Research Article

Rationally Tunable Phase Change Material Thermal Properties Enabled by Three-Dimensionally Printed Structural Materials and Carbon-Based Functional Additives

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Passive cooling using phase change materials (PCMs) is a promising solution to address thermal challenges for modern electronics, electric vehicles, and energy storage systems. The high latent heat of PCMs can significantly decrease overheating or thermal shock; however, their low thermal conductivity and unstable shape limit their practical application. Herein, we report a multiscale rational design strategy for tuning the thermal properties of PCM (octadecane), enabled by 3D-printed structural materials and multiwalled carbon nanotubes (MWCNTs)/graphene nanoplatelets (GNPs), serving as PCM reservoirs and thermally functional additives. Octadecane, used as the PCM, was thermally reinforced with MWCNT/GNP functional additives using one- and two-dimensional thermal transport at the micro-/nanoscale, and the developed nanocomposite PCM was incorporated into the 3D-printed grid structures serving two purposes: thermal transport at the macroscale and mechanical support during the liquid–solid phase change. Thus, the fabricated 3D-printed structures with incorporated thermal energy management composites (3DS-TEMCs), with different infill density/MWCNT/GNP parameters, exhibited tunable latent heat/thermophysical properties and outstanding thermal conductivity (~0.45–0.79 W/(m K)) higher than that of pure octadecane (~0.15 W/(m K)). In passive cooling tests implemented in a local heating configuration, the 3DS-TEMCs inhibited overheating and thermal shock under transient thermal loads in the operating temperature ranges of electronic devices and batteries. The proposed 3DS-TEMC offers a tunable and scalable strategy to impart PCMs with advanced thermophysical characteristics compared to conventional PCMs.

1. Introduction

Increasing multiscale energy consumption in portable electronics, electronic vehicles, mobility platforms, and energy storage systems requires high energy conversion rates and power densities, leading to the generation of considerable amounts of heat [1]. Thus, rational management of internal thermal energy generation is necessary to ensure the best performance of such systems. Complex chipsets in confined structures must satisfy the mobility and portability requirements of miniaturized applications, while electronic vehicles and energy storage systems utilize highly reactive materials under repetitive charge–discharge cycling to increase power and energy densities. Although the reduction of power consumption can resolve the issue of heat management, it generally requires redesigning core components, such as semiconductor chips and battery cells, which is not generally considered a viable option [2]. Thus, local overheating or unexpected thermal shock is commonly mitigated using cooling components that consider the operating environment to prevent potential fire or explosion [3]. Among various cooling methods, passive cooling designs are becoming significantly important owing to their low volume occupation and no power consumption, compared to active cooling devices. Phase change materials (PCMs) have recently emerged as a promising solution for the effective control of
passive thermal energy distribution and mitigation of thermal shock [4]. PCMs serve as functional components that can store large amounts of thermal energy, owing to the large latent heat, and release this energy through solid-to-liquid or liquid-to-solid phase changes within a compact design/package [5]. Owing to their large heat capacity induced by remarkably high latent heat, PCMs can absorb a significant amount of thermal energy, transfer it in the transient state, and prevent overheating or thermal shock. Various PCM-based passive cooling systems have been widely explored as promising approaches for thermal management systems and energy storage platforms such as battery cooling components [6], solar thermal energy systems [7], thermal energy storage devices [8], or building [9].

The major drawback of PCM is low thermal conductivity, which limits the absorbing and releasing rate of thermal energy. Many studies have been conducted to solve this problem of PCM. First, in order to improve the thermal conductivity of PCM, a PCM nanocomposite was produced by mixing nanomaterials with high thermal conductivity filler such as tetra pod metal particles [10], carbon nanotube, and graphene into PCM [11]. For instance, Zhang et al. reported a mixed energy-storage composite of expanded perlite, multivalled carbon nanotubes (MWCNTs), and paraffin, which showed a higher thermal conductivity (0.516 W/(m K)) than pure paraffin (0.35 W/(m K)) [12]. The second method is to insert porous structures that can effectively transfer heat to the PCM. For instance, absorbing PCMs, such as paraffin, into porous foam structures (e.g., metal, melamine, CNTs, and graphene foams and various aerogels) has been explored as an effective mean to obtain composites with high latent heat and high physical and chemical stabilities [13, 14]. However, it is a challenging issue for the PCM nanocomposites to simultaneously utilize thermally conductive filler and porous structure. If thermally conductive fillers are embedded in PCM to increase thermal conductivity, the viscosity of the PCM nanocomposite increases, making it difficult to insert into highly porous structures [15]. In addition, foam or aerogel structures produced by freeze drying or supercritical extraction require complex and high-cost manufacturing processes and have low mechanical properties required to withstand the weight of PCM [16].

