

Solid-solid latent thermal energy storage in nanotube-reinforced pentaerythritol and pentaglycerine composites

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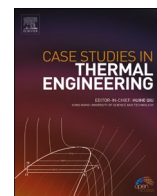
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# Solid-solid latent thermal energy storage in nanotube-reinforced pentaerythritol and pentaglycerine composites

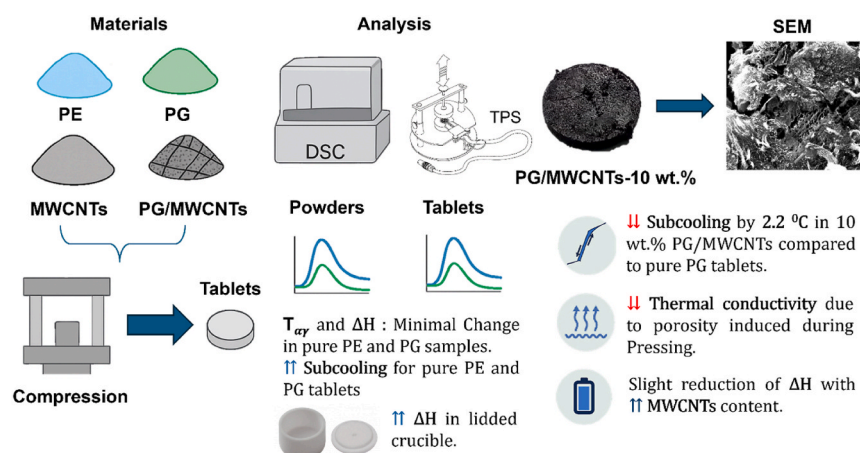
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Solid-solid phase change materials (SS-PCMs) offer promising capabilities for thermal energy storage due to their high latent heat density, minimal volume change, and inherent form-stability.

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Pentaerythritol  
 Pentaglycerine  
 MWCNTs  
 Thermal energy storage  
 Thermal conductivity

This study investigates an experimental case study of the solid-solid phase transition of pentaerythritol (PE) and pentaglycerine (PG) composites enhanced with multiwalled carbon nanotubes (MWCNTs) designed for low to high thermal energy storage systems. The materials were also fabricated as cold pressed tablets and evaluated their phase transition behaviour, subcooling characteristics, and effective thermal conductivity. The effect of MWCNTs on subcooling and their influence on thermal conductivity in cold pressed SS-PCM tablets are also investigated. Differential scanning calorimetry analysis of powders revealed that pure PE exhibits a solid-solid transition at approximately 199 °C with latent heat around 280 kJ/kg in a closed experimental setup, significantly reducing mass loss. Pure PG demonstrated a stable phase transition at about 95 °C with latent heat of approximately 183 kJ/kg. Tablets prepared by cold pressing showed increased subcooling effects, notably mitigated by the addition of up to 10 wt% MWCNTs, which reduced subcooling by about 2.2 °C. However, thermal conductivity decreased unexpectedly from 0.364 W/(m K) for pure PG to 0.269 W/(m K) at 10 wt% MWCNT loading. This reduction is attributed to increased porosity introduced during tablet fabrication, which enhances phonon scattering and counteracts the intrinsically high thermal conductivity of the MWCNTs. Numerical modelling supported the dominant role of porosity on thermal transfer performance. Despite the reduced thermal conductivity, nanotube-reinforced composites retained high latent heat capacities (>150 kJ/kg), highlighting the potential of PE-based composites for high-temperature applications and PG-based composites for low-temperature thermal energy storage. The results demonstrate the critical influence of fabrication induced microstructure on thermal performance and provide insights for optimizing filler content and densification strategies in solid-solid latent heat storage systems. Future research should focus on optimizing filler content and porosity reduction to enhance thermal conductivity without sacrificing latent heat performance.

