fabrication methods and sample compositions used across studies, all of which could greatly affect the basis of comparison. One example would be the different methods used to measure the k of the samples. The different methods used, such as the Hot disk TPS2500 [26], [105], or laser flash

apparatus [83] or in-house measurement rigs [28], [32], [56], and the different environmental conditions of each measurement was conducted would result in unaccountable errors across studies. A systematic study was therefore conducted with controlled experimental factors such as graphene content in composite, type of PCM used, quality of graphene used, and the k measurement method, to systematically compare the thermal properties of PCM filled with 3D-C and GP. Thermal properties as well as shape stability of 3DCPCM and GPPCM over initial thermal cycling were studied and compared with neat PCM.

4.2.1 Materials preparation and characterisation

3D-C/10/1.5 with apparent density of 0.0128 g/cm^3 was used in this study. 3DCPCM was fabricated according to the method in section 3.2.1. The $\varphi_{(3DCPCM)}$ was found to be 1.5 wt. %. GPPCM were fabricated with $\varphi_{(GPPCM)} = 1.5 \text{ wt. \%}$ according to the methods described in section 3.2.2.

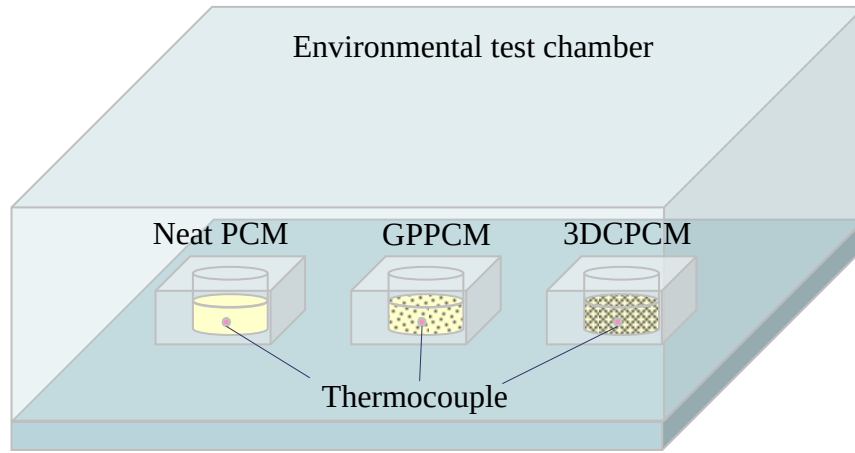
The morphologies of 3D-C and GP were characterised with SEM and Raman spectroscopy. DSC measurements were conducted on the PCM composites according to the methods in section 3.3.3. k measurements were conducted on the PCM composites using the Lee's disc method described in section 3.3.2.1.

4.2.2 Thermal cycling characteristics

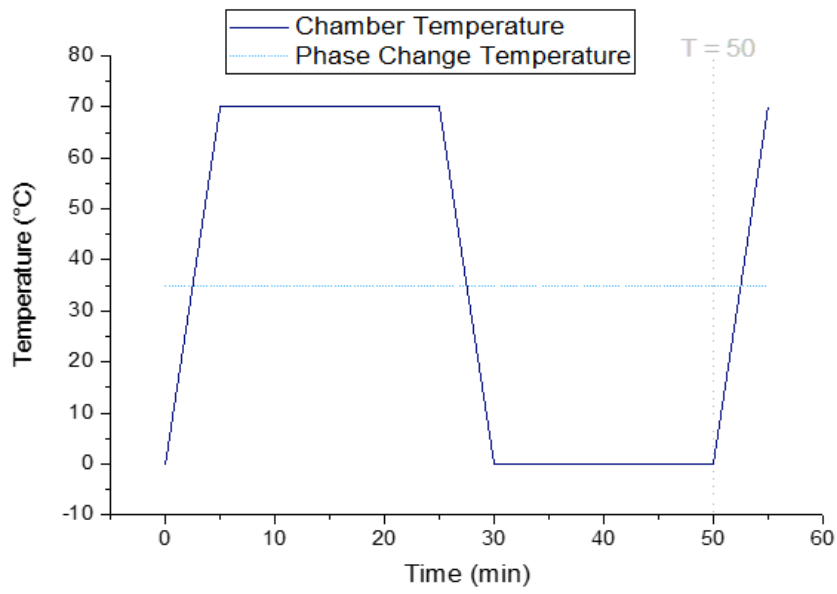
Assuming a 1-year service lifetime of CubeSats and 1 phase change cycle per orbit, the PCM would likely go through close to 5000 phase change cycles in its service lifetime. The aim of this experiment was to study the physical characteristics of 3DCPCM and GPPCM over a few initial thermal cycles, to compare the shape-stabilizing effects between an interconnected scaffold and a discrete filler due to solidification and melting of the PCM at regular intervals. In this experiment, 3DCPCM, GPPCM and neat PCM samples were

compared. Thermal cycling was conducted in Thermotron SE300-6-6 environmental temperature test chamber.

Typically, 9.65 ± 0.01 g of each sample were prepared and placed in similar glass trays with a thermocouple attached to the inner glass walls. The samples were thermally cycled through their melting points over nine complete phase-change cycles. A schematic of the setup is shown in Figure 4.4 (a). The environmental test chamber was first cooled and held at 0 °C for 20 min, after which the chamber was rapidly heated from 0 to 70 °C over 5 min and held for 20 min until the 3DCPCM, GPPCM, and neat PCM samples fully melted. The chamber was then rapidly cooled to 0 °C over 5 min and held for 20 min to ensure that all samples had fully solidified. Figure 4.4 (b) shows the chamber temperature history profile described. 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 min may not be sufficient for samples to reach the steady-state temperature, the sample with the highest k would have attained the highest and lowest temperatures. Figure 4.4 (c) shows the samples used before thermal cycling.



(a)



(b)



(c)

Figure 4.4. (a) Schematic of the set-up for thermal cycling in the environmental test chamber. (b) Temperature profile of thermal chamber of one cycle period. (c) Samples for thermal cycling (left) neat PCM, (centre) 3DCPCM, (right) GPPCM.

4.2.3 Results and Discussion

4.2.3.1 Morphology

Figure 4.5 shows the morphology of 3D-C and GP captured using SEM. The SEM image of GP, Figure 4.5 (a), shows distinctly separated flakes of graphene less than 200 μm in diameter. The SEM image of 3D-C, Figure 4.5 (b), shows that 3D-C consists of open pores and continuous interconnected structure. The open pores in 3D-C would allow liquid PCM to flow freely throughout the 3D-C network during infusion resulting in a higher fill fraction as compared to a scaffold with some closed pores. The cross-section of fractured 3D-C strut in Figure 4.5 (c) and (d) show that the strut was hollow and had a distinct inner and outer layer. The reason for two macro layers of strut walls can be inferred from the original fabrication process of the Ni foam template used for CVD synthesis of 3D-C. Ni foam was fabricated via CVD on a porous polyurethane (PU) template [106] followed by sintering to remove the PU. This process produces Ni foam with hollow struts. Subsequently, during the CVD synthesis of 3D-C, the carbon atoms dissolved in Ni would have been deposited and precipitated on both the inner and outer surface of the hollow Ni strut based on the mechanism of graphene growth on Ni [107], thus the distinct inner and outer macro layer of graphene. Figure 4.5 (e) and (f) show the SEM image of the corresponding hollow fractured struts of 10 mm thick Ni foam that could have resulted in the 3D-C structure in Figure 4.5 (c) and (d) after CVD of graphene and HCl etching. Figure 4.6 shows a schematic of the synthesis process of 3D-C from PU. There were certain bumps and uneven surfaces on the outer surface of 3D-C which were evident to have been caused by the bumps and uneven surfaces on the Ni foam.

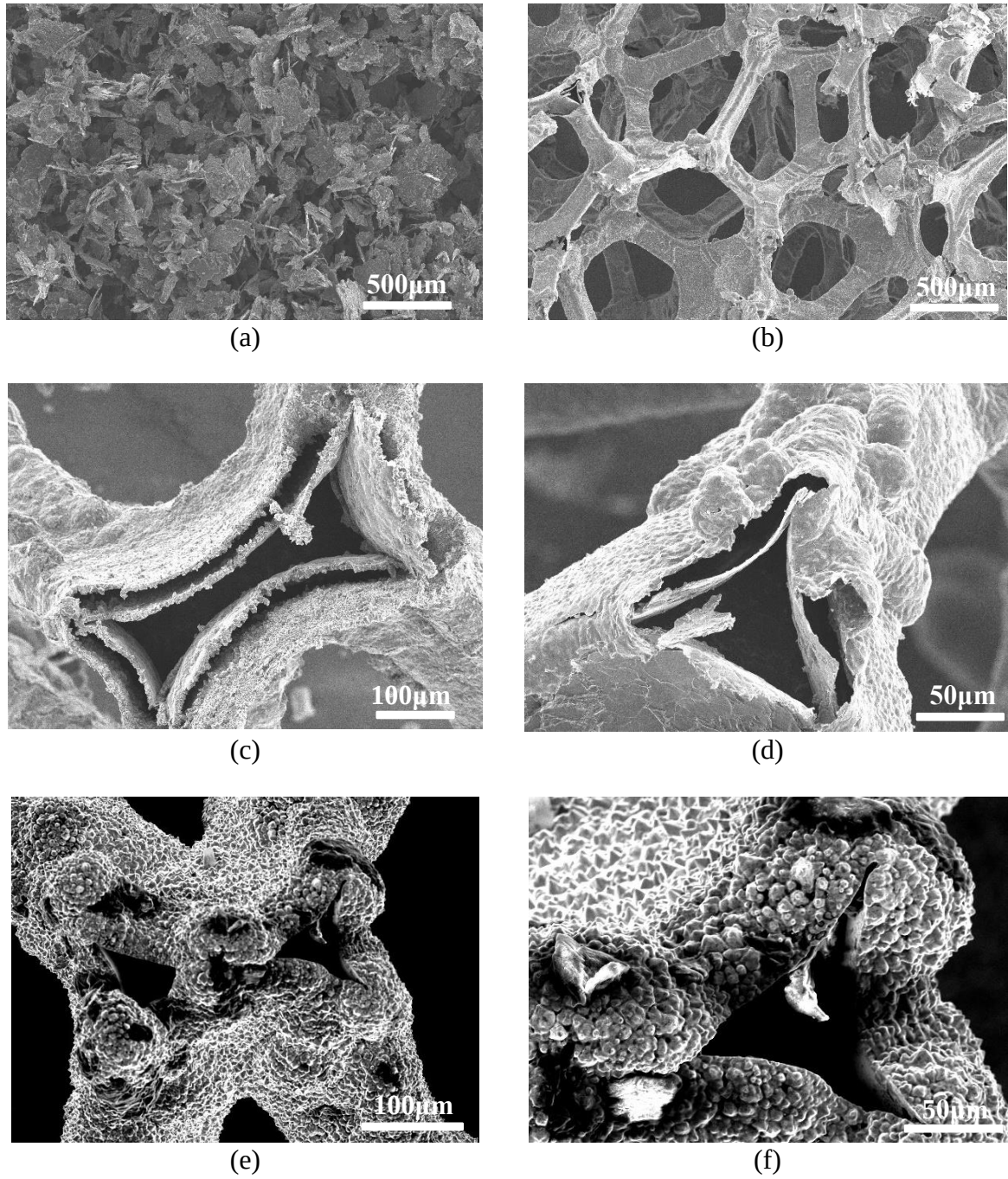


Figure 4.5 SEM image of (a) GP, showing distinctly separated flakes. (b-d) showing 3D-C interconnected struts and open pores, (e-f) 10 mm Ni foam fracture surface

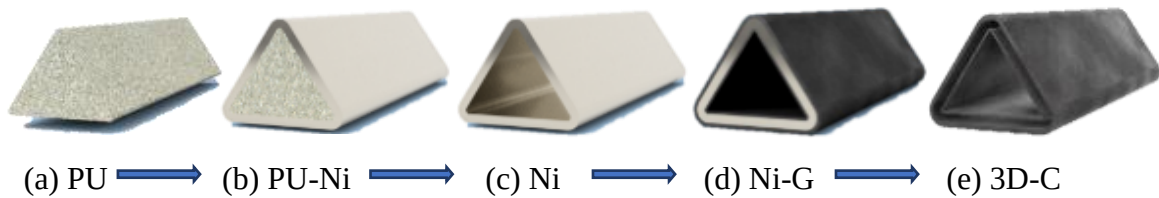


Figure 4.6 Strut cross-section schematic of the synthesis process of 3D-C from polyurethane (PU). (a) PU, (b) PU coated with Ni after CVD, (c) Ni shell remains after PU is removed via sintering, (d) Graphene coats Ni on both inner and outer surface after CVD. (e) 3D-C strut with distinct outer and inner layer after removal of Ni via HCl etching.

Figure 4.7 shows the Raman spectra for 3D-C and GP. A D peak at 1350 cm^{-1} was observed for GP, indicating the presence of crystal defects [108]–[110]. The D peak for 3D-C 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 3D-C. 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 3D-C and GP consist of high-quality graphene.

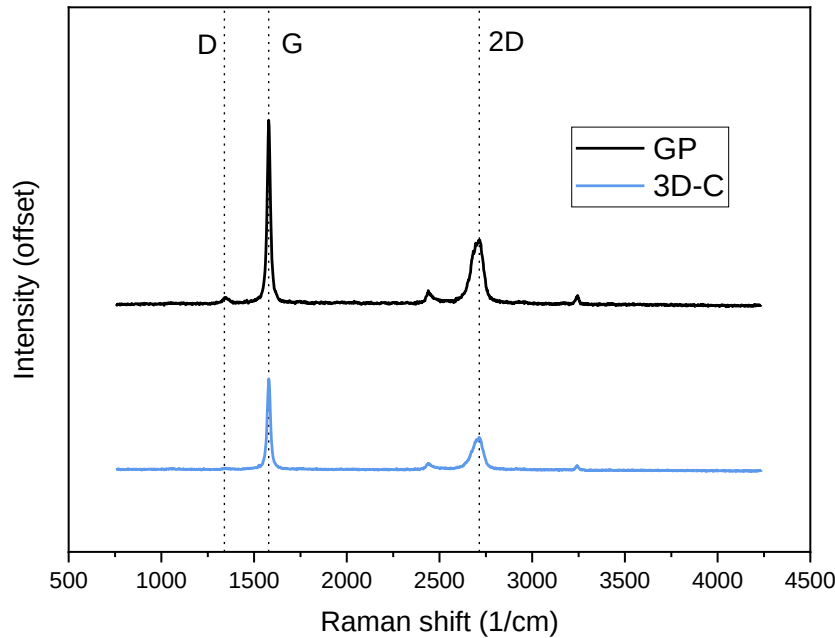


Figure 4.7 Raman spectroscopy of 3D-C and GP

4.2.3.2 Thermal conductivity and latent heat of fusion measurements

Thermal conductivity measurements of the samples are shown in Table 4.2. The k of neat PCM was measured 0.25 W/mK , in agreement with the commercial datasheet [97]. k of 3DCPCM was measured to be 1.01 W/mK , with a relative k of 4.0. On the other hand, the k of GPPCM was measured to be 0.41 W/mK at the same graphene loading as 3DCPCM, with relative k of 1.6. This significant difference in k measurement at the same graphene loading confirms that the interconnected struts of 3D-C provide a reliable thermal network and

significantly improve the efficiency of k as compared to discrete fillers of similar quality and loading. The non-dimensional k values of 3DCPCM relative to the neat PCM, RT35HC, were reported to reduce systematic bias arising from the k measurement method so that the results could be compared across studies.

The H_f measurement of the samples are shown in Table 4.2 as well. The DSC plots for the samples are shown in Figure 4.8. The H_f of neat PCM was measured to be 226.8 kJ/kg, which is similar to that reported in the datasheet [97]. There were negligible changes in H_f after the infusion of fillers in both GPPCM and 3DCPCM. The absolute H_f per unit mass of PCM have been calculated in previous works [9], [16], [58] where carbon based fillers such as carbon nanotubes and discrete graphene were used as fillers. The absolute H_f of paraffin in these works were observed to have exceeded that of neat paraffin at low loadings. Such phenomenon was attributed to the C-H $\cdots\pi$ bond interactions [58]. In this study, the relative absolute H_f was calculated to be 1.04 that of neat PCM for both GPPCM and 3DCPCM samples. 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 3DCPCM is a confirmation that the two samples have identical graphene filler loading.

The combined results of k and H_f of the samples show that at low loading, the inclusion of 3D-C scaffold increase the k of the composite by more than 4 times at 1.5 wt. % of 3D-C or at a 3D-C apparent density of 12.8 mg/cm³, while having negligible changes in its energy density as shown by the H_f measurements.

Table 4.2 Thermal conductivity and latent heat of fusion (H_f) measurements of the samples.

Sample	ϕ (wt. %)	k (W/mK)	Relative k , $\frac{k}{k_{(paraffin)}}$	H_f (kJ/kg)	Relative H_f , $\frac{H_f}{H_{f(paraffin)}}$	$H_{f(absolute)}$ (kJ/kg)	Relative $H_{f(absolute)}$
Neat PCM	0.0	0.25	1.0	226.8	1.00	226.8	1.00
GPPCM	1.5	0.41	1.6	232.2	1.02	235.7	1.04
3DCPCM	1.5	1.01	4.0	232.3	1.02	235.8	1.04

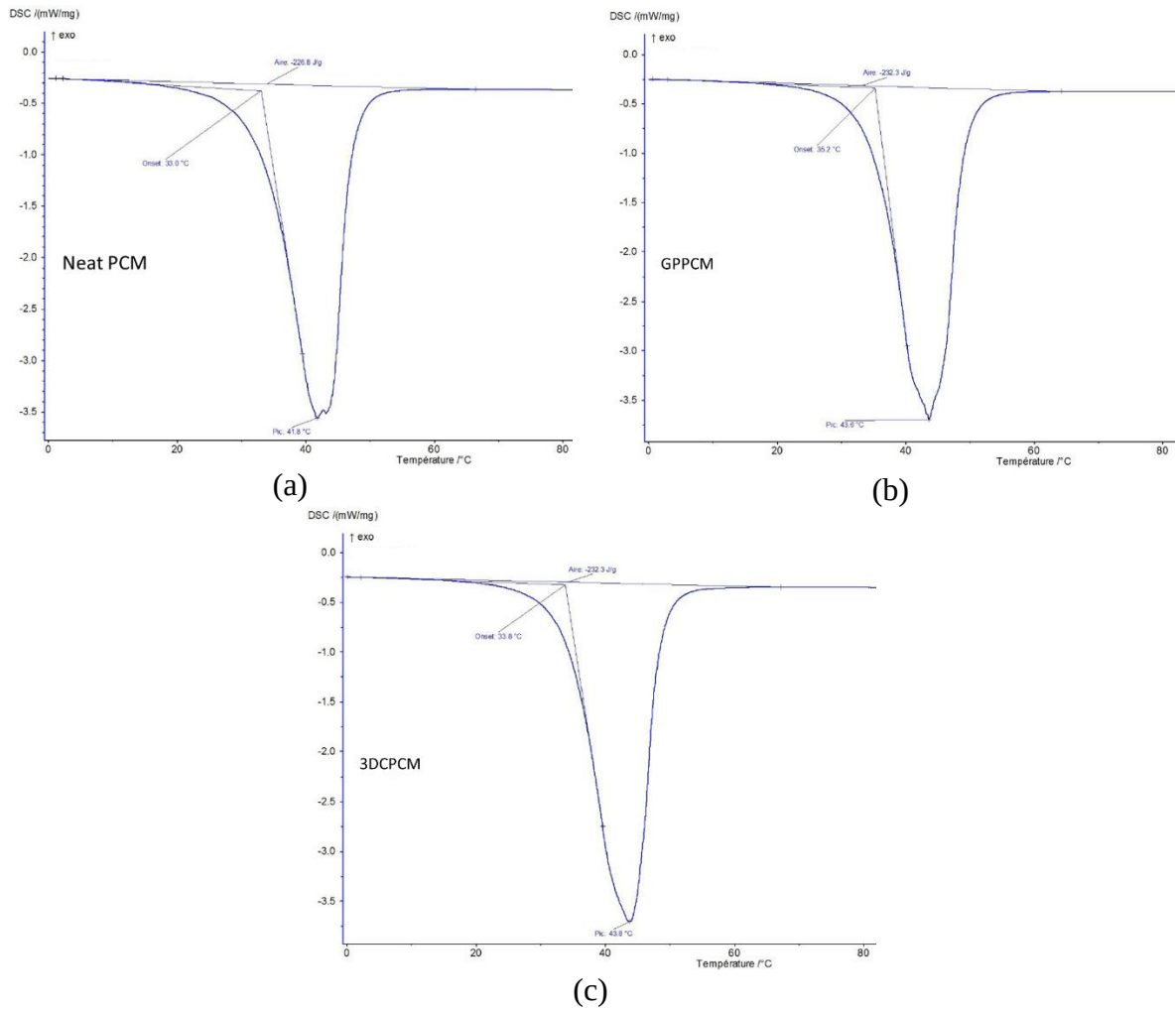


Figure 4.8 DSC plots for (a) Neat PCM, (b) GPPCM, (c) 3DCPCM.

4.2.3.3 Thermal cycling characteristics

The temperature profiles of each sample for all nine cycles were recorded in Figure 4.9 (a). Figure 4.9 (b) 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 3DCPCM and GPPCM as compared to neat PCM. At the points of peak temperature, it was consistent that 3DCPCM has the highest temperature at each peak, followed by GPPCM and then neat PCM. A similar trend is observed at the points of trough temperature, where 3DCPCM consistently hit the lowest temperature, followed by GPPCM and then neat PCM. This is indicative that 3DCPCM and GPPCM has a faster response with the environmental temperature change and hence a higher k than neat PCM. In the first cycle, the temperature profile of GPPCM followed closely to that of 3DCPCM. The largest difference between the temperature profiles of 3DCPCM 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 were observed after the GPPCM was heated beyond its melting temperature. In addition, the temperature profile of GPPCM also deviated further from 3DCPCM, 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 neat PCM sample were attributed to the irregular melting of paraffin wax. It was observed that the neat PCM sample was a melting solid block surrounded by liquid paraffin during the period of temperature fluctuations. Due to the low k of paraffin wax, there would 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 was no temperature fluctuation when the neat PCM sample was solidifying, since convection does not occur in solids.

During, melting, the solid portion of the neat paraffin was observed to float in the liquid, suggesting the solid paraffin block is less dense than the liquid, which was not true according to the datasheet, where the density of solid and liquid paraffin, RT35HC, should be

0.88 g/cm³ and 0.77 g/cm³ respectively. This could be explained by the presence of air bubbles trapped within the voids of neat paraffin, which would decrease the bulk density of the solid paraffin block and hence cause the solid paraffin block to float. These air bubbles were also observed to escape the melting solid paraffin during the melting period, which caused the solid paraffin to be perturbed randomly. This movement would also cause mixing of the paraffin resulting in temperature fluctuation.

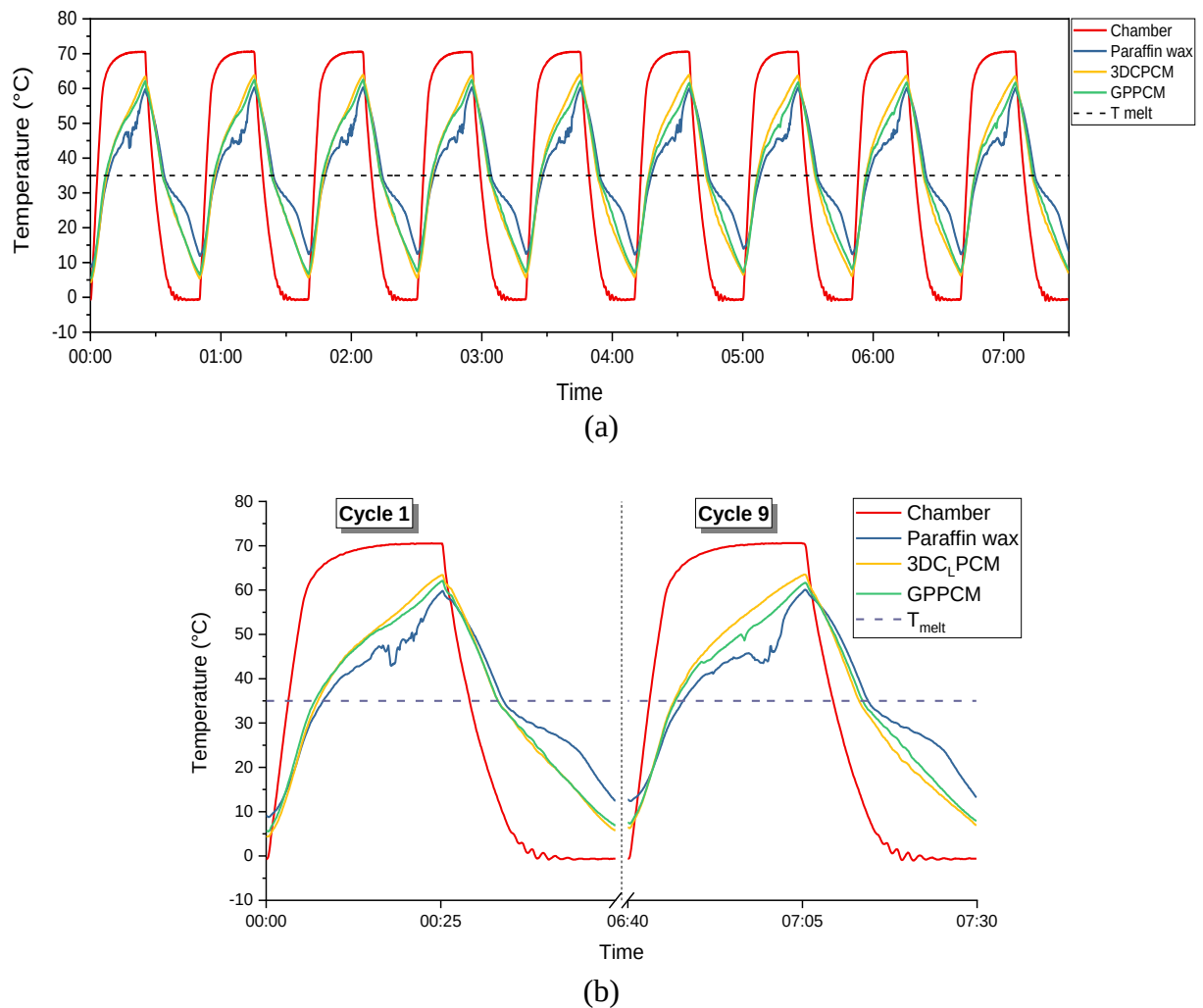


Figure 4.9 (a) Temperature profile of all nine cycles of thermal cycling for 3DCPCM, GPPCM and neat PCM samples. (b) Temperature profile of the 1st and 9th cycle of thermal cycling. Neat PCM has a distinct fluctuation of temperature during melting. After 9 cycles, the temperature profile suggests that GPPCM has deviated from its original temperature profile in the 1st cycle.

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 like the neat PCM sample. For 3DCPCM, the porous 3D-C network would have hindered much of the convection currents, thus resulting in a smooth temperature rise.

Furthermore, the high bulk thermal conductivity of 3DCPCM would ensure a smaller thermal gradient within the sample and hence a more uniform melting.

The physical characteristics over phase change of each sample was studied and compared before and after nine phase change cycles. The cross-section of each sample was also examined after the experiment. The results are shown in Figure 4.10.

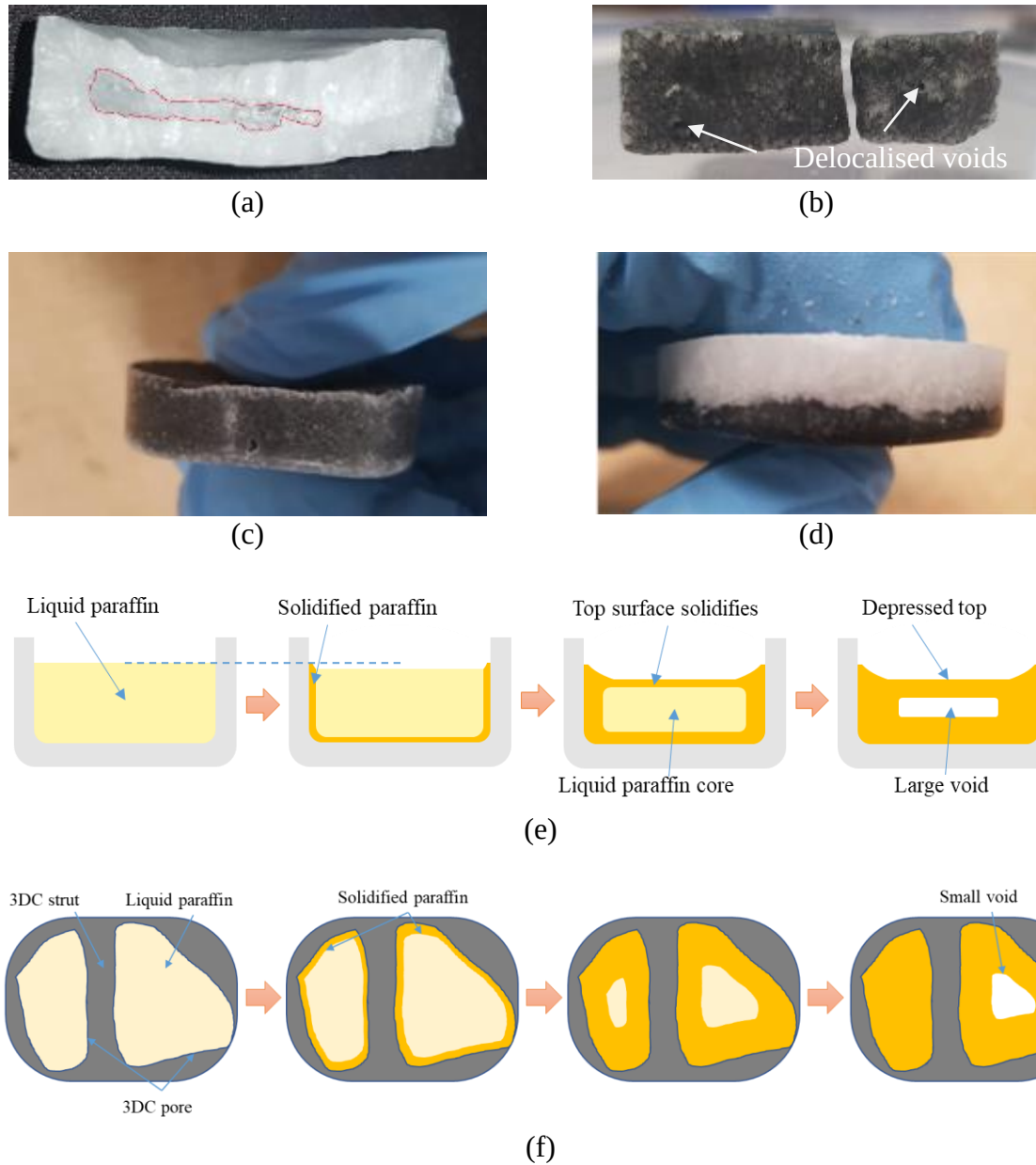


Figure 4.10 Cross-section of (a) neat PCM sample and (b) 3DCPCM after thermal cycling. The thickness of the neat PCM sample is noticeably smaller near the centre as compared to the sides, forming a depressed top surface. The single large void in the neat PCM sample is outlined in red and the delocalized voids in 3DCPCM are indicated. Side profile of GPPCM (c) before and (d) after thermal cycling, showing the distinct phase separation of GP and PCM with GP settling to the base of the glass tray. (e) Schematic of the cross-sectional view of neat paraffin solidification process in the glass tray. (f) Schematic of paraffin solidification at the 3D-C pores.

During the solidification procedure in the test, observations were made on the neat PCM 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 4.10 (a). This observation was consistent with the concaved ullage space reported by Weinstein et al. [36] and Namkoong et al. [90]. The cross-sectional view of the neat PCM sample revealed a single large void at the core, which has not been reported in previous studies. 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 neat PCM sample during solidification, which is a material property of paraffin wax, working in tandem with the solidification process of the neat PCM sample in the glass tray. A schematic of the cross-sectional view of neat PCM solidification process in the glass tray is shown in Figure 4.10 (e). RT35HC contracts by 14 % in volume during solidification [97]. As the neat PCM 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 neat PCM 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 neat PCM 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 3DCPCM sample.

GPPCM had the most noticeable physical difference amongst the samples. Initially, the GP was well distributed within the GPPCM as shown in Figure 4.10 (c). After thermal cycling, a distinct phase separation of fillers and PCM could be observed in GPPCM. The graphene particles had settled at the base of the sample, leaving a distinct white paraffin layer at the top of the sample, as seen in Figure 4.10 (d). 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 settled 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 ground-based effects of thermal cycling are still relevant. During the terrestrial testing, the GP would have settled and change the properties of GPPCM already. Therefore, GPPCM is unreliable for space applications.

The 3DCPCM sample was cut at multiple points to reveal the cross-sections. Small voids were observed at random pores of 3DCPCM as shown in Figure 4.10 (b). The voids were expected to form after rapid thermal cycling because 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 3D-C skeleton provided multiple low energy barrier surfaces for paraffin to nucleate heterogeneously. The interconnected open pores in 3D-C allow liquid paraffin to flow freely to compensate the decrease in volume during solidification. This happened until the paraffin in most of the pores was fully solidified, effectively enclosing the remaining liquid paraffin within the corresponding pores. Voids form when this

remaining paraffin has solidified and contract within the closed pores. A schematic of paraffin solidification at the pores of 3D-C to depict this phenomenon is shown in Figure 4.10 (f). Unlike neat PCM, the voids in 3DCPCM were delocalised and dispersed, and hence the mechanical strength and high bulk k of the sample would be retained even after multiple phase change cycles. This interaction showed surface compatibility of 3D-C with the paraffin wax, and that 3D-C stabilized the shape of the PCM, hence 3D-C 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 [74], [75]. This makes 3D-C 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.

4.2.3.4 Conclusions

High quality 3D-C micro-skeletal was synthesized using templated assisted CVD growth on Ni foam. The micro-skeletal and its grounded powder was infused into PCM at the same graphene loading to form a PCM composite, 3DCPCM and GPPCM. The k and H_f as well as thermal response and shape-stability effects over multiple phase change of each PCM composite were compared. 3DCPCM and GPPCM had identical H_f , indicating that the graphene loading for each sample is identical. 3DCPCM had a larger relative k of 4.0 as compared to 1.6 in GPPCM. From the results, it was concluded that the interconnected structure of 3D-C makes use of the high intrinsic k of graphene more efficiently as compared to GP of identical quality and graphene loading. The 3D-C scaffold also retains the shape of PCM composite through multiple phase changes, therefore helps retain thermal contact and

reduces melt pressures within PCM containers, making 3D-C 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 agglomeration and settling of GP, therefore the thermal performance and physical behaviours, such as void formation, of GPPCM became similar to that of neat PCM, hence making GPPCM less reliable than 3DCPCM for applications that requires thermal cycling. With these results, it was concluded that 3D-C is a superior substitute to GP filler variations. Given that PCM goes through about 5000 phase change cycles over its service lifetime in CubeSats, these results helps to quickly eliminate GPPCM as a potential space-grade PCM candidate and provide confidence that 3DCPCM has good thermal cycling stability. The properties of GPPCM also indicates the worst-case scenario should all the interconnected network in 3DCPCM be damaged, be it during fabrication or within lifetime of usage.

4.3 Thermal properties of 3DCPCM with different graphene loading

In this study, 3D-C of different graphene loadings were fabricated and infused within PCM. 3D-C with higher density has the advantage of better handleability and increased k , however the trade-offs include lower porosity thus larger displacement of PCM. The objective of this study is to determine the optimal loading of 3D-C, and to formulate a model specific to 3D-C to numerically predict the k of 3DCPCM.

4.3.1 Materials preparation

3D-C was fabricated according to the method in section 3.2.1. Eleven 3DCPCM samples were fabricated according to the method in section 4.1.2 using 3D-C samples of various apparent density with the growth time group of 1.5, 2.0, 4.5, 6.5 and 7.5 hours. The material properties of each sample are shown in Table 4.3. The naming convention of 3DCPCM sample is “3DCP- n / (apparent density of 3D-C)”, where n is the sample number.

Table 4.3 Material properties of 3D-C and its corresponding 3DCPCM samples.

3D-C sample name	3DCPCM sample name	Density ρ_{3D-C} (mg/cm ³)	Graphene loading, ϕ	Porosity, ϕ_{3D-C}
3D-C/10/1.5	3DCP-1/12.8	12.8	1.5	0.994
	3DCP-2/12.5	12.5		
	3DCP-3/12.5	12.5		
3D-C/10/2.0	3DCP-4/20.7	20.7	2.5	0.991
	3DCP-5/20.1	20.1		
	3DCP-6/20.1	20.1		
3D-C/10/4.5	3DCP-7/42.6	42.6	5.5	0.981
	3DCP-8/42.4	42.4		
	3DCP-9/43.0	43.0		
3D-C/10/6.5	3DCP-10/63.8	63.8	8.0	0.972
3D-C/10/7.5	3DCP-11/74.7	74.7	9.0	0.967

4.3.2 Characterisation

A small sample of 3D-C from each density was used for characterisation. Raman spectroscopy was performed on each growth time group of 3D-C. The exfoliated flakes of 3D-C samples with the lowest and highest growth time, 3D-C/10/1.5 and 3D-C/10/7.5, was studied using TEM to characterise and compare their lattice and crystalline structure. DSC measurements were conducted according to the methods discussed in section 3.3.3. k measurements were conducted using the MTPS method described in section 3.3.2.2. The MTPS was used as the k of the 3DCPCM samples were expected to be above 2.0 W/mK.

4.3.3 Results and Discussion

4.3.3.1 Morphology

Figure 4.11 (a)-(d) shows TEM images for samples of 3DC/10/7.5 and 3DC/10/1.5, the 3D-C samples with the highest and lowest apparent density, respectively. The graphene flakes that were derived from 3DC/10/7.5 were thicker than that from 3DC/10/1.5 as observed by the darker contrast in their bright-field images in Figure 4.11 (a) and (c). The selected area

electron diffraction (SAED) on both samples, inset of Figure 4.11 (a) and (c), shows 6 diffracted spots which confirms the hexagonal lattice structure. Figure 4.11 (b) and (d) shows the high-resolution images taken at the edge of the flake. The interlayer spacing for both samples were measured to be about 0.35 nm, which was consistent with that of multi-layer graphene. From the TEM image, the thickness of the 3D-C/10/1.5 sample flake was measured to be ~24 nm. The 3D-C/10/7.5 sample flake was too thick to be measured by high resolution imaging. Using the weight ratio difference between the 3D-C/10/7.5 and 3D-C/10/1.5, the thickness of the 3D-C/10/7.5 was estimated to be ~140 nm. Both the Raman and TEM characterization results indicate that apart from the difference in thickness, the crystallinity in both 3D-C/10/7.5 and 3D-C/10/1.5 were identical. A high resolution TEM (HR-TEM) and the fast Fourier transform (FFT) of the HR-TEM was taken within the interior of the flake for sample A1, as shown in Figure 4.11 (e). The hexagonal lattice structure of graphene can be clearly seen in the HR-TEM. These results verify that multiple and prolonged CVD growths did not compromise the high graphene quality in 3D-C samples.

The Raman spectroscopy of each 3D-C, shown in Figure 4.11 (f), were consistent with high quality graphite.