The development of three-dimensional (3D) printing has enabled facile and precise fabrication of periodically arranged porous structures. Whereas the porous foams incorporating the PCMs like aerogels or randomly oriented, sponge-like structures maintain the weak solid-like structure over the melting temperature regime of the PCMs, they could not provide mechanically reinforced characteristics against external forces such as compression or impact. Meanwhile, the 3D-printed lattice (truss) and gyroid structures may be used to complement foam structures in terms of their mechanical properties and scalability [17]. They can partition internal space into desired shapes, thus enabling the adjustment of the pore volume fraction and backbone material to obtain the desired mechanical characteristics. However, structures fabricated using resin-based 3D printing methods have poor intrinsic thermal properties induced by the low thermal conductivity and stability of the polymeric backbone structures [18].

Herein, we report thermally tunable and scalable passive-cooling composite structures consisting of 3D-printed periodic porous structures and nanocomposite PCMs with carbon-based functional additives (Figure 1). The structures 3D-printed using thermally conductive fillers were employed as simple yet effective porous housing (with adjustable infill density) to store octadecane, selected as the core PCM. Meanwhile, MWCNTs/graphene nanoplatelets (GNPs) mixed at various ratios were incorporated as functional additives to enhance the thermal conductivity of the PCM. The hybrid thermal network, provided by onedimensional (1D) MWCNTs and two-dimensional (2D) GNPs led to further advancement of thermal conductivity, within a low filler ratio. The 3D-printed structure incorporating thermal energy management composite (3DS-TEMC) was designed and fabricated by filling an adjustable 3D-printed porous housing with PCM nanocomposites containing a small amount of filler (MWCNT/GNP) and low viscosity. The thermophysical and physicochemical properties of the 3DS-TEMCs were investigated using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and laser flash analysis. The ability of the 3DS-TEMC to mitigate overheating and thermal shock was demonstrated under transient thermal loads at the operating temperatures of electronic devices and batteries, simulated as local heating configurations via a film heater. In addition, compared to other previous studies, the 3DS-TEMCs have relatively high thermal conductivity and latent heat, while facile rapid prototyping and shape production are capable of using the developed 3D printing processes. The findings of this study provide insights for the development of new composites of PCMs and 3D-printed porous structures, which are expected to benefit rapid prototyping and packaging of passive cooling components.

2. Materials and Methods

2.1. Materials and Equipment. Octadecane (C_{18}H_{38}, >99% purity, Alfa-Aesar, USA) with a melting point of 28–29°C was used as the PCM incorporated into the 3D-printed porous structures. The melting point that induces the transition between the solid and liquid phases was selected to maintain the threshold temperature using latent heat under rational temperature levels for both portable/wearable electronics and battery systems. Thermally conductive 3D printing filament (Ice9™ Flex model; density: 1500 kg/m^3; specific heat: 1300 J/kg-K; tensile strength: 15 MPa; diameter: 1.75 mm; TCPoly, USA) was based on thermoplastic elastomers (TPEs) which had flexibility, nontoxicity, recyclability, and excellent resistance for chemical, flexural fatigue, tearing, and temperature change within the phase change temperature range of octadecane. A fused filament fabrication (FFF) 3D printer (TL-D3 Pro, nozzle diameter = 0.8 mm, TENLOG, China) was used to fabricate 3D-printed structures with different porosity. MWCNTs (95 wt.% purity; outer diameter: 20–40 nm; length: 5–20 μm; JEIO, Korea) and GNPs (particle size: average 5 μm; surface area: 120–
150 m²/g; Sigma-Aldrich, USA) were used as filler materials to increase thermal conductivity of octadecane.

2.2. Fabrication of 3DS-TEMCs. The fabrication of 3DS-TEMCs was conducted using three steps to fabricate 3DS-TEMCs with different infill densities (3D-printed diagonal grid structures) and filler concentrations (MWCNTs and GNPs). Infill density is the reciprocal of the porosity of the 3D-printed structure. By filling the inside of the 3D-printed structure with diagonal grid structure, the time, cost, and amount of filament used in 3D printing can be controlled. The infill density was chosen to cover a wide range of porosity for the inclusion of PCM because it can significantly exhibit specific transitions depending on porosity. The first step was to fabricate periodically porous backbones from thermally conductive filaments. Based on the screening of the optimal dimensions, a nozzle of 0.8 mm in diameter was selected to obtain smooth thermally conductive backbones. The base parameters of the 3D printing process were set to the values provided by the filament manufacturer, while the nozzle and bed temperatures were set to 250 and 70°C, respectively. The printing and travel speeds were 20 and 30 mm/s, respectively. The external dimensions of the 3D-printed porous structures were 12.7 × 12.7 mm² with a height of 5 mm and single-faced open; the diagonal grid structures and their spacing with infill densities of 30, 60, and 80% were fabricated within the squares to provide adjustable PCM nanocomposite (Figure 2(a)). Because the most representative design pattern employing the mechanically functional 3D printing object containing other raw materials was the grid structure, it was selected as the combined structure considering the scalability and tunability for broad applications. Furthermore, the grid structures comprising the TPEs fabricated by the 3D printing process could effectively complement the mechanical strength of the 3DS-TEMCs, compared with the porous foam-based backbones. The modulus, tensile strength, and elongation at break of the TPE-based filaments were previously investigated as 20–100 MPa, 20–50 MPa, and 200–300% that could support the ample mechanical reinforcement for the PCM in the liquid phase [19]. Three infill densities were determined to provide sufficient range for the evaluation of the relationship between thermal conductivity and latent heat.