## 1. Introduction

Solid-solid phase change materials (SS-PCMs) hold significant promise for thermal energy storage applications due to their advantageous properties. These materials exhibit high latent heat storage density and minimal volume changes. Moreover, SS-PCMs undergo an isothermal phase transition, ensuring a constant temperature during both heat storage and release processes. Notably, they exhibit inherent form-stability, eliminating the need for encapsulation, which simplifies integration and reduces potential leakage concerns [1,2]. While SS-PCMs offer several compelling advantages for thermal energy storage, their successful implementation in real-world applications demands consideration of several factors, such as subcooling, thermal conductivity, reliability, mechanical and thermal stability. Subcooling refers to the phenomenon observed during the cooling process of a PCM, wherein the material undergoes a phase transition at a temperature lower than its theoretical or anticipated phase transition temperature. Consequently, significant temperature differentials are required to fully exploit stored energy. Furthermore, low thermal conductivity may hinder the charging and discharging rate. Reliability, mechanical and thermal stability are fundamental attributes essential for materials in practical applications, particularly those exposed to numerous thermal cycles over prolonged periods [3–5].

Several classes of materials hold promise for SS-PCM applications, including polymeric SS-PCMs [6], perovskites [7,8], and polyalcohols [9,10]. Polymeric SS-PCMs can be synthesized through various methods such as chain grafting [11], cross-linking copolymerization [12], facile bulk polymerization [13], and block polymerization [14]. Alkan et al. [15] synthesized polyurethane (PUs) SS-PCMs using three types of diisocyanate molecules and polyethylene glycols with three different molecular weights. They demonstrated that these PUs exhibit solid-solid transition properties with enthalpies as high as 179 kJ/kg at temperatures ranging from 19 to 60 °C, indicating their potential for use as solid-state PCMs in thermal energy storage systems. Zhou et al. [16] introduced a novel method for fabricating crosslinked PU-based SS-PCM reinforced with graphene oxide. This innovation resulted in a PU-based SS-PCM with exceptional light-thermal conversion capabilities. However, the synthesis of polymeric SS-PCMs often faces challenges, including the use of toxic organic solvents, intricate procedures, and time-consuming reaction, which may limit their environmental sustainability and economic viability.

On the other hand, perovskites, a class of organometallic compounds, exhibit a sandwich-like crystalline structure characterized by alternating inorganic and organic components [7,8]. Di et al. [8] synthesized two perovskite compounds ( $(1-C_{15}H_{13}NH_3)2CdCl_4(s)$  and  $(1-C_{16}H_{33}NH_3)2CdCl_4(s)$ ) and characterized their crystalline structures using X-ray crystallography and low-temperature heat capacities via adiabatic calorimetry. They also examined their thermodynamic properties associated with their solid-solid phase transitions. In another study [7], two additional crystalline compounds,  $C_{10}Cu(s)$  and  $C_{11}Cu(s)$  were fabricated via a liquid-phase reaction, with their solid-solid phase transition thermodynamics determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) techniques. Despite the promising structure of perovskites, their phase change enthalpy typically ranges from 62.6 to 153.8 kJ/kg, which is considered insufficient for TES applications [17].

Consequently, polyalcohols have emerged as the most promising candidates for SS-PCMs. These materials undergo reversible solid-solid phase transitions from a low temperature ordered layered structure to a high temperature orientationally disordered structure. These materials are often referred to as *plastic crystals* [18–20]. Extensive literature exists concerning the investigation of the thermodynamic properties of these materials [21–24]. The most commonly used polyalcohols for TES applications include mainly pentaerythritol (PE), pentaglycerine (PG), neopentylglycol (NPG) and tris(hydroxymethyl)amino methane (TAM). While polyalcohols offer high latent heat and reasonable transition temperatures, several key factors must be considered for practical implementation.

These include thermal conductivity and subcooling. Researchers are exploring avenues to improve thermal conductivity by incorporating various additives [25–27]. PE, with its favourable transition temperature of 180 °C, has emerged as a prime candidate for industrial applications. Studies have investigated the effects of incorporating various fillers, such as alumina particles and copper nanoparticles, on the thermal performance of PE-based composites [28–30]. However, recent research has shifted focus toward utilizing carbon-based materials as a potentially superior method for enhancing thermal conductivity in PE.