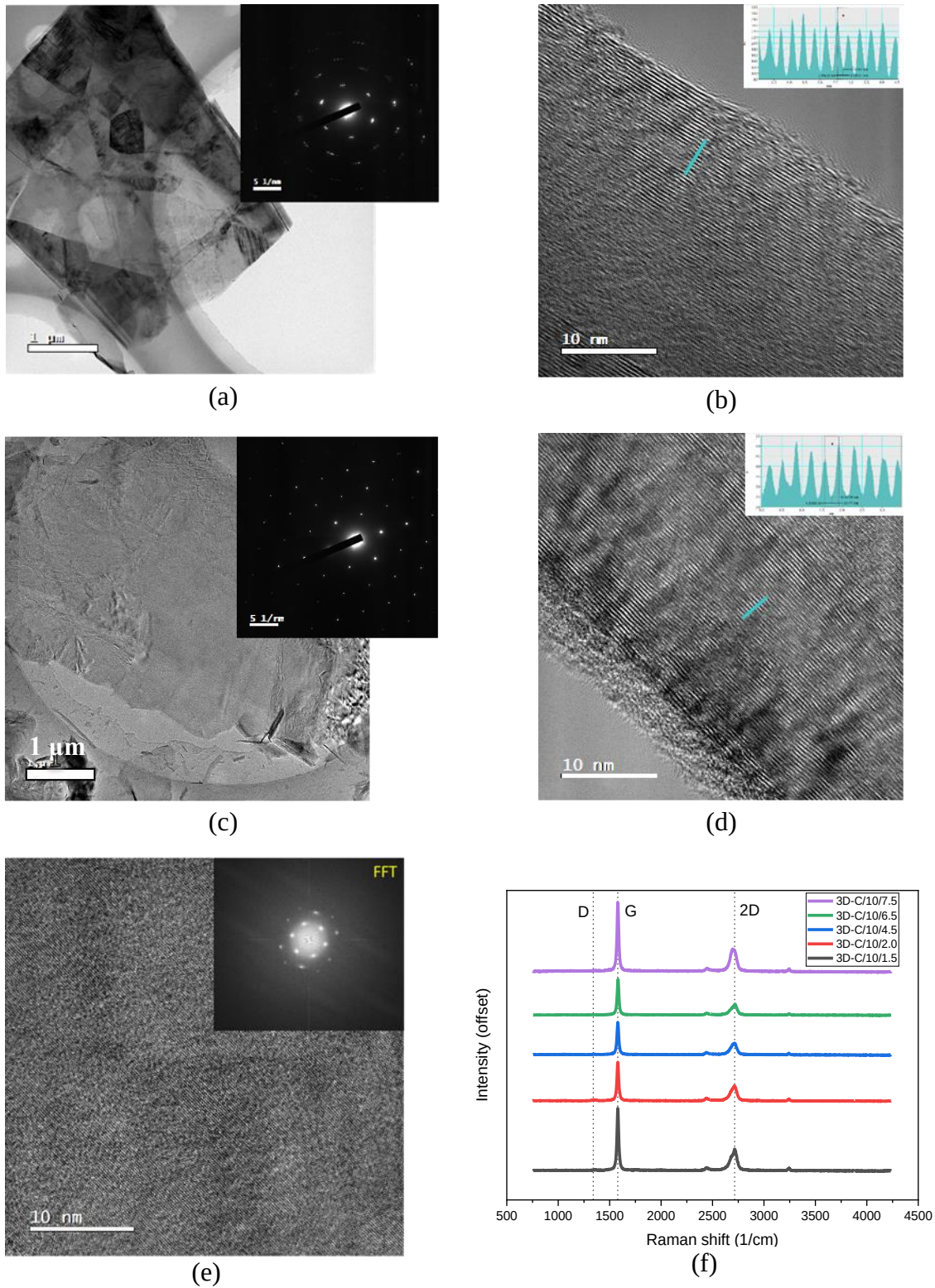


Figure 4.11 (a) & (c) Image of exfoliated graphene flakes and inset shows the selected area electron diffraction (SAED) of 3DC/10/7.5 (a) and 3DC/10/1.5 (c). SAED of both samples confirms the hexagonal lattice structure of the flakes. (b) & (d) High-resolution image, showing interlayer spacing of the flakes taken from the edge of the flake from sample. The interlayer spacing was measured to be ~ 0.35 nm, consistent with multilayer graphene. (e) High resolution TEM (HR-TEM) of the interior of the flake for sample 3DC/10/7.5. Inset shows the fast Fourier transform (FFT) of the HRTEM. (f) Raman spectroscopy of 3D-C samples.

4.3.3.2 Thermal conductivity and latent heat of fusion measurements

The results of the k and the H_f of each sample is shown in Table 4.4. The k of neat PCM measured 0.25 W/mK, in agreement with datasheet and results in section 4.2.3.2. The k of each 3DCPCM sample is plotted with respect to sample 3D-C apparent density in a scatter plot in Figure 4.12 (a). There was a general increasing trend with increasing apparent density of 3D-C and 3DCPCM relative k . This phenomenon coincides with the trends reported in literature [39], [81], [111], [112]. The relative k reached a maximum of 9.20 in sample 3DCP-11/74.7. Figure 4.12 (b) shows the graph of average relative H_f and $H_{f(absolute)}$ against ϕ . From the data collected, relative H_f of each sample was within ± 0.05 of the PCM loading, and relative $H_{f(absolute)}$ of each sample was within 1.00 ± 0.05 . Hence it can be concluded that 3D-C and PCM in all samples underwent a physical mixing with negligible chemical interactions. 3DCPCM can also be assumed to be homogeneous and mass specific material properties of 3DCPCM sample such as H_f and c_p can be calculated from the product of component properties and their respective loading fraction.

Table 4.4 Thermal conductivity and latent heat of fusion (H_f) measurements of the samples.

Sample name	ϕ (wt. %)	k (W/mK)	Relative k	H_f (kJ/kg)	Relative H_f	$H_{f(absolute)}$ (kJ/kg)	Relative $H_{f(absolute)}$
Neat RT35HC	-	0.25	1.00	226.8	1.00	226.8	1.00
3DCP-1/12.8	1.5	1.61	6.44	232.3	1.02	235.8	1.04
3DCP-2/12.5		0.80	3.20	231.9	1.02	235.4	1.04
3DCP-3/12.5		1.02	4.08	232.1	1.02	235.6	1.04
3DCP-4/20.7	2.5	1.29	5.16	223.4	0.99	229.1	1.01
3DCP-5/20.1		1.11	4.44	221.6	0.98	227.3	1.00
3DCP-6/20.1		1.11	4.44	222.1	0.98	227.8	1.00
3DCP-7/42.6	5.5	1.62	6.48	213.4	0.94	225.8	1.00
3DCP-8/42.4		1.61	6.44	213.5	0.94	225.9	1.00
3DCP-9/43.0		1.95	7.80	211	0.93	223.3	0.98
3DCP-10/63.8	8.0	1.99	7.96	209.5	0.92	227.7	1.00
3DCP-11/74.7	9.0	2.3	9.20	208.9	0.92	229.6	1.01

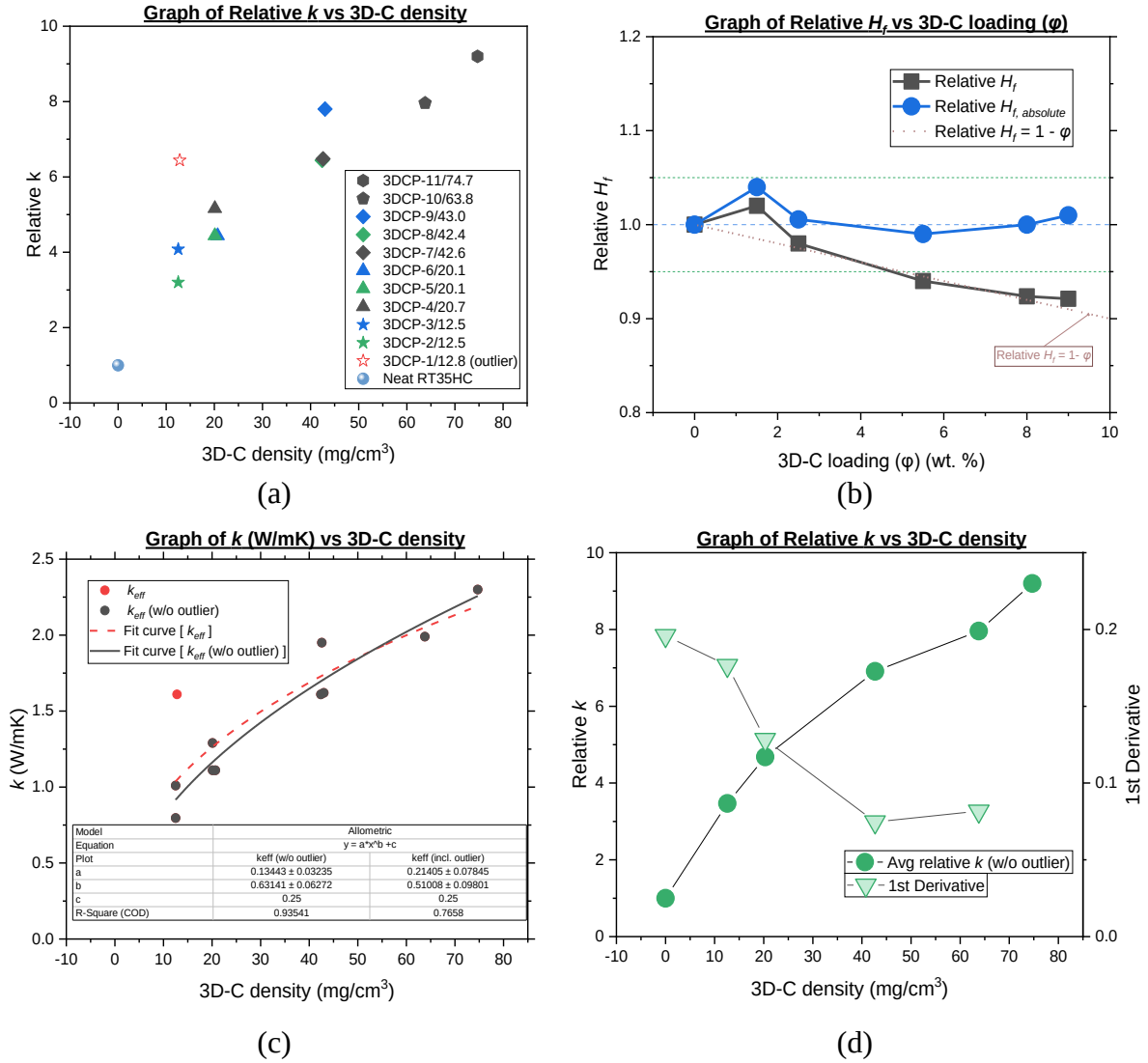


Figure 4.12 (a) Scatter diagram of relative k of each 3DCPCM sample against 3D-C density. (b) Scatter + line plot of average relative H_f and $H_{f(\text{absolute})}$ against ϕ . (c) Scatter diagram of k_{eff} of 3DC samples against 3D-C density, with allometric curve fit. (d) Scatter + line plot of average relative k (left y-axis) and the 1st derivative (right y-axis) against 3D-C density.

k value of sample 3DCP-1/12.8 was identified as an outlier. Allometric curve fitting of the scatter plot “ k vs 3D-C density”, shown in Figure 4.12 (c), indicates a significantly higher R^2 value of 93.5% when data from sample 3DCP-1/12.8 was excluded as compared to 76.6% included. The result of the allometric curve fitting without outlier gives equation (4.1).

$$k_{\text{eff}} = 0.134(\rho_{(3D-C)})^{0.631} + 0.25 \quad (4.1)$$

k_{eff} represents the effective k of the 3DCPCM. The constant coefficients were calculated with values of $\rho_{(3D-C)}$ in mg/cm^3 . The first term, $a(\rho_{(3D-C)})^b$, was the contribution from 3D-C. The second term of the equation, $c = 0.25$ W/mK, was the contribution from neat

PCM. The relation of k with density of open-cell foam as proposed by Ashby et. al [113], [114] is shown in equation (4.2).

$$k \approx k_s(\rho/\rho_s)^q \quad (4.2)$$

where k_s is the thermal conductivity of the bulk material, in this case graphite. ρ_s is the theoretical density of graphite 2.26 g/cm³ [115], [116]. ρ is the apparent density of 3D-C in g/cm³ and q is a constant. Comparing equations (4.1) and (4.2), k_s was calculated to be approximately 17.5 W/mK and $q = 0.631$. These values enable approximation of k of 3DCPCM infused with 3D-C of various apparent densities grown using methods mentioned in section 3.1.1 and infused with PCM using the immersion method described in section 3.2.1.

Figure 4.12 (d) shows the average relative k of 3DCPCM against 3D-C density. The slope between each point indicates the efficiency of increasing relative k with 3D-C density in the units of (mg/cm³)⁻¹. The slope was found to be steepest at 0.196 (mg/cm³)⁻¹ from 0 to 12.6 mg/cm³ (0 to 1.5 wt.%) followed by 0.177 (mg/cm³)⁻¹ from 12.6 to 20.3 mg/cm³ (1.5 to 2.5 wt.%). This indicates that 3D-C is most effective in increasing k of 3DCPCM composite at 1.5 or 2.5 wt.% in terms of k /(mg/cm³) of 3D-C. Beyond that loading, k still increases but at a lower rate per density of 3D-C. 3D-C density is proportional to the resources and time input required to grow, and a higher 3D-C loading both increases the bulk 3DCPCM mass and decreases H_f , therefore the optimal 3D-C loading was determined to be between 1.5 - 2.5 wt.%, or with 12.5 – 20.7 mg/cm³ for mass sensitive smallsats applications. Further study would be required to assess the sufficiency of k improvement at 1.5 – 2.5 wt.% for specific applications.

The combined results of H_f and k shows that the k of 3DCPCM can be tuned by using 3D-C of a different apparent density, with a minor trade-off in H_f that is directly proportionate to the mass fraction of 3D-C in the composite.

4.3.3.3 Conclusions

High quality 3D-C micro-skeletal with apparent densities of 12.5 – 74.7 mg/cm³ was synthesized using template assisted CVD. 3D-C of higher apparent densities was synthesized using a scalable method of increasing the precursor deposition time. Morphology study on the 3D-C samples using Raman spectroscopy and TEM indicates that the 3D-C consist of high-quality polycrystalline graphite and showed that the increase in precursor deposition time increased the layers of graphene on 3D-C and retained the graphene crystallinity in the 3D-C synthesized. k of the corresponding 3DCPCM composites increased with the apparent density of 3D-C infused, and average relative k ranged from 3.47 at 12.5 mg/cm³ (1.5 wt.%) to 9.20 at 74.7 mg/cm³ (9 wt.%). The traded-off was a small decrease in H_f that was linearly proportionate to the mass fraction of 3D-C infused. The optimal mass fraction of 3D-C that maximizes relative k increase per unit mass of 3D-C was found to be between 1.5 to 2.5 wt. % of 3D-C. A model was formulated using experimental results and theory proposed by Ashby to approximate the k of 3DCPCM using the apparent density of 3D-C.

4.4 Summary

In this Chapter, two studies were presented. In the first systematic study, 3DCPCM and GPPPCM were synthesized using the same batch of 3D-C with the same graphene loading of 1.5 wt.%. The samples were benchmarked using the measured material properties, k , H_f , and thermal cycling stability. In the second study, 3D-C of apparent densities of 12.5 – 74.7 mg/cm³ were infused into PCM and characterized. The main conclusions of this Chapter are listed hereafter.

- The minimum 3D-C apparent density to produce a free-standing 3D-C was found to be 9.7 mg/cm³ for the 10 mm thick sample and 16.3 mg/cm³ for the 5 mm thick sample.

- The interconnected structure of 3D-C makes use of the high intrinsic k of graphene more efficiently as compared to GP of identical quality and graphene loading. The 3D-C scaffold also retains the shape of PCM composite through multiple phase changes, therefore helps retain thermal contact and reduces melt pressures within PCM containers, making 3D-C a potential solution for operating the PCM in microgravity environments. It was concluded that 3D-C is a superior substitute to GP filler variations.
- The k of 3DCPCM composites increased with the apparent density of 3D-C infused. The traded-off was a small decrease in H_f that was linearly proportionate to the mass fraction of 3D-C infused. The optimal mass fraction of 3D-C that maximizes relative k increase per unit mass of 3D-C was found to be between 1.5 to 2.5 wt. % of 3D-C. A model was formulated using experimental results and theory proposed by Ashby to approximate the k of 3DCPCM using the apparent density of 3D-C.

5. Phase Change Material Demonstrator Analysis

It is crucial to analyse the performance of the PCM within its packaging to obtain use-case specific thermal management performance. This Chapter records the performance and analysis of the optimal configuration of 3D-C micro-skeletal enhanced PCM, as determined in the previous Chapter, enclosed within a use-case packaging. An in-house experimental set-up was designed to directly compare multiple PCMs in packaging at the same time with the same environmental conditions and heat inputs. As such, PCMs can be benchmarked with each other.

A 3D thermal model of 3DCPCM within the packaging was generated with COMSOL Multiphysics using material properties obtained from the material analysis. Thermal simulation was done on the model and was verified with experimental results. This model contributes to various parametric studies, such as PCM packaging with various dimensions and effect of PCM with various material properties.

5.1 Experimental Methods

5.1.1 Aluminium PCM packaging

The computer numerical control (CNC) milled aluminium packaging for PCM was designed according to satellite use-case provided by Thales Alenia Space. The specifications provided by the end-user regarding the design of the packaging is shown in Table 5.1.

Table 5.1 Specifications of hermetically sealed PCM module

PCM module attachment	Direct contact with subsystem of interest, with TIM
Contact surface area dimensional limit	100 * 40 mm ²
PCM module height limit	35 mm
Container thickness (Recommended)	1.5 – 3.0 mm

A sample of the fabricated aluminium packaging is shown in Figure 5.1. The main body of the packaging consist of a bottom open container fabricated from Al-6061-T6. Each main body has an opening measuring $94 * 34 \text{ mm}^2$ at the base, interior depth of 27 mm, wall thickness of 3 mm, and a standardized interior capacity of 86.2 cm^3 after considering the 2 mm radius fillet in the interior edges. The top exterior surface of $100 * 40 \text{ mm}^2$ would be the surface in full contact with the satellite subsystem of interest. The bottom of the container had an extended plate with dimensions $74 \text{ mm} * 134 \text{ mm} * 3 \text{ mm}$ surrounding the bottom opening and had ten M3 holes. Figure 5.1 (a) & (b) shows the fabricated top portion of the packaging at various angles. The average mass of 8 such main bodies was $138.0 \pm 1.4 \text{ g}$.

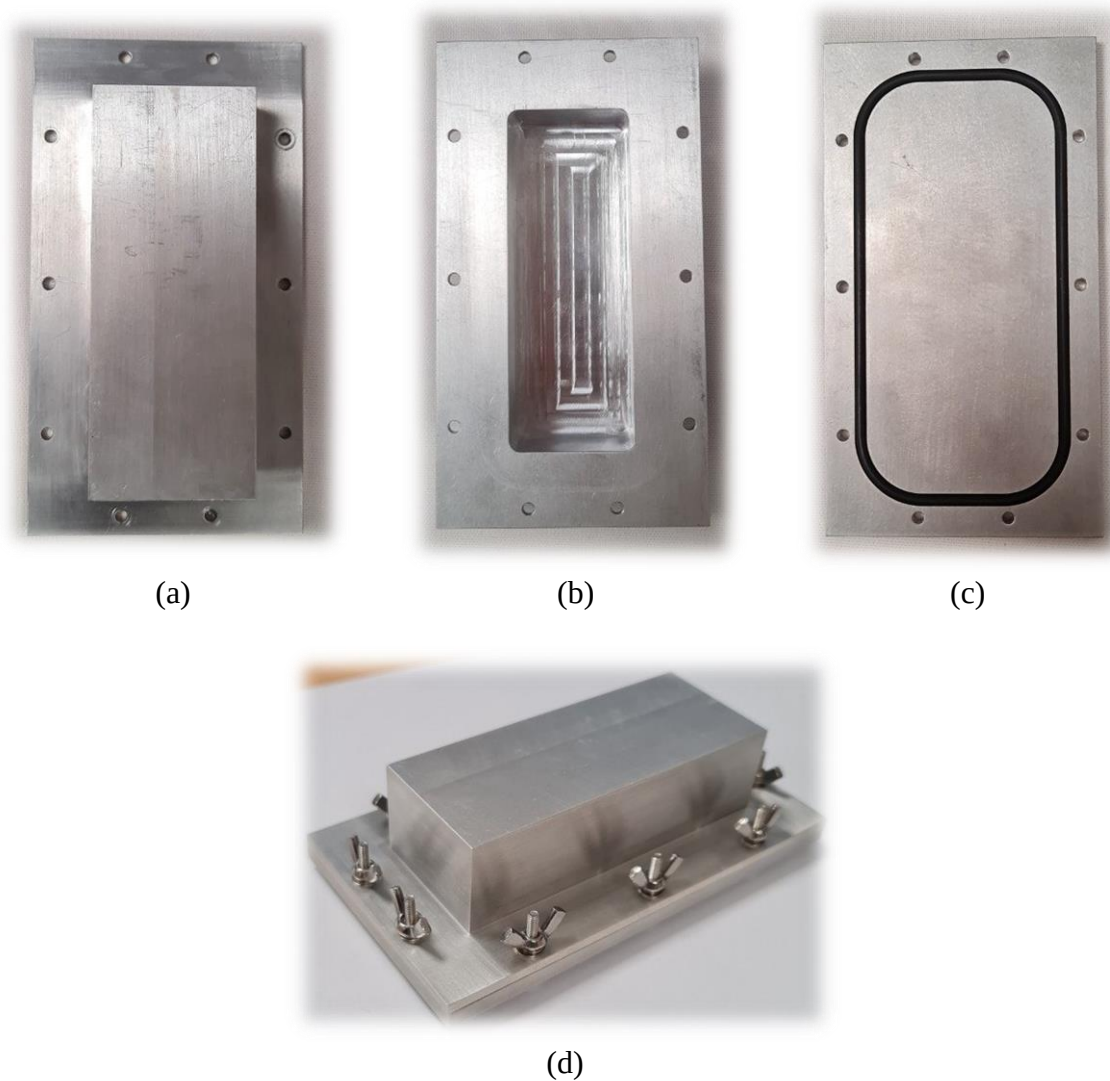


Figure 5.1 Aluminium PCM container. (a) Top view of main body. (b) Interior view of main body. (c) Bottom cover. (d) Assembled PCM container.

The bottom cover portion of the packing, also made of Al-6061-T6, had a thickness of 5 mm, and was fitted with grooves for 3.0 mm thick Viton O-ring of outer diameter of 95 mm and ten M3 holes aligned with the top container. The bottom cover would be secured to the Al container using ten M3 screws and wing nuts, each tightened with 1.10 Nm of torque. This would provide an effective hermetic seal to the contents within the container, standardized across all samples. The average mass of 8 of such bottom covers was 130.5 ± 0.1 g. Figure 5.1 (c) shows the fabricated bottom cover portion of the packaging, and Figure 5.1 (d) shows the fully assembled PCM packaging. The overall dimensions were within the limits specified in Table 5.1.

5.1.2 Sample preparation

Three samples were prepared and compared in this portion of the experiment, neat RT35HC, 3DCPCM and GPPCM. 3DCPCM and GPPCM were prepared according to the methods described in section 3.2.1 and 3.2.2 respectively.

To achieve a consistent volumetric fill rate throughout the PCM container samples, the mass of PCM required was calculated by the product of container interior capacity (V_i), porosity of filler/scaffold material (ϕ) and PCM liquid density ($\rho_{(PCM,l)}$), as shown in equation (5.1). In the case of neat PCM, porosity value will be equivalent to 1.

$$m_{(PCM)} = V_i \times \phi \times \rho_{(PCM,l)} \quad (5.1)$$

The mass of neat PCM required was calculated to be 66.3 g. The PCM container was placed on an electronic balance and liquid PCM was added with a beaker initially till PCM was about 1 g below the required mass, or 65 g. Liquid PCM was then added drop wise using a dropper until the mass of PCM was within 0.5 g of the required mass, which gives a mass error of less than 1%. The final mass of PCM added was 66.47 g. After the PCM solidify completely, the PCM container was sealed with the bottom cover.

3DCPCM was fabricated within the aluminium packaging in-situ using 10 mm thick 3D-C micro-skeletal and RT35HC. 3D-C of 17.5 mg/cm^3 was shaped to the axial-plane dimension of $94 \text{ mm} * 34 \text{ mm}$ to fit the opening of the PCM container and gently pushed to the base of the container. A total of three stacks of 3D-C were used to fill the PCM container. The mass of the 3D-C used was 1.51 g. The effective porosity of the 3D-C in the PCM container was calculated to be 99.2 %. The mass of PCM required was calculated to be 65.8 g. The final mass of PCM added was 65.72 g, and the mass of PCM composite was 67.23 g. Mass fraction of 3D-C was calculated to be 2.2 wt.%.

GPPCM was prepared at a filler loading of 2.2 wt.%. The mass of GPPCM required would be identical to that of 3DCPCM. The mass of GPPCM added was 67.40 g.

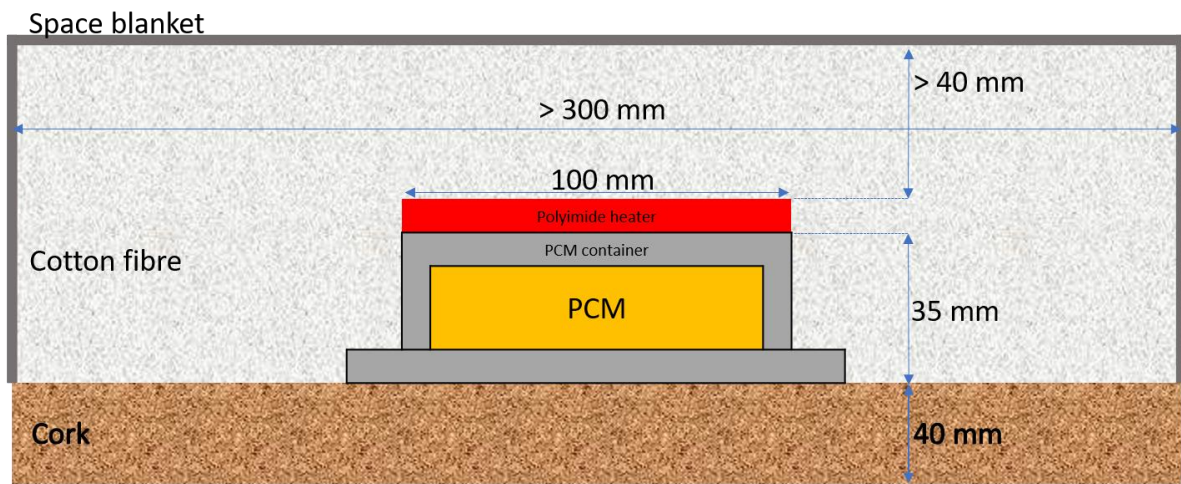
5.1.3 Experimental setup

Polyimide (PI) heater mat with dimensions $25 * 100 * 0.2 \text{ mm}^3$ and resistance of 36Ω sourced from RS component was used to simulate the heat inputs experienced by the PCM container from the subsystem of interest in use-case scenarios. One PI heater mat was adhered to the top surface of each PCM container, shown in Figure 5.2 (a). Each PI heater mat was connected in parallel and powered by a power supply capable of outputting 360 W. The power supply was calibrated to supply 10, 15 and 20 W to a maximum of 4 PI heaters simultaneously at fixed voltage settings of 19.6, 24.0 and 27.9 V respectively. The corresponding heat flux are 2500, 3750 and 5000 W/m^2 respectively. The 3 power settings were chosen to represent the typical power dissipation of the use-case provided by Thales Alenia Space, and 20 W was the highest power dissipation expected from the use-case. Thermocouples were attached to the top surface of the PCM container to measure the temperature-time ($T-t$) profile. This $T-t$ profile would be representative of that of the subsystem in which the PCM container would be attached to in use-case scenarios.

The PCM container were carefully insulated to reduce the heat losses due to conduction, convection, and radiation. Each PCM container was placed, heater side up, on a 40 mm thick insulative cork board base. A few layers of insulative raw cotton were placed around each PCM container and a larger cotton blanket was used to cover the top of the containers. Cotton fibre and cork traps air and has a bulk k of 0.04 W/mK [117], hence reducing heat loss due to conduction and convection. Finally, a reflective space blanket was used to cover the whole setup to reduce heat losses due to radiation. Each PCM container sample was positioned 200 mm apart from each other. All 4 PCM containers were heated to 100 °C and the external temperature of the space blanket, cotton blanket and the bottom side of the corkboard was measured to be within 0.5 °C of the ambient temperature. The ambient temperature was maintained at 24 °C. The schematic of the experimental setup is shown in Figure 5.2 (b).



(a)



(b)

Figure 5.2 (a) Sealed PCM container with polyimide heater attached. (b) Schematic of PCM container sample with insulation.

At each power setting, the samples were heated simultaneously beyond their melting point. To ensure the PCM in the packaging has fully melted, the temperature of the top surface (T_{top}) of the sample with neat PCM was observed for 10, 15 and 20 W with a thermocouple attached to the top surface. Temperature readings were recorded at 2 seconds interval. The T - t profile was observed to have reached the sensible heat regime when the rate of change of temperature had increased from the phase change regime and had reached a relative constant rate of increase. Samples were heated beyond a specific temperature for each power setting. For 10 W, samples were heated till T_{top} reaches at least 60 °C and at 15 and 20 W, samples were heated till the T_{top} reaches 70 °C. The samples were left to cool at room

temperature for at least 4 hours without insulation to ensure all the PCM had solidified and were at a constant temperature before the next heat load. The experiment was repeated at each power rating and have their T - t profile compared for repeatability. Repeatability was achieved when T - t profile of each re-run were within 1.0 °C of each other.

5.1.4 Analysis of temperature-time curve

The parameters that the samples were characterised on 1) the steepness and stability of the T - t gradient during melting regime ($dT/dt_{(m, avg)}$) and 2) practical H_f , denoted as $H_{f(\Delta T)}$, calculated using the time taken for T_{top} to increase from T_{melt} to $(T_{melt} + \Delta T)$, denoted as $\Delta t_{(Tm+\Delta T)}$. ΔT is the temperature offset from T_{melt} , determined by end user. For this analysis, calculations were done for $\Delta T = 5$ and 10 °C. Finally, a figure of merit (FOM) was used to consolidate the characterisations and rank the samples.

5.1.4.1 Formulation of average melting temperature-time gradient

The steepness of $dT/dt_{(m, avg)}$ was calculated using T_{top} and time at phase change onset and end, shown in equation.

$$\frac{dT}{dt}_{(m, avg)} = \frac{T_{(m, end)} - T_{(m, onset)}}{t_{(m, end)} - t_{(m, onset)}} \quad 5.2)$$

The phase change onset and end points were determined by the intersection of 2 tangent lines before and after the points of onset. The instantaneous dT/dt during melting was mapped out against time in a graph to determine stability. This post-processing was done using Origin graphing tools.

A gentle gradient in the melting regime is favoured in application as it corresponds to a subsystem temperature that is closer to the melting temperature of PCM selected during melting. Temperature fluctuation is not favoured as it adds to the uncertainty in predicting the subsystem temperature.

Where needed, the percentage of PCM that had undergone phase change was calculated using equation (5.3).

$$\%melt = \frac{t - t_{(m,onset)}}{t_{(m,end)} - t_{(m,onset)}} \quad (5.3)$$

Where t was the time in seconds of the data point and $t < t_{(m,end)}$. This formulation assumes melting occur linearly with time.

5.1.4.2 Formulation of practical latent heat of fusion

$H_{f(\Delta T)}$ was calculated using first principles. The energy equation in the range of $t_{(T_m)} < t < t_{(T_m+\Delta T)}$ is,

$$\int_{t_{T_m}}^{t_{T_m+\Delta T}} (P_{in} - \dot{Q}_{loss}) dt = C_{p(t)} \Delta T + m_{(PCM)} H_{f(\Delta T)} \quad (5.4)$$

Where P_{in} is the power input to the PI heater, $\dot{Q}_{loss}$ is the rate of heat loss of the PCM container in unit of (W), $C_{p(t)}$ is the total heat capacity of the PCM container sample in the unit of (J/K), ΔT is the temperature offset from T_{melt} , and $m_{(PCM)}$ is the mass of the PCM composite in the PCM container for each sample. P_{in} was assumed to be constant. $P_{in} - \dot{Q}_{loss}$ was evaluated over the sensible heat regime after latent heat regime.

The formulation of $C_{p(t)}$ is,

$$C_{p(t)} = m_{(PCM)} [(1 - \varphi) c_{p(PCM)} + \varphi c_{p(3D-C)}] + m_{(container)} c_{p(Al6061)} + m_{(screws)} c_{p(ss304)} \quad (5.5)$$

Where φ is the mass fraction of 3D-C in the PCM composite. $c_{p(x)}$ is the specific heat capacity of various component x in the units of (J/gK). The values of each component are shown in Table 5.2.

Table 5.2 Values of individual components of PCM container

Component	Value	Units
$m_{(Neat\ PCM)}$	66.47	g
$m_{(3DCPCM)}$	67.23	g
$m_{(GPPCM)}$	67.40	g
$\varphi_{(3DCPCM)}, \varphi_{(GPPCM)}$	2.2	Wt. %
$m_{(container)}$	266.4 – 269.7	g
$m_{(screws)}$	36.4	g
$m_{(t, neat\ PCM)}$	372.2	g
$m_{(t, 3DCPCM)}$	373.3	g
$m_{(t, GPPCM)}$	370.8	g
$C_{p(PCM)}$	3.0	J/gK
$C_{p(3D-C)}, C_{p(GP)}$	0.7077 [116]	J/gK
$C_{p(Al6061)}$	0.896 [118]	J/gK
$C_{p(ss304)}$	0.5 [119]	J/gK
$C_{p(t, Neat\ PCM)}$	460.0	J/K
$C_{p(t, 3DCPCM)}$	457.8	J/K
$C_{p(t, GPPCM)}$	457.8	J/K

The energy equation in the sensible heat regime immediately after melting is,

$$(P_{in} - \dot{Q}_{loss}) = C_{p(t)} \frac{dT}{dt}_{(pm)} \quad (5.6)$$

Where $(dT/dt_{(pm)})$ is the temperature-time gradient after phase change in the unit of (K/s). Assuming constant $(P_{in} - \dot{Q}_{loss})$ over the period of phase change, the product of C and $dT/dt_{(pm)}$ thus gives the net input power to the PCM container during phase change. Combining equations (5.4) and (5.6) gives a formulation for $H_{f(\Delta T)}$, as shown in equation (5.7),

$$H_{f(\Delta T)} = C_{p(t)} \left(\frac{dT}{dt}_{(pm)} \times \Delta t_{(Tm+\Delta T)} - \Delta T \right) / m_{PCM} \quad (5.7)$$

Where $\Delta t_{(T_m+\Delta T)}$ is defined as the time required for T_{top} to reach $(T_{melt} + \Delta T)$ °C from T_{melt} .

$$\Delta t_{(T_m+\Delta T)} = t_{(T_m+\Delta T)} - t_{(T_m)} \quad (5.8)$$

The rationale for using $H_{f(\Delta T)}$ was that in application scenario, the PCM phase change temperature would be chosen with a slight offset from the optimal temperature of the subsystem. In the case of melting PCM, a longer $\Delta t_{(T_m+\Delta T)}$, and therefore a large $H_{f(\Delta T)}$, would be favoured as it indicates that the subsystem temperature would be within ΔT of the PCM melting for a longer period. Depending on the use-case condition, ΔT could be set accordingly, for example ΔT would be -5 and -10 °C when analysing the solidification of PCM samples, and for temperature sensitive subsystems, ΔT could be as low as ± 1.0 °C. The Δt term and hence the $H_{f(\Delta T)}$ term in equation (5.7) would change accordingly. In this report, the temperature offset would be 5 or 10 °C above T_{melt} .

Furthermore, a PCM container mass specific $H_{f(\Delta T)}$, denoted $H_{f,t(\Delta T)}$, would be generated according to equation (5.11).

$$H_{f,t(\Delta T)} = H_{f(\Delta T)} \times \frac{m_{(PCM)}}{m_{(t)}} \quad (5.9)$$

Where $m_{(t)}$ is the total mass of the sample.

5.1.4.3 Formulation of figure of merit

A FOM was generated to numerically grade the performance of each samples. The parameters used and the FOM were accepted as key performance indicator by the end-user.

The FOM formulation is shown in equation (5.10).

$$FOM_{\Delta T} = \frac{dT/dt_{(pm)}}{dT/dt_{(m,avg)}} \times \frac{H_{f,t(\Delta T)}}{H_{fo}} \quad (5.10)$$

Where H_{fo} is the H_f of neat PCM indicated in the datasheet.

The FOM was formulated using use-case practical performance markers introduced in previous sections, $dT/dt_{(m,avg)}$ and $H_{f(\Delta T,t)}$. A lower $dT/dt_{(m, avg)}$ was favourable, hence $dT/dt_{(m,avg)}$ would be inversely proportionate to the FOM. Conversely, a higher $H_{f,t(\Delta T)}$ was favourable, hence $H_{f,t(\Delta T)}$ would be directly proportionate to the FOM. $dT/dt_{(pm)}$ was used to account for the different power input level and to non-dimensionalise $dT/dt_{(m, avg)}$. A neutral term, H_{fo} , was used to non-dimensionalise $H_{f,t(\Delta T)}$.

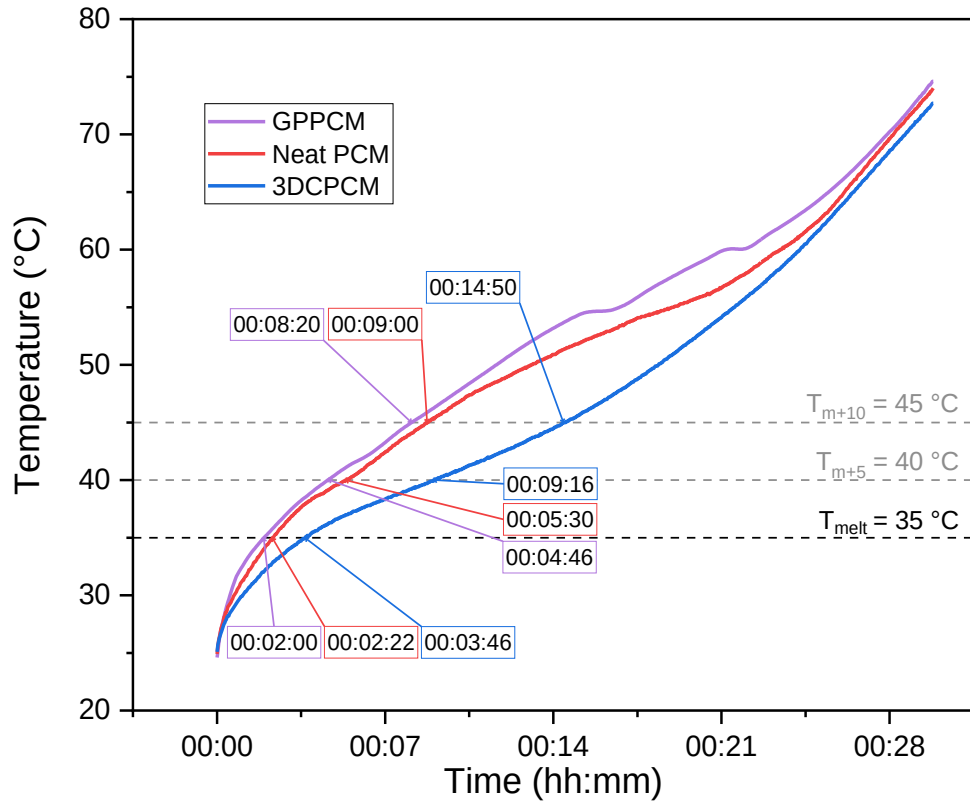
5.2 Results and Discussion

5.2.1 Temperature-time profile analysis – 20 W

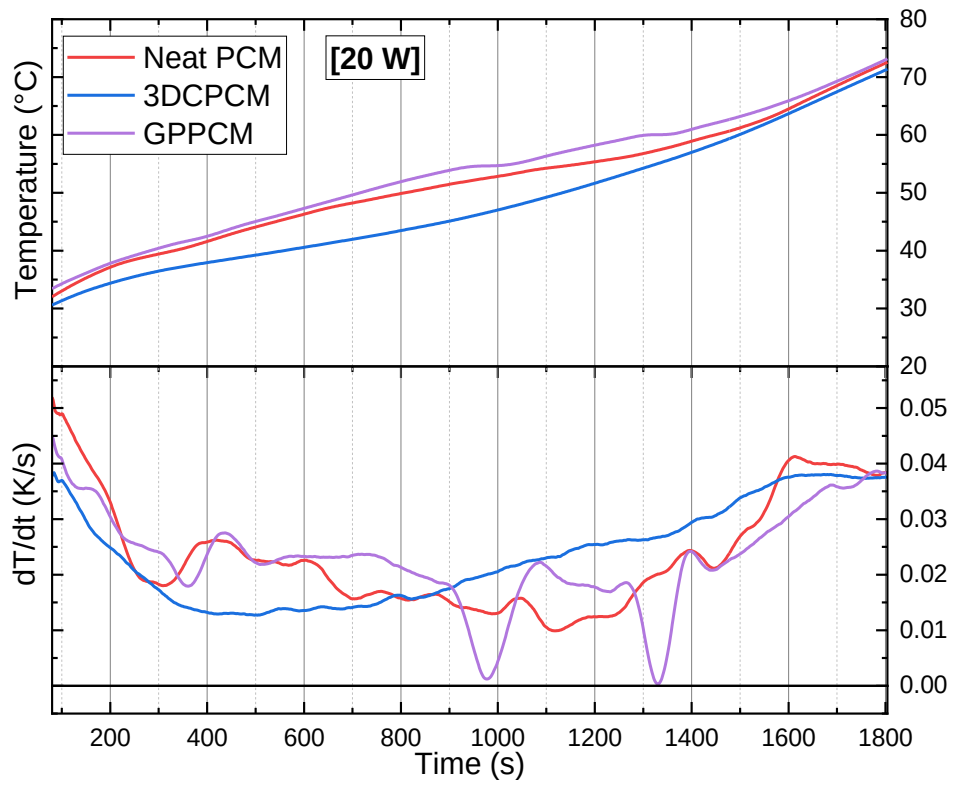
The T_{top} against time curve of the 3 samples for 20 W is shown in Figure 5.3 (a) and the corresponding gradient in the melting regime is shown in Figure 5.3 (b). The numerical gradients, $t_{Tm+\Delta T}$, $H_{f(\Delta T)}$ and $FOM_{(\Delta T)}$ of each sample are shown in Table 5.3. The results for 15 and 10 W would be presented in the subsequent sections.

Table 5.3 Temperature-time gradients, $t_{(Tm+\Delta T)}$, $H_{f,t(\Delta T)}$ and $FOM_{(\Delta T)}$ of each sample for 20 W power input.