In the second step, thermally complemented PCMs were developed through the addition of desirable ratios of MWCNTs and GNPs to the PCM. The target operating temperature to be maintained by passive cooling with the 3DS-TEMCs was approximately 30°C because this threshold level is the most acceptable heat configuration for portable electronic devices and batteries, without deteriorating performance. Thus, considering its melting point (28–29°C) and high latent heat (224 kJ/kg), octadecane was selected as the PCM for 3DS-TEMCs. The low thermal conductivity (0.15 W/(m K)) of octadecane was complemented by the high thermally conductive functional additives: MWCNTs and GNPs. In PCM nanocomposite, the mixed percolation networks of one-dimensional and two-dimensional nanomaterials can exhibit synergistic effects in terms of thermal conductivity and stability owing to their improved interfacial characteristics [20]. The MWCNT/GNP network can improve the thermal conductivity of PCM with a small amount of thermal conductive filler, so it has low viscosity and can be easily filled into the 3D-printed porous structure produced previously [11]. The PCM nanocomposite containing MWCNT/GNP mixed with octadecane was produced using the solution intercalation method which was generally used to evenly disperse polymer materials and nanomaterials [21]. MWCNTs and GNPs were added to acetone and thoroughly mixed by bath sonication for 2 h at 20°C. During the process of sonicating MWCNTs and GNPs, the MWCNTs and GNPs, which were bound together by the van der Waals forces and electrostatic forces, could be dispersed in acetone, and the MWCNTs and GNPs were uniformly mixed. Then, 20 g of the melted octadecane was mixed with the MWCNT/GNP acetone
solution for 6 h at 80°C, using a hot plate and a magnetic stirrer, until the acetone had completely evaporated (Figure 2(b)). Through the solution insertion process, a PCM nanocomposite with GNPs and MWCNTs uniformly dispersed inside the octadecane. When the weight percent of GNPs exceeded 2% of the weight of octadecane, the PCM nanocomposites could not fill the porous structure of 3DS-TEMC, so all GNP concentrations were fixed at 2%. The compositions of the PCM nanocomposites with the mixed MWCNT/GNP nanofillers are listed in Table 1.

In the third step, the octadecane-based MWCNT/GNP nanocomposites were integrated into the 3D-printed diagonal grid structures. The liquefied PCM nanocomposites were poured into glass beakers, and the 3D-printed porous structures were immersed in the liquid. Vacuum permeation at 60°C for 4 h facilitated the absorption of the PCM nanocomposite into the 3D-printed porous structures, and the resulting products were dried at 20°C for 24 h, thereby obtaining the 3DS-TEMCs (Figure 2(c)).

2.3. Characterization of 3DS-TEMCs. Diverse characterization methods were used to elucidate the structural, physicochemical, thermophysical, and thermal properties of 3DS-TEMCs. The microstructures and surface morphologies of the 3D-printed porous structures comprising differently mixed MWCNTs and GNPs were examined using field emission SEM (Quanta 250 FEG) under low-vacuum conditions. The individual constituents of the conductive backbone were extended to implement precise characterization during the measurement. FTIR was used to precisely investigate the physicochemical compatibility of the 3DS-TEMCs in the range of 600–4000 cm⁻¹ using a PerkinElmer Spectrum 100 spectrometer. The KBr pellet method was also used for more precise measurements. Thermophysical properties (melting/freezing temperatures and respective latent heats) of the 3DS-TEMCs with different infill densities and MWCNT/GNP ratios were measured using DSC (Q20, TA Instruments). The DSC measurements were conducted at a rate of 5°C/min in the range of −10 to 70°C and nitrogen flow of 50 mL/min. Thermal degradation durability and weight ratios of the constituents of the 3DS-TEMCs were explored using TGA (TGA Q500, TA Instruments) at a heating rate of 10°C/min from −20 to 650°C under a nitrogen environment. The effects of the infill density and functional additives composition on thermal conductivity were estimated using the laser flash method, which was used to measure thermal diffusivity according to the ASTM E1461 standard. The thermal diffusivity (LFA 447 NanoFlash, NETZSCH) was measured at 20°C, considering the PCM melting characteristics. Once the thermal diffusivity was obtained, the thermal conductivity was calculated by considering intrinsic density and specific heat. Thermal stability of the 3DS-TEMCs was investigated under the long-time exposure (~36 h) to 40°C and repetitive changes of ambient conditions.