Liu et al. [31] investigated the doping of PE with graphene powders, at concentrations of up to 3 wt%, and compared its effectiveness with that of alumina particles. Their analysis revealed that the expanded carbon atom spacing in graphene facilitated enhanced interaction with PE, leading to improved heat transfer. Zhang et al. [32] introduced a novel approach for fabricating composite solid-solid PCMs with improved thermal conductivity by incorporating expanded graphite (EG) as a nanofiller into PG. The fabrication process involved ball milling for initial homogenization, followed by complete melting of the PG at 300 °C and subsequent solidification. The study investigated the impact of varying EG weight fractions (up to 4 wt%) on the thermal properties of the solid-solid PCM. They found a substantial increase in thermal conductivity, reaching 0.944 W/mK compared to 0.35 W/mK for neat PG. This improvement was achieved with a minor decrease (3.55–4%) in the latent heat storage capacity and a reduction in subcooling, with a minimal temperature difference of 5.8 °C. Building on this work, Zhang et al. [1] explored the effects of graphene nanoplatelets (GnPs) on the structure and thermal behaviour of PG-based composites. They examined the influence of varying GnP concentrations (up to 4 wt%) by melt-mixing the PG-GnP mixture and grinding it to achieve homogeneity. Their findings indicated a physical interaction between PG and GnPs, suggesting that these nanofillers could enhance the thermal performance of PG composites. Notably, incorporating 4 wt% GnPs reduced PG subcooling by up to 3.78 °C and increased thermal conductivity to 0.574 W/mK, demonstrating the potential of these composites for advanced thermal management applications.

Singh et al. [33] reported the one-step synthesis and characterization of NPG/EG microcomposites for enhanced TES applications. They employed a uniform mixing process with varying weight ratios of NPG and EG to improve the thermal performance of the PCM. The morphological and structural characterization of the NPG/EG composites revealed the formation of worm-like structures. These structures leverage the high absorption properties of expanded graphite, contrasting with the sheet-like morphology of natural graphite. Comprehensive characterization using FESEM, FTIR, Raman spectroscopy, and DSC techniques confirmed the successful shape stabilization of the microcomposites. Notably, a significant enhancement in thermal conductivity was achieved, reaching up to ten times that of pure NPG. Similarly, Dai et al. [34] investigated the use of multiwalled carbon nanotubes (MWCNTs) to enhance the performance of the NPG. Their research identified 3 wt% MWCNTs as the optimal loading ratio for the NPG composite. This composite demonstrated a significant reduction in subcooling (by 6 K) without compromising latent heat storage density. Characterization under a pressure of 40 MPa revealed a change in entropy of  $0.39 \text{ kJ K}^{-1} \text{ kg}^{-1}$  and a temperature change of 9.9 K. Furthermore, the minimum pressure required to induce the reversible barocaloric effect was reduced by 19.2%. The composite also exhibited a significant increase in thermal conductivity (approximately 28%), leading to a substantial reduction in heat exchange time during a barocaloric refrigeration cycle. The study further explored the impact of GnPs on the phase transition behaviour, finding that higher GnPs concentrations increased the activation energy for the phase transition and accelerated the transformation of PG from a plastic to a more ordered crystalline phase. Interestingly, the study also revealed nanoconfinement effects that resulted in lower latent heat values compared to the theoretical predictions. This finding highlights the potential of carbon-based materials as prominent doping agents for enhancing the thermal performance of PCMs. However, their practical implementation can be limited by agglomeration and poor dispersion within the composite, which may reduce the uniformity of heat transfer and constrain the overall effectiveness of the filler.

This study presents an application oriented evaluation of PE and PG materials as solid-solid phase change materials for low to high thermal energy storage systems, with a particular focus on solid-solid phase transition kinetics, latent heat, and subcooling behaviour. The investigation includes multiple analyses using DSC to measure the latent heat associated with their solid-solid phase change temperature. To simulate the practical integration conditions, the materials were fabricated into cold pressed tablets to evaluate the impact of densification on their thermal properties. To address the mass loss in PE material, a closed system was employed to ensure repeatable and reliable performance. Furthermore, we also examine the influence of the pressing process and doping with MWCNTs on the thermal properties of PG-based composites. The effect of MWCNTs on subcooling and their influence on thermal conductivity in cold-pressed SS-PCM tablets are also investigated. SEM was employed to characterize the structure and elemental composition of the PG/MWCNTs PCMs. Finally, thermal conductivity measurements were conducted at room temperature for both pristine and MWCNT-doped PG tablets to evaluate the effects of processing and filler addition, thereby providing design relevant insights for optimization of solid-solid thermal energy storage systems.