Sample	$dT/dt_{(pm)}$ (K/s)	$dT/dt_{(melting, avg)}$ (K/s)	$\Delta t_{(Tm+5)}$ (s)	$\Delta t_{(Tm+10)}$ (s)	$H_{f(+5)}$ (kJ/kg)	$H_{f(+10)}$ (kJ/kg)	$FOM_{(+5)}$ (10^{-1})	$FOM_{(+10)}$ (10^{-1})
Neat PCM	0.0388	0.0188	188	398	15.9	37.7	0.244	0.579
3DCPCM	0.0379	0.0183	330	664	51.1	103.3	0.798	1.61
GPPCM	0.0383	0.0200	166	380	9.22	30.9	0.134	0.449



(a)



(b)

Figure 5.3 (a) T-t curve of Neat PCM, 3DCPCM and GPPCM at 20 W power input. (b) dT/dt vs time of each curve.

The change and convergence in gradient at $55\text{ }^{\circ}\text{C} < T < 70\text{ }^{\circ}\text{C}$ in all samples indicate that the PCMs had gone through a complete phase change from solid to liquid. The gradient after phase change for all three samples were similar, indicating that the power input and C_p of each sample were similar. Overall, the $\text{FOM}_{(+5)}$ and $\text{FOM}_{(+10)}$ for 3DCPCM was the highest among the 3 samples at $0.798\text{E-}1$ and $1.61\text{E-}1$ respectively, and GPPCM had a lower performance than neat PCM at both $\Delta T = 5$ and $10\text{ }^{\circ}\text{C}$.

In the melting regime, T_{top} of 3DCPCM was significantly lower and dT/dt was more stable than neat PCM or GPPCM as observed in Figure 5.3 (b). The more stable and lower T_{top} could be attributed to the presence of the high k interconnected 3D-C micro skeletal in 3DCPCM. 3D-C evenly increase the k throughout the sample, resulting in more even heating of PCM and more efficient usage of H_f to absorb the heat energy from the top surface of the PCM box as compared to GPPCM and neat PCM. The temperature fluctuation in GPPCM and neat PCM was attributed to the movements of the melting solid block of PCM as mentioned in section 4.2.3.3.

The Δt_{Tm+10} of 3DCPCM was significantly longer at 664 seconds compared to neat PCM and GPPCM of 398 and 380 seconds, respectively. This meant that 3DCPCM could keep temperatures below $10\text{ }^{\circ}\text{C}$ from melting point for 67% longer than neat PCM. The same trend was noticed for Δt_{Tm+5} , this time 3DCPCM extend temperature below $5\text{ }^{\circ}\text{C}$ for 75.6% longer time than neat PCM. At 20 W , the $H_{f(+10)}$ of the PCM container with 3DCPCM was 103.2 kJ/kg , 2.74 times that of neat PCM, and utilised 43.0 % of H_{fo} . $H_{f(+5)}$ of the PCM container with 3DCPCM was 51.1 kJ/kg , 3.22 times that of neat PCM, and utilised 21.3 % of H_{fo} .

These results indicate numerically how much better 3DCPCM utilises the PCM volume compared to neat PCM. The presence of 3D-C allowed more PCM to melt and expend the latent heat within the practical range of $10\text{ }^{\circ}\text{C}$ from T_{melt} to absorb the power

dissipation from the top surface. At 20 W, a PCM container with 3DCPCM could sustain the subsystem temperature for 664 seconds between T_{melt} and T_{m+10} and for 330 seconds between T_{melt} and T_{m+5} .

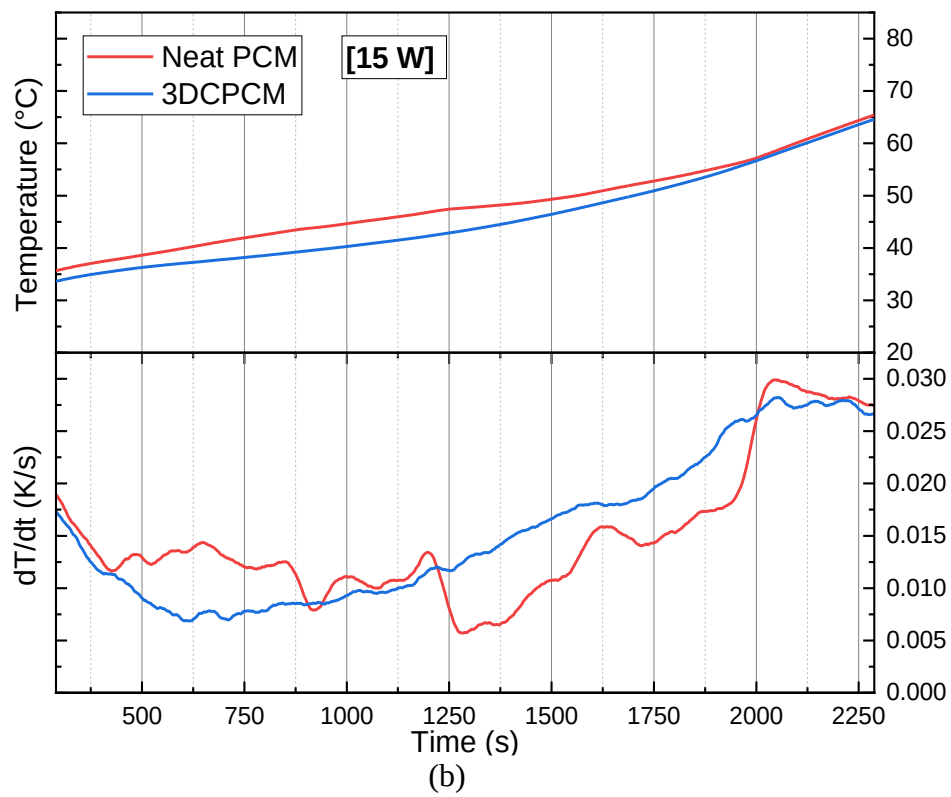
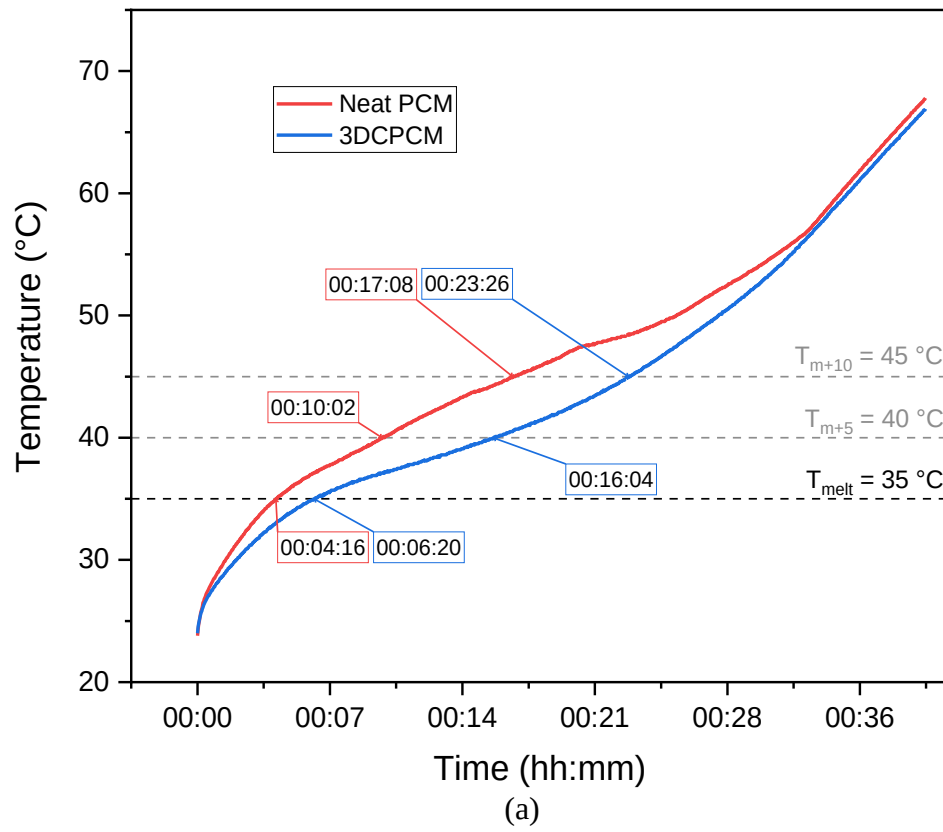
GPPCM had a performance worse than neat PCM at 20 W, indicating that the GP in the composite has already settled during the experiment and did not improve the heat spread of the PCM composite. This hypothesis was supported by the similar T - t profile of GPPCM in the second 20 W run. As such, GPPCM was excluded for the 15 and 10 W experiment.

5.2.2 Temperature-time profile analysis – 10 W and 15 W

The T_{top} against time curve of neat PCM and 3DCPCM samples for 15 and 10 W are shown in Figure 5.4(a) and (c) respectively. and the corresponding gradients in the melting regime are shown in Figure 5.4 (b) and (d) respectively. The numerical gradients, $t_{Tm+\Delta T}$, $H_{f,t(\Delta T)}$ and $FOM_{(\Delta T)}$ of are shown in Table 5.4.

Table 5.4 Temperature-time gradients, $t_{(Tm+\Delta T)}$, $H_{f,t(\Delta T)}$ and $FOM_{(\Delta T)}$ of each sample for 15 and 10 W power input.

P_{in} (W)	Sample	dT/dt (pm) (K/s)	dT/dt (melting, avg) (K/s)	Δt (T_{m+5}) (s)	Δt (T_{m+10}) (s)	$H_{f(+5)}$ (kJ/kg)	$H_{f(+10)}$ (kJ/kg)	FOM ($+5$) (10^{-1})	FOM ($+10$) (10^{-1})
15	Neat PCM	0.0281	0.0120	346	772	32.7	80.9	0.568	1.41
	3DC PCM	0.0274	0.0116	584	1026	74.9	123.3	1.33	2.19
10	Neat PCM	0.0182	0.00643	660	1590	48.0	129.7	1.01	2.73
	3DC PCM	0.0179	0.00563	1120	1718	102.5	141.3	2.46	3.39



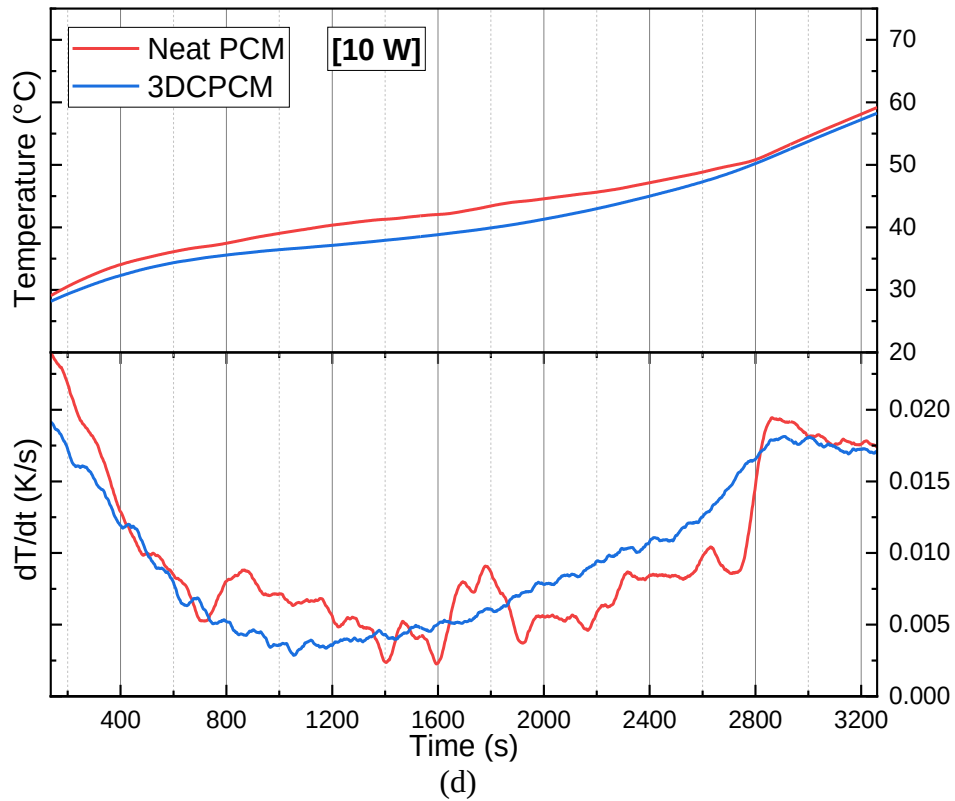
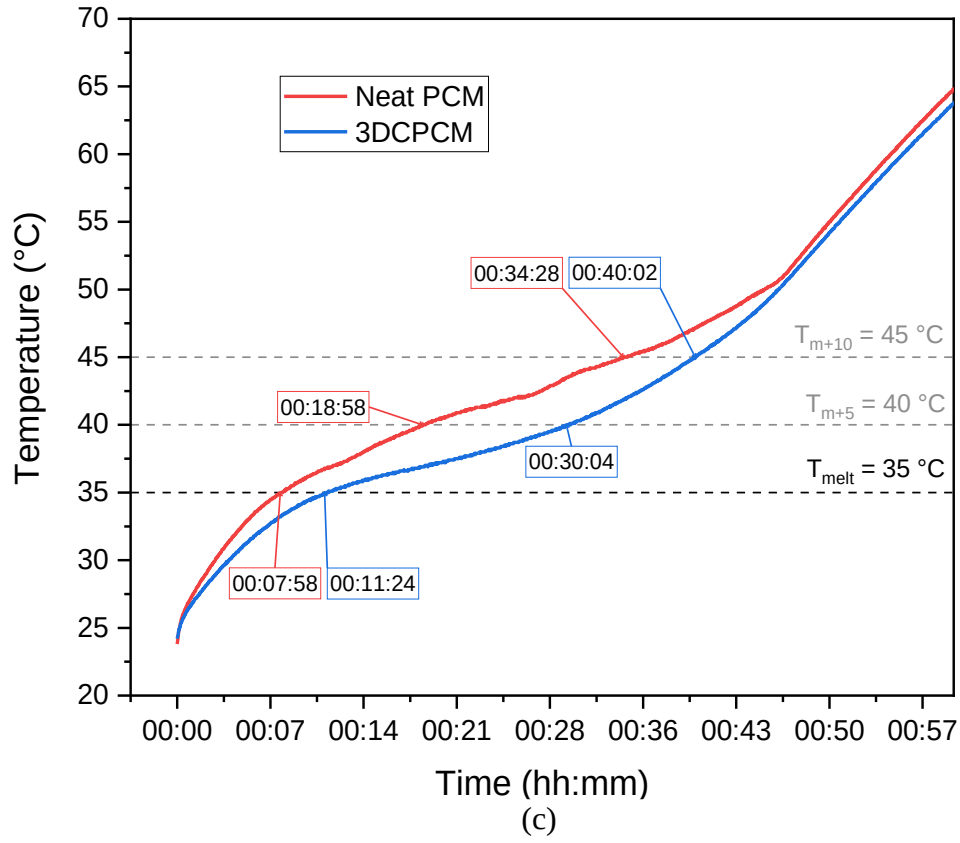


Figure 5.4 (a) T-t curve of Neat PCM, 3DCPCM at 15 W power input. (b) dT/dt vs time at 15 W power input (c) T-t curve of Neat PCM, 3DCPCM at 10 W power input. (d) dT/dt vs time at 10 W power input.

At both power inputs, there was a decrease in dT/dt when $T_{top} = 35\text{ }^{\circ}\text{C}$, indicating the onset of phase change, and subsequently an increase to a similar $dT/dt_{(pm)}$ unique to each power input. The latter indicated that the samples have completed the phase change in each experiment, and the power inputs across the samples were similar for each experiment. 3DCPCM samples had a more stable dT/dt during melting with less fluctuations than neat paraffin at both power inputs. Hence the melting T_{top} of 3DCPCM were more stable than neat PCM across 10, 15 and 20 W. This showed that the inclusion of 3D-C consistently improves the predictability of melting T_{top} , and extension, the subsystem temperature in application. The $FOM_{(\Delta T)}$ of 3DCPCM was consistently higher than neat PCM at each ΔT setting and power setting, hence in application, for 10 – 20 W power dissipation, 3DCPCM would consistently outperform PCM with melting T_{top} closer to T_{melt} and a longer $t_{(Tm+\Delta T)}$.

Across the experiments, the $FOM_{(\Delta T)}$ of both samples were observed to have an increasing trend with decreasing power. This was realistic because with a lower power dissipation, heat energy input would be slower and heat can spread more evenly throughout the PCM, resulting in a longer $t_{(Tm+\Delta T)}$ and a more gentle $dT/dt_{(melting, avg)}$ and thus a larger $FOM_{(\Delta T)}$. The $FOM_{(+10)}$ of 3DCPCM sample decreased by 36% from 10 to 15 W and 26% from 15 to 20 W. $FOM_{(+5)}$ of 3DCPCM sample decreased by a larger extent at 46% and 40% respectively. The $FOM_{(\Delta T)}$ of neat PCM sample in general had a greater decrease than 3DCPCM. $FOM_{(+10)}$ of neat PCM sample decreased 48% from 10 to 15 W and 59% from 15 to 20 W, while $FOM_{(+5)}$ decreased by 44% and 57% respectively. These results showed that the impact of a higher k PCM composite was more significant at a higher power dissipation.

Across all P_{in} , the performance of 3DCPCM was 1.25 to 2.79 times that of neat paraffin based on $FOM_{(+5)}$ and 2.31 to 3.27 times that of neat paraffin based on $FOM_{(+5)}$.

5.2.3 Physical characteristics post experiment

After 3 phase change cycles, the samples were removed from the PCM container and examined. Neat PCM and GPPCM samples were bisected from the top to bottom along the shorter width to expose the cross-sectional view. The close-up images of the samples are shown in Figure 5.5. A single large elliptical shaped air pocket was observed at the top surface in both neat PCM and GPPCM sample, indicated by the red outline in Figure 5.5 (a) and (c). An air pocket was observed at the centre of the neat PCM cross-section, shown in Figure 5.5 (b). An agglomeration of GP was observed at the base of the top surface air pocket. GP was observed to have largely agglomerated at the bottom of the GPPCM sample. There was no observable air pocket present at the cross-section of GPPCM sample, shown in Figure 5.5 (d). Multiple smaller air pockets that follow the outlines of the 3D-C pores were observed spread out on the top surface, instead of a single large air pocket, as shown in Figure 5.5 (f) and (h). The largest air bubble on 3DCPCM sample was observed along a corner of the top surface, shown in Figure 5.5 (f). The 3D-C struts observed in this air bubble all had a coating of PCM, thus resembling 3D-C pore-sized air pockets. Figure 5.5 (g) showed that the bottom surface of the 3DCPCM sample was smooth and had no air pockets. No air pockets were observed at the bottom surface of neat PCM and GPPCM as well.

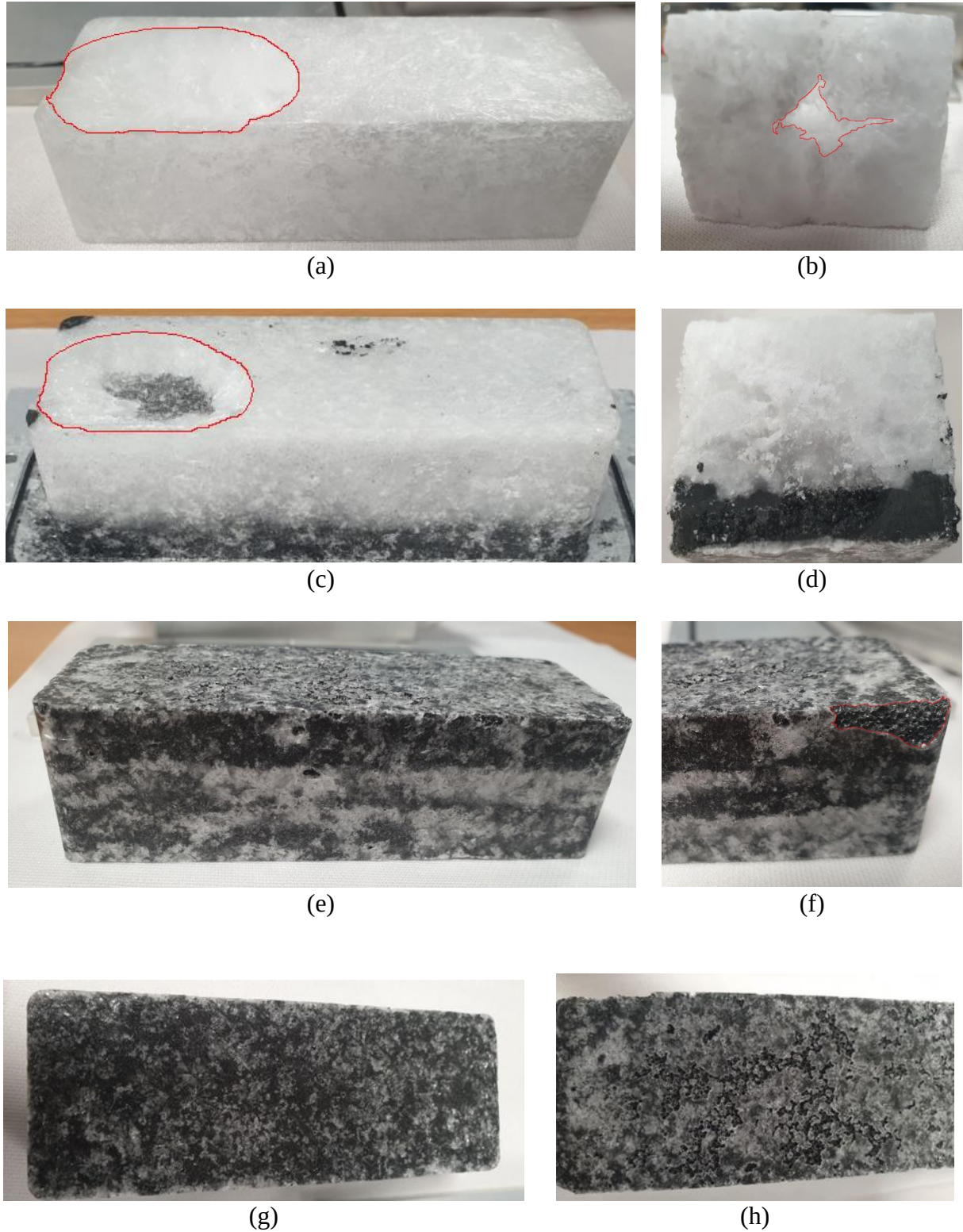


Figure 5.5 Images of samples (a) overview of neat PCM sample, (b) cross-section view of neat PCM sample, (c) overview of GPPCM sample, (d) cross-section view of GPPCM sample, (e) overview of 3DCPCM sample, (f) close-up view of air-gaps in 3DCPCM sample in the top surface, (g) bottom view of 3DCPCM sample, (h) top surface view (surface closest to T_{top}) of 3DCPCM sample.

The air pocket on the top surface of neat PCM and GPPCM was an indication that air had been trapped in the container during the sealing. Therefore, while the PCM was in liquid state, the trapped air would gather on the top surface in one large air bubble, as air is less

dense than the PCM. The pressure in this air bubble would be higher than atmospheric pressure due to the expansion of PCM during melting. The elliptical air pocket would have been formed after the PCM solidified around the pressurized air bubble. This explanation is substantiated by the fact that there were no air bubbles on the bottom surface of the samples. The formation of air pocket in neat PCM and GPPCM in a sealed container was similar to the observation of a depressed top surface made in section 4.2.3.3. This would result in a decrease in effective contact surface with the container walls and hence lower heat transfer rate from the container, and in extension, from the subsystem of interest.

The air pocket observed at the centre of the neat PCM sample cross-section was formed due to the shrinking of PCM during solidification, as explained in section 4.2.3.3. Cooling occurred from the container walls towards the centre, hence the core of the neat PCM at the centre of the container would be the last to solidify and shrink, thus forming the air pocket.

The presence of GP at the base of the top surface air pocket in GPPCM sample indicate that surface energy of the pressurized air bubble was compatible with GP, thus a portion of the GP agglomerated at the base of the air pocket, even after 3 phase change cycles. The large GP agglomerate at the bottom of the GPPCM sample was similar to that observed in section 4.2.3.3, thus further supporting GPPCM with GP diameter of 200 μm was not suitable for space application.

As mentioned in section 4.2.3.3, air bubbles would be present in 3DCPCM due to the changing density of paraffin over phase change. Air bubble formation is an issue under microgravity conditions as well [13], [90]. The presence of 3D-C effectively delocalised the air bubbles, hence, helps retain surface contact with container walls and mitigates the reduced k across air bubbles. This was shown in the spread of smaller air pockets at the top surface instead of a single large air pocket as observed in the other samples. 3D-C would have

constricted the pressurized air from forming a single large air bubble as seen in the other samples. The lack of observable air pockets at the bottom surface of 3DCPCM sample affirms that the top surface air pockets was caused by pressurized air. The coating of PCM on 3D-C in the air pockets indicate the favourable surface energy of PCM and 3D-C. This characteristic ensures contact between high k scaffold and PCM and retains the shape stability of 3DCPCM samples even in large samples. These results showed the physical characteristics of the PCM samples sealed in atmospheric pressure after 3 phase change cycles.

5.2.4 Conclusions

The results of the T - t profile analysis of PCM demonstrator container with neat PCM, 3DCPCM and GPPCM were presented in this section. GPPCM performed the worst amongst the 3 samples, according to ranking by $FOM_{(+10)}$ and $FOM_{(+5)}$ at 20 W power input. The addition of GP to PCM was shown to be detrimental to the performance during melting, and further supports the fact that GP is unsuitable for space applications. This was further supported by the physical characteristics of GPPCM after 3 phase change cycles. Conversely, 3DCPCM performed significantly better than neat PCM in every power setting, with better relative performance at higher power. 3DCPCM was also shown to retain surface contact with the container walls, and thus retain the heat transfer rate with container walls. Therefore, 3DCPCM in hermetically sealed containers would be suitable for space applications.

5.3 Thermal Model for PCM demonstrator

To further investigate the effect of PCM thermal properties on T_{top} , a FE analysis was conducted using COMSOL Multiphysics based on a 3D model of the PCM demonstrator. The computer-aided design (CAD) model is shown in Figure 5.6.

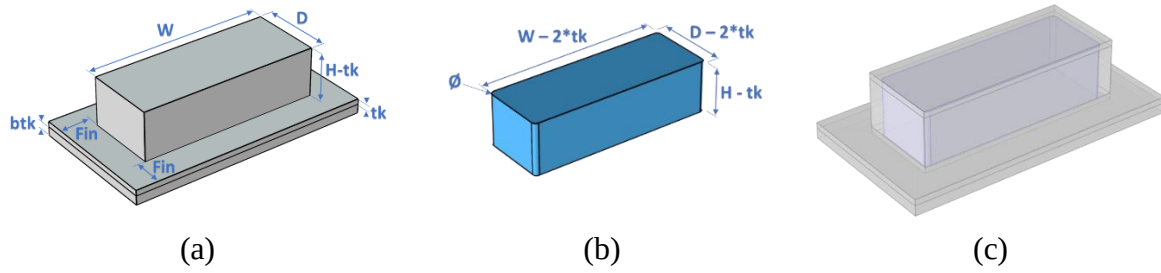


Figure 5.6 CAD model of (a) PCM container (b) PCM composite (c) PCM container + PCM assembly

5.3.1 Geometrical parameters and meshing

The values of the parameters used in the 3D model are listed in Table 5.5.

Table 5.5 Values of geometrical parameters in CAD model

Parameter	Description	Value (mm)
W	Width	100
D	Depth	40
H	Height	30
tk	Thickness of container wall	3
Fin	Fin length	34
btk	Thickness of bottom cover	5
$\emptyset$	Fillet radius	2

The 3D model was generated with the following features and assumptions,

- The 10 screws/nuts, O-ring and the respective cut-outs were not included
- Perfect contact between PCM composite, interior container wall and bottom cover
- Bulk homogeneous properties for PCM composite
- Shape stable PCM composite
- No convection in liquid PCM

A predefined mesh with maximum and minimum element size of 0.0107 and 0.00134 m respectively was used.

5.3.2 Governing equations and boundary conditions

The 3D governing energy equations of the 3D model are,

$$\rho c_p \frac{\partial T}{\partial t} |_{(container)} = \nabla \cdot (k \nabla T) |_{(container)} \quad (5.11)$$

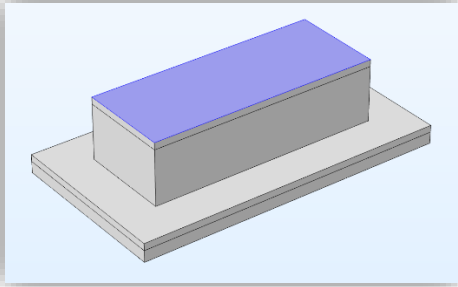
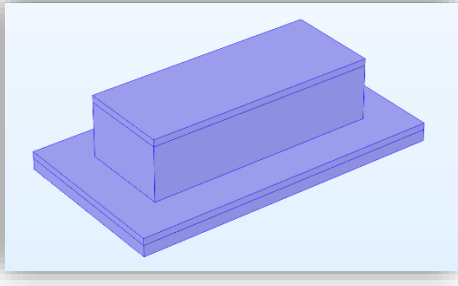
$$\rho (c_p \frac{\partial T}{\partial t} + H_f \frac{\partial f_2}{\partial t}) |_{(PCM)} = \nabla \cdot (k \nabla T) |_{(PCM)} \quad (5.12)$$

Where f_2 is the fraction of PCM in the liquid phase (phase 2), as shown in equation (5.13).

$$f_2 = \begin{cases} 0, & T < T_1 \\ \frac{T - T_1}{\Delta T_{1 \rightarrow 2}}, & T_1 \leq T \leq (T_1 + \Delta T_{1 \rightarrow 2}) \\ 1, & T > (T_1 + \Delta T_{1 \rightarrow 2}) \end{cases} \quad (5.13)$$

The boundary conditions for external surfaces are shown in equation (5.14) and (5.15) in Table 5.6.

Table 5.6 Boundary conditions for thermal model

	$-\mathbf{n} \cdot \mathbf{q} = P \quad (5.14)$
	$-\mathbf{n} \cdot \mathbf{q} = \frac{(T_\infty - T(t, x, y, z))}{R_m} \quad (5.15)$

Where $\mathbf{n}$ refer to the directional vector parallel to the boundary, $\mathbf{q}$ is vector of heat flux with units (W/m²), P is the heat flux with units (W/m²), R_m is the mean insulation resistivity constant with units (Km²/W), T_∞ is the external ambient temperature, $T(t,x,y,z)$ is the temperature of the node on the boundary and A_e is the external surface area of the PCM container. The conductance constant of the insulation, $1/R_m$, was used as input to the 3-D model. Equation (5.14) was applied to the top surface of the PCM container model. The product of P and top surface area, A_{top} , would simulate P_{in} . Equation (5.15) would simulate the insulation around the PCM container.

5.3.3 Validation methods of 3-D model

The FE analysis of the 3-D model was validated in two stages. In stage one, the 3-D model of the Al6061 PCM container was validated and in stage two, the combined model of the container and PCM was validated.

5.3.3.1 Stage One: Validation of PCM container model

The thermal analysis of the 3D model requires 3 basic heat transfer properties of each solid materials for simulation, ρ , c_p and k . The typical thermal properties of Al6061-T6 were used [120]. The 3D model of the PCM container was validated using experimental results of PCM containers filled with DI water, a material with well-defined properties. 86.1 g of DI water was added into an empty PCM container at room temperature and carefully sealed. The DI water sample was tested according to the methods described in section 5.1.3 at $P_{in} = 10, 15$, and 20 W power input. The T_{top} over time was recorded with a thermocouple attached to the top surface and a data acquisition system. The PCM composite component in the 3D model was replaced with properties of DI water and simulation was conducted at equivalent $P_{in} = 10, 15, 20$ W. A parametric study with a range of $1/R_m$ values from 2.0 to 4.0 W/m²K with a 0.5 W/m²K interval was conducted at each P_{in} . The average temperature at T_{top} was extracted over

time at 30 s interval and compared with the respective experimental results to determine the best fit R_m . The formulation of the material properties of DI water used in the 3D model, where T was the absolute temperature of the node in Kelvins (K), is shown in Table 5.7.

Table 5.7 Formulation of DI water properties for 3-D model

Parameter	Description	Value	Units
DI water			
$\rho_{(DI\ water)}$	Density	$838.466135 + 1.40050603T - 0.0030112376T^2 + 3.71822313 \times 10^{-7}T^3$	g/cm ³
$C_{p(DI\ water)}$	Specific heat capacity	$12010.1471 - 80.4072879T + 0.309866854T^2 - 5.38186884 \times 10^{-4}T^3 + 3.62536437 \times 10^{-7}T^4$	J/gK
$k_{(DI\ water)}$	Thermal conductivity	$-0.869083936 + 0.00894880345T - 1.58366345 \times 10^{-5}T^2 + 7.97543259 \times 10^{-9}T^3$	W/mK
$\mu_{(DI\ water)}$	Dynamic viscosity	$1.3799566804 - 0.021224019151T + 1.3604562827 \times 10^{-4}T^2 - 4.6454090319 \times 10^{-7}T^3 + 8.9042735735 \times 10^{-10}T^4 - 9.0790692686 \times 10^{-13}T^5 + 3.8457331488 \times 10^{-16}T^6$	Pa·s
Al6061-T6			
$\rho_{(Al6061)}$	Density	2.7	g/cm ³
$C_{p(Al6061)}$	Specific heat capacity	0.896	J/gK
$k_{(Al6061)}$	Thermal conductivity	167	W/mK
Miscellaneous parameters			
$1/R_m$	Insulation conductance	2.0 – 4.0 (0.5 interval)	W/m ² K
P	Heat flux	2550; 3810; 5160	W/m ²
T_{ext}	External temperature	23.0	°C
T_i	Intital temperature	Adjusted accordingly for each experiment	°C

5.3.3.2 Stage Two: Validation of PCM container + PCM model

To validate the 3D model of the PCM, three sets of 3DCPCM with different melting temperature ranges were fabricated using the method described in section 5.1.2. PCM from Rubitherm, RT35HC, RT44HC and RT54HC [97], [121], [122], with melting point of 34 – 36 °C, 40 – 44 °C and 53 – 54 °C were used as PCM. 3D-C with density of 16.5 - 22.0 mg/cm³ was used. Experiments using the methods described in section 5.1 using the three sets of PCM were conducted at 10, 15, and 20 W power input. For this section, the naming convention of samples used in the experiments was “3DC/P(melting point)/(P_{in})”.

The experimental results for the T - t profile of T_{top} was compared to the numerical simulation of the 3D model for each 3DCPCM sample using the best fit R_m value. Data was recorded at 30 s interval. In addition to ρ , c_p and k , the thermal analysis of PCM require additional parameters, such as H_f , phase change temperature ($T_{(pc1 \rightarrow 2)}$), and transition interval ($\Delta T_{(1 \rightarrow 2)}$). $T_{(pc1 \rightarrow 2)}$ and $\Delta T_{(1 \rightarrow 2)}$ values were taken from material datasheets. The k of each 3DCPCM were determined using the Lee’s disc method described in section 3.3.2.1 using 3 copper plates with dimensions of 94 mm * 34mm * 5mm. The ρ of each 3DCPCM sample was calculated by dividing each $m_{(3DCPCM)}$ by the internal volume of the PCM container. The c_p and H_f of each 3DCPCM sample were calculated using equation (5.16) and (5.17).

$$c_{p(3DCPCM)} = (1 - \varphi)c_{p(PCM)} + \varphi c_{p(3D-C)} \quad (5.16)$$

$$H_{f(3DCPCM)} = (1 - \varphi)H_{f(PCM)} \quad (5.17)$$

The experimental material properties of the 3DCPCM samples, material properties of Al6061-T6, other parameters used in the 3-D model are documented in Table 5.8.

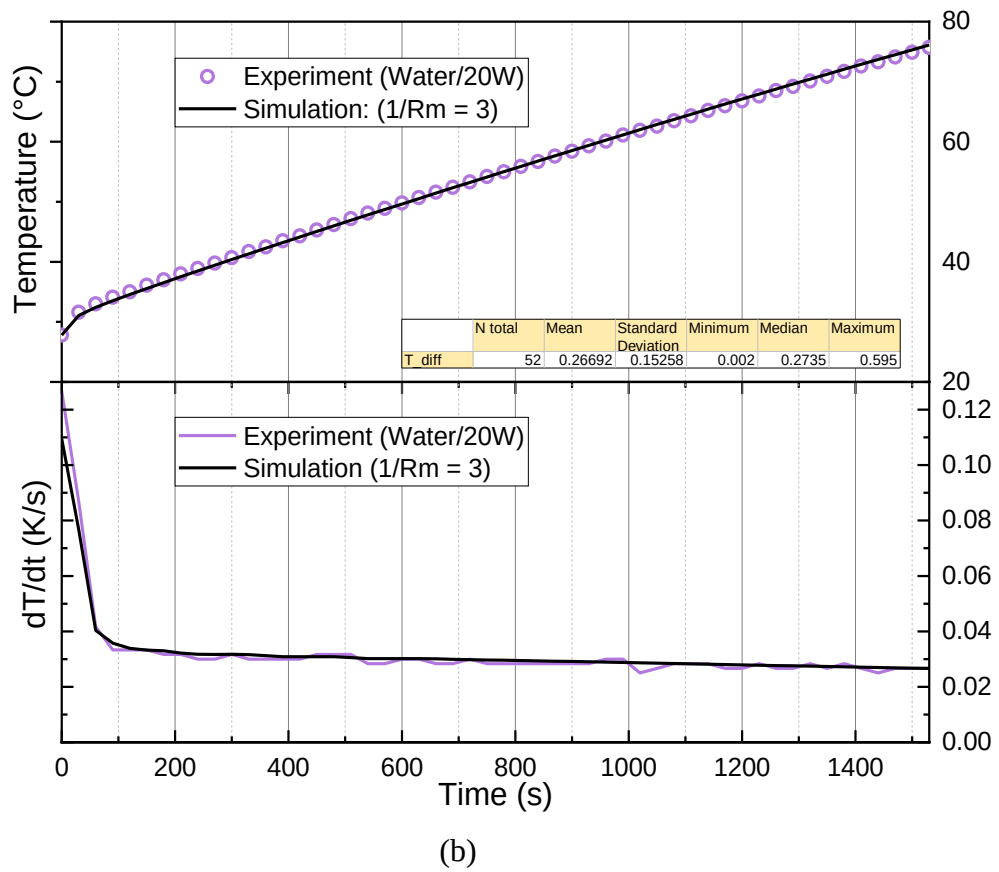
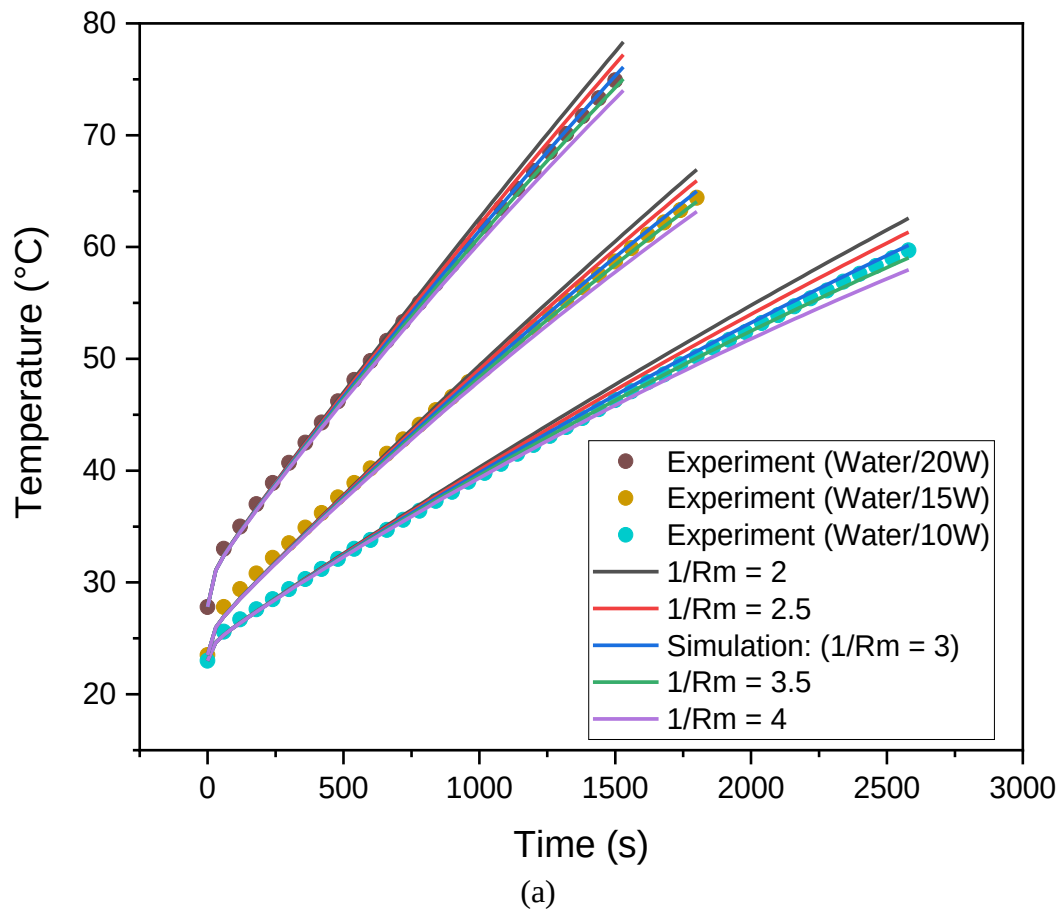
Table 5.8 Experimental material properties used for 3D model.