Table 1: Octadecane-based PCM nanocomposites with MWCNT/GNP nanofillers.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Octadecane</th>
<th>MWCNT</th>
<th>GNP</th>
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<tbody>
<tr>
<td>3DS-TEMC 2%/1%</td>
<td>20.000 g</td>
<td>0.400 g</td>
<td>0.200 g</td>
</tr>
<tr>
<td>3DS-TEMC 4%/1%</td>
<td>20.000 g</td>
<td>0.800 g</td>
<td>0.200 g</td>
</tr>
<tr>
<td>3DS-TEMC 6%/1%</td>
<td>20.000 g</td>
<td>1.200 g</td>
<td>0.200 g</td>
</tr>
<tr>
<td>3DS-TEMC 8%/1%</td>
<td>20.000 g</td>
<td>1.600 g</td>
<td>0.200 g</td>
</tr>
</tbody>
</table>

Figure 2: Fabrication of 3DS-TEMCs. (a) 3D-printed diagonal grid structures with different infill densities (30, 60, and 80% of the printed objects) as thermally conductive backbone structures for 3DS-TEMCs. (b) Preparation of the octadecane-based MWCNT/GNP nanocomposites. (c) Incorporation of 3D-printed porous structures and phase change nanocomposites to obtain 3DS-TEMCs.
temperature conditions. All 3DS-TEMCs maintained their initial structure and design without the specific leakage of the PCMs (Figure S1). Thereafter, testing environments of overheating and thermal shock were experimentally conducted using local heating with a film heater. The passive cooling capabilities of the 3DS-TEMCs were demonstrated under transient thermal loads, which reflect thermal conditions in batteries and electronic devices. Real-time temperature changes were recorded using a data acquisition device (GL840 data logger, Graphtec) and thermocouples (TT-K-30-SLE k-type thermocouple, OMEGA). The characterization of 3DS-TEMC and uncertainty about passive cooling capabilities were obtained through error propagation method in Table S1.

3. Results and Discussion

3.1. Morphological and Physicochemical Properties of 3DS-TEMCs. The morphologies of the TPE filaments, MWCNTs, and GNPs show the structural characteristics of the 3D-printed backbones and thermally functional additives comprising the 3DS-TEMCs (Figure 3). The 3D-printed porous diagonal grid structures solidly adhere to each other, whereas rough surfaces are observed in the SEM image (Figure 3(a)). The raw MWCNTs and GNPs before mixing with octadecane present randomly oriented networks of 1D structures and layered 2D structures of plate-like shapes (Figures 3(b) and 3(c)), respectively. After the solution intercalation process of octadecane, MWCNTs, and GNPs, the PCM nanocomposites were absorbed into the voids in the prefabricated 3D-printed diagonal porous structures. The cross-sectional areas of the hybridized composite structures, which were prepared by cutting the 3DS-TEMCs, reveal the characteristics of the prepared materials (Figure 3(d)). The integrated structures of the PCM nanocomposites and TPE backbones show distinctive interfacial boundaries, which are shown as light gray and dark gray. The light-gray regions indicate the PCM nanocomposites, and the dark-gray area is a 3D-printed backbone. Furthermore, 3DS-TEMCs are forcibly disassembled to investigate the MWCNTs/GNPs networks in octadecane (Figures 3(e) and 3(f)). 3DS-TEMCs with infill density/MWCNT/GNP of 60%/6%/1% (Figure 3(e)) and 60%/8%/1% (Figure 3(f)) exhibit the entangled MWCNTs and plate-like GNP percolation networks in the octadecane. In the PCM nanocomposites, the capillary force and surface tension between the nanofoils and liquefied octadecane supported interface formation [22]. The sample with a higher concentration of MWCNTs reveals more entangled with GNP networks; octadecane as a PCM is apparently located in the micro-/nanoporous structures [23]. It is generally accepted that dense networks of one- and two-dimensional nanostructures can facilitate the formation of thermal transport pathways through direct heat conduction paths. At the same time, exceedingly high concentrations of functional nanostructures may cause severe agglomeration of individual constituents. Such agglomerated hybrids of the octadecane and MWCNT/GNP additives appear in the 3DS-TEMCs with 8% MWCNTs, possibly decreasing the thermal conductivity (Figure 3(f) and Figure S2). Thus, the thermal conductivity of the 3DS-TEMCs with the too high concentration of MWCNTs could result in the low thermal conductivity.

Physicochemical transitions during the fabrication of 3DS-TEMCs were examined to detect the occurrence of unexpected chemical reactions and compositional changes. Thus, FTIR analysis was used to characterize the constituents of 3DS-TEMCs (Figure 4). Octadecane, MWCNTs, GNPs, and 3DS-TEMC with an infill density/MWCNT/GNP of 60%/6%/1% were selected as representative FTIR samples to elucidate the presence of unanticipated transitions. First, the peak spectrum of octadecane appears at 716, 1471, and 2912 cm⁻¹ corresponding to the rocking, bending, and asymmetric stretching vibrations of C–H, respectively [24]. Because MWCNTs and GNPs are both carbon-based materials, their FTIR spectra are similar, with the peaks at 3428, 1633, and 1098 cm⁻¹ [25], while only the MWCNTs indicate the stretching vibrations of C=O and C–O bond peaks at 2917 and 2849 cm⁻¹ corresponding to the stretching vibration of C–H [26]. The transmittances of MWCNTs and GNPs have a relatively small magnitude in the composites compared to that of octadecane, which suggests a small effect on the composite material. Finally, the FTIR spectrum of the 3DS-TEMCs presents major peaks reflecting the constituent materials and elements. Overall, additional peaks or unusual trends did not appear in the FTIR measurements, thereby validating the absence of chemical reactions and specific bonding during the fabrication of the 3DS-TEMCs.