## 2. Materials and methods

### 2.1. Materials

2,2-Bis(hydroxymethyl)propane-1,3-diol, commonly known as PE and 1,1,1-Tris(hydroxymethyl)ethane, commonly known as PG, were obtained from Sigma-Aldrich with a purity of 99% and investigated as solid-solid PCMs. Additionally, commercially available highly conductive MWCNTs were selected as an additive for PG. These MWCNTs have a purity exceeding 95%, an outer diameter of less than 8 nm, and a length ranging from 10 to 30  $\mu\text{m}$ .

### 2.2. Fabrication of tablets

The experimental characterization involved two sample configurations: loose powders and compacted tablets of neat PE and PG

materials. Tablet preparation was carried out using a uniaxial cold pressing technique, in which the powders were compressed within a cylindrical stainless-steel die using a hydraulic press. This approach offers advantages such as high production rate and cost-effectiveness, though it is limited in shaping flexibility. The compaction mold, specifically designed for tablet preparation, had a diameter of 10 mm. PE and PG powders were loaded into the die cavity, and uniaxial compaction was achieved by applying 510 MPa with the top die. The compacted tablets were then ejected using the upward movement of the bottom punch (see Fig. 1).

For composite tablets, PG and MWCNTs were manually pre-mixed in predetermined weight ratios. The resulting mixtures were then compressed into tablets using the same uniaxial cold pressing technique described earlier. To examine the influence of MWCNT content, PG was reinforced with varying weight percentages (wt.%) of MWCNTs: 1%, 5%, and 10%. The resulting composite PCMs were designated as PG/MWCNTs-1%, PG/MWCNTs-5%, and PG/MWCNTs-10%, respectively, as shown in Fig. 2.

## 2.3. Experimental characterization

### 2.3.1. Differential scanning calorimetry

The solid-solid phase transition temperatures and associated enthalpies of both powders and tablets were determined using DSC (DSC7, PerkinElmer). The DSC can operate with heating and cooling rates adjustable from 0.1 °C/min to 500 °C/min in 0.1 °C increments. The instrument provided a temperature accuracy of  $\pm 0.1$  °C and a calorimetric accuracy of  $\pm 1\%$ , corresponding to standard uncertainties of approximately  $\pm 0.058$  °C and  $\pm 0.577\%$  of the measured value, respectively. The reported accuracies were calculated using the formula [35]:

$$u = \frac{a}{\sqrt{3}}, \quad (1)$$

where,  $u$  represents the standard uncertainty, and  $a$  is the accuracy of the equipment.

Prior to the DSC measurements, the instrument was calibrated using standard reference samples. To minimize thermal lag and ensure sample equilibrium, both heating and cooling ramps were applied. For PE samples, the temperature range was set to 20–250 °C, while for PG and PG/MWCNTs samples it was 0–130 °C, with a heating/cooling rate of 10 °C/min. A 1-min isothermal hold was implemented at the end of each ramp to facilitate thermal equilibration. Nitrogen gas, flowing at 20 mL/min, was used as the carrier gas throughout all experiments. Transition temperatures were identified from the onset points of the DSC curves, and enthalpies were calculated by integrating the exothermic and endothermic peaks using a linear baseline. Sample preparation involved placing both powder and tablet forms of the material into aluminium crucibles. Approximately 20 mg of each sample was precisely weighed and dispensed into the crucibles, which were then inserted into the DSC apparatus for analysis. It should be noted that, despite these precautions, thermal lag and non-equilibrium effects may slightly influence the measured latent heat and transition temperatures.

### 2.3.2. Bulk and true density

The density of neat PE and PG tablets was evaluated using two complementary techniques. First, the bulk density was determined by measuring the diameter, height, and mass of five cylindrical samples for each material. Second, the true density of the PE and PG tablets was measured using Archimedes' principle.