Parameter	Description	Value			Units
		3DC/P35	3DC/P44	3DC/P54	
$T_{(pc1 \rightarrow 2)}$	Phase change temperature	34	40	53	°C
$\Delta T_{1 \rightarrow 2}$	Transition interval	2	4	1	°C
$m_{(3DCPCM)}$	Mass of 3DCPCM	67.23	65.06	69.77	g
$m_{(3DC)}$	Mass of 3D-C	1.51	1.89	1.42	g
$\phi_{(3DC)}$	Mass fraction of 3D-C	2.2	2.9	2.0	wt%
$\rho_{(3DCPCM)}$	Density of 3DCPCM	0.780	0.755	0.810	g/cm ³
$c_{p(3D-C)}$	Specific heat capacity of 3D-C	0.7077			J/gK
$c_{p(3DCPCM)}$	Specific heat capacity of 3DCPCM	2.84	2.93	2.95	J/gK
$k_{(3DCPCM)}$	Thermal conductivity of 3DCPCM	1.0	0.65	0.60	W/mK
$H_{f(3DCPCM)}$	Latent heat of fusion of 3DCPCM	234.7	242.8	196	J/g
$m_{(t, 3DCPCM)}$	Total mass of sample (measured)	373.3	371.3	375.6	g

5.4 Results and Discussion

5.4.1 Stage one: Validation of PCM container model

The numerical fitting results of the parametric study of $1/R_m$ for $P_{in} = 10, 15$ and 20 W of PCM container and DI water are shown in Figure 5.7. Figure 5.7 (a) shows an overview of the $T-t$ curves at T_{top} comparison for $1/R_m = 2.0 - 4.0$ W/m²K for all P_{in} settings, and the respective experimental $T-t$ curves. The curve of each $1/R_m$ value was colour coded and shown using solid lines. The experimental results are shown in solid circle scatters. Throughout all three P_{in} settings, the curve with $1/R_m = 3.0$ W/m²K was closest to experimental values.



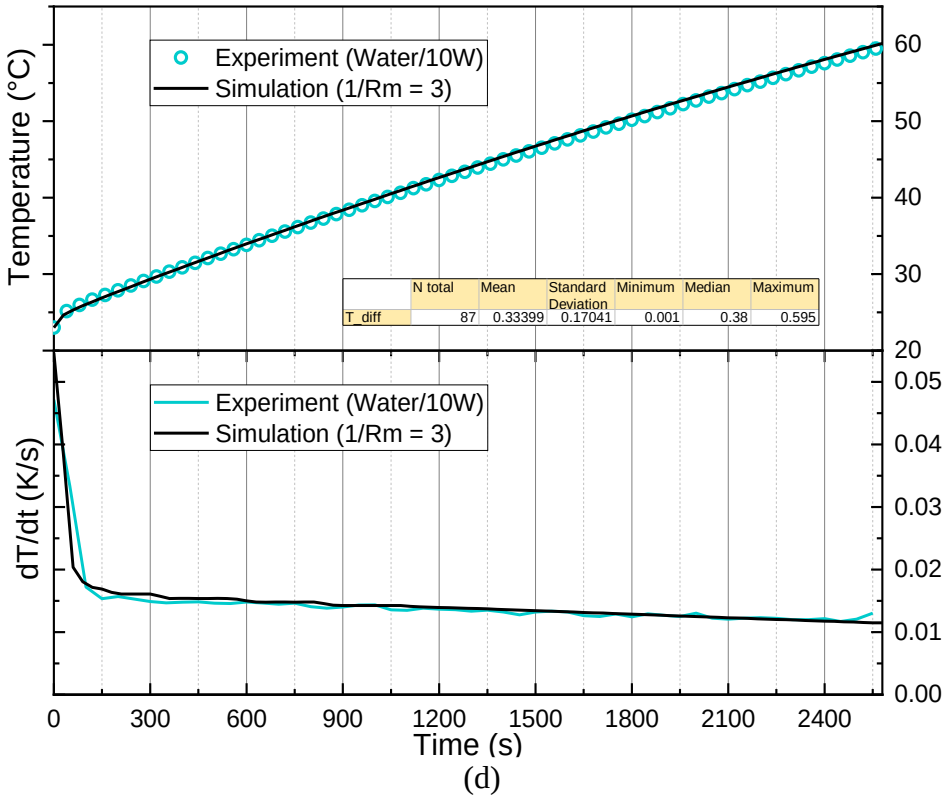
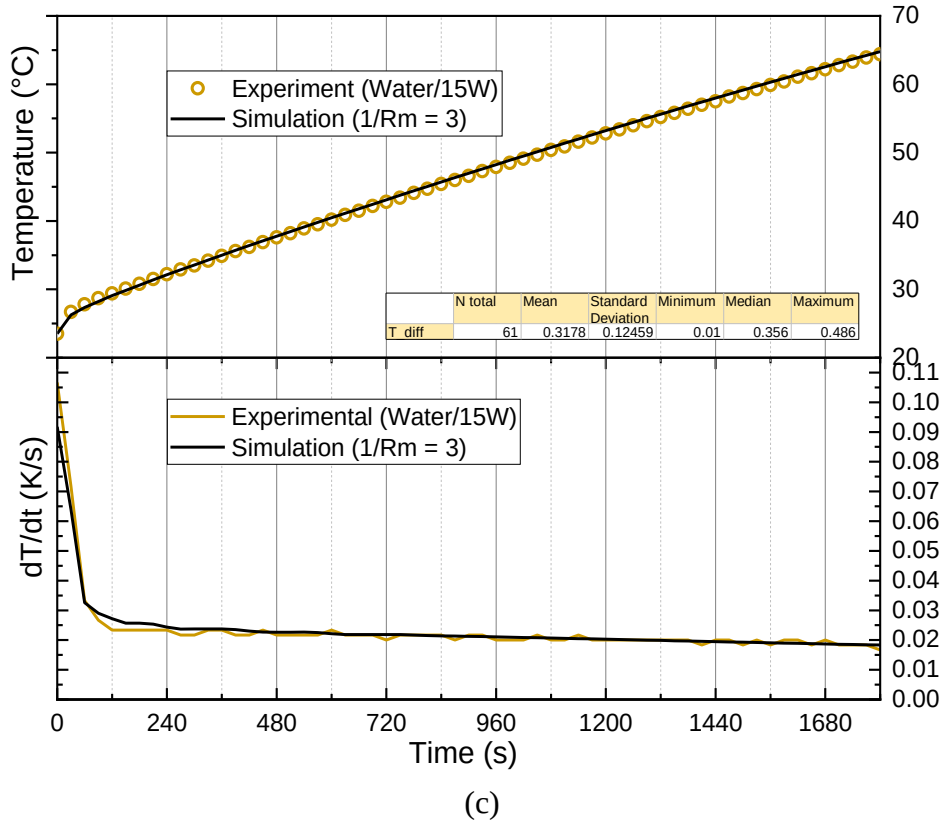


Figure 5.7 (a) Overview of the numerical fitting with experimental T - t curves at T_{top} comparison for $1/R_m = 2.0 - 4.0$ W/m^2K . Numerical simulation curve in solid lines, each $1/R_m$ value was uniquely colour coded for every P_{in} setting. Experimental results shown in solid circle scatter. (b) – (d) T - t curve of numerical vs experimental for $1/R_m = 3.0$ on top graph, and dT/dt vs time curve at the bottom graph for $P_{in} =$ (b) 20 W, (c) 15 W and (d) 10 W. Inset (b) – (d) Statistical study of T_{diff} of experiment and simulation results.

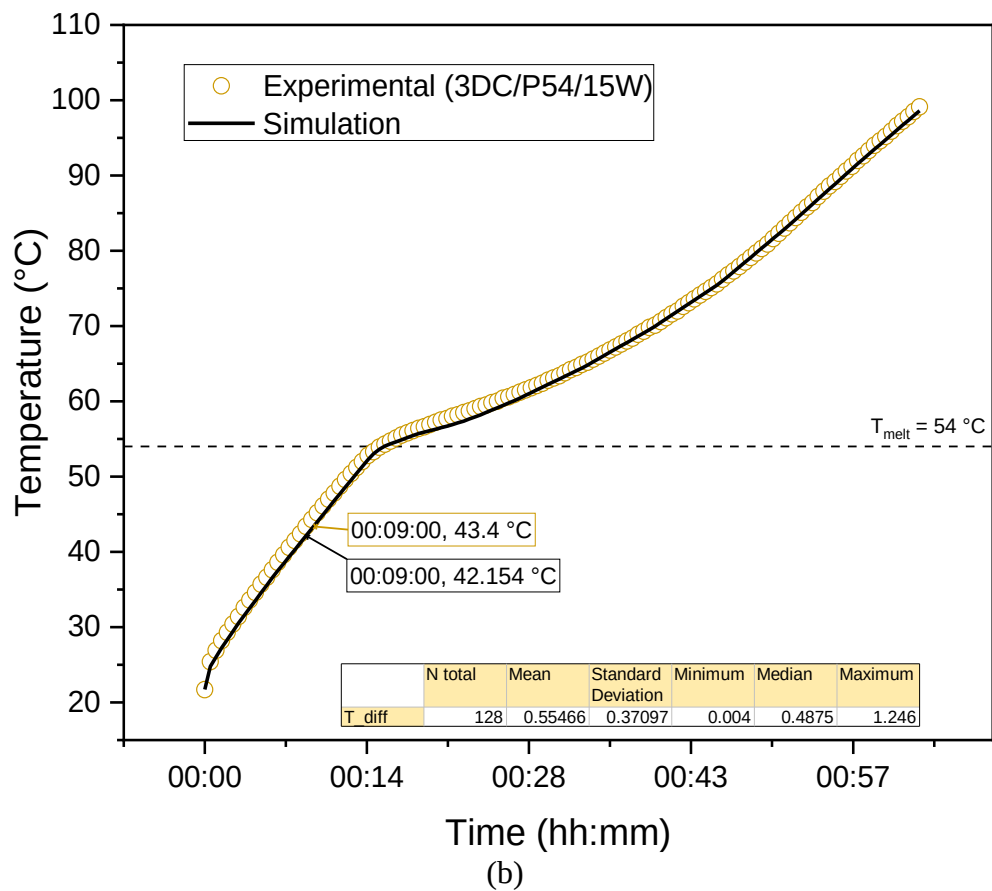
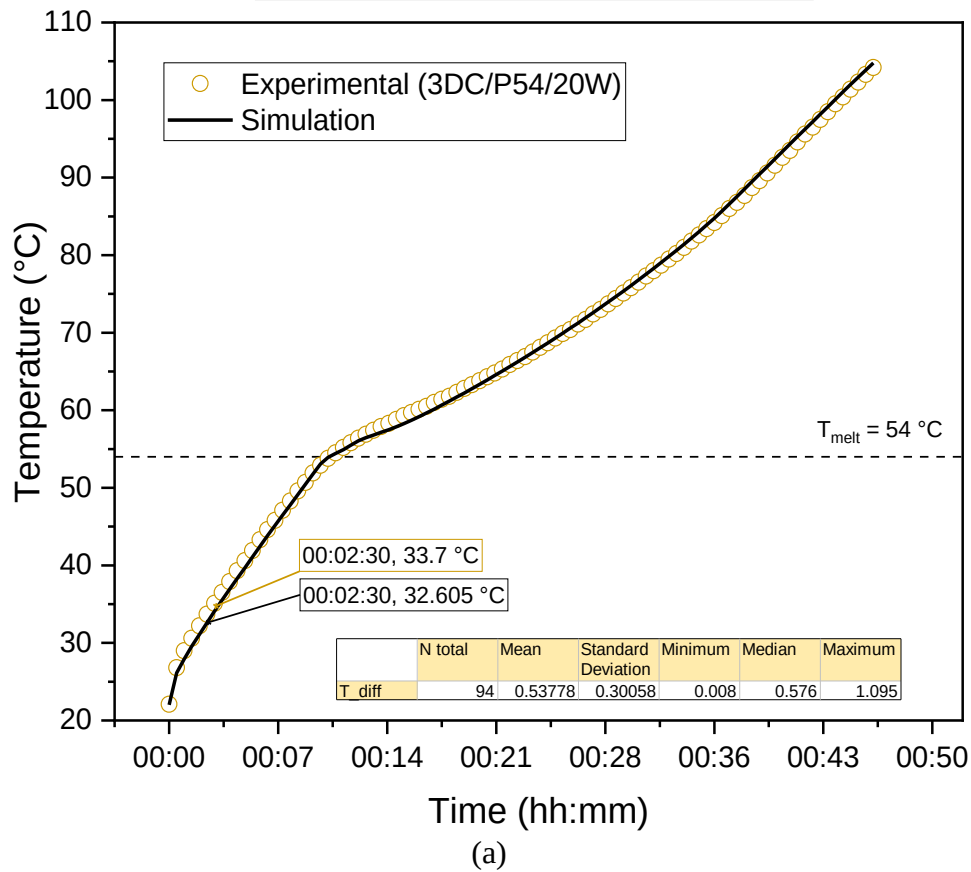
Figure 5.7 (b)–(d) shows the numerical fitting with experimental T_{top} against time curve for $1/R_m = 3.0 \text{ W/m}^2\text{K}$ at the top graph and the respective dT/dt against time curve for 20 – 10 W at the bottom graph. From the results, the largest error in dT/dt difference between numerical and experimental results occur at the initial transient rate of heating stage. After the heating rate stabilized, the gradient of the curves quickly converges. The inset of Figure 5.7 (b)–(d) records the statistical study of the temperature difference, T_{diff} , of experiment and simulation results, shown in equation (5.18).

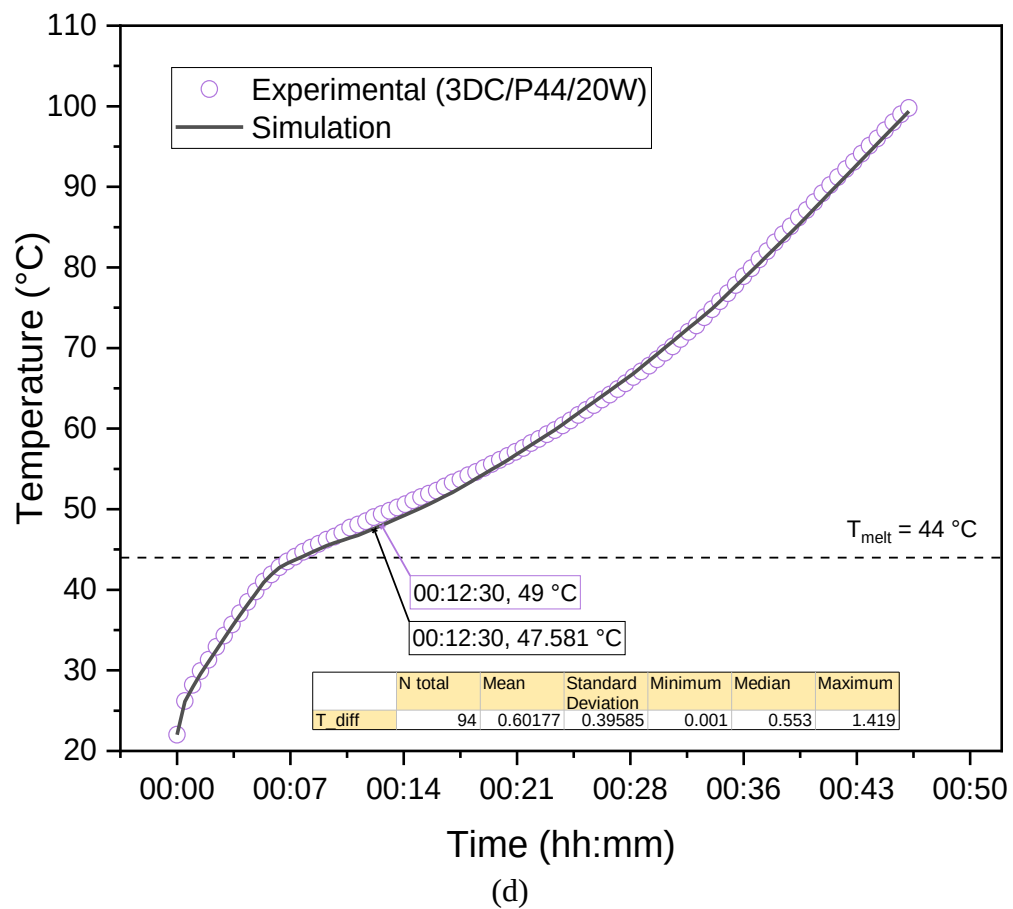
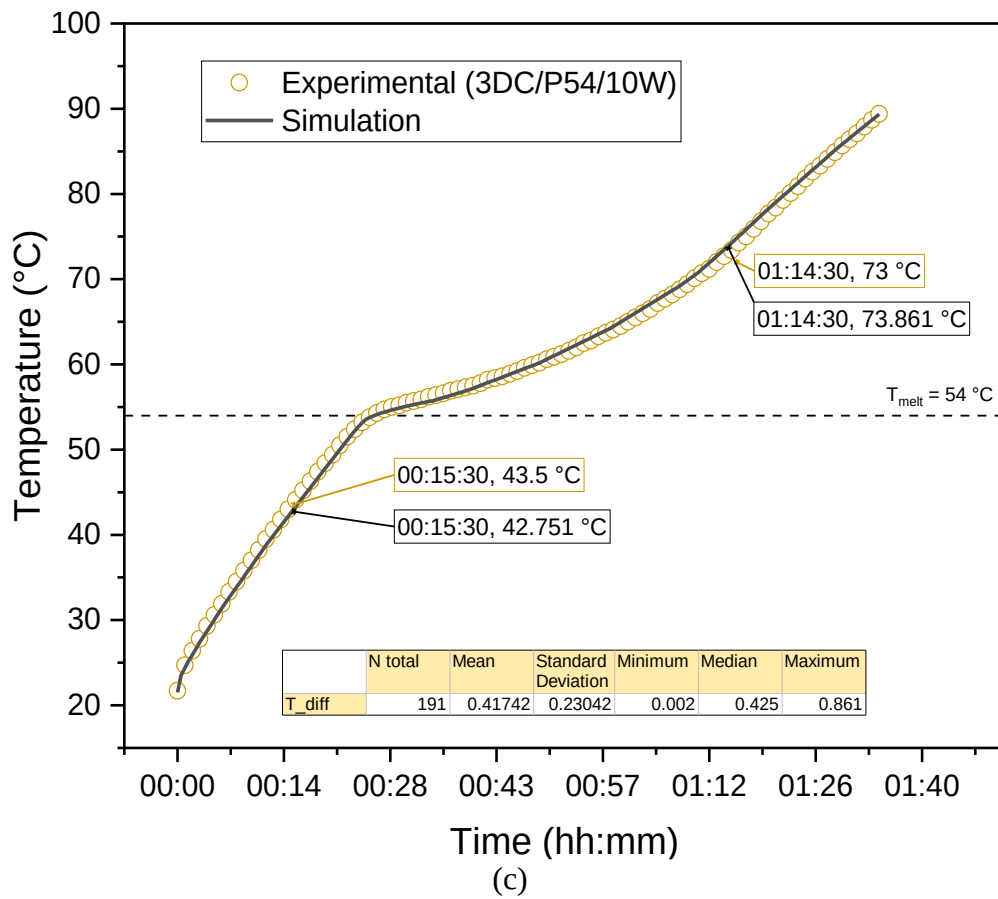
$$T_{diff} = |T_{experiment} - T_{simulation}| \quad (5.18)$$

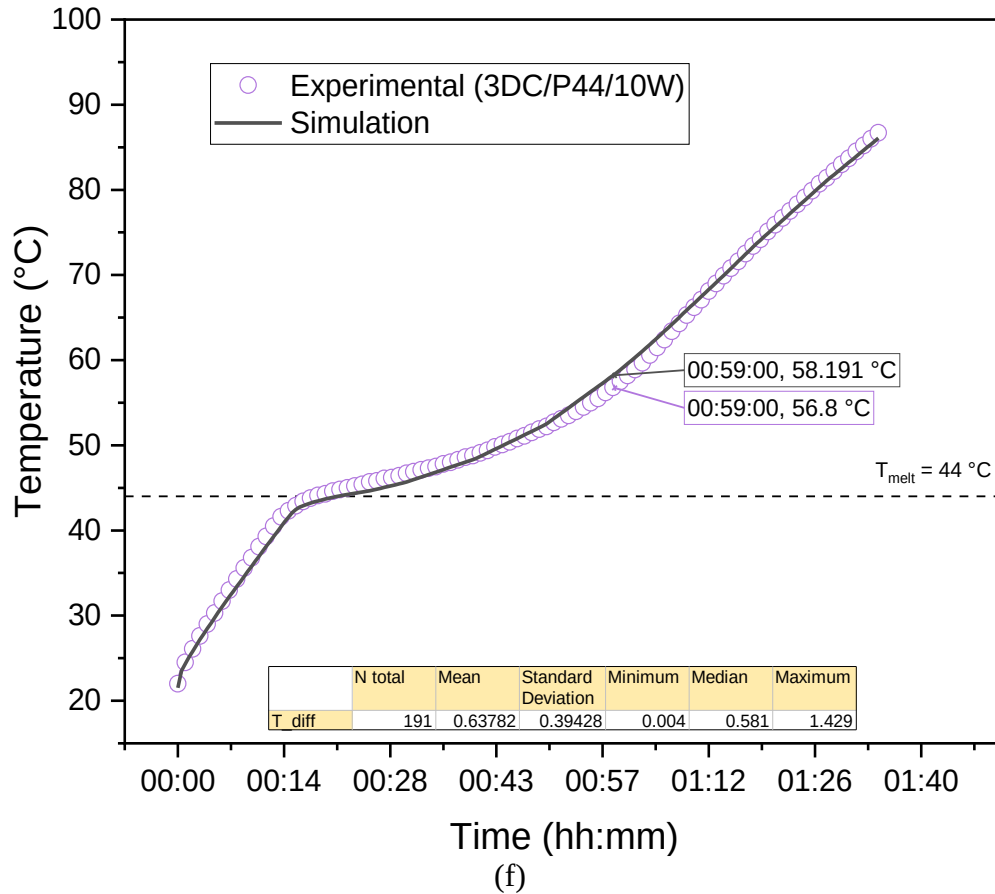
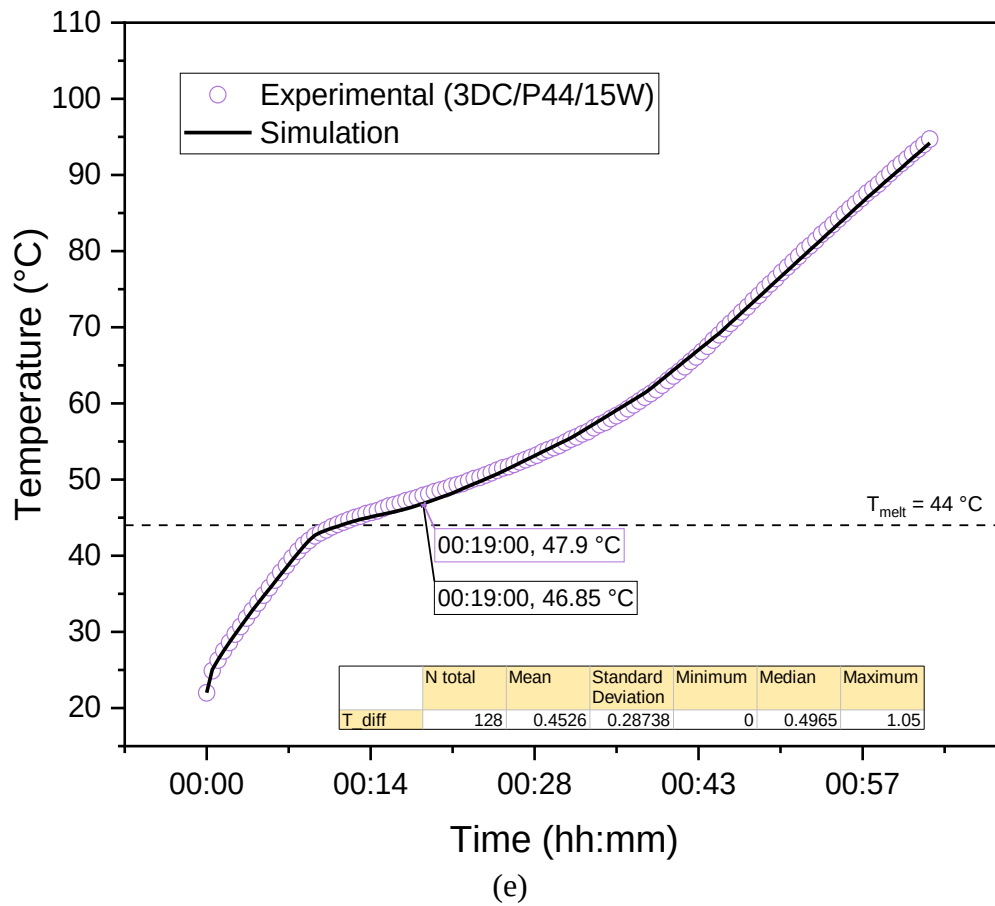
The numerical fitting results showed a very good fit with experimental values. The mean T_{diff} was 0.267, 0.318 and 0.334 °C for 10, 15 and 20 W, respectively, with a low standard deviation of 0.170, 0.125 and 0.153 °C, respectively. The maximum T_{diff} was 0.595 °C for 10 and 20 W and 0.486 °C for 15 W, hence the uncertainty of the T - t curve generated was less than ± 0.6 °C from experimental results. These results validated the FE analysis on the 3-D model of the Al6061 PCM container with $1/R_m = 3.0 \text{ W/m}^2\text{K}$. Numerical fitting of 3DCPCMs

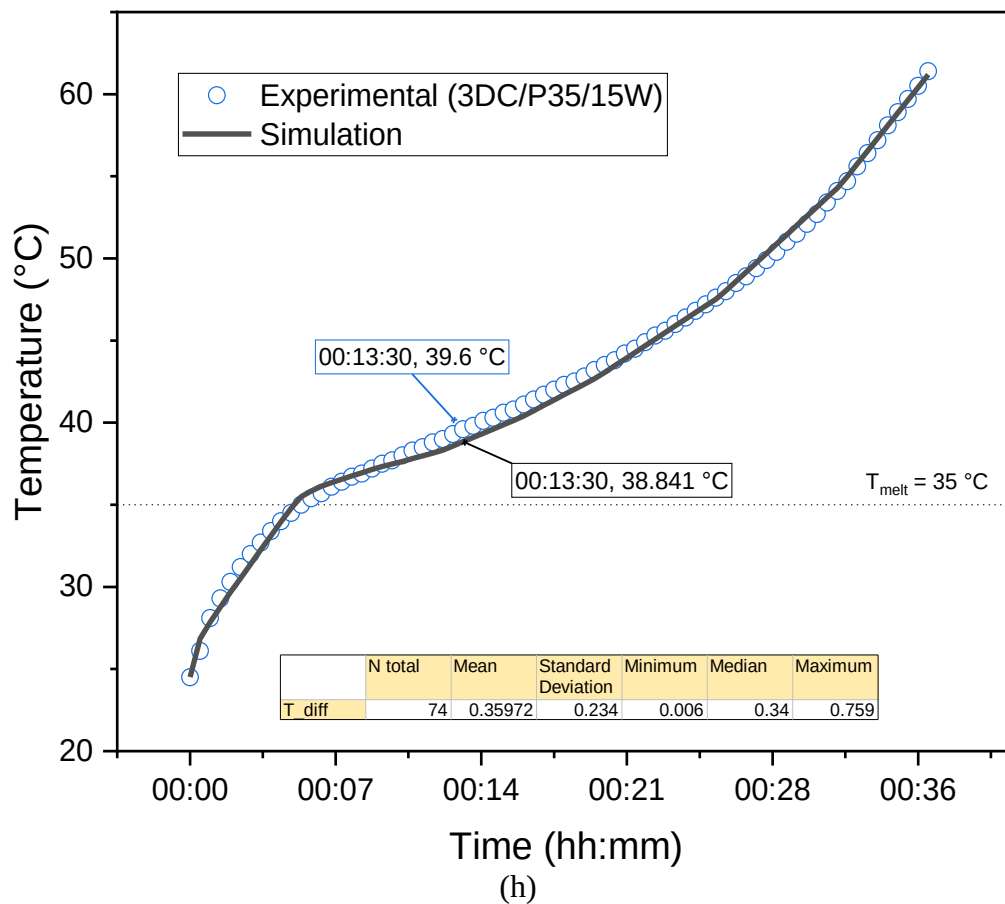
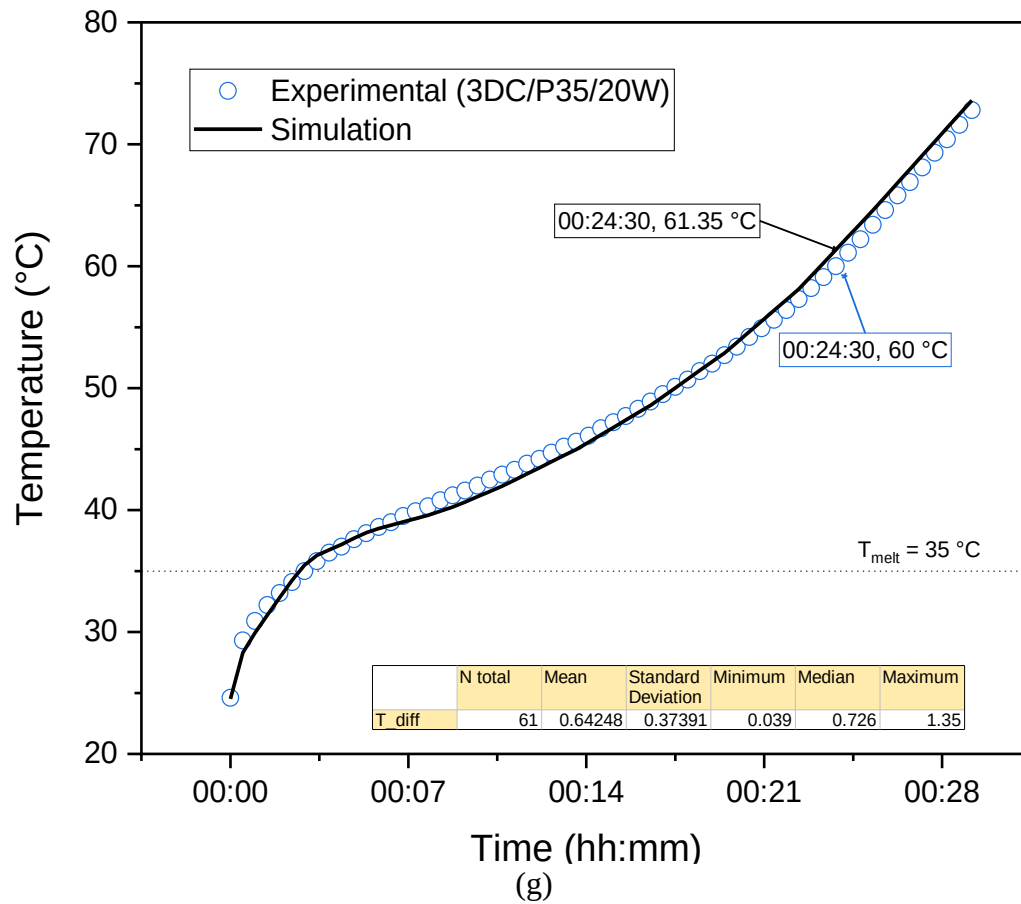
5.4.2 Stage Two: Validation of PCM container + PCM model

The numerical fitting results of 3DCPCM with $T_{(pc1 \rightarrow 2)}$ at 35, 44 and 54 °C are shown in Figure 5.8. The results of the statistical study of T_{diff} are shown in the inset of each graph in Figure 5.8, and the consolidated results are shown in Table 5.9. The point of the largest T_{diff} of each graph was annotated.









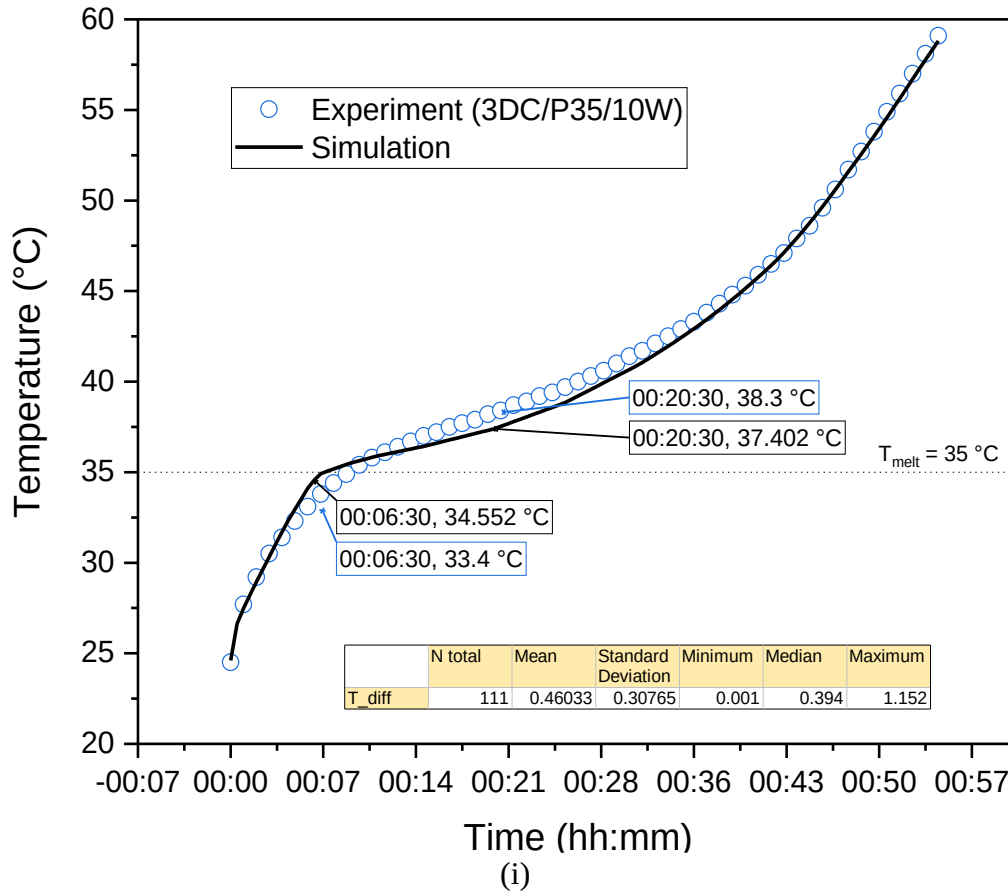


Figure 5.8 Numerical fitting of T-t curve at $P_{in} = 20, 15$ and 10 W for (a)-(c) $T_{(pc1 \rightarrow 2)} = 54$ °C, (d)-(f) $T_{(pc1 \rightarrow 2)} = 44$ °C, (g)-(i) $T_{(pc1 \rightarrow 2)} = 35$ °C. Inset: Statistical study of T_{diff} of experiment and simulation results.

Table 5.9 Results of statistical study on T_{diff} of each power setting and phase change temperature

Power (W)	$T_{(pc1 \rightarrow 2)}$ (°C)	Mean (°C)	Standard deviation (°C)	Minimum (°C)	Maximum (°C)
20	54	0.538	0.301	0.008	1.095
	44	0.602	0.396	0.001	1.419
	35	0.642	0.374	0.039	1.350
15	54	0.555	0.371	0.004	1.246
	44	0.453	0.287	0	1.05
	35	0.360	0.234	0.006	0.759
10	54	0.417	0.230	0.002	0.861
	44	0.638	0.394	0.004	1.429
	35	0.460	0.308	0.001	1.152

The overall numerical fitting of T - t curve showed a good fitting in every case. Across all cases, the mean difference ranged from 0.360 – 0.642 °C and the standard deviation ranged from 0.230 – 0.396 °C. The maximum T_{diff} generally occurred during the phase change regime for 3DC/P35 and 3DC/P44, and during the solid phase for 3DC/P54. The largest T_{diff} occurred in 3DC/P44/10W and 3DC/P44/20W at 1.429 and 1.419 °C. The uncertainty for the FE analysis on the combine 3D model therefore is within ± 1.5 °C.

The fitting results validated the FE analysis on the 3D model of Al6061 PCM container and PCM sample. Hence the combined model could be used to predict the melting T - t curve at T_{top} of PCM containers with PCMs of different parameters, such as $T_{(pc1 \rightarrow 2)}$, $\Delta T_{1 \rightarrow 2}$, k and H_f , and at different heating rates with temperature accuracy within ± 1.5 °C.

5.4.3 Conclusions

The FE analysis of 3D model of PCM demonstrator was in this section. Experiments were conducted with 4 different PCM containers, one containing DI water and the other each containing 3DCPCM with different thermal properties ($T_{(pc1 \rightarrow 2)}$, $\Delta T_{1 \rightarrow 2}$, k and H_f) at 3 different P_{in} of 10, 15 and 20 W. The 3D model of the Al6061 container and DI water was validated with experimental results by fitting of T - t curves for T_{top} , with maximum errors of ± 0.6 °C across all three P_{in} settings and the numerical value of $1/R_m$ was found to be 3.0 W/m²K. The combined 3D model of the Al6061 container and PCM was similarly validated with experimental results, with maximum errors of ± 1.5 °C across all three P_{in} settings. The 3D model could therefore be used to predict the melting T - t curve of T_{top} for PCM containers with PCM of different parameters. It was noted that the model assumes shape stability during melting and hence could not be used to predict the results for PCMs where the melting solid phase moves randomly within the container during melting.

5.5 Summary

In this Chapter, an in-house PCM demonstrator set-up was introduced to identify the impact of the PCMs in use-case packaging, and a FE analysis was conducted using COMSOL Multiphysics based on a 3D model of the PCM demonstrator and numerically fitted to experimental results for validation. The main points of the Chapter are listed.

- GPPCM, 3DCPCM and neat paraffin was used as samples and various output parameters was generated at three typical P_{in} values to simulate heat inputs from subsystems of interest in use-case scenarios. The $T-t$ curve of T_{top} was generated in each case to represent the temperature profile of the subsystem surface. Various practical output parameters were generated from the $T-t$ curve and two FOMs was calculated to benchmark each sample. Addition of GP to PCM was found to be detrimental to the performance. PCM container with 3DCPCM was found to 1.25 to 2.79 times that of neat paraffin based on $FOM_{(+5)}$ and 2.31 to 3.27 times that of neat paraffin based on $FOM_{(+10)}$ respectively. The physical characteristics of each samples examined after the experiment showed that neat PCM sample had a large air gap at the top surface and an elongated air gap at the core of the sample. Conversely 3DCPCM sample had air gaps that were spread out due to the 3D-C scaffold and maintained its shape and thus thermal contact with the container.
- FE analysis base on 3D model of the PCM demonstrator was conducted for 3DCPCM. The model was validated in two-stages with experimental results of PCM container + DI water for stage one and experimental results of PCM container + three 3DCPCM with different $T_{(pc1 \rightarrow 2)}$, $\Delta T_{1 \rightarrow 2}$, k and H_f . The overall 3D model was validated to predict the melting $T-t$ curve of T_{top} for PCM containers with PCM of different parameters with the accuracy of ± 1.5 °C.

6. Novel Composite: Carbon Honeycomb 3DCPCM

In the previous Chapters, it was established that 3DCPCM is a viable PCM composite for space applications. The key factor was the lightweight, interconnected structure of 3D-C micro-skeletal acting both as shape-stabilizing scaffold and as thermal transport highways to spread heat rapidly throughout the PCM. Two main concerns were identified through the demands of applying 3DCPCM to use-cases. Firstly, the current use-case PCM module demand samples thicker than the thickness of the 3D-C available. In our case, three 3D-Cs was stacked to fulfil the required dimensions and fabricated 27 mm thick 3DCPCM for the PCM container demonstrator. The break in thermal contact between each stack layer would disrupts heat transfer between 3D-C layers, and thus reduce the effectiveness of heat transfer throughout the sample. The outer metal packaging would assist heat spread between layers at the outer surface of the 3DCPCM sample, however, the effect would be less pronounced further away from the outer packaging, i.e., at the centre of the 3DCPCM sample. The second concern lies in the launch vibrations that liquid phase 3DCPCM experience. The launch vibrations were hypothesized to induce sloshing of liquid PCM within the PCM module, thus compromise the structural integrity of the 3D-C micro-skeletal, and thereby diminish the excellent properties of 3DCPCM, such as shape-stability and high k .

In this Chapter, a novel material, CH3DCPCM, was introduced. The dimensions of honeycomb structures can be fabricated according to the dimensions of the use-case module. High k CH cells walls enclose a small volume of 3DCPCM and act as fins that spread heat rapidly between the 3D-C layers. In the launch environment, honeycomb cells walls could dampen the spread of momentum and reduce sloshing, and thus protect the structural integrity of the 3D-C. Additionally, honeycomb sandwich panels are used in primary and secondary structures in satellites [123], thus CH3DCPCM could be integrated into the structures of the satellite for more efficient packaging.