3.2. Thermophysical Properties of 3DS-TEMCs. Efficient thermal management using 3DS-TEMCs requires an understanding of their thermophysical properties (latent heat and phase change temperatures). Thus, DSC analyses were conducted to measure the melting latent heat (Hₘ), melting temperature (Tₘ), freezing latent heat (Hₖ), and freezing temperature (Tₖ) of octadecane and the 3DS-TEMCs with different infill density/MWCNT/GNP parameters (Figure 5 and Table 2). The thermal energy storage material, octadecane, exhibits melting and freezing temperatures of 27.8 and 24.98°C, while the latent heats of solid–liquid and liquid–solid phase changes are 222.60 and 218.50 J/g, respectively, and the obtained numbers almost match the intrinsic properties of octadecane [27]. After characterizing the octadecane, all 3DS-TEMCs with diverse infill density/MWCNT/GNP parameters were investigated to obtain the thermophysical properties. Owing to the sample volume and mass limitation of DSC, these data were obtained by cutting a portion of the diagonal grid section of the 3DS-TEMCs considering the infill density. The melting and freezing temperatures of the 3DS-TEMCs are 27.07–27.33 and 25.07–25.33°C, like those of octadecane. These results indicate that the phase change temperatures of 3DS-TEMCs are determined by the thermal energy storage material, even though other functional additives and supportive structures were introduced. At the same time, the latent heats of solid–liquid and liquid–solid phase changes show ranges of 87.3–171.5 and 86.96–167.3 J/g, respectively, depending on the infill density/MWCNT/GNP parameters. As the infill density indicating low porosity increases, the available
volume for the PCM nanocomposite becomes smaller. The obtained thermophysical properties of octadecane and 3DS-TEMCs are listed in Table 2.

Evidently, infill density and MWCNT/GNP ratio determine the overall differences between the properties of 3DS-TEMCs and those of octadecane. First, at the same MWCNT/GNP ratio, increasing the infill density significantly reduces the latent heat, and the effect is nearly unit proportional. For example, the latent heat of the 3DS-TEMC with 30% infill density is 185% higher than that of the 3DS-TEMC with 80% infill density. It is reasonable that the higher infill density of the 3D-printed objects results in lower latent heat because the amount of octadecane as a PCM in the 3DS-TEMCs decreases with increasing infill density. In the temperature range near the melting temperature of octadecane, the TPE backbones do not contribute to the latent heat; thus the total amount of octadecane is the determining factor for latent heat. The 3DS-TEMCs with 30 and 80% infill densities exhibit a 195% difference in the relative weight ratios of octadecane. Notably, the latent heat estimated using the weight ratio is within a 0.59% uncertainty from the experimentally measured DSC results (Table S1) [28]. Next, at a fixed in fill density, the MWCNT/GNP contents affect the latent heat, although the differences are smaller than those at different infill densities. Increasing the amount of MWCNT/GNP results in a decrease in the latent heat of the 3DS-TEMCs. At the constant GNP content (~1%) and infill density, the change in the MWCNT addition from 2 to 8% leads to a reduction in the proportion of octadecane by 5.1% in the 3DS-TEMCs, thereby decreasing the latent heat during the phase change. Moreover, this reduction in latent heat is almost proportional to the decrease in the mass ratio of octadecane. Meanwhile, the increment in the MWCNT/GNP ratio results in a slight increase in the melting and decrease in the freezing temperatures of the 3DS-TEMCs, respectively, owing to the mutually formed heat transfer networks between the backbone, functional additives, and PCMs. However, the PCM nanocomposite with more than 8% of the MWCNT ratio might lead to a severe agglomeration of the additives and could not uniformly fill the voids of the 3D-printed diagonal grid structures in the 80% infill density case (Figure 3(f) and Figure S2). Therefore, the effects on melting and freezing temperatures are limited because of weak physical bonding with the printing surface and aggregation of internal fillers.

The thermal stability of the 3DS-TEMCs, which correlates with durability and resistance to high temperatures, was assessed using TGA (Figure 6). Because all 3DS-TEMCs were

Figure 3: Morphological analysis of 3DS-TEMCs constituents. SEM images of (a) 3D-printed TPE backbones, (b) MWCNTs, and (c) GNPs before integrating them into the 3DS-TEMCs. Cross-sectional images of (d) the locally hybridized TPE backbones and the PCM nanocomposites consisting of octadecane and MWCNT/GNP functional additives. The dark- and light-gray areas classified by yellow lines indicate the TPE backbone and the PCM nanocomposites, respectively. Disassembled structural images of 3DS-TEMCs with infill density/MWCNT/GNP of (e) 60%/6%/1% and (f) 60%/8%/1%.