### 2.3.3. Morphology

To assess the morphological characteristics of both neat PG and PG/MWCNTs composite tablets, Scanning Electron Microscope (SEM) analysis was performed with the FEI QUANTA INSPECT 200LV microscope (Hilboro, USA) equipped with an Energy Dispersive X-Ray Analysis (EDAX) detector. The system was interfaced with xT Microscope Control and GENESIS Spectrum version 6.04 from Edax Inc (Mahwah, NJ, USA). The SEM was operated in low vacuum mode at 20 kV and equipped with a backscattered electron

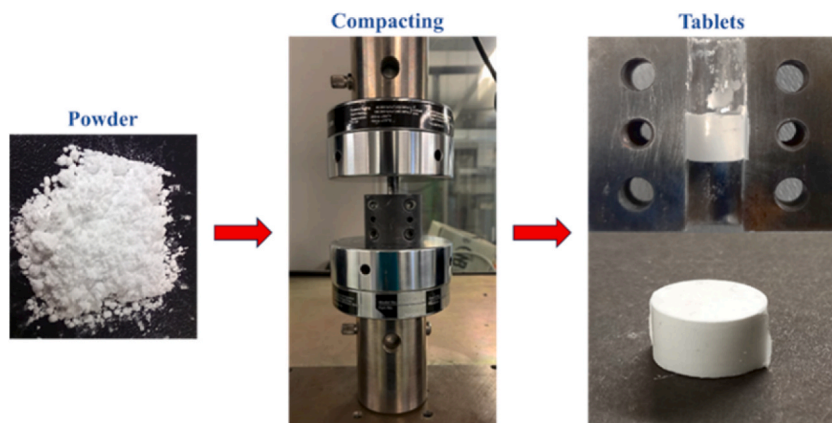


Fig. 1. Stages of tablet forming process.

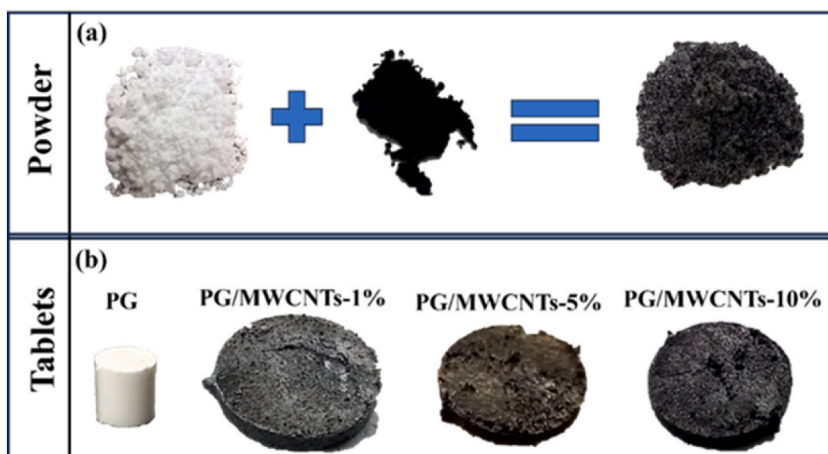


Fig. 2. (a) SS-PCMs and MWCNTs samples in powder form. (b) Snapshots of pelletized composite SS-PCMs for thermal energy storage.

detector (BSED). Operational parameters were carefully configured to prevent any thermal effects that could cause melting of the PG and PG/MWCNTs tablets during the characterization. Prior to observation, all samples were sputtered with a thin layer of gold to enhance conductivity and facilitate clear imaging under the electron beam.

#### 2.3.4. Thermal conductivity

The thermal conductivity of neat PG and PG/MWCNTs samples was measured using the hot disk technique as illustrated in Fig. 3. For this purpose, the samples were compressed into cylindrical tablets with a thickness of 11 mm and a diameter of 20 mm. This method utilizes a transiently heated, disk-shaped sensor that is sandwiched between two identical PG or PG/MWCNTs composite tablets. The sensor consists of a thin double metal spiral sealed between two sheets of Kapton, which serve as electrical insulators. The sensor has four electrical connections: two carry the heating current, while the other two function as a resistance thermometer to measure the voltage drop across the coil. An electrical current pulse is applied to the sensor, causing a temperature increase of several degrees within the sample. Simultaneously, the change in electrical resistance of the spiral, which correlates with its temperature rise through a well-defined thermal coefficient of resistance, is monitored over time. By applying a parameter estimation method that minimizes the deviation between the measured data and a theoretical model, both the thermal conductivity and thermal diffusivity of the sample can be accurately determined.

To ensure compliance with the Hot Disk ISO 22007-2:2015 standard, careful selection of sample and sensor dimensions was carried out. The measurement system consisted of a Hot Disk TPS 500 instrument equipped with a Kapton® sensor (type 5465 F2, radius 3.2 mm). Thermal conductivity measurements were performed at room temperature, with power levels between 20 and 50 mW, and measurement durations spanning from 20 s to 80 s, in accordance with ISO standard recommendations. To ensure reliable data, all thermal properties were measured three times for each sample. The average value with standard deviation was then calculated and reported for each experimental result.