In this Chapter, the design of experiments to test the hypothesis that high k carbon honeycombs improve heat spread of 3DCPCM between 3D-C layers is presented and the relevant results and discussion are documented. The experiments to test the launch environment will be presented in Chapter 7.

6.1 Minimum density of 3D-C for CH+3DC

To identify the minimum density of 3D-C required, 3D-C of different apparent densities were used to physically merge with CH to fabricate CH+3D-C scaffold. In section 4.3, it was concluded that the optimal mass fraction of 3D-C that maximizes relative k increase per unit mass of 3D-C was found to be between 1.5 to 2.5 wt.% of 3D-C. Therefore, the corresponding 10 mm 3D-Cs of densities 12.8 and 20.1 mg/cm³, named 3D-C/10/1.5 and 3D-C/10/2.0 respectively, was selected to be physically merged with CH using the method described in section 3.2.3.1. CH3DCPCM was fabricated thereafter using the method described in section 3.2.3.2

6.1.1 Results and Discussion

The images of the fabricated CH+3D-C scaffolds and CH3DCPCM are shown in Figure 6.1.

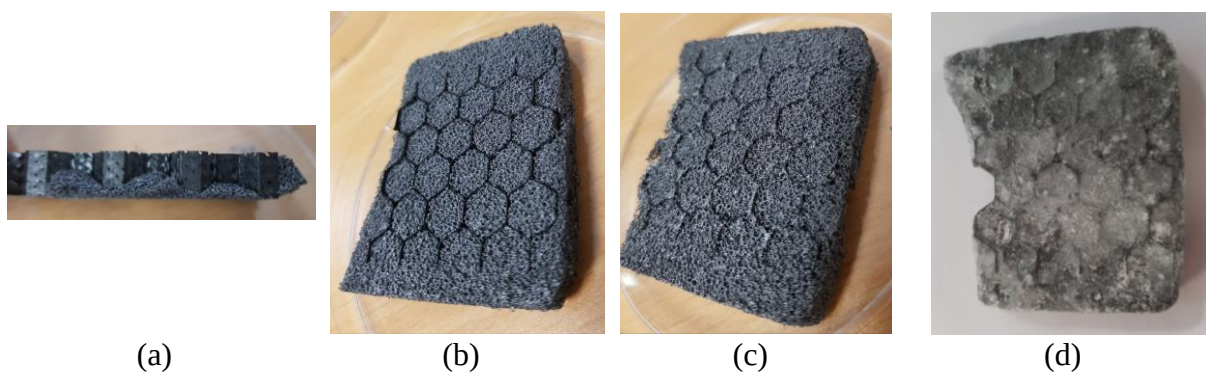


Figure 6.1 (a) Side view of CH + 3D-C/10/1.5, showing that the 3D-C had been deformed and compressed in the attempt to merge with CH. (b) Top view of CH + 3D-C/10/2.0. (c) Bottom view of CH + 3D-C/10/2.0. Distinct regions of compressed 3D-C in the hexagonal outline of the CH were observed. (d) 10 mm thick CH3DCPCM.

Figure 6.1 (a) shows the side view of sample CH+3D-C/10/1.5. The CH was observed to have deformed and compressed the 3D-C instead of slicing through. This indicates that 3D-C/10/1.5 at the apparent density of 12.8 mg/cm^3 was insufficiently rigid for the fabrication method described in section 3.2.3.1.

Figure 6.1 (b) and (c) shows, respectively, the top and bottom view of a successfully fabricated CH+3D-C/10/2.0. The 3D-C was observed to retain its shape within the CH cell. Distinct regions of compressed 3D-C in the hexagonal outline of the CH were observed on the bottom of CH+3D-C/10/2.0, in Figure 6.1 (c). The 3D-C in the scaffold was observed to retain its position after the CH region was tapped with a spatula. This meant that the frictional force between the CH and 3D-C interface was sufficient to hold the 3D-C in place despite the perturbation. These observations showed that good physical contact between the interface of CH and 3D-C can be assumed. Therefore, the minimum apparent density of 3D-C to fabricate CH+3D-C scaffold is 20.1 mg/cm^3 .

The sample of CH3DCPCM fabricated from CH+3D-C/10/2.0 is shown in Figure 6.1 (d). PCM showed good wettability with the CH+3D-C scaffold. There was no observable air bubble on the surfaces of CH3DCPCM and there was no separation between the CH cells and the 3DCPCM. Hence the interconnected thermal path remained intact in CH3DCPCM. One half hexagonal cell of 3DCPCM on the edge of the CH3DCPCM was observed to have fallen off from the sample, centre left of Figure 6.1 (d). Cross-referencing the corresponding half-cell in the CH+3D-C scaffold, shown in Figure 6.1 (b) and (c), there was insufficient overhanging 3D-C from adjacent cells holding on to the 3D-C in that half-cell. The 3D-C in that half-cell had fallen off during the infusion process. For a whole CH3DCPCM sample to be well fabricated for characterisation, sufficient overhanging 3D-C at the edges of the CH+3D-C scaffold was required. This was taken into consideration when fabricating the

subsequent CH3DCPCM sample for k measurements. Subsequent samples of CH3DCPCM have the appearance of the ideal sample as shown in Figure 3.6 (d).

6.2 Thermal conductivity of CH3DCPCM

A sample of CH3DCPCM was fabricated with CH+3D-C/10/2.0 scaffold and RT35HC as PCM with the methods described in section 3.2.3. k measurements were conducted using the MTPS method described in section 3.3.2.2.

6.2.1 Results and Discussion

The measured properties of CH3DCPCM, sample name CH+3DCP/20.1, are listed in Table 6.1.

Table 6.1 Properties of components of CH+3DCP/20.1

Sample	3D-C mass (g)	CH mass (g)	Sample mass (g)	Volume (cm ³)	$\rho_{(3D-C)}$ (mg/cm ³)	k (W/mK)
CH+3DCP/20.1	0.24	0.40	10.33	12.25	20.1	1.34

The k of CH+3DCP/20.1 was 1.34 W/mK. Based on equation (4.1), with the $\rho_{(3D-C)}$ of 20.1 mg/cm³, the k was predicted to be 1.14 W/mK. Based on these results, the addition of CH improves k of sample marginally by 17.5%, at the expense of 4% additional mass, calculated based on specific gravity. Due to the extent of non-homogeneity of the sample with the addition of CH, the H_f of CH3DCPCM could not be measured using the traditional DSC method, and hence comparison of H_f needs to be done in the bulk material. This would be addressed in section 6.3.3.2.

6.2.1.1 Conclusions

Novel material CH3DCPCM was introduced in this section. Commercially sourced CH was merged with 3D-C to form the CH+3D-C scaffold. It was found that 3D-C with

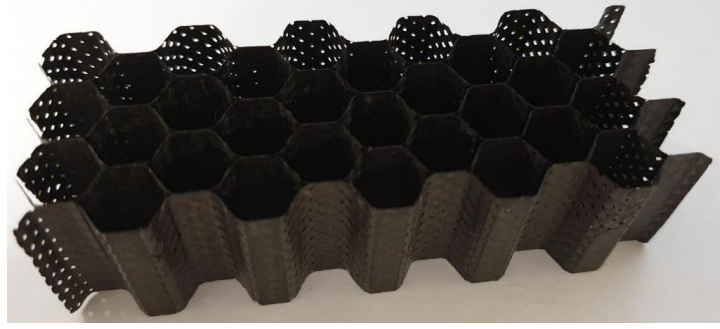
apparent density of 20.1 mg/cm^3 was required such that the 3D-C remains freestanding after merging with CH. No separation nor air bubbles were observed in the samples of CH3DCPCM fabricated, hence the interconnected thermal path within the sample was retained. The addition of CH to 3DCP/20.1 improved k of sample by 17.5% at the expense of 4% additional mass to the PCM composite. These results indicate that CH3DCPCM was a promising improvement over 3DCPCM.

6.3 Benchmarking CH3DCPCM with PCM demonstrator

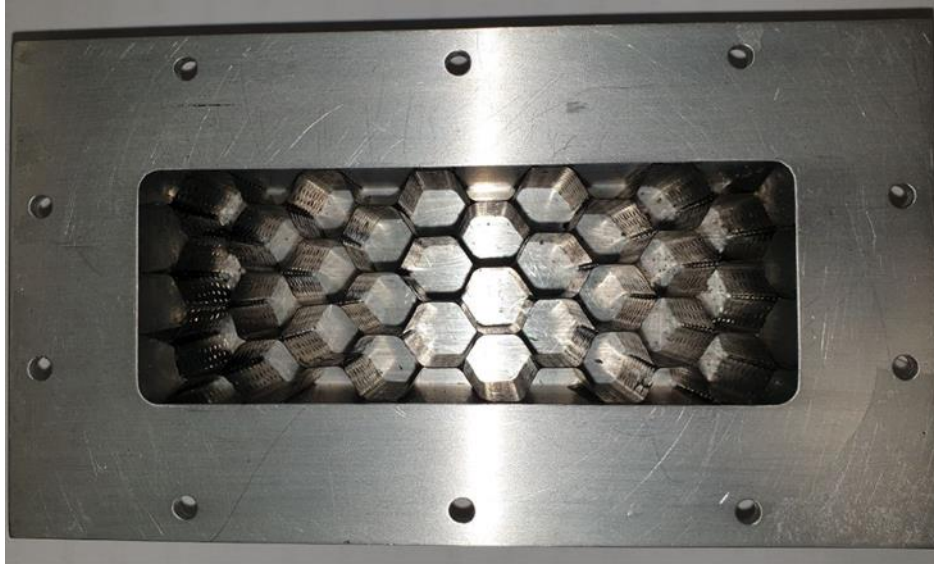
To compare the in-application performance of the novel composite, CH3DCPCM was benchmarked against 3DCPCM using the PCM demonstrator. An additional sample with only CH and PCM, named CHPCM, was fabricated as well to identify the impact of CH alone.

6.3.1 Sample preparation

Two additional samples, CH3DCPCM and CHPCM, were prepared in PCM container. RT35HC was used as PCM. CHs of dimensions $94 \text{ mm} * 34 \text{ mm} * 27 \text{ mm}$ thick, sourced from Ultracor Inc., with properties as described in section 3.1.2 was used to prepare the samples. An image of the CH sample is shown in Figure 6.2 (a). The mass of CH used to prepare CH3DCPCM and CHPCM was 2.74 g and 3.07 g, respectively.



(a)



(b)

Figure 6.2 (a) CH of 94 mm * 34 mm * 27 mm thick from Ultracor Inc. (b) CH after fitting into PCM container.

CHPCM was prepared by inserting CH directly into the PCM container, as seen in Figure 6.2 (b), and subsequently filling it with neat PCM. In order to achieve a consistent volumetric fill rate throughout the PCM container samples, $m_{(PCM)}$ was calculated according to equation (5.1). Porosity of CH, $\phi_{(CH)}$, was calculated as shown in equation (6.1).

$$\phi_{(CH)} = 1 - \frac{m_{(CH)}}{V_i \times \rho_{(CF)}} \quad (6.1)$$

Density of the carbon fibre, $\rho_{(CF)}$, was measured to be 1.4 g/cm³ using Archimedes' principle. The mass of neat PCM required for CHPCM sample was calculated to be 64.7 g. The final mass of PCM added was 65.26 g. The mass of CHPCM composite was 68.33 g.

To maintain comparability, 3D-C of a similar apparent density as that used to fabricate 3DCPCM in section 5.1.2 was used to fabricate CH3DCPCM. CH+3D-C was fabricated using a similar method as described in section 3.2.3.1. CH was placed on top of a single stack 3D-C of a slightly larger width and length. This was done to ensure the 3D-C along the sides of the CH does not break away. CH was gently tapped until it had sliced through the thickness of the 3D-C. The process was repeated with a second stack and third stack of 3D-C of identical width and length. The 3D-C from the first stack was observed to be pushed gradually to the top of the CH. There was ~3 mm thick excess 3D-C from the third stack. A schematic of the scaffold with the 3D-C is shown in Figure 6.3. The excess 3 mm 3D-C as well as the excess 3D-C along the sides of the scaffold act as TIM when compressed between the scaffold and the PCM container walls. 3D-C TIM had been shown to improve cooling from 20 - 30% [50]. The excess 3D-C along the sides of the scaffold was compressed towards the scaffold before the scaffold was inserted into the PCM container with the excess 3mm 3D-C protruding from the top of the PCM container. The CH+3D-C scaffold weighed 4.05 g, which meant 1.31 g of 3D-C was added in the fabrication of the CH+3D-C scaffold. The mass of neat PCM required was calculated to be 64.4 g. The final mass of PCM added was 64.96 g. The mass of CH3DCPCM was 69.01 g. After liquid PCM had been added to the PCM container, the lid was closed while the PCM was still liquid, thus the excess 3D-C was compressed and act as TIM between the lid and the scaffold.

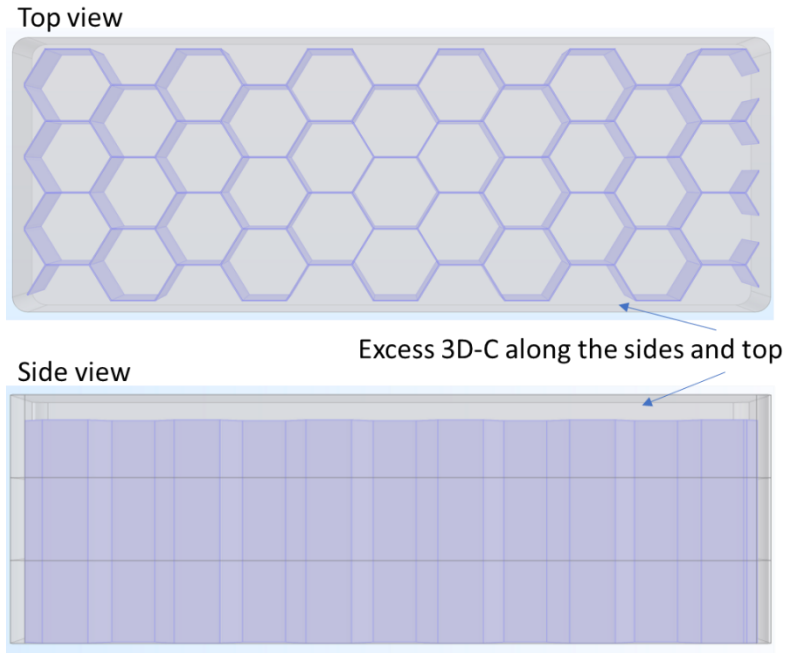


Figure 6.3 Schematic of the CH+3D-C scaffold with excess 3D-C along the sides and the top.

6.3.2 Experimental setup

The experiment was set up as described in section 5.1.3. Four samples, CH3DCPCM, neat PCM, 3DCPCM and CHPCM were test simultaneously at $P_{in} = 10, 15$ and 20 W. In addition to the heating $T-t$ data, the cooling $T-t$ data was also recorded.

6.3.3 Analysis of temperature-time curve

Two techniques were used to analyse the $T-t$ data collected. The first technique, FOM analysis, was introduced in section 5.1.4. The second technique, H_f analysis, was used to extract the average H_f from the heating and cooling $T-t$ data using energy equation.

6.3.3.1 Figure of merit analysis

The analysis technique and parameters described in section 5.1.4 was used to formulate $FOM_{(\Delta T)}$ at $\Delta T = 5$ and 10 °C to benchmark the 4 samples. The formulation of $C_{p(t)}$ for CH3DCPCM and CHPCM is,

$$C_{p(t)} = m_{(PCM)}[(1 - \varphi_{(3D-C)} - \varphi_{(CH)})c_{p(PCM)} + \varphi_{(3D-C)}c_{p(3D-C)} + \varphi_{(CH)}c_{p(CH)}] \\ + m_{(container)}c_{p(Al6061)} + m_{(screws)}c_{p(ss304)} \quad (6.2)$$

Where $\varphi_{(3D-C)}$ and $\varphi_{(CH)}$ is the mass fraction of 3D-C and CH, respectively, in the PCM composite. In the case of CHPCM, $\varphi_{(3D-C)} = 0$.

A second figure of merit, $FOM_{PCM(\Delta T)}$, was formulated based on the $m_{(PCM)}$ instead of $m_{(t)}$ as shown in equation (6.5) and (6.6).

$$FOM_{PCM(\Delta T)} = \frac{dT/dt_{(pm)}}{dT/dt_{(m,avg)}} \times \frac{H_{f(\Delta T)}}{H_{fo}} \quad (6.3)$$

$$FOM_{PCM(\Delta T)} = FOM_{(\Delta T)} \times \frac{m_{(t)}}{m_{(PCM)}} \quad (6.4)$$

$FOM_{PCM(\Delta T)}$ was a measure of PCM module performance with a focus on the mass of PCM used rather than the entire packaging. The relative $FOM_{\Delta T}$ and $FOM_{PCM(\Delta T)}$, against neat PCM, would be compared to show the prevalent trends of both FOM for the samples tested. In application, $FOM_{(\Delta T)}$ based on the combined mass of the packaging and PCM would be more practical in case of ranking PCM packaging effectiveness of different forms and mass of packaging that encase the same mass of PCM composite.

The values of each component required for calculation are shown in Table 6.2.

Table 6.2 Values of individual components of PCM container

Component	Value	Units
$m_{(CH3DCPCM)}$	69.01	g
$m_{(Neat PCM)}$	66.47	g
$m_{(3DCPCM)}$	67.23	g
$m_{(CHPCM)}$	68.33	g
$\varphi_{(CH, CH3DCPCM)}$	4.0	wt%
$\varphi_{(3D-C, CH3DCPCM)}$	1.9	wt%
$\varphi_{(3D-C, 3DCPCM)}$	2.2	wt%
$\varphi_{(CH, CHPCM)}$	4.5	wt%
$m_{(container)}$	266.4 – 269.7	g
$m_{(screws)}$	36.4	g
$m_{(t, CH3DCPCM)}$	371.8	g
$m_{(t, neat PCM)}$	372.2	g
$m_{(t, 3DCPCM)}$	373.3	g
$m_{(t, CHPCM)}$	371.7	g
$C_{p(PCM)}$	3.0	J/gK
$C_{p(CH)}$	1.13 [124]	J/gK
$C_{p(3D-C)}$	0.7077	J/gK
$C_{p(Al6061)}$	0.896	J/gK
$C_{p(ss304)}$	0.5	J/gK
$C_{p(t, CH3DCPCM)}$	456.9	J/K
$C_{p(t, Neat PCM)}$	460.0	J/K
$C_{p(t, 3DCPCM)}$	457.8	J/K
$C_{p(t, CHPCM)}$	457.7	J/K

6.3.3.2 Latent heat of fusion analysis

In addition to the analysis to obtain FOM, a new analysis method to estimate the H_f of the PCM composite using the heating and cooling $T-t$ data is documented. Traditional DSC would not be able to measure H_f of non-homogeneous samples such CH3DCPCM, hence a bulk measurement method was required to cater to such samples.

The assumptions of the analysis are listed:

- i. Properties such as R_m , c_p , k and ρ of the PCM composite and PCM container, and geometrical dimensions remained constant throughout the experiment.
- ii. Rate of change of temperature, dT/dt , measured by the thermocouple on the top surface of the PCM container was representative of the dT/dt throughout the sample.
- iii. Latent heat of fusion for melting and freezing were identical.

To justify assumption (ii), the regions of analysis would be limited to regions beyond the initial transient dT/dt .

The energy equations used for the analysis is shown in equation (6.5)

$$\int_{t_a}^{t_b} (P_{in} - \dot{Q}_{loss}) dt = \int_{\theta_a}^{\theta_b} C_{p(t)} d\theta + m_{(PCM)} H_f \quad (6.5)$$

Where $\theta(t) = T(t) - T_\infty$ and $d\theta = dT$. Subscripts a and b are dummy coefficients.

The $\dot{Q}_{loss}$ term could be defined as,

$$\int_{t_a}^{t_b} \dot{Q}_{loss} dt = \left(\frac{S}{R_m}\right) \int_{t_a}^{t_b} \theta(t) dt \quad (6.6)$$

Where S is the external surface area in contact with the insulation. Figure 6.4 shows a typical heating and cooling θ - t curve for $P_{in} = 20$ W. A_1 and A_2 are sum of area under the curve with the following formulas,

$$A_1 = \int_{t_1}^{t_2} \theta(t) dt \quad (6.7)$$

$$A_2 = \int_{t_3}^{t_4} \theta(t) dt \quad (6.8)$$

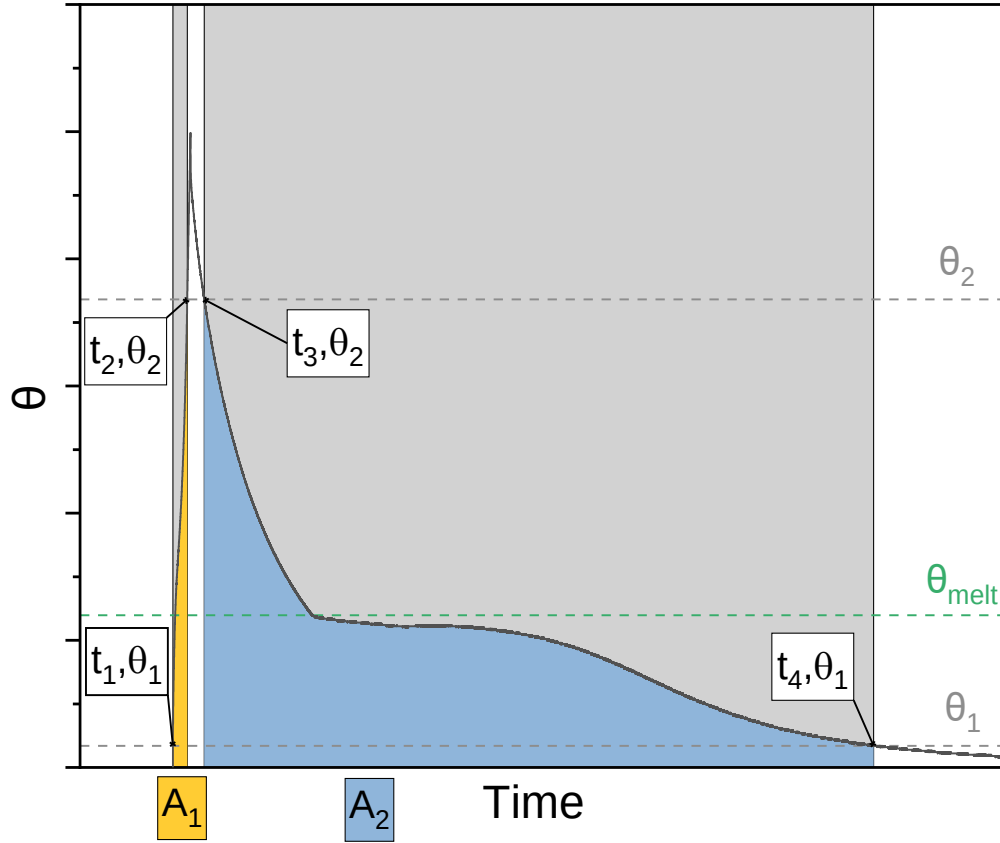


Figure 6.4 Typical heating and cooling θ - t curve for $P_{in} = 20$ W. A_1 and A_2 are sum of area under the curve for t_1 to t_2 and t_3 to t_4 , respectively

For each P_{in} , θ_1 and θ_2 were determined to be the points beyond the transient temperature transition and the PCM was 100% solid and 100% liquid, respectively. The selected regions in between θ_1 and θ_2 would encompass the full phase change transition of the PCM. Therefore, points between t_2 and t_3 were omitted as there would be transient temperature transition after the temperature peak. Points beyond t_4 were omitted as the PCM was deemed to have completed the phase change transition and was 100% solid, indicated by the increase in temperature gradient, $\frac{d\theta}{dt}$, beyond θ_{melt} . From the results of the θ - t curve, equation (6.6) can be simplified as,

$$\frac{S}{R_m} \int_{t_1}^{t_2} \theta(t) dt = \frac{S}{R_m} A_n \quad (6.9)$$

When the heater was turned on, the energy equation is,

$$P_{in}(t_2 - t_1) - \frac{S}{R_m} A_1 = C_{p(t)}(\theta_2 - \theta_1) + m_{(PCM)}H_f \quad (6.10)$$

When the heater was turned off the energy equation is,

$$\frac{S}{R_m} A_2 = C_{p(t)}(\theta_2 - \theta_1) + m_{(PCM)} H_f \quad (6.11)$$

$$\frac{S}{R_m} = \frac{C_{p(t)}(\theta_2 - \theta_1) + m_{(PCM)} H_f}{A_2} \quad (6.12)$$

Substituting (6.12) into (6.10), the equation becomes,

$$P_{in}(t_2 - t_1) - \frac{A_1}{A_2} [C_{p(t)}(\theta_2 - \theta_1) + m_{(PCM)} H_f] = C_{p(t)}(\theta_2 - \theta_1) + m_{(PCM)} H_f \quad (6.13)$$

By making H_f the subject, equation (6.13) becomes,

$$H_f = \frac{(A_c)P_{in}(t_2 - t_1) - C_{p(t)}(\theta_2 - \theta_1)}{m_{(PCM)}} \quad (6.14)$$

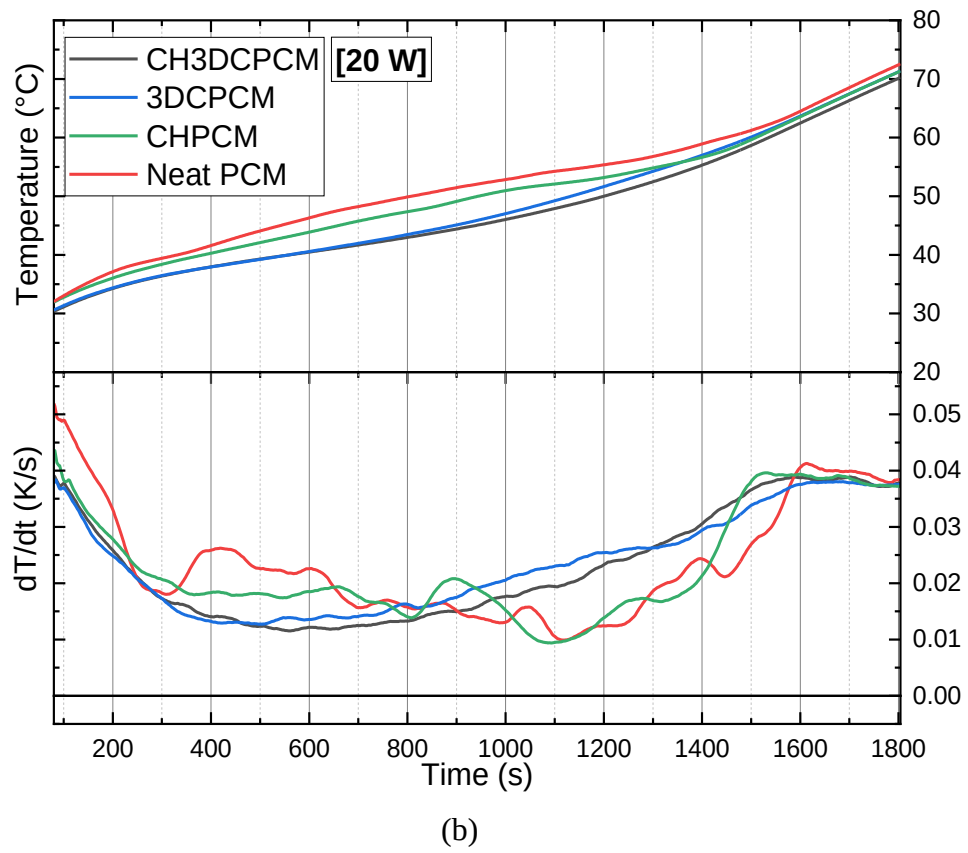
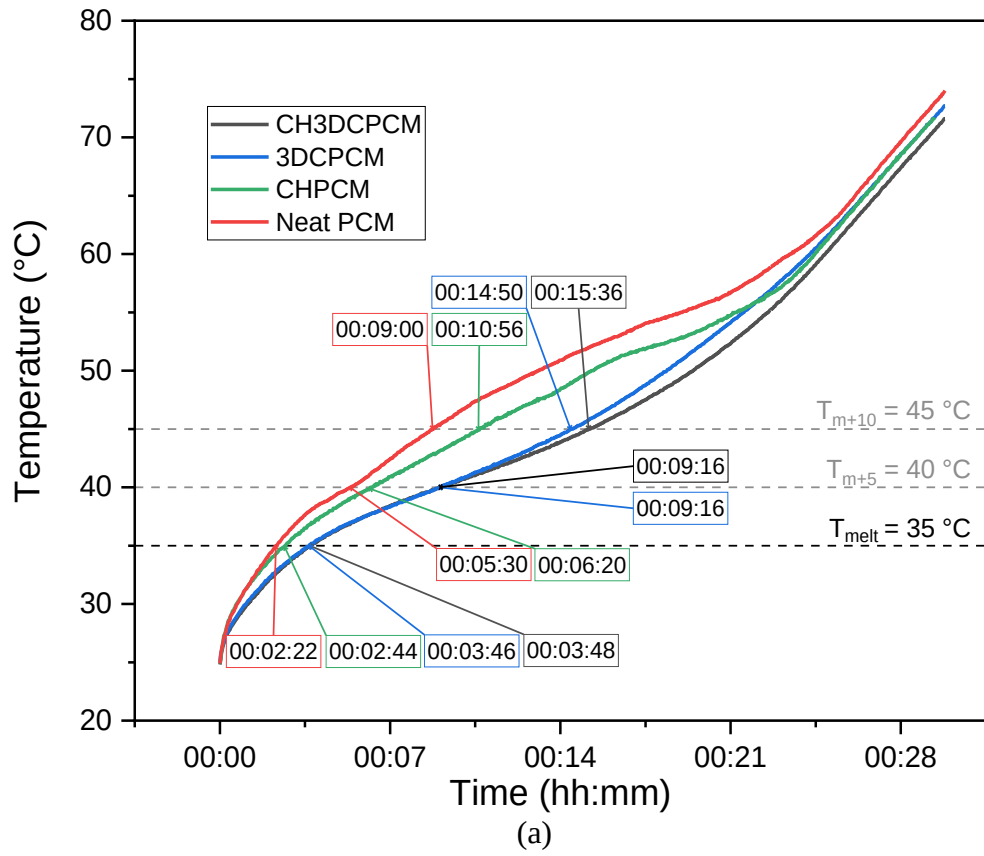
$$A_c = \frac{A_2}{A_2 + A_1} \quad (6.15)$$

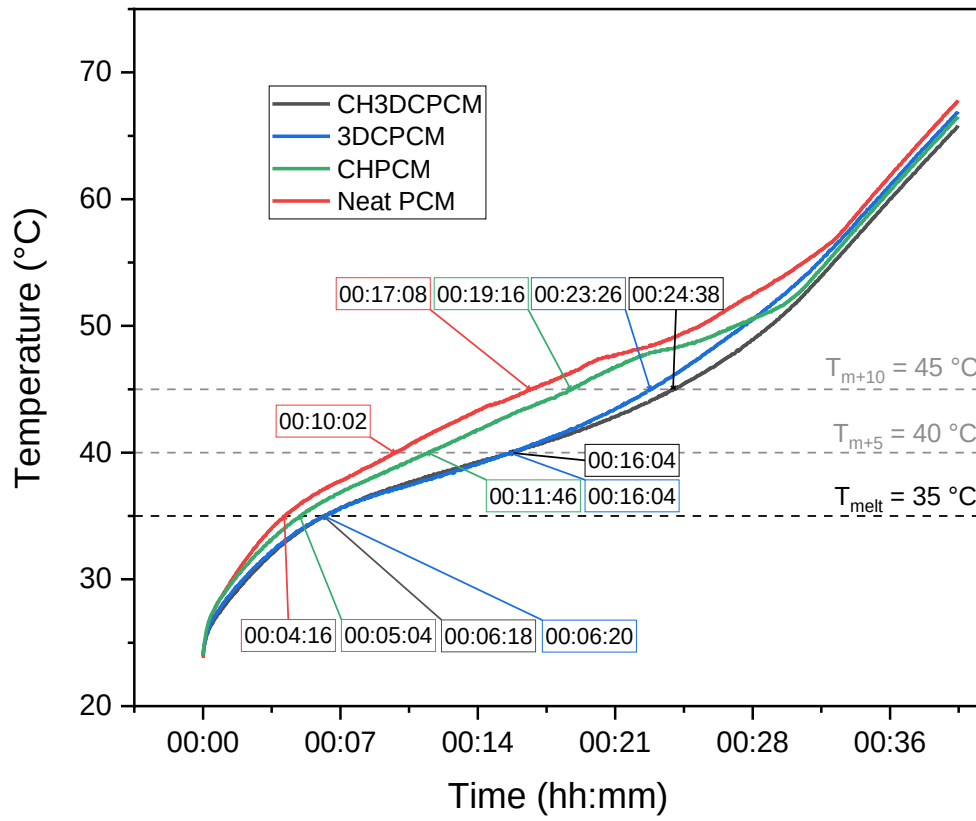
With equation (6.14), the H_f of the PCM composite from the θ - t curve for each P_{in} could be extracted.

6.3.4 Results and Discussion

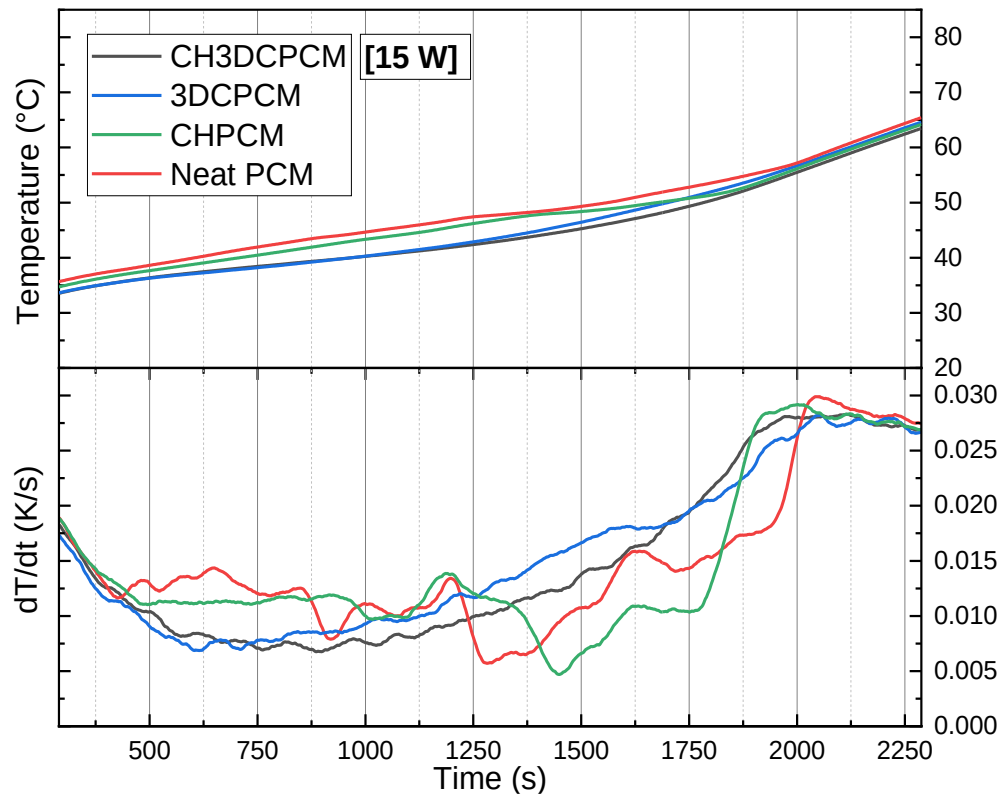
6.3.4.1 Figure of merit analysis

The T_{top} against time curve of the 4 samples for $P_{in} = 20, 15$ and 10 W is shown in Figure 6.5 (a), (c) and (e), respectively, and the corresponding gradient in the melting regime is shown in Figure 6.5(b), (d) and (f), respectively.





(c)



(d)

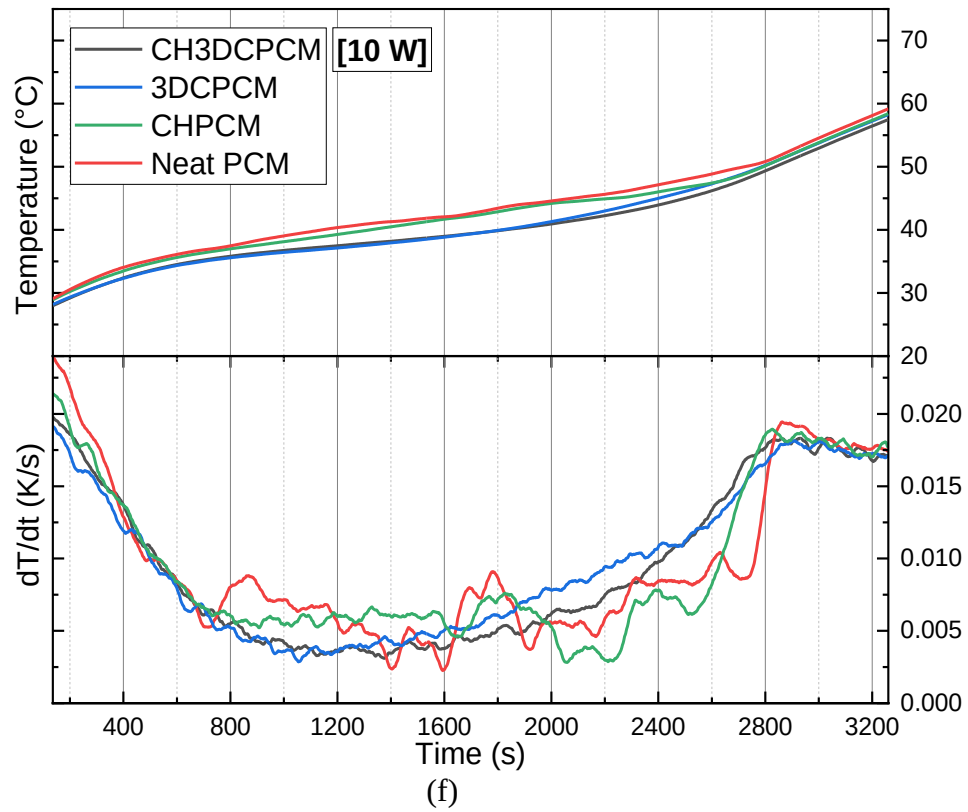
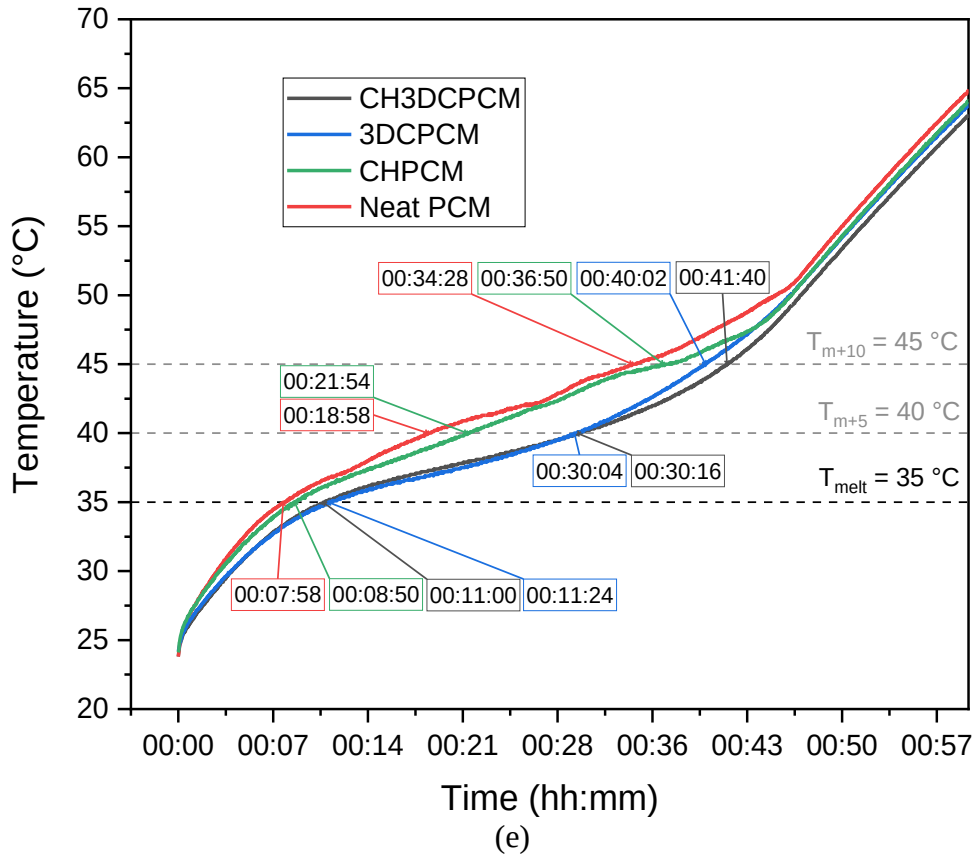


Figure 6.5 (a) T-t curve of CH3DCPCM, 3DCPCM, CHPCM and neat PCM at 20 W power input. (b) dT/dt vs time at 20 W power input (c) T-t curve of CH3DCPCM, 3DCPCM, CHPCM and neat PCM at 15 W power input. (d) dT/dt vs time at 15 W power input (e) T-t curve of CH3DCPCM, 3DCPCM, CHPCM and neat PCM at 10 W power input. (f) dT/dt vs time at 10 W power input.