Figure 4: FTIR spectra of octadecane, MWCNTs, GNPs, and 3DS-TEMC with infill density/MWCNT/GNP of 60%/6%/1%.
composed of the same materials (i.e., TPE, octadecane, MWCNTs, and GNP), the 3DS-TEMC with infill density/MWCNT/GNP of 30%/6%/1% was selected as representative. The TPE, octadecane, and PCM nanocomposites with the same filler ratio of the representative 3DS-TEMC were separately analyzed to elucidate the individual contributions to the thermal decomposition. During the TGA at 25–650°C at a rate of 10°C/min in a nitrogen environment, the TPE backbone lost 56.8% of its weight via thermal decomposition. Meanwhile, the pristine octadecane and PCM nanocomposite show weight losses of 99.9 and 93.1%, respectively. The difference in the percentages is similar to the MWCNT/GNP content, thereby demonstrating the thermal durability of carbon-based fillers under the nitrogen environment. Lastly, the 3DS-TEMC (infill density/MWCNT/GNP of 30%/6%/1%) was subjected to the TGA, and a two-step weight loss of 77% is observed, which is the thermal decomposition of the octadecane at 234.5°C and TPE backbone at 410.1°C. Based on the TGA results, considering the primary pyrolysis, the estimated octadecane content by mass is 57.1%; at the same time, considering the ratio of secondary pyrolysis and final residue, the TPE backbone comprises 36.7% of the total weight of the 3DS-TEMC. In addition, the mass content of the MWCNT/GNP conductive networks is estimated to be 5.1%. Owing to the sample volume limitation of TGA, these data were obtained by cutting a portion of the diagonal grid section of the 30%/60%/1% 3DS-TEMC considering with the infill density. From these results, thermal stability of 3DS-TEMC was confirmed within 40°C to 50°C, which is the threshold temperature for electronic device operation.

The thermal conductivity of the 3DS-TEMCs is a significant factor in improving the passive cooling capability in comparison with pure octadecane. The broad interest in the application of PCM nanocomposites in electronics,

**Figure 5:** DSC analysis of 3DS-TEMCs with different infill density/MWCNT/GNP parameters. (a) MWCNT 2%/GNP 1%, (b) MWCNT 4%/GNP 1%, (c) MWCNT 6%/GNP 1%, and (d) MWCNT 8%/GNP 1%.
Table 2: Quantitative summary of DSC analyses for 3DS-TEMCs with different infill density/MWCNT/GNP parameters. $T_M$, $H_M$, $T_F$, and $H_F$ indicate the melting temperature, melting temperature latent heat, freezing temperature, and freezing temperature latent heat, respectively.

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<th>3DS-TEM C</th>
<th>Infill/MWCNT/GNP</th>
<th>Heating period $T_M$ (°C) $H_M$ (J/g)</th>
<th>Cooling period $T_F$ (°C) $H_F$ (J/g)</th>
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Figure 6: Thermal degradation durability of the constituents of 3DS-TEMCs, examined by TGA. The black, blue, dark yellow, and red curves indicate the decomposition of TPE backbones, 3DS-TEMCs with infill density/MWCNT/GNP of 30%/6%/1%, octadecane incorporated with 6%/1% MWCNTs/GNPs, and pure octadecane.

wearable devices, batteries, and construction lies in the range from room temperature (~25°C) to a threshold temperature of less than 40–50°C [29]. Thus, the enhanced thermal dissipation and fast phase transition of the solid and liquid phases under the same thermal loads or intermittent thermal loads can be promoted by improving the thermal conductivity of thermal energy storage composites. In the 3DS-TEMCs, the MWCNT/GNP functional additives complement the thermal conductivity of octadecane via one- and two-dimensional networks comprising thermal transport pathways, whereas the 3D-printed conductive TPE backbones boost the thermal conductivity between adjacent pockets of nanocomposite PCM. The laser flash method enabled the direct measurement of density (ρ), specific heat (C_p), and thermal diffusivity (α) for each specimen at a specific temperature (T). Then, the product of the measured properties could be confirmed as the obtained thermal conductivity (λ) according to the ASTM 1461 standard, as follows:

$$\lambda(T) = \rho(T) \times C_p(T) \times \alpha(T).$$ (1)