The numerical gradients, $t_{Tm+\Delta T}$ and $H_{f,(\Delta T)}$ of each sample are shown in Table 6.3.

Table 6.3 Temperature-time gradients, $t_{(Tm+\Delta T)}$ and $H_{f,(\Delta T)}$ of each sample for 20, 15 and 10 W power input.

P_{in} (W)	Sample	dT/dt ($_{pm}$) (K/s)	dT/dt (melting, avg) (K/s)	$\Delta t_{(Tm+5)}$ (s)	$\Delta t_{(Tm+10)}$ (s)	$H_{f(+5)}$ (kJ/kg)	$H_{f(+10)}$ (kJ/kg)
20	CH3DCPCM	0.0379	0.0161	328	708	49.2	111.4
	3DCPCM	0.0379	0.0183	330	664	51.1	103.3
	CHPCM	0.0387	0.0166	216	492	22.5	59.2
	Neat PCM	0.0388	0.0188	188	398	15.9	37.7
15	CH3DCPCM	0.0279	0.0098	586	1100	75.1	137.0
	3DCPCM	0.0274	0.0116	584	1026	74.9	123.3
	CHPCM	0.0282	0.0106	402	852	42.4	91.7
	Neat PCM	0.0281	0.0120	346	772	32.7	80.9
10	CH3DCPCM	0.0180	0.00484	1156	1840	104.7	153.1
	3DCPCM	0.0179	0.00563	1120	1718	102.5	141.3
	CHPCM	0.0179	0.00584	784	1620	60.3	126.9
	Neat PCM	0.0182	0.00643	660	1590	48.0	129.7

With the results of 3DCPCM and CHPCM, the effects of each scaffold on key parameters could be isolated. At all power inputs, there was a decrease in dT/dt when $T_{top} = 35\text{ }^{\circ}\text{C}$, indicating the onset of phase change, and subsequently an increase and convergence to a similar $dT/dt_{(pm)}$ unique to each power input. The latter indicated that the samples have completed the phase change in each experiment, and the power inputs across the samples were similar for each experiment. The CH core did not significantly correct the fluctuation in

T_{top} during melting observed in neat PCM sample. Both CH3DCPCM and 3DCPCM had a more stable dT/dt during melting with less fluctuations than neat PCM and CHPCM. This affirms the conclusion made in section 5.2 that the improvement in stability in dT/dt and predictability of T_{top} during melting was due to the shape stabilizing effects of the 3D-C scaffold.

In the initial part of melting, T_{top} and dT/dt of 3DCPCM and CH3DCPCM had a similar value and trend. However, at approximately the point of T_{m+5} , after a significant portion of PCM composite was liquid, the T_{top} and dT/dt of 3DCPCM begin to increase faster than CH3DCPCM. This improvement could be attributed to 1) 3DCPCM has a lower H_f than CH3DCPCM, 2) the liquid phase k of CH3DCPCM was higher than 3DCPCM or 3) the 3D-C TIM in CH3DCPCM improved the heat conduction between the container walls and PCM composite in the liquid phase. Due to the higher scaffold loading in CH3DCPCM, the H_f of 3DCPCM would likely not be lower than CH3DCPCM. It was more likely that while solid k of 3DCPCM and CH3DCPCM may be similar, the k of liquid 3DCPCM was lower than the liquid CH3DCPCM. Furthermore, k of liquid PCM reported to be lower than that of solid, according to previous studies [125], [126]. Harish et al. [125] reported that k of liquid PCM was 40% that of solid PCM for 1.0 vol.% GNP + lauric acid PCM. Wang et al. [126] reported that k of liquid PCM ranged from 50 – 75% that of solid in paraffin samples infused highly percolated micron-size graphite flakes. Wang also observed that the drop in k from liquid to solid was smaller in at a higher filler loading. These reports support that liquid PCMs have a lower k , and k enhancement effects of graphite-based fillers were less effective in the liquid state. In the current study, the reason k of liquid CH3DCPCM was higher than 3DCPCM was likely due to the sturdier CH retaining the phonon dominated heat transfer, leading to the gentler dT/dt of CH3DCPCM compared to 3DCPCM in the liquid state, hence the better end-of-melting performance.

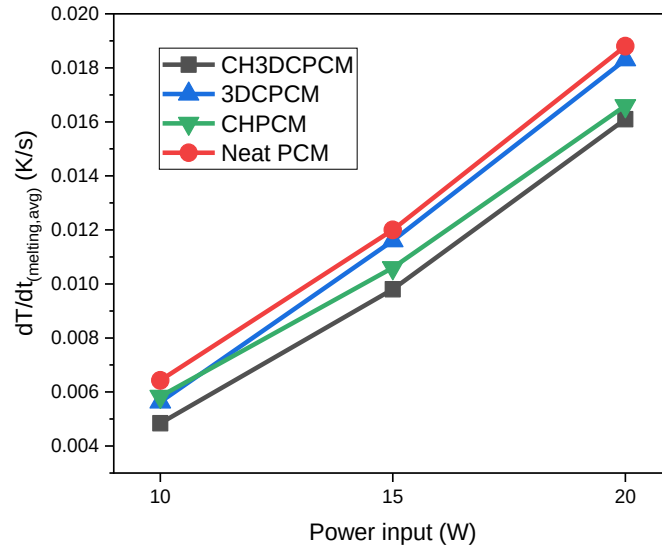
The comparison between $FOM_{(\Delta T)}$ and $FOM_{PCM(\Delta T)}$ and their neat PCM relative comparison ($rFOM_{(\Delta T)}$ and $rFOM_{PCM(\Delta T)}$) are shown in Table 6.4.

Table 6.4 $FOM_{(\Delta T)}$, $FOM_{PCM(\Delta T)}$ and neat PCM relative comparison of each sample for 20, 15 and 10 W power input.

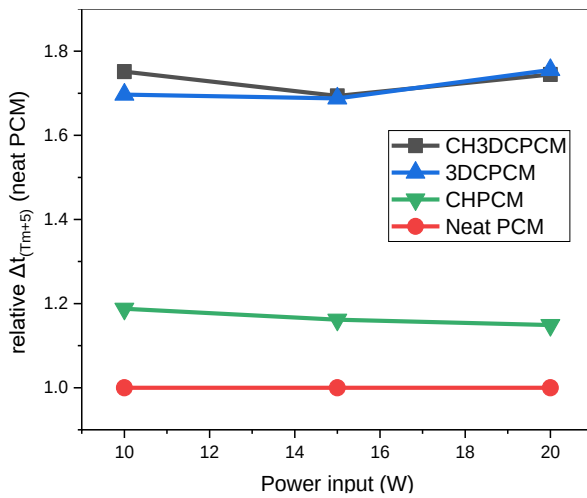
P_{in} (W)	Sample	$FOM_{(+5)}$ (10^{-1})	$FOM_{PCM(+5)}$	$FOM_{(+10)}$ (10^{-1})	$FOM_{PCM(+10)}$	$rFOM_{(+5)}$	$rFOM_{PCM(+5)}$	$rFOM_{(+10)}$	$rFOM_{PCM(+10)}$
20	CH3DCPCM	0.897	0.483	2.03	1.09	3.68	3.53	3.51	3.36
	3DCPCM	0.798	0.441	1.61	0.890	3.27	3.22	2.78	2.75
	CHPCM	0.402	0.219	1.06	0.576	1.65	1.60	1.83	1.78
	Neat PCM	0.244	0.137	0.579	0.324	1.00	1.00	1.00	1.00
15	CH3DCPCM	1.65	0.892	3.02	1.63	2.90	2.81	2.14	2.07
	3DCPCM	1.33	0.734	2.19	1.21	2.34	2.31	1.55	1.54
	CHPCM	0.864	0.470	1.87	1.02	1.52	1.48	1.33	1.29
	Neat PCM	0.568	0.318	1.41	0.788	1.00	1.00	1.00	1.00
10	CH3DCPCM	3.01	1.62	4.40	2.37	2.98	2.87	1.61	1.55
	3DCPCM	2.46	1.36	3.40	1.87	2.44	2.41	1.25	1.22
	CHPCM	1.42	0.770	2.98	1.62	1.41	1.36	1.09	1.06
	Neat PCM	1.01	0.565	2.73	1.53	1.00	1.00	1.00	1.00

Across all power inputs, the ranking, unanimous determined by all FOM terms, was consistently first CH3DCPCM, followed by 3DCPCM, CHPCM and neat PCM. To better visualize the degree of improvement, the graphical comparison of $dT/dt_{(melting, avg)}$ and neat PCM relative $\Delta t_{(T_m + \Delta T)}$, $H_{f(\Delta T)}$, $FOM_{(\Delta T)}$ and $FOM_{PCM(\Delta T)}$ of each sample are shown in Figure 6.6. For $dT/dt_{(melting, avg)}$, a lower value was favourable as it reflects a slower rate of increase in temperature throughout melting. The graph of $dT/dt_{(melting, avg)}$ against power input shows that

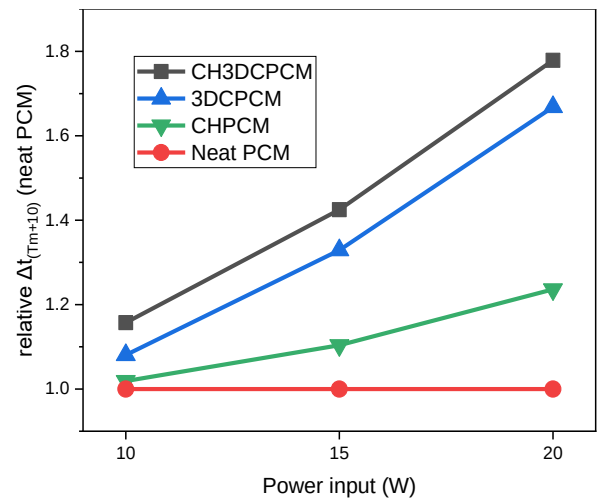
at $P_{in} = 15$ and 20 W, the $dT/dt_{(melting, avg)}$ for 3DCPCM, at 0.0116 and 0.0183 K/s respectively, was slightly lower than neat PCM, at 0.0120 and 0.0188 K/s respectively, and a more significant drop in $dT/dt_{(melting, avg)}$ for CHPCM, at 0.0106 and 0.0166 K/s respectively, followed by CH3DCPCM, at 0.0098 and 0.0161 K/s respectively. At $P_{in} = 10$ W, $dT/dt_{(melting, avg)}$ for neat PCM was 0.00643 K/s. $dT/dt_{(melting, avg)}$ for CHPCM and 3DCPCM were similar and slightly lower than neat PCM at 0.00584 and 0.00564 K/s respectively, and CH3DCPCM was the lowest at 0.00484 K/s. This showed that the presence of CH in the composite played a significant role in decreasing the $dT/dt_{(melting, avg)}$ as compared to 3D-C scaffold. The graphical comparison shown in Figure 6.6 (a) clearly depict the trend mentioned.



(a)



(b)



(c)

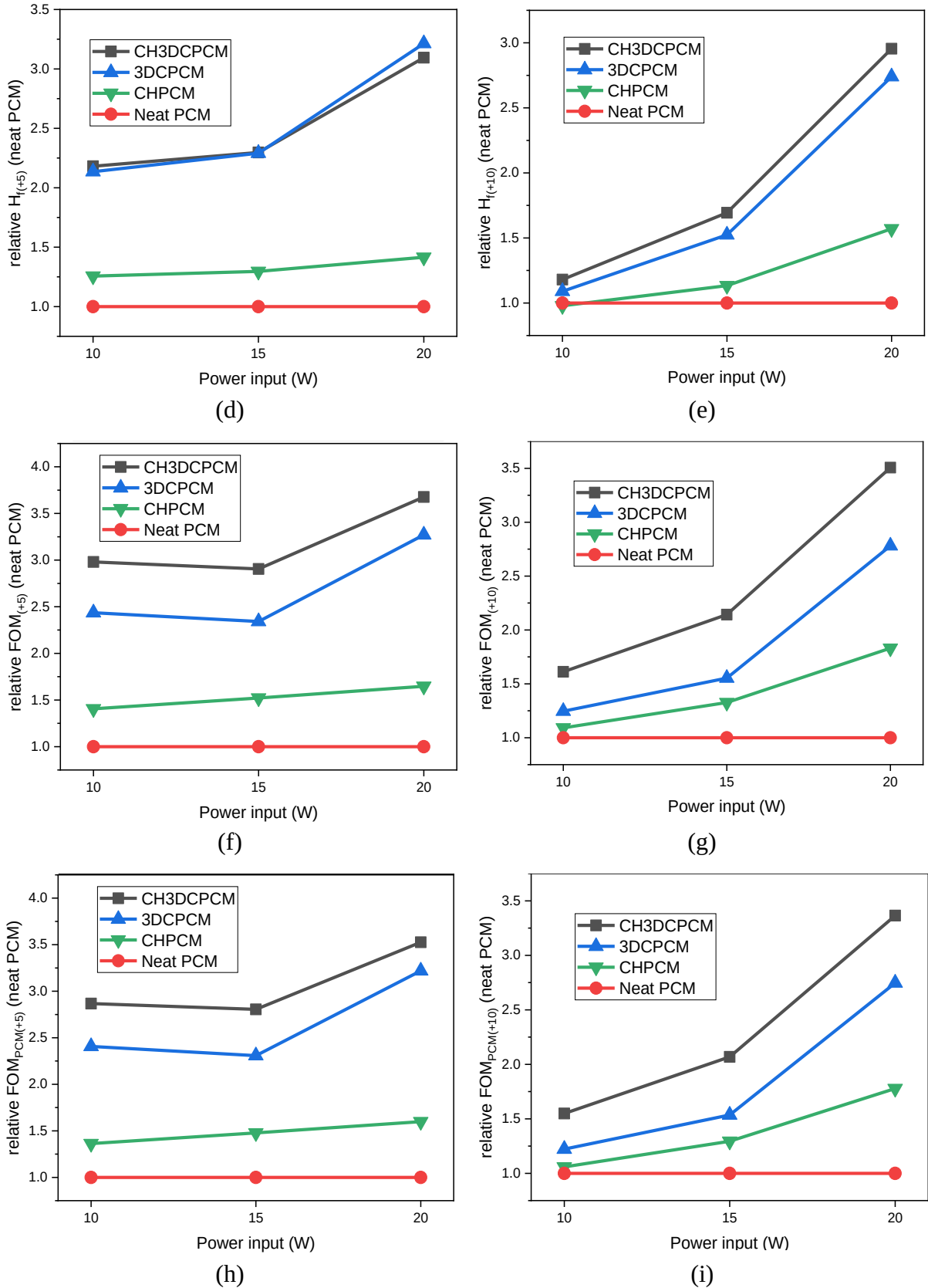


Figure 6.6 Graph against Power input of (a) $dt/dt_{(melting,avg)}$ of samples, (b) neat PCM relative $\Delta t_{(Tm+5)}$, (c) neat PCM relative $\Delta t_{(Tm+10)}$, (d) neat PCM relative $H_{f(+5)}$, (e) neat PCM relative $H_{f(+10)}$, (f) neat PCM relative $FOM_{t(+5)}$, and (g) neat PCM relative $FOM_{t(+10)}$, (h) neat PCM relative $FOM_{PCM(+5)}$, and (i) neat PCM relative $FOM_{PCM(+10)}$.

The relative $\Delta t_{(T_m+5)}$ results, shown in Figure 6.6 (b), indicated that each sample had a relatively similar improvement over neat PCM at every P_{in} . CHPCM had a 1.15 – 1.19 times improvement from neat PCM. The improvement was more pronounced in 3DCPCM and CH3DCPCM at 1.69 – 1.76 times. The relative $\Delta t_{(T_m+10)}$ results, shown in Figure 6.6 (c), showed that each sample had a relatively smaller improvement over neat PCM at $P_{in} = 10$ W, at 1.02, 1.08 and 1.16 times for CHPCM, 3DCPCM and CH3DCPCM respectively. There was an increasingly larger improvement for each sample at $P_{in} = 15$ and 20 W, at 1.10 and 1.24 times for CHPCM, 1.33 and 1.67 times for 3DCPCM and 1.42 and 1.78 times for CH3DCPCM, respectively. The relative $\Delta t_{(T_m+10)}$ results indicate that the scaffold inclusion had a larger impact at a higher heating rate. Cross-referencing to Figure 6.5 (a), (c) and (e), the results suggest that the carbon scaffolds resulted in the largest improvements in $\Delta t_{(T_m+\Delta T)}$ at the start to the mid-section of PCM melting regime. Towards the end of the melting, the T_{top} of each sample would converge, hence reducing the difference in Δt between samples.

The relative $H_{f(+5)}$ results, shown in Figure 6.6 (d), indicated that CHPCM had a 1.26 – 1.42 times improvement over neat PCM. Both CH3DCPCM and 3DCPCM had similar improvements over neat PCM at each power level, at 2.14 – 3.21 times improvement. The improvements were more significant at 20 W. The relative $H_{f(+10)}$ results, shown in Figure 6.6 (e), had a similar trend as the relative $\Delta t_{(T_m+10)}$ results. 3DCPCM and CH3DCPCM had a small improvement over neat PCM at $P_{in} = 10$ W, at 1.09 and 1.18 times, respectively. CHPCM, on the other hand, performed slightly worse than neat PCM, at 0.978 times, at $P_{in} = 10$ W. The improvements were much larger at $P_{in} = 15$ and 20 W, at 1.13 and 1.57 times for CHPCM, 1.52 and 2.74 times for 3DCPCM and 1.69 and 2.95 times for CH3DCPCM, respectively.

The rFOM values by dividing FOM value by the respective FOM of neat PCM in each case. As such, the rFOM for neat PCM would always be equivalent to 1. The rFOM results

showed very similar trends for $rFOM_{PCM(\Delta T)}$ and $rFOM_{(\Delta T)}$ across samples and P_{in} , as observed in Table 6.4 and Figure 6.6 (f) – (i). The $rFOM_{PCM(\Delta T)}$ values were slightly smaller in magnitude as compared to $rFOM_{(\Delta T)}$. This observation was due to the similar $\frac{m(t)}{m_{(PCM)}}$ values across all samples. Since there were little difference between the trends across samples and P_{in} , the discussion would be based on $rFOM_{(\Delta T)}$.

The $rFOM_{(+5)}$ results, shown in Figure 6.6 (f), showed an improvement over neat PCM of all samples at all P_{in} . CHPCM improved 1.41, 1.52 and 1.65 times, 3DCPCM improved 2.44, 2.34 and 3.27 times, and CH3DCPCM improved 2.98, 2.90 and 3.68 times at $P_{in} = 10, 15$ and 20 W, respectively. The relative $FOM_{(+10)}$ results, shown in Figure 6.6 (g) also showed an improvement over neat PCM of all samples at all P_{in} that was slightly lower than $FOM_{(+5)}$. CHPCM improved 1.09, 1.33 and 1.83 times, 3DCPCM improved 1.25, 1.55 and 2.78 times, and CH3DCPCM improved 1.61, 2.14 and 3.51 times at $P_{in} = 10, 15$ and 20 W respectively. The results consistently show that the ranking of samples to be, from worst to best performing, neat PCM, CHPCM, 3DCPCM and CH3DCPCM. The combined addition of CH and 3D-C scaffold further improved the practical performance of PCM than either CH or 3D-C alone. The results also showed that the impact of the addition of the scaffolds were more pronounced when only a small portion of the PCM was utilised at the points of analysis. This was evident from the results of the parameters with the least restrictive conditions, $FOM_{(+10)}$ at $P_{in} = 10$ W, where more than 70% of the neat PCM have melted at the selected data points, as compared to the parameters with the most restrictive conditions, $FOM_{(+5)}$ at $P_{in} = 20$ W, where only approximately 12% of the neat PCM has melted.

The results shown in Figure 6.6 overall indicated that the improvements to neat PCM at more restrictive conditions, namely $\Delta T = +5$ at all P_{in} and $\Delta T = +10$ at $P_{in} = 20$ W where the region of analysis was near the initial point of melting, were largely due to 3D-C rather than CH. However, CH was better than 3D-C at decreasing $dT/dt_{(melting, avg)}$ at higher P_{in} . Therefore,

the combination of CH and 3D-C resulted in further improvements over neat PCM in all parameters than just CH or 3D-C alone. Hence the novel material, CH3DCPCM, was a remarkable improvement to 3DCPCM and CHPCM in application.

6.3.4.2 Latent heat of fusion analysis

The calculated H_f from equation (6.14) and the corresponding parameters for each sample are listed in Table 6.5. The graph of calculated H_f against P_{in} is shown in Figure 6.7

Table 6.5 Calculated H_f and the corresponding parameters for each sample at $P_{in} = 10, 15$ and 20 W

Sample	P_{in} (W)	A_1 (Ks)	A_2 (Ks)	$t_2 - t_1$ (s)	$\theta_2 - \theta_1$ (K)	H_f (kJ/kg)	$H_f / H_{f(neat PCM)}$ (same P_{in})
CH3DC PCM	20	30851.2	707119.0	1546	34.8	209	0.99
	15	40534.8	790959.4	2156	35	218	0.98
	10	60130.5	690637.5	3398	34.9	225	0.98
3DC PCM	20	30588.4	700281.0	1504	34.8	202	0.96
	15	40212.2	781480.0	2116	35	215	0.98
	10	59271.5	680879.1	3352	34.9	224	0.98
CHPCM	20	34250.2	718324.4	1510	34.8	199	0.94
	15	44493.2	759054.4	2124	35	210	0.95
	10	63555.9	710058.9	3346	34.9	219	0.96
Neat PCM	20	33848.0	713893.0	1490	34.8	211	1.0
	15	44936.4	774349.2	2092	35	221	1.0
	10	64278.9	692362.5	3298	34.9	229	1.0

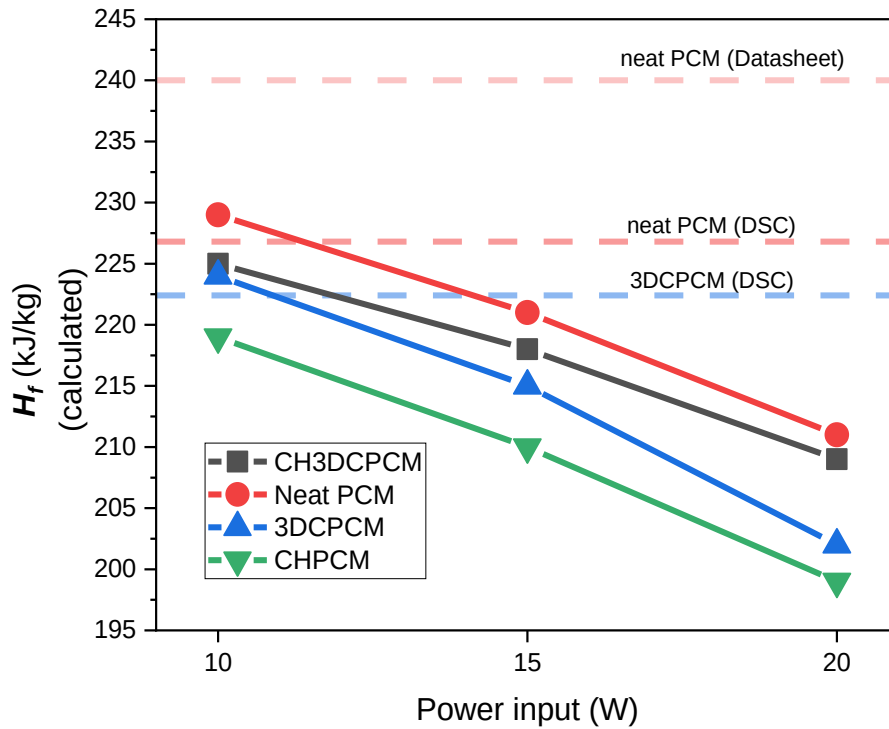


Figure 6.7 Graph of calculated H_f (kJ/kg) against P_{in} (W)

Overall, all the H_f values of neat PCM were within 14 % of the H_f value reported in the material datasheet, or within 29 kJ/kg of the 240 kJ/kg reported. The H_f value of each sample were within -6% of neat PCM at the corresponding P_{in} . The results of each P_{in} consistently show neat PCM to have the largest calculated H_f , followed by CH3DCPCM, 3DCPCM and lastly CHPCM. For each sample, it was observed that the calculated H_f increases 4 – 6% from 20 W to 15 W calculations and increases another 3 – 4% from 15 W to 10 W. This difference was a result of assumption (ii) stated in section 6.3.3.2 that the rate of change of temperature, dT/dt , measured by the thermocouple on the top surface of the PCM container was representative of the dT/dt throughout the sample. At a higher input heat, such as $P_{in} = 20$ W, there would be a larger differential in dT/dt measured at the top surface of the PCM container and the rest of the sample. Therefore, the temperature profile of T_{top} would overestimate the dT/dt of the sample and hence the calculated H_f would be underestimated. This meant that at a lower heating rate, the calculated H_f would converge closer to the actual H_f of the PCM, which was evident from the decreasing rate of increase of the calculated H_f .

To better ascertain the accuracy of the calculated H_f , the calculated H_f of neat PCM and 3DCPCM was compared to H_f previously measured with DSC in section 4.3.3.2. The comparison is also shown graphically in Figure 6.7, The H_f of neat PCM measured with DSC was of 226.8 kJ/kg, and the average H_f of 2.5 wt% 3DCPCM was 222.4 kJ/kg. The calculated H_f of neat PCM was 211, 221 and 229 kJ/kg for 20, 15 and 10 W, respectively. These results were, respectively, +7%, +2.6% and -1% of the DSC results. The calculated H_f of 3DCPCM was 202, 215 and 224 kJ/kg for 20, 15 and 10 W, respectively. These results were, respectively, +9%, +3% and -0.7% of the DSC result. The calculated H_f at 10 W was consistently within 1% margin of error of the measured DSC results. Hence the calculated H_f results at 10 W would be a close estimate for the actual H_f of the PCM composite. Therefore, the H_f of CH3DCPCM and CHPCM could be estimated to be 225 and 219 kJ/kg, respectively. The expected H_f of CH3DCPCM and CHPCM based on filler loading of 5.9 wt.% and 4.5 wt.% respectively, was 225.8 and 229.2 kJ/kg respectively, assuming a neat PCM H_f of 240 kJ/kg. The deviation of H_f between calculated and expected were 0.35% and 4.45% respectively for CH3DCPCM and CHPCM, hence within the 7.5% error margin of H_f results reported in the datasheet [97]. These show that the method to calculate H_f based on test bench analysis results at 10 W heat input is highly accurate for this design of containers.

It should be noted that the accuracy of this method at 10 W is specific to this PCM container design. Assumption (ii) from section 6.3.3.2 assumes the change in temperature at the measured surface represents that throughout the sample. The validity of this assumption depends on the design of the container as well as the boundary conditions applied. Hence the maximum P_{in} found for this study should not be directly applied to a different PCM container design, but it can be used as a starting point for future studies. The strategy of lowering heat load is aligned to reducing thermal gradient in a conduction dominant heat transfer.

The relative uncertainty of H_f was calculated to be $\sim 2.2\%$ using the formula in equation (6.16).

$$\frac{\delta H_f}{H_f} = \sqrt{\left[\frac{\left[\sqrt{\left(\frac{\delta A_c}{A_c} \right)^2 + \left(\frac{\delta P_{in}}{P_{in}} \right)^2 + \left(\frac{\delta(t_2 - t_1)}{t_2 - t_1} \right)^2} \times A_c P_{in}(t_2 - t_1) \right]^2 + \left[\sqrt{\left(\frac{\delta C_{p(t)}}{C_{p(t)}} \right)^2 + \left(\frac{\delta(\theta_2 - \theta_1)}{\theta_2 - \theta_1} \right)^2} \times C_{p(t)}(\theta_2 - \theta_1) \right]^2}{A_c P_{in}(t_2 - t_1) - C_{p(t)}(\theta_2 - \theta_1)} \right]^2 + \left[\frac{\delta m_{(PCM)}}{m_{(PCM)}} \right]^2} \quad (6.16)$$

6.3.4.3 Conclusions

The results from the FOM and H_f analysis showed a significant advantage of CH3DCPCM over the other samples tested. From the results of the FOM analysis, the addition of CH into PCM improved the $dT/dt_{(melting, avg)}$ and 3D-C scaffold improved the $\Delta t_{(T_m + \Delta T)}$, $H_{f(\Delta T)}$ and $FOM_{(\Delta T)}$ of the PCM container sample. The addition of CH had insignificant effects on CH3DCPCM under more restrictive conditions, such as $\Delta T = +5$ and $P_{in} = 20$ W, where the region of analysis was near the initial point of melting. At less restrictive conditions, CH3DCPCM performed better than 3DCPCM. The FOM ranking show that the CH3DCPCM was superior to the other PCM composites tested. It was noted that $FOM_{\Delta T}$ and $FOM_{PCM(\Delta T)}$ produced similar results and would lead to the same conclusion in this case where the $\frac{m(t)}{m_{(PCM)}}$ factor was similar for each sample. $FOM_{\Delta T}$ would be a better comparison of performance between PCM packaging of different mass encasing the same mass of PCM composite.

The calculated H_f results showed that CH3DCPCM had a higher H_f than 3DCPCM and CHPCM. The calculated H_f results of 3DCPCM and neat PCM were compared to DSC results, and when calculated from the θ - t curve at $P_{in} = 10$ W, the H_f results were within 1% error margin of DSC results, hence most accurate.

6.4 Summary

In this section, the strategy to address the issue of disconnected thermal pathway due to stacking of 3D-C in PCM module was presented, in the form of a novel material CH3DCPCM. The fabrication method and characterization were discussed. CH3DCPCM was also benchmarked against neat PCM, 3DCPCM and CHPCM using the FOM analysis described in the previous Chapter. A new method to obtain H_f was introduced based on first principles. The main conclusions of the Chapter are listed below.

- Commercially sourced CH was merged with 3D-C to form CH+3D-C scaffold. 3D-C with apparent density of 20.1 mg/cm^3 was required such that the 3D-C remains freestanding after merging with CH. No separation nor air bubbles were observed in the samples of CH3DCPCM fabricated.
- The addition of CH to 3DCP/20.1 improved k of sample by 17.5% at the expense of 4% additional mass to the PCM composite, calculated based on specific gravity. These results indicate that CH3DCPCM was a promising improvement over 3DCPCM.
- From the results of the FOM analysis, adding CH into PCM improved the $dT/dt_{(melting, avg)}$ and adding 3D-C scaffold improved the $\Delta t_{(T_m + \Delta T)}$, $H_{f(\Delta T)}$ and $FOM_{(\Delta T)}$ of the PCM container sample. The addition of CH had insignificant effects on CH3DCPCM under more restrictive conditions, such as $\Delta T = +5$ and $P_{in} = 20 \text{ W}$, where the region of analysis was near the initial point of melting. The FOM ranking show that the CH3DCPCM was superior to the other PCM composites tested.
- The calculated H_f results showed that CH3DCPCM had a higher H_f than 3DCPCM and CHPCM. The calculated H_f results of 3DCPCM and neat PCM were compared to DSC results, and when calculated from the θ - t curve at $P_{in} = 10 \text{ W}$, the H_f results were within 1% error margin of DSC results, hence most accurate.

7. Space environment qualification

In this Chapter, two space environment tests conducted on the PCM samples, 3DCPCM and CH3DCPCM are presented. The first was a launch vibration qualification test and the second was an extreme temperature thermal cycling test. The tests were conducted with the PCM samples fabricated in the PCM container described in section 5.1.

7.1 Vibration qualification test

Based on the prelaunch environmental conditions defined by the NASA Space Launch System Mission Planner's Guide [127], the maximum pre-launch environmental temperatures were 54.4 °C during rollout, 38.3 °C while on-pad and 31.1 °C during launch and ascent. If the PCM chosen had a melting point lower than these temperatures, the PCM would likely be in the liquid state during launch. In the case where the PCM composite used was 3DCPCM, the launch vibrations experienced might induce sloshing of liquid PCM sufficient to damage the structure of the 3D-C micro-skeletal and thereby negatively impact the thermal efficiency of the PCM module. In such cases, the vibration damping properties of CH in the novel material CH3DCPCM was hypothesized to isolate the movement of liquid PCM and protect the encased 3DCPCM, hence retain the structural integrity and heat transfer rate in the 3D-C in CH3DCPCM. The vibration qualification test was thus designed to subject the PCM module with liquid state PCM to the maximum predicted vibration environment experienced during launch to verify the above-mentioned hypothesis.

7.1.1 Experimental methods

The two test subjects were 3DCPCM and CH3DCPCM, each hermetically sealed in the PCM container and fabricated using the methods described in section 5.1.2 and 3.2.3, respectively. The test samples were individually mounted in a fixed position onto a mechanical shaker and were subjected to random and sinusoidal vibrations in each of the 3

orthogonal axes according to the parameters specified in the Polar Satellite Launch Vehicle (PSLV) user manual [128] and followed the standards described in section 6.3.5 of SMC-S-016 (year 2014) [129]. The detailed qualification specification of the random and sinusoidal vibration tests are listed in Table 7.1 and Table 7.2, respectively. Since the final orientation of the PCM module on satellite was not known, the more stringent longitudinal qualification criteria on the sinusoidal vibration test would be applied at each axis. The test samples would each undergo 100 sweeps of sinusoidal vibration across frequency range of 5-100 Hz.

Table 7.1 Random vibration qualification specification.

Frequency (Hz)	Qualification
	Power Spectrum Density - PSD (g^2/Hz)
20	0.002
110	0.002
250	0.034
1000	0.034
2000	0.009
Root-mean-square acceleration (g RMS)	6.7
Duration	2 min/axis

Table 7.2 Sinusoidal vibration qualification specification.

	Frequency Range (Hz)	Qualification
Longitudinal Axis	5-8	34.5 mm (DA)
	8-100	4.5 g
Lateral Axis	5-8	24 mm (DA)
	8-100	3 g
Sweep rate	2 Oct/min	

7.1.1.1 Equipment – Vibration test system

The vibration test would be conducted on TIRA vibration test system TV 55240/LS. The system was programmable using the included software to apply the required magnitude across the frequency ranges for random and sinusoidal vibration qualification test. Figure 7.1 shows the mechanical shaker component. The top of the shaker features the circular steel vibration plate with multiple M8 threaded inserts at 50, 100 and 150 mm for the mounting of base plate and sample fixture. The movement of the vibration plate was limited to axis perpendicular to the circular plate. Hence the PCM container needs to be manually mounted at the different orientations to fulfil the qualification criteria at all axes. The frequency and amplitude of the vibration would be picked up by a sensor attached to the vibration plate or the objects mounted on it.



Figure 7.1 Mechanical shaker, part of the TIRA vibration test system TV 55240/LS.

7.1.1.2 PCM container sample set-up

To ensure that the PCM in the PCM container remains in liquid state, 3 PI heaters were attached to the PCM container, as shown in Figure 7.2. The PI heaters attached on the side walls of the PI heater were of similar specification as the PI heater attached on the top surface.

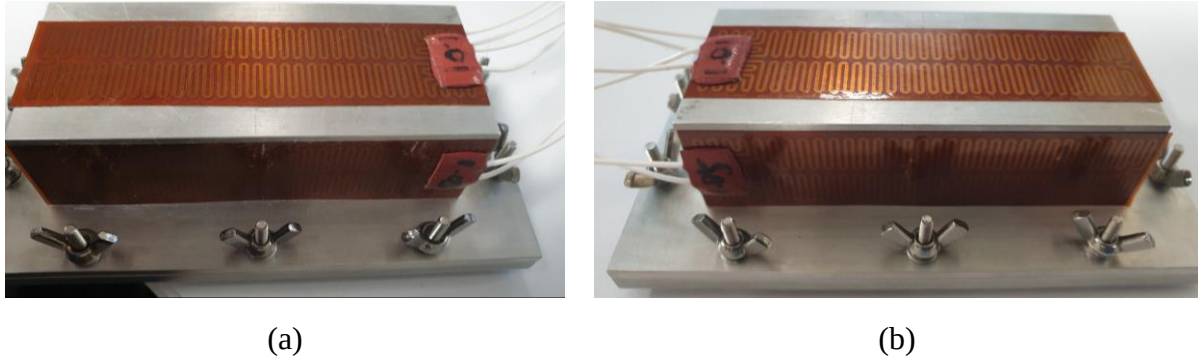


Figure 7.2 PCM container with 3 PI heaters attached

7.1.1.3 Mounting plate and fixture

A mounting plate and fixture were designed and fabricated to securely mount the PCM container sample onto the shaker in all three orthogonal axes. The fabricated mounting plate is shown in Figure 7.3. The mounting plate had a diameter of 180 mm and thickness of 15 mm. It was made from stainless steel, SS304, and had eight M8 sized attachment points distributed evenly around its circumference at a 150 mm radius, and two M8 thread inserts between two opposite M8 attachment points, aligned along the diameter 45 mm from the M8 attachment points.



Figure 7.3 Stainless steel mounting plate with eight M8 attachment points along a 150 mm circumference for attachment to the shaker vibration plate and two M8 threaded inserts for mounting of the PCM fixture. (a) top view (b) bottom view, in contact with the shaker vibration plate.

A fixture was designed and fabricated to securely clamp the PCM container in place and while mounted on the mounting plate in the three axes. The fixture was made of Al6061 and consist of a main body, which was an opened cuboid container as shown in Figure 7.4, and a clamp lid as shown in Figure 7.5. The main body had a pair of M8 sized attachment holes at each of the -Z, -Y and -X faces as shown in Figure 7.4 (b), (d) and (f). These attachment hole pairs correspond to the two threaded M8 inserts on the mounting plate. The PCM container was designed to be inserted with the top side, with an attached PI heater, facing the base of the main body container. The laser cut indentation on the inner surface of the base, as seen in Figure 7.4 (a), was made to ensure the PI heater would not be damaged when the PCM container was being clamped in the fixture. The clamp lid could be secured to the main body through the eight M6 size threaded inserts on the +Z face of the main body, Figure 7.4 (a).

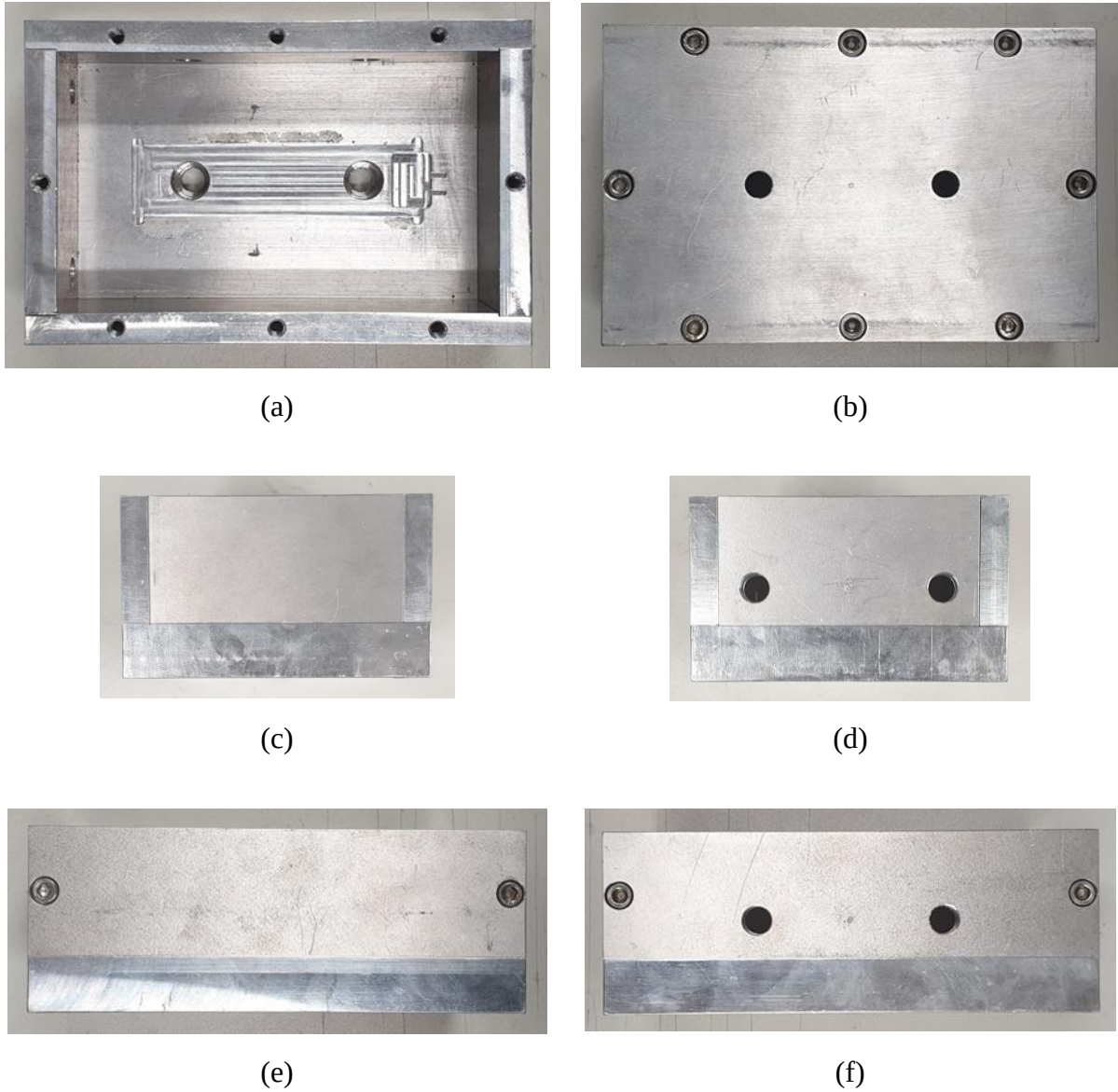


Figure 7.4 Fixture main body, open cuboid container. (a) +Z face, (b) -Z face, (c) +Y face, (d) -Y face, (e) +X face, (f) -X face. The attachment hole pair to the mounting plate were drilled on the -(minus) faces.

The cuboid extrusion on the bottom surface of the clamp, as seen in Figure 7.5 (a), (c) and (d) would be in contact with the bottom surface of the PCM container in the area bounded by the 10 M3 screws to ensure the PCM container was centralised and securely clamped. There would be a 1 mm gap between the clamp lid and main body at the rims when the PCM container was loaded.

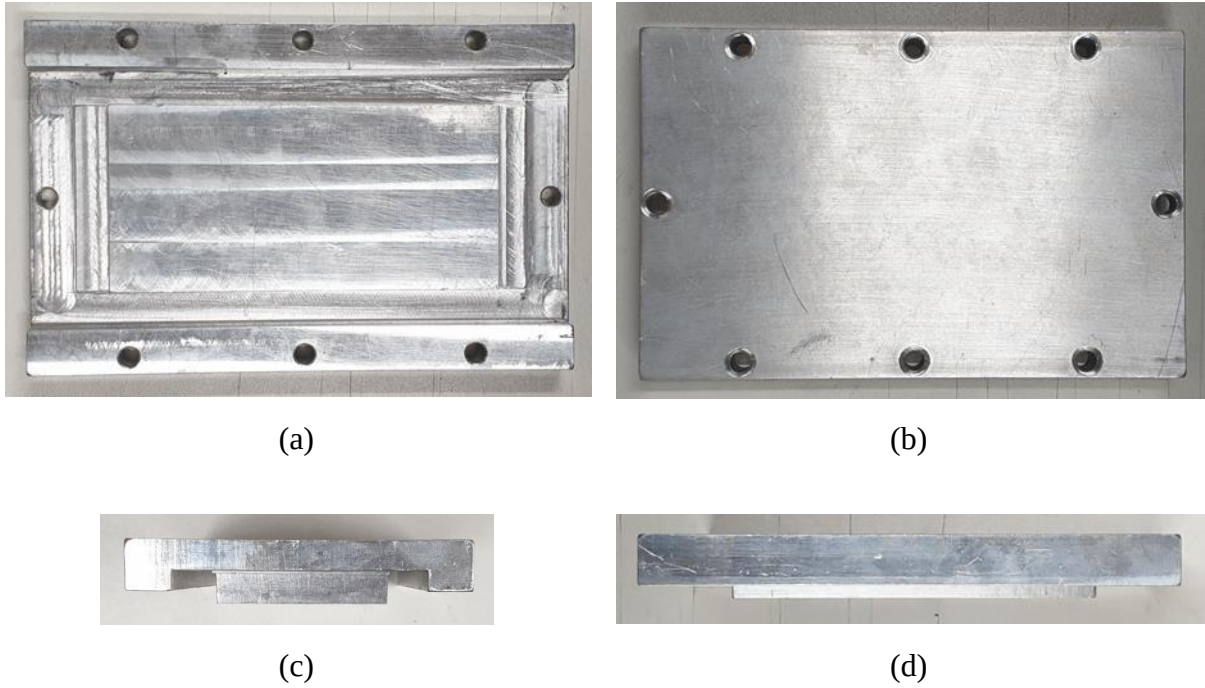


Figure 7.5 Clamp lid, (a) bottom sided, (b) top side, (c) Y facing side, (d) X facing side.

The PCM container, fixture and mounting plate assembly are shown in Figure 7.6.

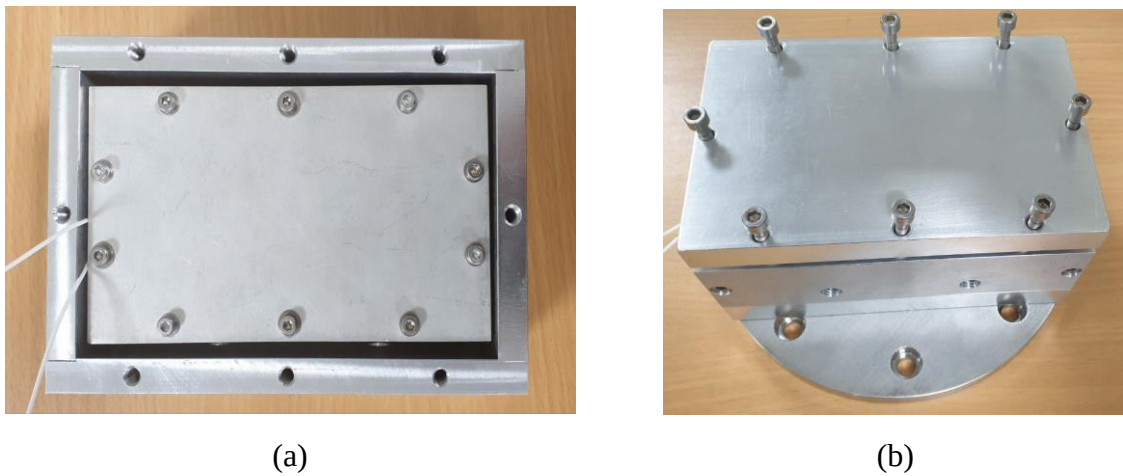


Figure 7.6 (a) PCM container loaded into the main body of the fixture. (b) Assembly of the mounting plate, fixture and PCM container for vibration test in the z-axis. The clamp lid here had not been fully tightened and was resting on top of the PCM

7.1.1.4 Vibration test system assembly

The PCM container, fixture and mounting plate assembly, mounted in the Z-, Y- and X-axis onto the vibration test system is shown in Figure 7.7.

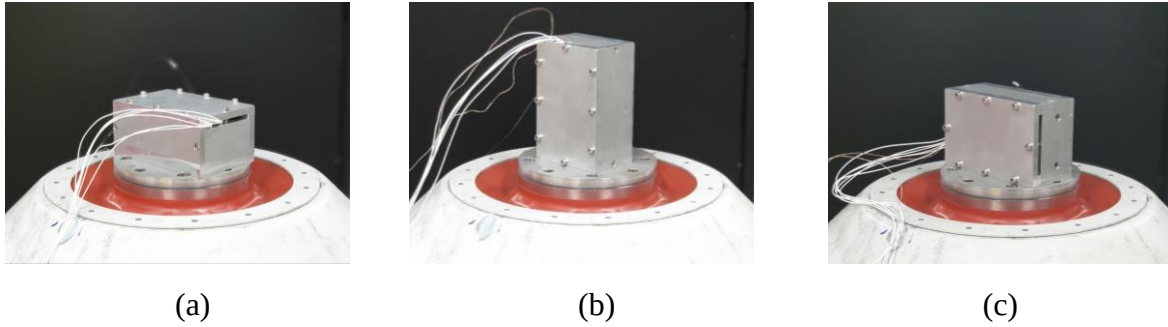


Figure 7.7 PCM container, fixture and mounting plate assembly on vibration test system, mounted in the (a) Z-axis, (b) Y-axis and (c) X-axis.

The PCM container, containing CH3DCPCM or 3DCPCM as fabricated in section 6.3.1, would be preheated to 50 °C before loading into the fixture main body. The temperature would be monitored by 2 thermocouples attached to various parts of the PCM container. After the fixture had been mounted onto the vibration test system, a total of 120 W would be supplied to the three PI heater mats attached to the PCM container. The vibration test would only start when the temperature of the PCM container had equilibrated to a temperature beyond the melting point of the PCM. For this set-up, the temperature at the PCM container walls equilibrated at about 70 °C. At this temperature, entire PCM in the PCM container was assumed to be in the liquid state. At each axis, the random vibration profile would first be applied for 2 minutes as required, followed by 100 sweeps of sinusoidal vibration profile. After the vibration tests for one axis had been completed, the heat was turned off, and the fixture was changed to the next axis. After that, the heater was turned back on and the next set of vibration test commenced after the PCM container temperature had equilibrated to 70 °C. After each sample had completed the required sets of shaker tests, the 2 PI heater mats on the sides of the PCM container were removed in preparation for the verification test.

7.1.1.5 Verification using figure of merit analysis

The verification of the test subjects would be fulfilled by demonstration and analysis using the FOM analysis method described in section 5.1.4. Before and after the vibration testing, the test samples underwent the FOM analysis to obtain the characteristic T - t curve at $P_{in} = 10, 15$ and 20 W. $FOM_{(\Delta T)}$ and its constituting parameters were recorded and the results before and after the vibration tests were statistically compared. Statistical study was carried out on the difference between $T(t)$ after and before shaker test across, denoted $\Delta T_{(a-b)}(t)$, where

$$\Delta T_{(a-b)}(t) = T_{(post-test)}(t) - T_{(pre-test)}(t) \quad 7.1)$$

The results of the comparison would indicate if there were a significant difference in PCM module performance after being subjected to the launch vibration.

7.1.2 Results and Discussion

7.1.2.1 Vibration profile

The various profiles of the random and sinusoidal vibration against frequency are shown in Figure 7.8. The profiles indicate that the resultant vibration profile of the fixture was within the reasonable range of error of the required vibration in the input.

There was no observable difference on the PCM containers containing 3DCPCM and CH3DCPCM before and after the shaker test.

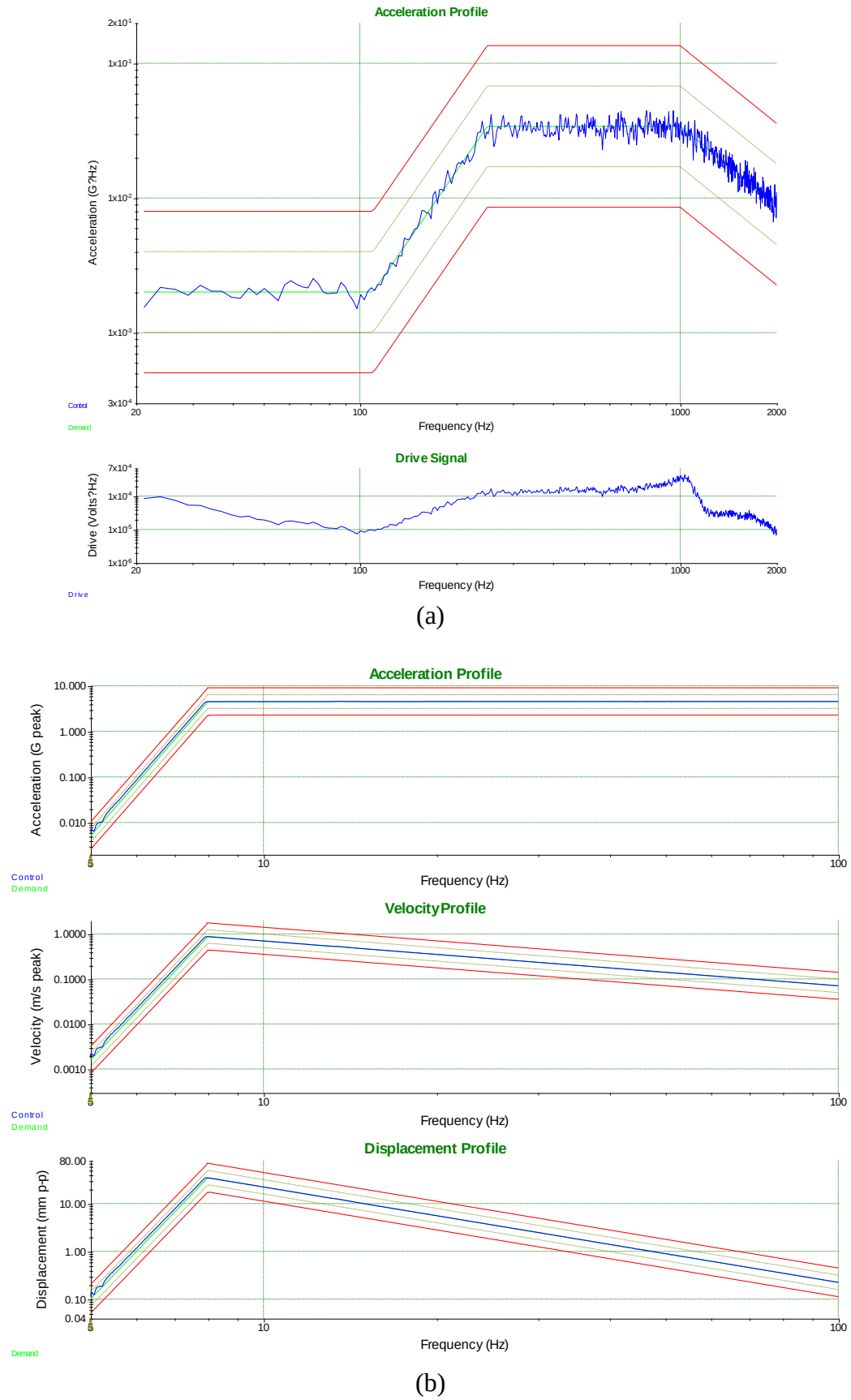
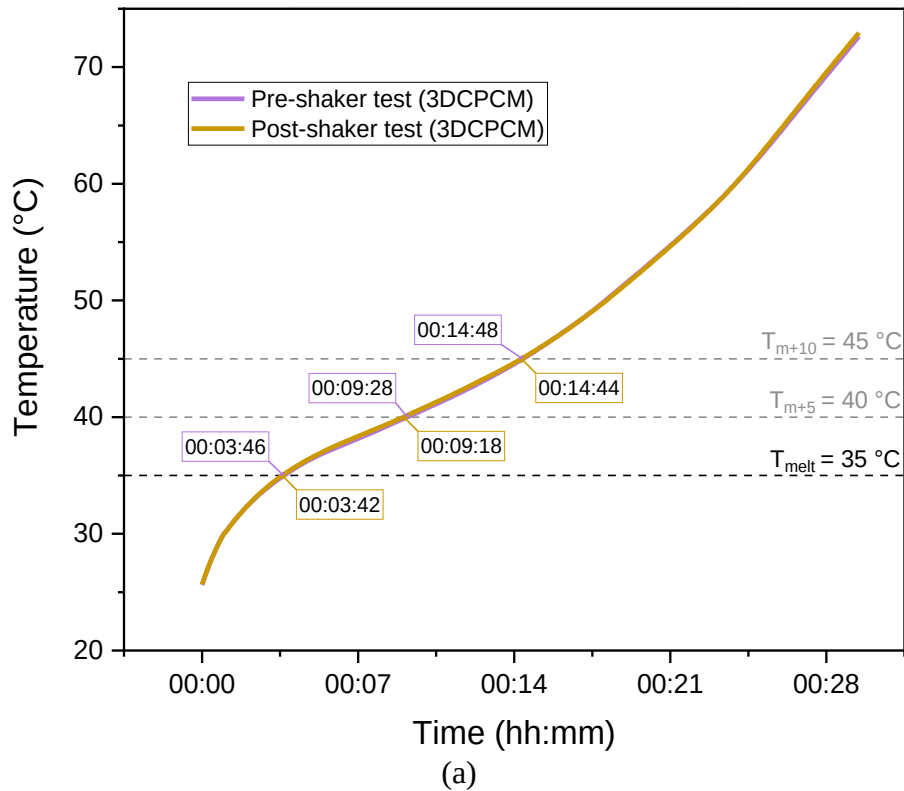
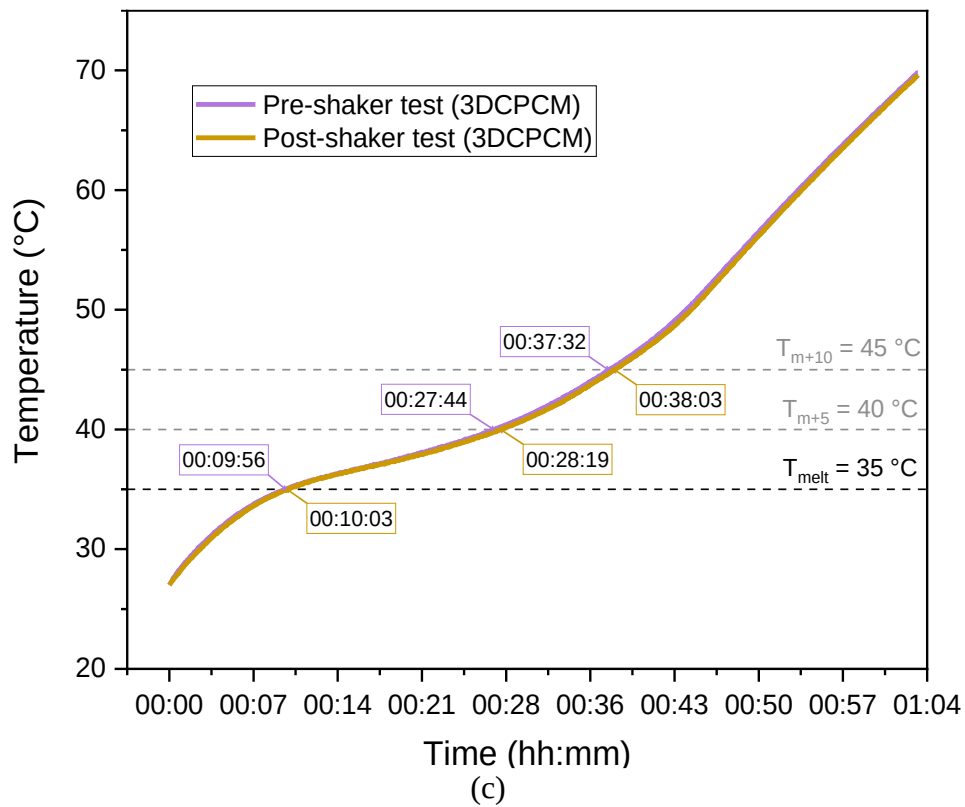
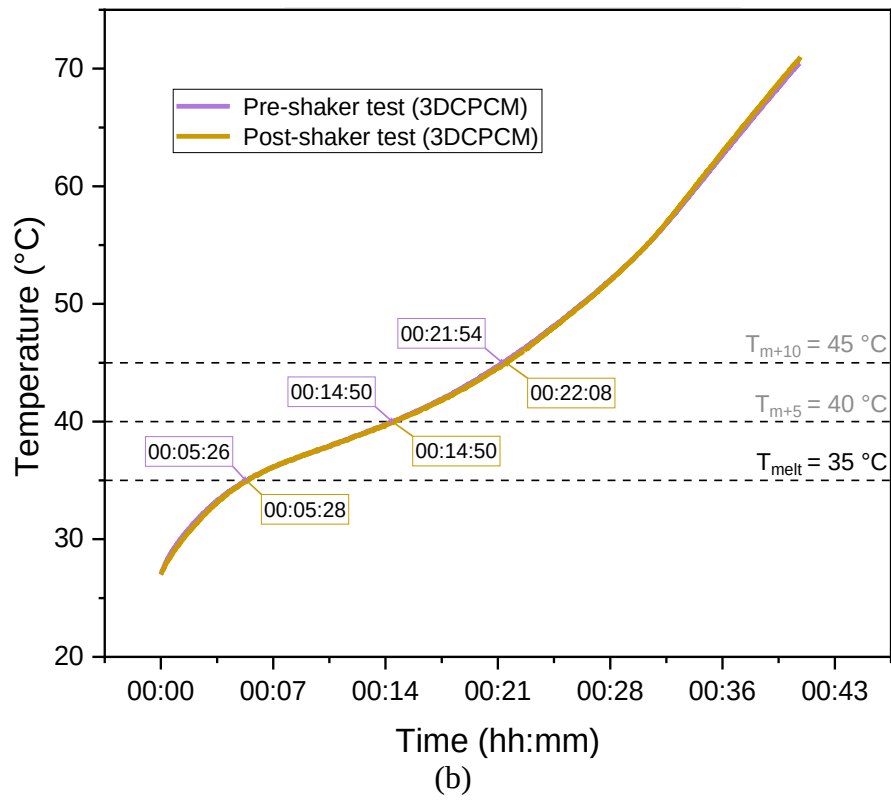


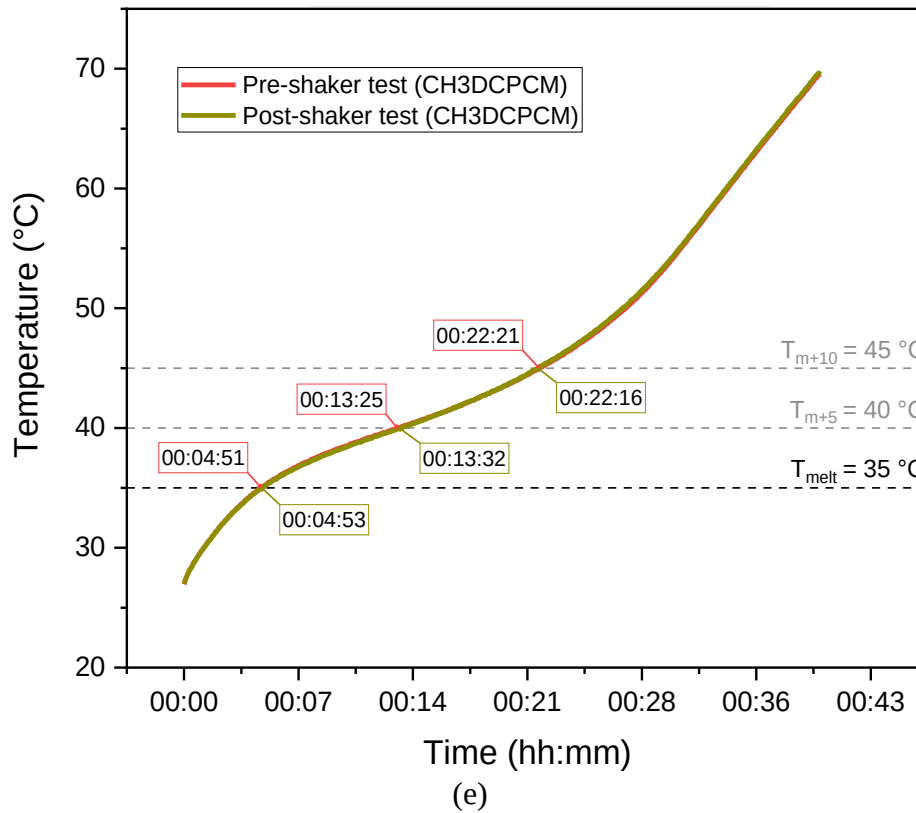
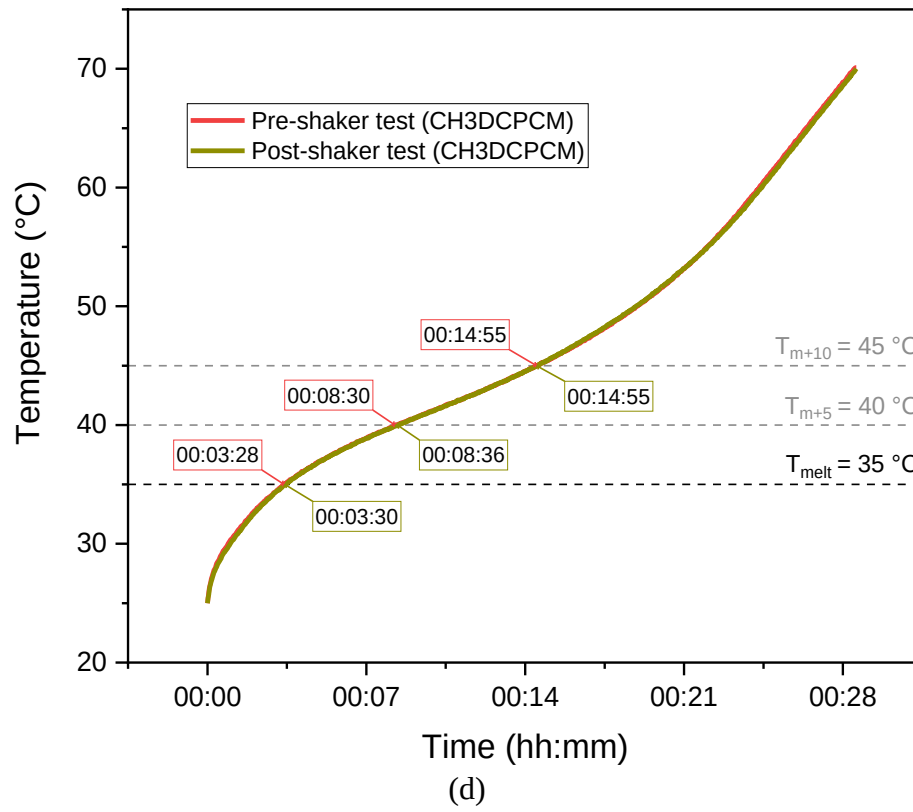
Figure 7.8 (a) Acceleration and drive against frequency profile for random vibration. (b) Acceleration, velocity, and displacement against frequency profile for sinusoidal vibration.

7.1.2.2 Verification using figure of merit analysis

The results of the pre-shaker and post-shaker test verification, in the form of T - t curves for 3DCPCM and CH3DCPCM at $P_{in} = 10, 15$ and 20 W are shown in Figure 7.9. From the T - t curve, there was little difference observable between the curve before and after the shaker test for both samples, for all P_{in} . The largest $\Delta T_{(a-b)}(t)$ across all cases was 0.5 °C which was an acceptably small margin. From the statistical analysis of the T - t curves, there were no significant difference in performance of 3DCPCM and CH3DCPCM after exposure to the qualification launch vibrations profile.







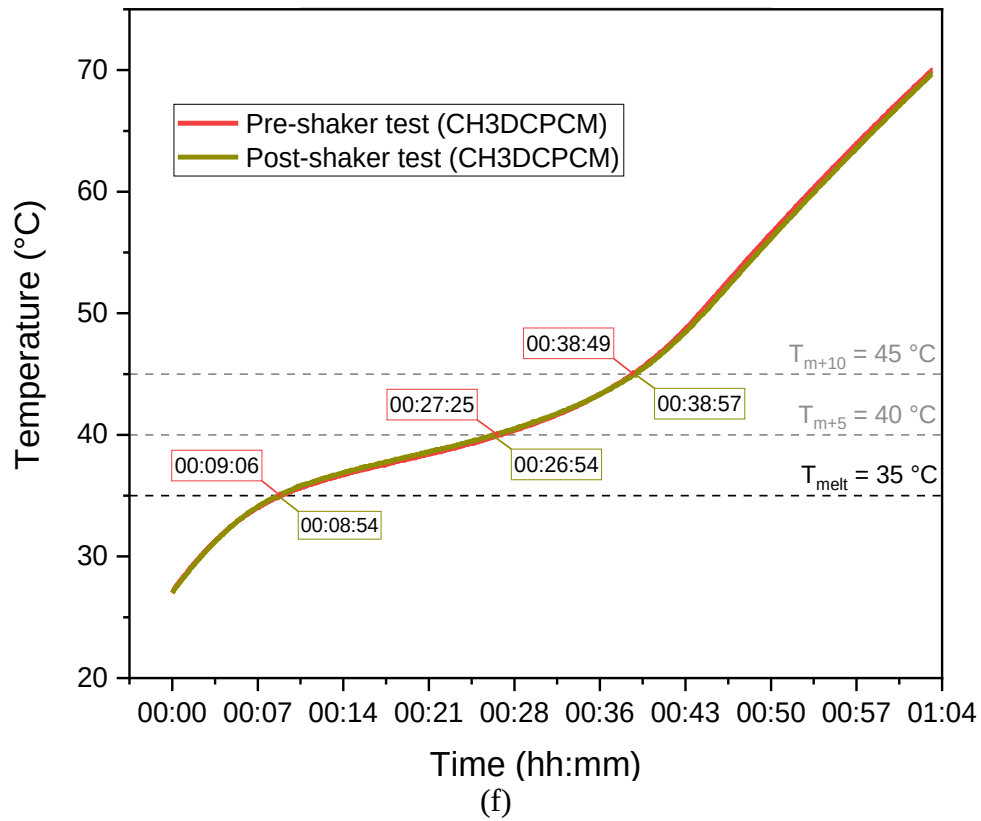


Figure 7.9 Before and after shaker test T-t curve for (a) 3DCPCM; $P_{in} = 20$ W, (b) 3DCPCM; $P_{in} = 15$ W, (c) 3DCPCM; $P_{in} = 10$ W, (d) CH3DCPCM; $P_{in} = 20$ W, (e) CH3DCPCM; $P_{in} = 15$ W, (f) CH3DCPCM; $P_{in} = 10$ W.

The $FOM_{(\Delta T)}$ at $\Delta T = 5$ and 10 °C and $P_{in} = 10, 15$ and 20 W, of PCM container samples, 3DCPCM and CH 3DCPCM, before and after the shaker test were calculated and shown in Table 7.3. The change factor, $\delta = \frac{FOM_{(\Delta T)post-test}}{FOM_{(\Delta T)pre-test}}$, would determine the changes in $FOM_{(\Delta T)}$, where a δ value above 1.00 indicates an improvement, and a value below 1.00 indicates a drop in performance.

Table 7.3 $FOM_{(+5)}$ and $FOM_{(+10)}$ of 3DCPCM and CH3DCPCM before and after shaker test at $P_{in} = 10, 15$ and 20 W

Sample	P_{in} (W)	$FOM_{(\Delta T)}$ (10^{-1})	Pre-test	Post-test	δ = Pre-test/Post-test
3DC PCM	20	$FOM_{(+5)}$	0.842	0.839	1.00
		$FOM_{(+10)}$	1.60	1.64	1.03
	15	$FOM_{(+5)}$	1.17	1.16	0.99
		$FOM_{(+10)}$	1.91	1.91	1.00
	10	$FOM_{(+5)}$	2.19	2.11	0.97
		$FOM_{(+10)}$	3.04	2.94	0.97
CH3DC PCM	20	$FOM_{(+5)}$	0.882	0.916	1.04
		$FOM_{(+10)}$	2.12	2.13	1.00
	15	$FOM_{(+5)}$	1.38	1.42	1.03
		$FOM_{(+10)}$	2.93	2.83	0.96
	10	$FOM_{(+5)}$	2.59	2.57	0.99
		$FOM_{(+10)}$	3.84	3.92	1.02

The δ for 3DCPCM ranged between 0.97 and 1.03 across all cases, and δ for CH3DCPCM ranged between 0.96 and 1.04 across all cases. The magnitude of change was within 5% of the performance before, and hence within the margin of error, for all cases. Therefore, from the results of the $FOM_{(\Delta T)}$ comparison, there was no significant difference in performance of 3DCPCM and CH3DCPCM after exposure to the qualification launch vibrations profile.

From all the T - t curve and $FOM_{(\Delta T)}$ comparison, it was concluded that after exposure to launch vibration qualification profile specified in section 7.1.1, 3DCPCM and CH3DCPCM had no statistically significant difference in performance. This meant that both samples could withstand the launch vibration and retain their performance. The two samples can therefore potentially be used for applications with vibration environment, such as missile

or airborne vehicles. Specific vibration profile of that particular application needs to be applied to the samples for full validation.

7.1.2.3 Conclusions

A launch vibration qualification test was conducted on PCM container with 3DCPCM and CH3DCPCM in accordance with standards provided by the PSLV handbook, based on the launch vibration test parameters of the PSLV and standards in SMC-S-16. A fixture and mounting system were designed and fabricated to secure the PCM container onto the mechanical shaker and mount the PCM container in 3 axes. PCM container was kept in the liquid state at 70 °C using the 3 PI heaters attached. Verification of performance was done using the PCM benchmarking test and was conducted 3 times, at each P_{in} = 10, 15 and 20 W, before and after the shaker test. No visible change was observed on the PCM container after the shaker test. The results of the PCM benchmarking test were shown in $T-t$ graphs and the corresponding $FOM_{(\Delta T)}$ at $\Delta T = 5$ and 10 °C results were calculated and compared. The largest $\Delta T(t)$ across all cases was 0.5 °C. From the $FOM_{(\Delta T)}$ analysis, the δ for 3DCPCM ranged between 0.97 and 1.03 across all cases, and δ for CH3DCPCM ranged between 0.96 and 1.04 across all cases, within the 5% margin of error. Therefore, it can be concluded that both 3DCPCM and CH3DCPCM had no statistically significant difference in performance after exposure to the random and sinusoidal launch vibrations specified by PSLV. This implied that the 3D-C structure in 3DCPCM was preserved after exposure to PSLV specific maximum predicted vibration environment in liquid PCM medium. The hypothesis that liquid PCM would induce sufficient sloshing due to launch vibrations, with respect to PSLV launch vibration requirements, to damage the structure of 3D-C micro-skeletal was hence rejected.

7.2 Extreme temperature thermal cycling

A thermal cycling test was designed to determine the resistance of the PCM to alternating high and low temperature extremes that a subsystem in a CubeSat would experience and quantify the effects of such exposure on the performance of the PCM.

7.2.1 Experimental methods

The two test subjects were 3DCPCM and CH3DCPCM, each encased in the PCM container, each screw was tightened with 1.10 Nm of torque. The thermal cycling tests were conducted based on the test conditions and procedures described in MIL-STD-883-1010.9 [130] and followed the standards described in section 6.3.8 of SMC-S-016 (year 2014) [129]. The test condition temperatures were 125 °C, with a tolerance of +15 and -0 °C for the hot case, denoted as '125(+15/-0) °C', and -55(+0/-10) °C for the cold case, according to test condition B of MIL-STD-883-1010.9. One thermal cycle was defined as 1) room temperature, 2) to hot (or cold) case temperature, 3) to cold (or hot) case temperature, 4) back to room temperature. The test samples were subjected to 50 thermal cycles, with a minimum of 10 thermal cycles in a single test run.

7.2.1.1 Equipment – Thermal environment chamber

The thermal cycling test were conducted in Thermotron SE-300-6-6 environment chamber. Both test samples were tested in the environment chamber simultaneously. The placement of the samples is shown in the schematic in Figure 7.10. Thermocouples were attached to the top and the bottom of each sample to track the temperature of the sample.

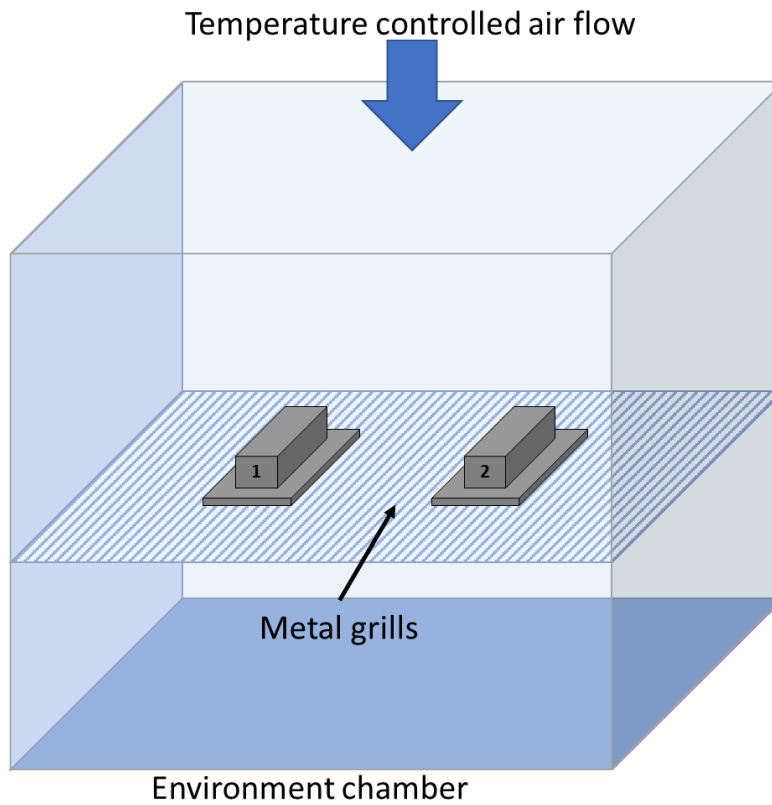


Figure 7.10 Schematic of sample placement in the environment chamber.

7.2.1.2 Test program input determination

A pre-test was conducted to identify test program input. PCM container with neat PCM was used as pre-test sample. According to the results in section 4.2.3.3, the neat PCM sample was expected to reach a lower peak temperature than 3DCPCM, and in extension CH3DCPCM, due to the neat PCM having the lowest k . Therefore, neat PCM was an ideal sample to determine the suitable test program. The test program input determined after the pre-test is shown in Table 7.4.

Table 7.4 Test program input for the environment chamber

Step	Description	Duration (mins)
1	Ramp to 135 °C from room temperature	1
2	Dwell at 135 °C	44
3	Ramp to -65 °C	1
4	Dwell at -65 °C	71
5	Ramp to 135 °C	1
6	Dwell at 135 °C	54
7	Repeat steps 3 - 6	$(n - 1)$ times $n = \text{no. of cycles}$
8	Ramp to 0 °C	1
9	Dwell at 0 °C	30
– End –		

A cycle was considered complete when the sample temperature reached room temperature. The first 3 cycles outcome of the pre-test with neat PCM is shown in Figure 7.11. The air and chamber temperatures were shown as well.

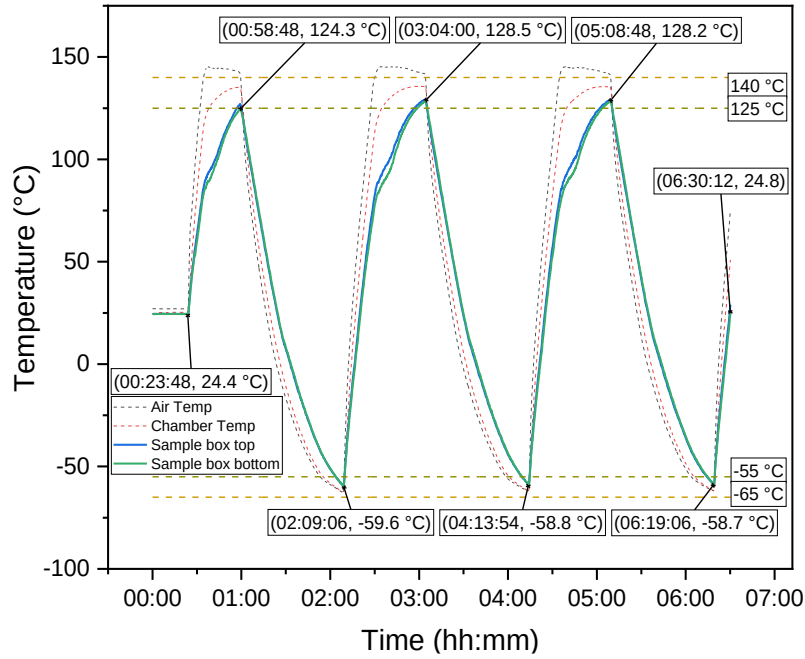


Figure 7.11 Three cycles of the pre-test with neat PCM sample in container.

The time of completion for the first cycle was slightly lower than the other cycles due to the shorter heating time from room temperature. An inflection of sample temperature, indicating the phase change of the PCM, could be observed between 80 to 105 °C in the heating step, indicating that PCM had completed its melting thereafter up till the next peak temperature. The inflection point observed in the 2nd and 3rd cycle at similar temperature ranges indicated that the PCM had a complete solidification in the cooling step. The results of the pre-test showed that the set of program inputs was able to cycle the PCM container to the required temperature of 125(+15/-0) °C and -55(+0/-10) °C within tolerance.

7.2.1.3 Verification using figure of merit analysis

The verification of the test subjects would be fulfilled by demonstration and analysis using the FOM analysis described in section 5.1.4. The procedures were similar in principle as described in section 7.1.1.5. Before and after the thermal cycling testing, the test samples underwent the FOM analysis to obtain the characteristic $T-t$ curve at $P_{in} = 10, 15$ and 20 W. $FOM_{(AT)}$ and its constituting parameters were recorded and the results before and after the

thermal cycling tests were compared. Statistical study was also carried out on $\Delta T_{(a-b)}(t)$. The results of the comparison would indicate if there were a significant difference in PCM module performance after being subjected to the extreme temperature thermal cycling.

7.2.2 Results and Discussion

The samples were inspected at the end of each 10 cycles. There were no cracks or leakage of PCM in the sample. After the first 10 cycles, one of the wing nuts along the centre of the 100 mm side was loose. This was the case for both samples. The nuts were retightened but came loose again after the 2nd 10 cycles. After which, the nuts were not retightened further for the 3rd 10 cycles onwards. The loose nuts did not loosen further after the 3rd 10 cycles. This was most likely due to the pressure build up due to the expansion of the PCM sample during heating. This revealed that the largest weakness in the sealed container at high temperature would be near the centre of the longest side.

7.2.2.1 Temperature-time profile

All peak and trough temperatures of each sample in the 50 cycles were checked and were found to be within tolerance of the temperature requirement of 125(+15/-0) °C and -55(+0/-10) °C. The temperature of the samples cycled in a sawtooth mode. The period of one cycle was approximately 2 h 8 mins. The last 10 cycles of the T - t profile of the 2 samples are shown in Figure 7.12. The temperature profile showed a consistent heating and cooling profile for all cycles. The results showed that the extreme temperature thermal cycle was conducted in an appropriate manner according to the required standards.