The thermal conductivity of 3DS-TEMCs exhibits remarkable dependence on the design parameters (infill density/MWCNT/GNP), as shown in Figure 7. The octadecane, TPE backbone, and 3DS-TEMCs with the different MWCNT proportions and infill densities were selected as the specimens to elucidate the correlation between the thermal conductivity and design parameters. They could reflect the working mechanisms of complementing thermal properties and the interfacial boundary consideration between the PCM nanocomposite/TPE structures. First, the thermal conductivity of the TPE backbone was measured to be 0.49 W/(m K), which is higher than that of conventional polymers [18], while the value of 0.15 W/(m K) for the octadecane was similar to that reported in previous studies [30]. TPE exhibits much higher conductivity than octadecane, thereby supporting the overall higher thermal conductivity of the 3DS-TEMCs compared with energy storage materials of a single composition. In this respect, 3DS-TEMCs with the infill density of only 30% show thermal conductivities of 0.45–0.57 W/(m K), which are approximately 2.5–3.2 times higher than that of octadecane. This implies that simply integrating the PCMs into the conductive backbone structure fabricated by 3D printing can remarkably improve the thermal conductivity, whereas the latent heat of the 3DS-TEMCs could be tuned by the infill density.
A more intriguing finding is that the thermal conductivity (~0.57 W/(m K)) of the 3DS-TEMC with a high concentration of MWCNTs (~6 wt.%) is higher than that of the thermally conductive TPE backbone (0.49 W/(m K)). This indicates that an optimal formulation of 3D-printed resin or filament incorporated with the MWCNT/GNP nanomaterials can significantly increase the thermal conductivity of the PCM, whereas the loss of latent heat can be minimized using functional additives at small weight percentages. However, an excess of MWCNT (~8%) is not effective in improving the thermal conductivity (~0.53 W/(m K)). At the MWCNT concentrations greater than 6%, the MWCNTs that connected the gaps in the GNP network aggregated together, forming unstable interfaces between the 3D-printed structures and infilled nanocomposite PCM, thereby reducing the thermal conductivity (Figure S2) [11]. Meanwhile, as the infill density increases from 60 to 80% at a constant 6% MWCNT content, the thermal conductivity also increases from 0.62 to 0.79 W/(m K). These values are 3.44 and 4.39 times higher, respectively, than the thermal conductivity of pure octadecane. This result confirms that using the TPE backbone structures in the 3DS-TEMCs could improve the heat transfer passing through the entire composites. The change in the infill density was still effective in improving the thermal conductivity because it only utilized the conductivity of the supportive backbone without agglomeration or interfacial contact resistance, despite the high occupancy (~80%). One of the critical issues in passive cooling using PCMs is their low thermal conductivity, while superb latent heat has attracted considerable attention for the timely management of thermal energy distribution. Thus, the 3DS-TEMCs incorporating conductive MWCNT/GNP filler into the 3D-printed conductive TPE backbone at the nano-/micro-/macroscale significantly improved the thermal conductivity of octadecane, thereby resolving the intrinsic limit of PCM-based passive cooling. The synergistic effects of the inner micro-/nanothermal conductive networks via MWCNT/GNP functional additives and the external macroconductive 3D-printed backbone housing enabled scalable and tunable thermophysical properties for PCMs [31].

3.3. Use of 3DS-TEMCs to Mitigate Overheating and Thermal Shock under Transient Thermal Loads. The developed 3DS-TEMCs showed higher thermal conductivity than conventional polymeric structures, while the latent heat was adjustable through the PCM fill rate. Herein, 3DS-TEMCs
were tested to absorb the local thermal energy generated during the operation of electronic devices or batteries. The prepared 3DS-TEMCs maintained their original shape and structure during the repetitive phase change cycles between the solid and liquid phases. Additional housing or enclosures for containing and sealing the PCM were not required, thereby providing versatile structural capabilities for passive cooling components. Mitigation of overheating and thermal shock experiment was demonstrated under transient thermal loads targeting the operating temperatures of electronic devices and batteries, simulated as local heating configurations via a film heater and 3DS-TEMC (30 mm × 30 mm × 5 mm, single-faced open) (Figure 8(a)). The experiment started with adiabatic natural convection at 20°C. First, the film heater, controlled by a power supply, consistently applied transient thermal load (~1 W) for 1800 s. Subsequently, the thermal load was terminated by turning off the film heater for a cooling duration of 1800 s (Figure 8). When bulk TPE was used as the cooling component, the maximum temperature reached 41.43°C without presenting a latent heat regime. Meanwhile, the maximum temperatures reached when using the 3DS-TEMCs with 30%/6%/1%, 60%/6%/1%, and 80%/6%/1% inll density/MWCNT/GNP were 38.48, 40.73, and 40.85°C, which are 2.95, 0.7, and 0.58°C lower than when using bulk TPE. Moreover, the shapes of the transient temperature curves indicate the presence of latent heat of fusion, confirmed by the sudden slope changes near the phase-change temperature points. It should be noted that the surface temperature of the film heater is constant during this period owing to the release of phase-change energy. Considering the 3DS-TEMC infll density, the 3DS-TEMC with 30% infll density exhibits the smallest temperature difference between the maximum and minimum points under the heating-cooling conditions because it contains the greatest amount of the PCM nanocomposite. The PCM in the 3DS-TEMCs could suppress overheating under the melting point of the PCM in a timely manner, while the enhanced thermal conductivity provided faster thermal transport, thereby extracting the local heat energy.