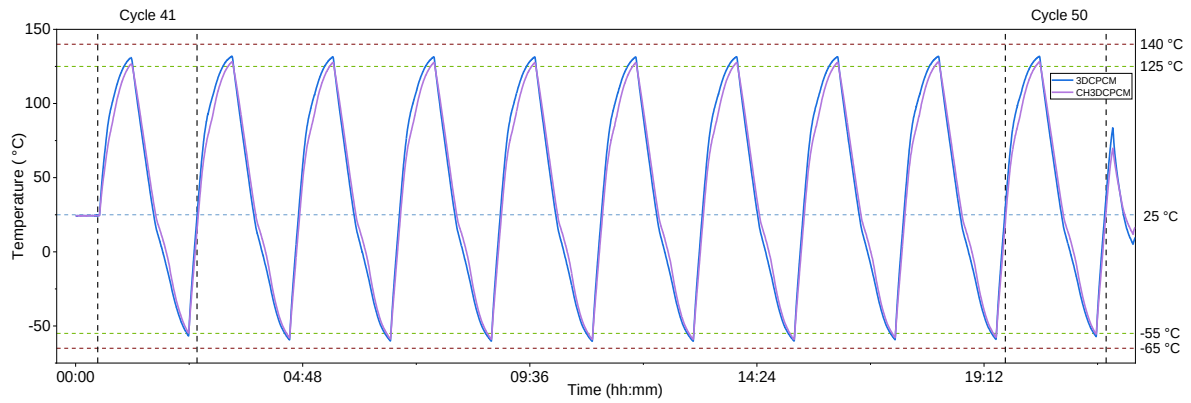
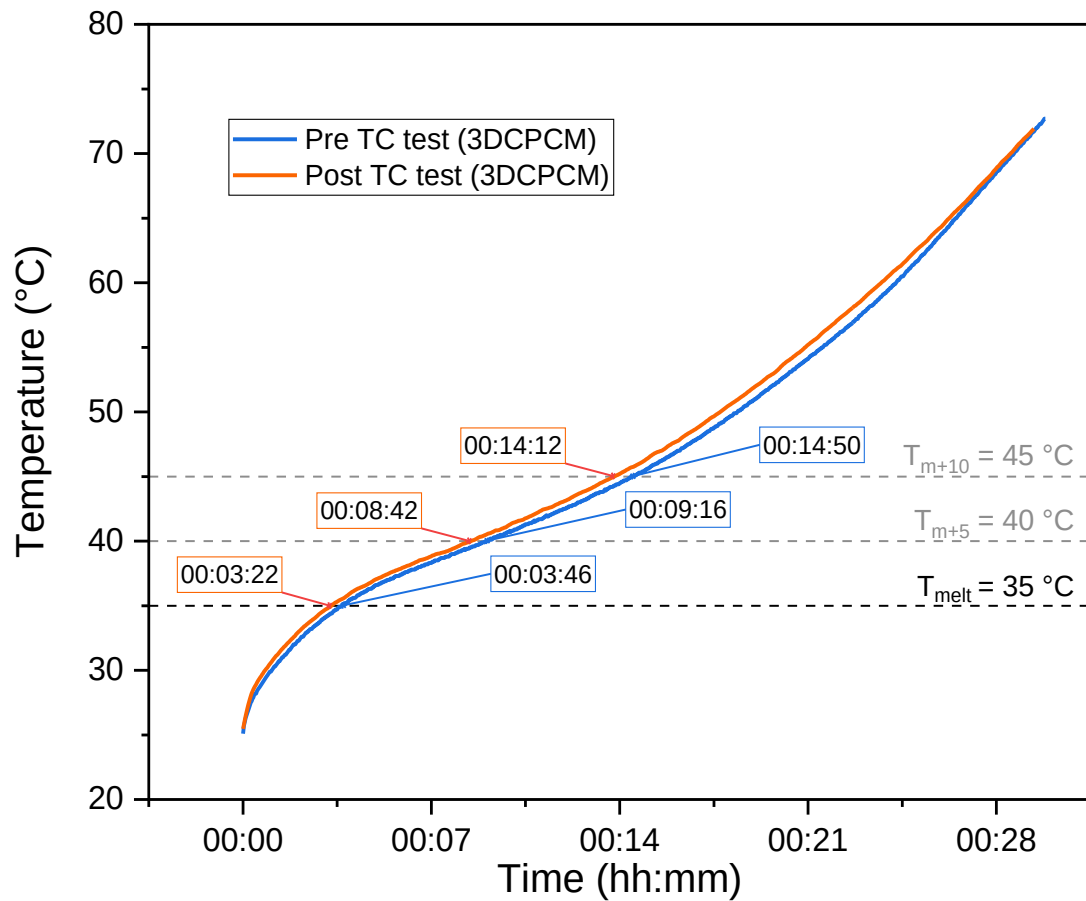


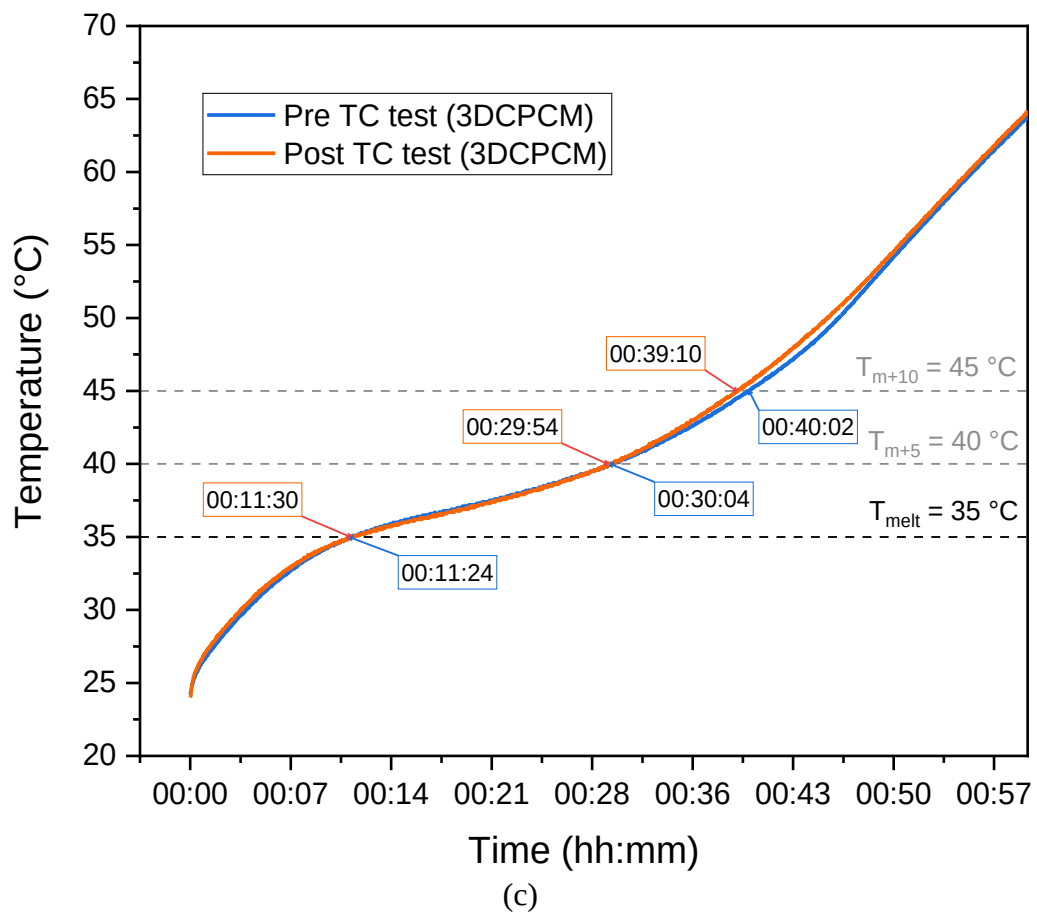
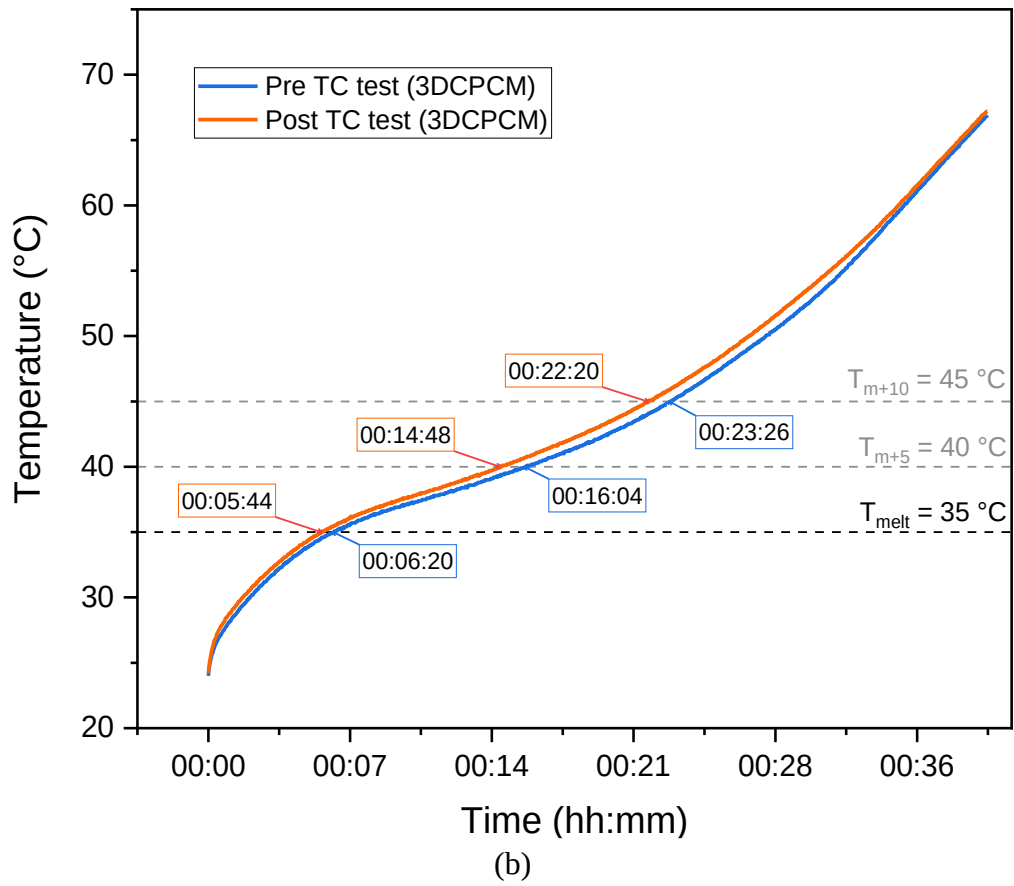
Figure 7.12 Temperature-time profile of 3DCPCM and CH3DCPCM sample cycle 41-50.

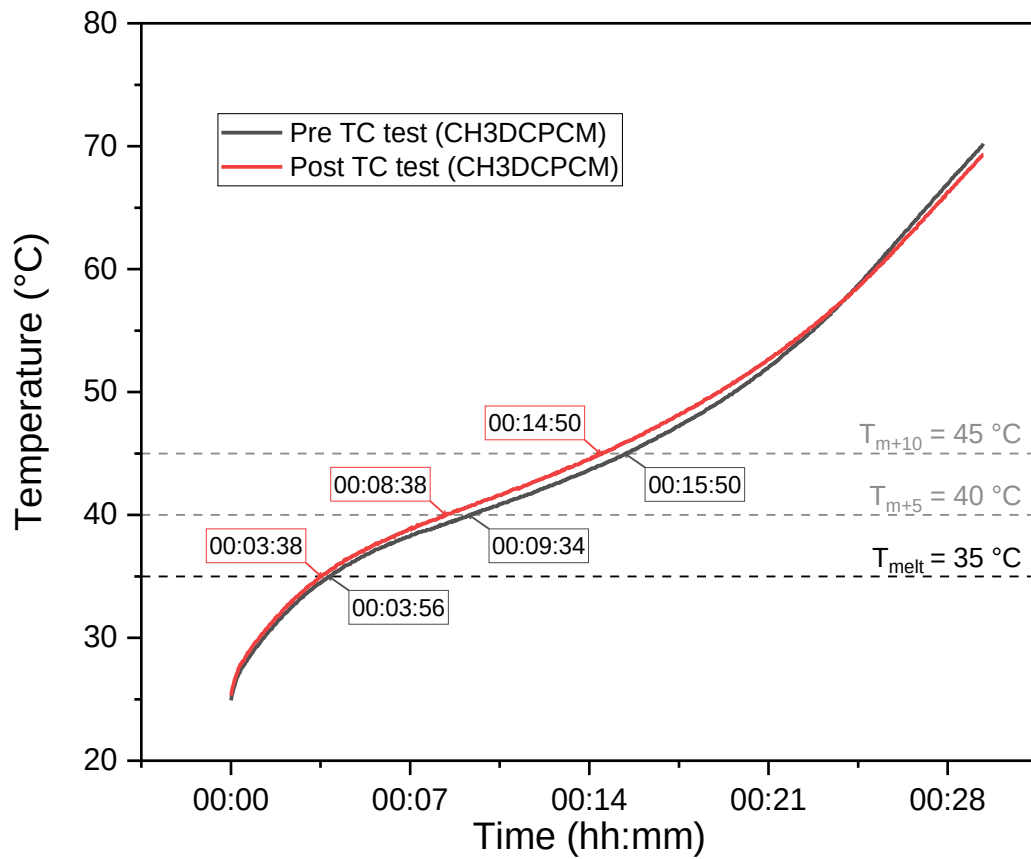
7.2.2.2 Verification using figure of merit analysis

The results of the pre-shaker and post-shaker test verification, in the form of T - t curves for 3DCPCM and CH3DCPCM at $P_{in} = 10, 15$ and 20 W are shown in Figure 7.13.

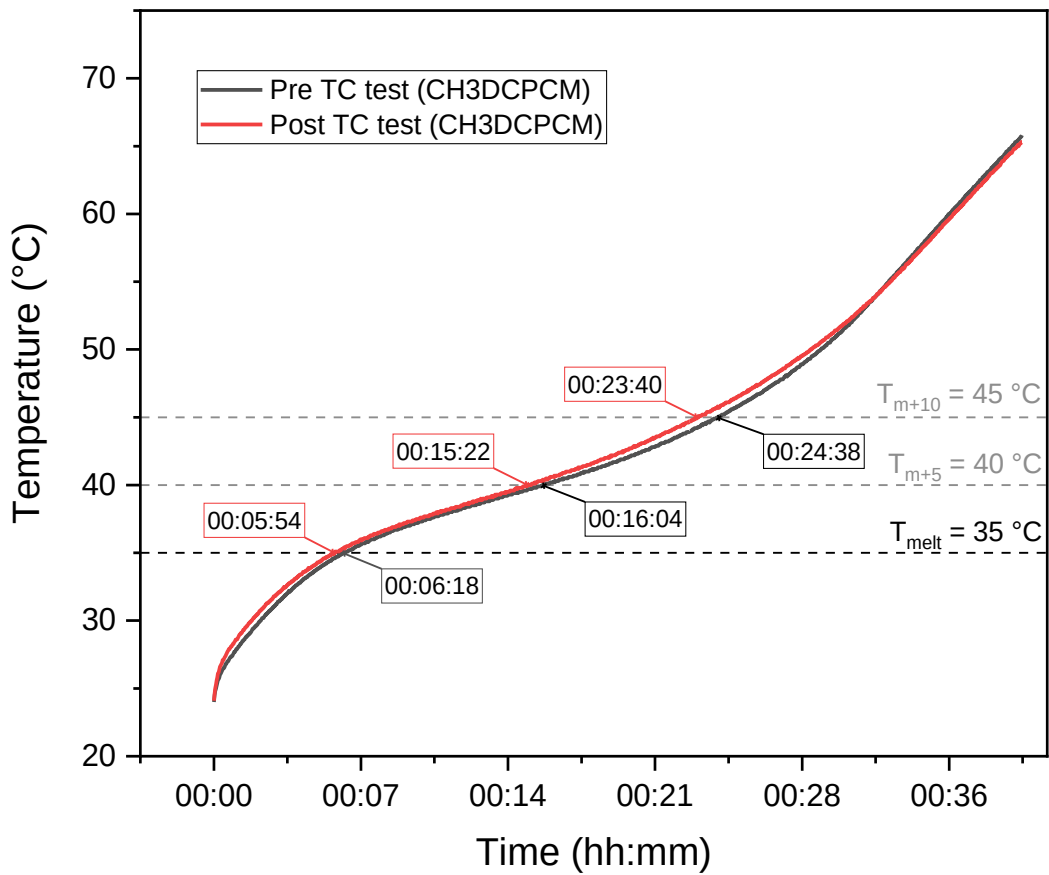


(a)





(d)



(e)

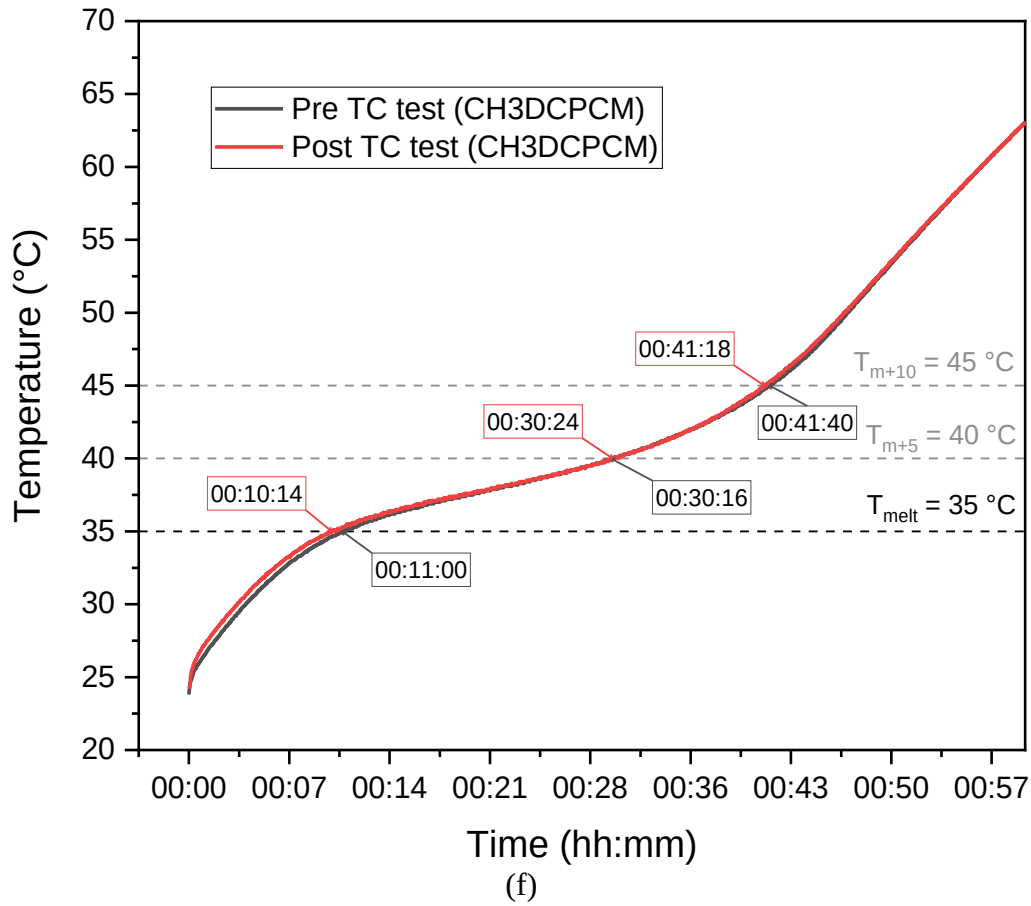


Figure 7.13 Before and after thermal-cycling test T-t curve for (a) 3DCPCM; $P_{in} = 20$ W, (b) 3DCPCM; $P_{in} = 15$ W, (c) 3DCPCM; $P_{in} = 10$ W, (d) CH3DCPCM; $P_{in} = 20$ W, (e) CH3DCPCM; $P_{in} = 15$ W, (f) CH3DCPCM; $P_{in} = 10$ W.

From the T - t graphs, both 3DCPCM and CH3DCPCM had a small difference at 10 W. The difference was more noticeable progressively at 15 and 20 W. The statistical analysis on $\Delta T_{(a-b)}(t)$ is shown in Table 7.5. For 3DCPCM, $\Delta T_{(a-b)}(t)$ was mostly positive, indicating a higher temperature at each point in time for $T_{(post-test)}(t)$ and hence a mostly poorer performance. The mean and maximum $\Delta T_{(a-b)}$ was higher at 20 and 15 W compared to 10 W, and the standard deviation from the mean was low at 0.23 – 0.26 °C. The trend was largely similar for CH3DCPCM for the various P_{in} . Compared to 3DCPCM, CH3DCPCM had a lower mean and maximum $\Delta T_{(a-b)}$ for all P_{in} . However, the deviation was slightly wider in CH3DCPCM, especially at $P_{in} = 20$ W, where deviation was 0.53 °C and the range of $\Delta T_{(a-b)}$ was -1.0 to 1.0 °C. Cross-referencing to the T - t graph in Figure 7.13 (d), the negative $\Delta T_{(a-b)}$ occurred near the end of the melting regime up till the sensible heat regime, which was

beyond the practical range used to calculate $FOM_{(\Delta T)}$. These results indicate that both 3DCPCM and CH3DCPCM had a statistically significant poorer performance after 50 extreme temperature cycles, and the magnitude of performance degradation in 3DCPCM was marginally larger than CH3DCPCM. The degradation would be shown numerically through the statistical analysis. The increase in post-test melting dT/dt observed in Figure 7.13 (a) – (e) suggest a decrease in k of the PCM composite, hence suggesting that the integrity of the high k 3D-C had been compromised.

Table 7.5 Statistical analysis on $\Delta T(t)$ for 3DCPCM and CH3DCPCM

Sample	P_{in} (W)	$\Delta T_{(a-b)}(t)$ (°C)			
		mean	standard deviation	minimum	maximum
3DCPCM	20	0.68	0.26	0	1.3
	15	0.69	0.23	0.2	1.2
	10	0.23	0.26	-0.3	0.9
CH3DCPCM	20	0.38	0.53	-1.0	1.0
	15	0.34	0.35	-0.5	0.8
	10	0.17	0.21	-0.2	0.8

The $FOM_{(\Delta T)}$ at $\Delta T = 5$ and 10 °C, at $P_{in} = 10, 15$ and 20 W of PCM container samples before and after the thermal cycling test were calculated and shown in Table 7.6. Based on the change factor, δ , both 3DCPCM and CH3DCPCM had a significant poorer performance after the thermal cycling test, with the exception of CH3DCPCM/10W/ $FOM_{(+5)}$ and CH3DCPCM/10W/ $FOM_{(+10)}$, which had a difference in performance of less than 5%. 3DCPCM had a lower average δ , at 0.86, than CH3DCPCM, at 0.91. This indicated that the CH3DCPCM had retained its performance better than 3DCPCM after extreme temperature thermal cycling. Furthermore, at each P_{in} , the $FOM_{(\Delta T)}$ of post-thermal cycling CH3DCPCM

were still higher than pre-thermal cycling 3DCPCM, which indicated that the improvement in performance due to the addition of CH in 3DCPCM was more significant than the performance degradation in CH3DCPCM after 50 extreme temperature thermal cycles.

Table 7.6 $FOM_{(+5)}$ and $FOM_{(+10)}$ of 3DCPCM and CH3DCPCM before and after thermal cycling test at $P_{in} = 10, 15$ and 20 W

Sample	P_{in} (W)	$FOM_{(\Delta T)}$ (10^{-1})	Pre-test	Post-test	$\delta = \text{Post-test/Pre-test}$
3DC PCM	20	$FOM_{(+5)}$	0.793	0.625	0.79
		$FOM_{(+10)}$	1.60	1.28	0.80
	15	$FOM_{(+5)}$	1.30	1.11	0.85
		$FOM_{(+10)}$	2.11	1.93	0.91
	10	$FOM_{(+5)}$	2.62	2.31	0.88
		$FOM_{(+10)}$	3.37	3.11	0.92
CH3DC PCM	20	$FOM_{(+5)}$	0.897	0.699	0.78
		$FOM_{(+10)}$	2.03	1.70	0.84
	15	$FOM_{(+5)}$	1.65	1.5	0.91
		$FOM_{(+10)}$	3.02	2.73	0.90
	10	$FOM_{(+5)}$	3.01	3.12	1.03
		$FOM_{(+10)}$	4.40	4.33	0.98

Figure 7.14 shows the δ against P_{in} for each sample at each $FOM_{(\Delta T)}$. For both samples, the lowest δ occurred at the highest power load of 20 W, followed by 15 and 10 W. For 3DCPCM, δ was always smaller for $FOM_{(+5)}$ as compared to $FOM_{(+10)}$ for all P_{in} .

The results for CH3DCPCM/10W/ $FOM_{(\Delta T)}$ shows a 2% decrease at $FOM_{(+10)}$ and a 3% improvement in performance at $FOM_{(+5)}$. Cross-referencing to Figure 7.13 (f), the $T-t$ graphs pre- and post-test were very similar and δ was within a 5% margin of error, therefore the $FOM_{(\Delta T)}$ at 10 W were considered similar and statistically insignificant. From the $FOM_{(\Delta T)}$

results, it was concluded that there was a significant performance degradation for both samples after extreme temperature thermal cycling with a more significant degradation in 3DCPCM. The numerical results confirmed that degradation was most pronounced at the higher heating load of 20 W. The higher degradation of performance at higher heat loads further confirms an overall decrease in k for both samples, since the effect of k difference is more prominent at higher heat loads according to Fourier's Law. This confirms that the high k 3D-C had degraded during the 50 extreme temperature cycles. The overall smaller degradation in CH3DCPCM suggest that the CH could retain the thermal network within the composite despite the degradation in 3D-C.

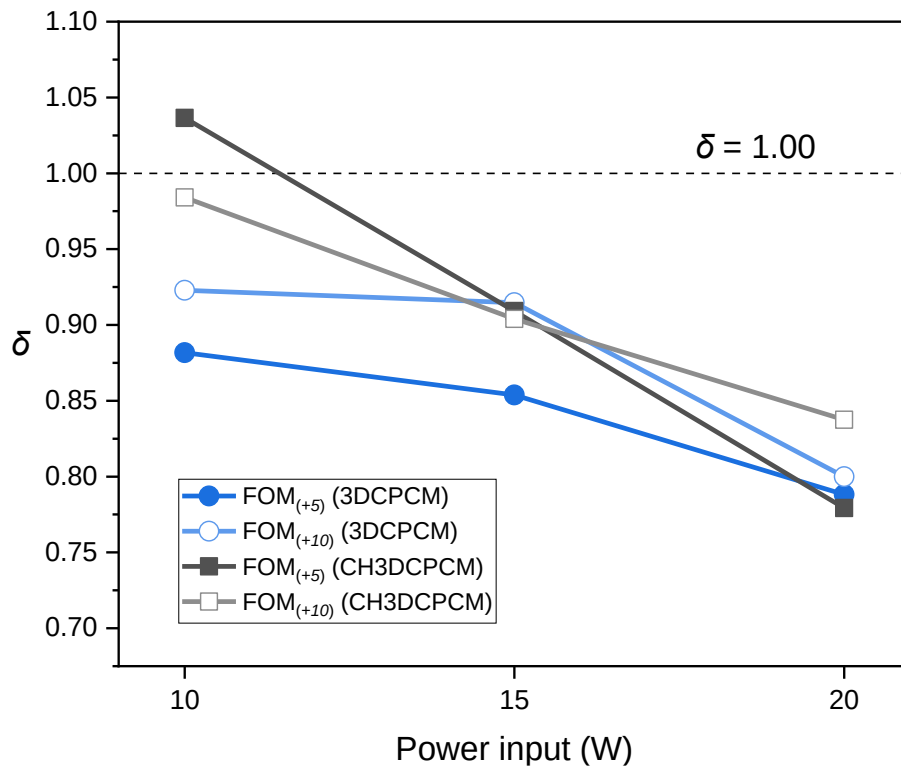


Figure 7.14 Graph of change factor, δ , against power input

7.2.2.3 Conclusions

An extreme temperature thermal cycling test was conducted on PCM container with 3DCPCM and CH3DCPCM based on the test conditions and procedures described in MIL-STD-883-1010.9 and followed the standards described in section 6.3.8 of SMC-S-16.

Samples were placed in a thermal environment chamber and were subjected to 50 cycles of alternate heating to $125(+15/-0)$ °C and cooling to $-55(+0/-10)$ °C. Verification of performance was done using the PCM benchmarking test and was conducted 3 times, at each $P_{in} = 10, 15$ and 20 W, before and after the thermal cycling test. One wing nut on each sample, at the centre of the longer side of the sample became loose after 10 cycles, indicating a high-pressure build-up within the sealed container and a possible structural failure location. The results of the PCM benchmarking test were shown in $T-t$ graphs and the corresponding $FOM_{(\Delta T)}$ at $\Delta T = 5$ and 10 °C results and at $P_{in} = 10, 15$ and 20 W were calculated and compared. Overall, there was a significant performance degradation for both samples after extreme temperature thermal cycling, with a more significant degradation in 3DCPCM. From the analysis of the $T-t$ graphs, $\Delta T_{(a-b)}$ for 3DCPCM had a larger positive mean and maximum as compared to CH3DCPCM at the corresponding P_{in} , indicating a larger degradation in performance for 3DCPCM than CH3DCPCM. From the $FOM_{(\Delta T)}$ analysis, 3DCPCM had a smaller average δ , at 0.86 , than CH3DCPCM, at 0.91 , indicating that the CH3DCPCM had retained its performance better than 3DCPCM. Furthermore, at each P_{in} , the $FOM_{(\Delta T)}$ of post-thermal cycling CH3DCPCM were higher than pre-thermal cycling 3DCPCM which indicated that the improvement in performance due to the addition of CH in 3DCPCM was more significant than the performance degradation in CH3DCPCM after 50 extreme temperature thermal cycles. Overall, CH3DCPCM was better buffered from degradation in extreme temperatures than 3DCPCM.

7.3 Summary

In this Chapter, the results of two space environment tests conducted on the PCM samples, 3DCPCM and CH3DCPCM, were presented. The first was a launch vibration qualification test conducted with PCM kept in the liquid phase and the second was an extreme

temperature thermal cycling test. The experimental methods according to the respective test standards were explained in detail, and the verification test results for both cases, using PCM benchmarking test, were shown. The main conclusions of the Chapter are listed below.

- The verification test results of the vibration qualification test showed statistically insignificant difference in performance for both 3DCPCM and CH3DCPCM. Hence both 3DCPCM and CH3DCPCM retained its performance after being subjected to random and sinusoidal vibration in three orthogonal axes according to the vibration qualification test standards of the PSLV, with PCM in the liquid phase.
- The verification test results of the extreme temperature thermal cycling test showed statistically significant difference in performance for both 3DCPCM and CH3DCPCM. The degradation was more pronounced in 3DCPCM than CH3DCPCM, and more pronounced at the highest heat load test at 20 W. This suggest a degradation of k in the samples as effects of a decreased k would more pronounced at a higher heat load.
- The $FOM_{(dT)}$ of post-thermal cycling CH3DCPCM were higher than pre-thermal cycling 3DCPCM which indicated that the improvement in performance due to the addition of CH in 3DCPCM was more significant than the performance degradation in CH3DCPCM after 50 extreme temperature thermal cycles.

8. Conclusions and Recommendations

8.1 Conclusions

The results reported in this thesis has advanced 3DCPCM as a viable PCM material for PCM-based TSU in smallsat application. For the first time, the interconnected 3D-C has been shown to be a superior filler material to the discrete counterpart GP for space application. Due to the interconnected thermal network of 3D-C, 3DCPCM has significantly more efficient k improvement, with a relative k of 4.0 as compared to 1.6 for GPPCM at the same filler loading of 1.5 wt.%. 3DCPCM also has better thermal cycling shape-stability than GPPCM. The work was also the first to report on the cross-section of PCM samples after thermal cycling and show that 3D-C delocalises the ullage that will otherwise be generated in neat PCM. The effect of increasing 3D-C loading in 3DCPCM was shown to produce an increasing trend in k_{eff} of 3DCPCM with a trade-off in H_f equivalent to the mass of PCM displaced. A model was formulated using experimental results and the theory proposed by Ashby to predict the k of 3DCPCM using the apparent density of 3D-C.

An in-house PCM demonstrator test bench was built to concurrently compare different PCM composites and identify their impact in use-case packaging. Subsequently a FE analysis was conducted using COMSOL Multiphysics based on a 3D model of the PCM container in the test bench boundary conditions. Results from the FE analysis were validated experimental results of three 3DCPCM with different T_{melt} . A FOM analysis was formulated and accepted by the end-user as key performance indicator of PCM in container. Overall, relative FOM of PCM container with 3DCPCM was found to 1.25 to 3.27 compared to neat PCM. At 20 W heat input, 3DCPCM ($k = 1.0$ W/mK) lasted 75.6 % longer than neat PCM ($k = 0.25$ W/mK) within 5 °C of melting temperature. This implies that with 3DCPCM, the passive TSU can be used for more temperature sensitive equipment that typically require active TMS, hence freeing up power budget for mission crucial subsystems.

The physical characteristics of each samples examined after the experiment showed that neat PCM sample had a large air gap at the top surface and an elongated air gap at the core of the sample. Conversely 3DCPCM sample had air gaps that were spread out due to the 3D-C scaffold and maintained its shape and thus thermal contact with the container. The FOM analysis creates the platform for performance validation should the PCM composite be required for qualification tests. FE analysis based on a 3D model of the PCM demonstrator with 3DCPCM was conducted. The resultant $T-t$ curve from the 3D model was found to correlate strongly with experimental results of 3DCPCM with variable input parameters such as k_{eff} , H_f , T_{melt} , ρ , and heat input, with the accuracy of ± 1.5 °C. This 3D thermal model of PCM demonstrator open the possibility of parametric and predictive analysis, for instance predicting the use-case efficiency of a 3DCPCM from its material properties or finding the range of material parameters that can fulfil a specific requirement related to $T-t$ curve from the end-user.

To address the disconnect between 3D-C stacks in thicker samples of 3DCPCM and the potential damage to the 3D-C structure due to launch vibration in liquid state, a novel composite consisting of CH+3D-C as scaffold infused with PCM, forming CH3DCPCM, was introduced. CH3DCPCM was also benchmarked against neat PCM, 3DCPCM and CHPCM using the FOM analysis. FOM of CH3DCPCM was found to be higher than 3DCPCM, especially at higher heat loads, hence showing that CH3DCPCM is an improvement from 3DCPCM. Since the H_f of more complex composites such as CH3DCPCM cannot be measured using standard DSC methods, a new method of H_f measurement derived from first principles using the results of the test bench analysis was formulated. The calculated H_f results of 3DCPCM and neat PCM were found to be most accurate at $P_{in} = 10$ W and were within 1% error margin of DSC results. The new method of H_f measurement will benefit further studies to determine H_f of more complex PCM composites with more complex packaging.

Finally, two space environment tests, launch vibration qualification and extreme temperature thermal cycling, were conducted on CH3DCPCM and 3DCPCM according to existing standards. The performance of both samples was compared before and after each environment test using the FOM analysis to verify change in performance. It was shown that the 3D-C structure was not compromised despite exposure to launch vibration conditions with PCM in the liquid state. This mean that 3DCPCM could potentially be used in applications with vibration environment, such as missile or airborne vehicles. Both 3DCPCM and CH3DCPCM showed significant performance difference after extreme temperature thermal cycling test. The FOM analysis indicated that the degradation was more significant at higher heat load, suggesting a decrease in k in both samples. However, the results from FOM analysis suggest that the improvement in performance of CH3DCPCM over 3DCPCM was more significant than the decrease in performance post-thermal cycling in CH3DCPCM. This show that CH+3D-C was a significantly superior scaffold compared to 3D-C to enhance k for PCM and was more resistant to performance degradation due to extreme temperature cycles.

Overall, this thesis has shown that 3DCPCM and CH3DCPCM have significant improvements over neat PCM and other filler materials in terms of the overall k , H_f and mass of the PCM packaging. A summary of the fulfilment of ideal characteristic of PCM for space application shown in Table 2.5 based on the findings of this thesis is shown in Table 8.1. Both samples are highly suitable for applications in smallsat PCM-based TSU. CH3DCPCM is an improvement over 3DCPCM with a higher overall performance and higher resistance to degradation over extreme temperature cycles.

Table 8.1 Fulfilment ideal characteristic of PCM for space application with findings from this thesis

Thermal properties	Physical properties	Chemical properties	Economic properties
• Appropriate T_{melt} for application (fulfilled by paraffin) • High H_f (fulfilled by paraffin and high porosity of 3D-C and CH) • High c_p (fulfilled by paraffin) • High k in both phases (fulfilled with addition of 3D-C and CH)	• High density (fulfilled by paraffin) • Low volume change during phase transition (3D-C shape-stabilizes PCM and retains thermal contact with container) • Low coefficient of expansion (fulfilled by CH) • No tendency to supercooling (fulfilled by paraffin) • Reversible solid-liquid transition (fulfilled by paraffin) • Low vapour pressure (fulfilled by paraffin) • High flash point (fulfilled by paraffin, 3D-C and CH) • No outgassing (fulfilled by paraffin, 3D-C and CH)	• Non-Toxic (fulfilled by paraffin) • Non-corrosive (fulfilled by paraffin) • Compatible with structural material (fulfilled by paraffin, 3D-C, CH and Al) • Identical chemical composition in solid and liquid phase (fulfilled by paraffin) • Thermal cycling stability (fulfilled with addition of 3D-C and CH)	• Abundant (fulfilled by paraffin) • Low cost (fulfilled by paraffin)

8.2 Recommendations for future work

To further improve on the performance and mature the TRL of the PCM composites, the following recommendations are suggested for future work.

8.2.1 Optimal cell size for CH3DCPCM

In Chapter 6, the novel composite CH3DCPCM was introduced and was shown to be an improvement to 3DCPCM. Since only a single cell size of CH was used in the fabrication, it was unknown if it was the optimal cell size to use to merge with 3D-C. The optimal cell size may be different for 3D-C of a different porosity and micro-structure. Parameters to decide the optimization can include FOM, total H_f and elimination of ullage. With the optimal cell size realised, the best performance of CH3DCPCM can be obtained and benchmarked against current PCM composites. Hexagonal CH core with different cell sizes (3/16, 1/4, 1/2 and 5/8 inch) with the same construction material as the one used in this work are readily available with customised bulk dimensions [131]. The overall loading of the CH core should be kept constant. It should be noted that a cell size that is smaller may require a 3D-C to be at a higher density to retain its structural integrity after physically merger with CH. Core shapes other than hexagonal can be considered after optimal cell size is known.

8.2.2 Further characterizations of PCM composites post-test

It was hypothesized in section 7.2.2 that the 3D-C had degraded due to the following observations:

- Evidence of steeper dT/dt during melting in most $T-t$ profile.
- Higher degradation scores at higher P_{in}

To prove this hypothesis, further verification must be conducted pre- and post-test. For instance, computed tomography scans of the PCM composite can be conducted to critically compare the microstructure within. Furthermore since it was known that both 3DCPCM and CH3DCPCM degrades in extreme temperatures, an extensive thermo-mechanical aging analysis should be conducted [132], [133], including modelling and testing which considers parameters such as leaks, pressure with container, fatigue etc. The theoretical thermo-

mechanical aging model of each sample can be generated to better predict the TSU lifespan in space conditions.

8.2.3 Further space qualification of PCM composites in final packaging

After the packaging of PCM has been finalised, the PCM composites should be permanently sealed in the packaging and fully tested for space qualification. This includes thermal cycling according to the requirements of the spacecraft, thermo-optical properties, AO exposure and outgassing. One key point to note would be mechanical failure of packaging due to the expansion of PCM during melting.

8.2.4 Auxetic CH3DCPCM

Auxetic honeycomb core structures have been widely researched on to provide mechanical strength equivalent to a regular honeycomb core across a curved surface [134]–[137]. Up till now, PCM-based TSU were fabricated in the cuboid shape [7]. With the introduction of CH core to 3DCPCM, auxetic re-entrant CH cores can be used such that the final packaging can be interfaced with curved equipment surface. Such CH cores are also readily available with various suppliers [138], [139]. This opens the possibility of a wide array of studies such as realising the impact of curvature of CH3DCPCM in packaging, thermal conductivity of auxetic CH3DCPCM at various curvatures etc. This would expand the range of application of CH3DCPCM to curved surfaces.

List of Publications

Journal Papers

1. **Wen Hao Li**, Lai-Iskandar Samson, Dunlin Tan, Luca Simonini, Jean-Paul Dudon, Fei Ni Leong, Roland Yingjie Tay, Siu Hon Tsang, Sunil Chandrakant Joshi, Edwin Hang Tong Teo, “Thermal Conductivity Enhancement and Shape Stabilization of Phase-Change Materials Using Three-Dimensional Graphene and Graphene Powder,” *Energy & Fuels*, vol. 34, no. 2, pp. 2435–2444, Feb. 2020.

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