The tunable ranges of the latent heat and thermal conductivity in the 3DS-TEMCs are plotted in Figure 9 along with those of other thermal energy storage materials reported in previous studies to compare the thermal properties. The use of the MWCNT/GNP functional additives and 3D-printed thermally conductive backbones allowed the 3DS-TEMCs to simultaneously exhibit good latent heat of fusion and thermal conductivity. The major purpose of the developed 3DS-TEMCs is improving the mechanical complement of the conventional PCMs, while it offers the advanced thermal functionality that optimizes the latent heat and thermal conductivity, as shown in Figure 9. For this purpose, the PCM (octadecane) infll density/MWCNT/GNP concentration in multiscale was selected to tune the thermal characteristics. Because the TPE backbone thermal conductivity is higher than that of the pure octadecane (Figure 7), the lower infll density results in the low thermal conductivity, whereas the latent heat increases. In terms of the MWCNT/GNP portions, increasing their concentration would provide thermal pathways along the percolation networks, thereby improving the heat transfer, until there is no severe agglomeration of the MWCNT/GNP fillers (MWCNTs ratio < 6%). The anisotropic structures of the 3DS-TEMCs might involve the directional dependence of the mechanical reinforcement and thermal conductivity. However, when the 3DS-TEMCs are compared with the sponge-like porous foam structures, the improved mechanical strength and modulus are secured in all directions [32]. The measured thermal conductivity (Figure 7) was averaged in all directions through the laser flash method, and the obtained value could represent the thermal property of the 3DS-TEMCs. Meanwhile, the latent heat (Table 2) highly depends on the infll density of the inner PCMs that experience solid-liquid and liquid-solid phase changes, whereas the MWCNT/GNP portions do not significantly contribute to manipulating the corresponding values. This result implies that effective nanofillers and externally supportive structures can extend thermophysical properties that are potentially useful for advanced passive cooling components.

4. Conclusions

We demonstrated the tunability of the thermal properties of PCMs through the use of 3D-printed thermally conductive diagonal porous structures and MWCNT/GNP functional additives as complementary conductive constituents on the macro-/micro-/nanoscale. Nanocomposite PCMs were fabricated by combining octadecane with MWCNT/GNP nanomaterials to form internally conductive percolation networks and the supportive structures using 3D-printed TPE filaments as thermally conductive external supports and housing for containing the nanocomposites. The solution intercalation method was used to improve the uniform distribution of MWCNTs and GNPs that could promote heat
transfer, boosted by the synergistic effect of one-dimensional and planar thermal transports. Vacuum permeation enabled the integration of the nanocomposites into the porous backbone structures. Thus, 3DS-TEMCs with different preparation parameters (3D-printed backbone infill density/MWCNT/GNP) were fabricated to investigate the individual contributions of the constituents to variations in the thermophysical properties. The dependency of morphological transition on the MWCNT/GNP ratios provided the optimal filler concentrations (~6%/1% of MWCNT/GNP) to form percolation networks without the agglomeration of the nanomaterials. The compositional transitions in the 3DS-TEMCs were examined through FTIR spectra, confirming the absence of chemical reactions or the presence of other materials during fabrication. Considering thermophysical properties, the latent heat and thermal conductivity were adjusted by choosing the appropriate infill density/MWCNT/GNP parameters. The thermal decomposition of the 3DS-TEMCs was used to evaluate the thermal stability of the composite as well as its constituents through thermal decomposition rates and corresponding temperatures. The latent heat was tunable in the range between the values for PCM and TPE backbone (100% and 0% cases in terms of PCM occupancy), and the 3DS-TEMCs exhibited highly enhanced thermal conductivity (3.44–4.39 times that of pure octadecane), enabled by incorporating the thermally conductive constituents at nano-/micro-/macroscale. The plot of the thermal conductivity and latent heat for 3DS-TEMCs revealed new areas of complementary thermophysical properties compared with previously reported thermal energy storage materials for passive cooling applications. Finally, the 3DS-TEMCs were directly applied to mitigate overheating and thermal shock under transient thermal loads, which simulated the threshold temperatures and cyclic heating and cooling of electronic devices and batteries. It was confirmed that the size of 3DS-TEMC can be easily changed, and the maximum temperature of 3DS-TEMCs (30%/6%/1%) was 2.95°C lower than that of the only TPE backbone structure, while the temperature rising rate was the lowest among the control samples. The rational design of tunable and scalable 3DS-TEMCs using multiscale conductive supports and additives is expected to yield new thermal energy storage materials for versatile passive cooling applications, potentially useful for electronics, wearable platforms, mobility platforms, and energy conversion/storage systems.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this study.

Authors’ Contributions

Chanho Song and Jaemin Lee contributed equally to this work.

Acknowledgments

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Supplementary Materials

Additional figures present thermal stability of 3DS-TEMCs under long-time exposure to 40°C (Figure S1) and MWCNT networks in 3DS-TEMCs with different MWCNT concentrations (Figure S2). Table S1 presents uncertainty of characterization and passive cooling capabilities test of 3DS-TEMC. (Supplementary Materials)

References