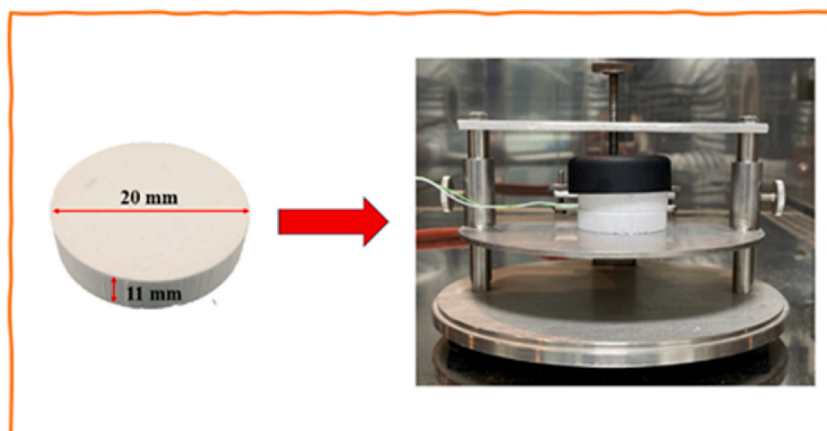


Fig. 3. Thermal conductivity measurement of PG tablet.

## 2.4. Numerical methods

Several effective medium theories have been developed to predict the effective thermal conductivity of polymeric composites. However, due to the distinctive interfacial and interference characteristics of SS-PCMs and MWCNTs, dedicated models are required to accurately describe SS-PCM/MWCNTs composite systems. Moreover, a practical approach for estimating thermal resistance based on bulk properties remains necessary. During the pressing process used to fabricate both neat PG and PG/MWCNT composite tablets, pore defects were inevitably introduced. These porous structures reduced the effective thermal conductivity of the resulting materials. To account for the effects of porosity and interfacial thermal resistance, numerical models were employed to interpret experimental results.

Islam et al. [36] developed one such model by modifying the classical Maxwell–Eucken-I framework. The original Maxwell model was formulated to estimate the electrical conductivity of systems in which one phase is dispersed within an infinite continuous medium, assuming no interaction among the dispersed particles [37]. Eucken subsequently extended this model to predict thermal conductivity, yielding the Maxwell–Eucken (ME) model, which accommodates composites containing more than one dispersed phase [38]. However, the porous structure of the composites examined in this study deviates from the fundamental assumptions of the ME model. In porous materials, heat transfer is governed not only by the intrinsic properties of the solid phase but also by the size, morphology, and spatial distribution of the pores. Consequently, determining the effective thermal conductivity of such systems is inherently complex, as it necessitates consideration of multiple heat transfer mechanisms and the structural characteristics of each constituent phase. To capture the influence of porosity on effective thermal conductivity, Islam et al. proposed a modified ME model, expressed by the following equation:

$$k_e = k_s \frac{2k_s + k_a - 2(k_s - k_a)\varphi}{2k_s + k_a + (k_s - k_a)\varphi}. \quad (2)$$

Here,  $k_s$  represents the thermal conductivity of the solid phase,  $k_a$  is the thermal conductivity of the air, and  $\varphi$  denotes the porosity. In this model, the thermal conductivity of solid phase ( $k_s$ ) is calculated as the weighted harmonic mean of the thermal conductivity of the individual solid components comprising the materials:

$$k_s = \frac{\sum_{i=1}^n v_i}{\sum_{i=1}^n \frac{v_i}{k_i}}, \quad (3)$$

where,  $v_i$  is the volume fraction of the  $i$ -th solid component, and  $k_i$  is its corresponding thermal conductivity. Since the total volume fraction of all solid components sums to unity, Equation (3) can be rewritten as:

$$k_s = \frac{1}{\sum_{i=1}^n \frac{v_i}{k_i}}. \quad (4)$$

While this model accounts for the effect of porosity, it does not consider the influence of interfacial thermal resistance or the aspect ratio of the fillers. To address these factors, Nan et al. [39] proposed a model for predicting the thermal conductivity of CNT-based composite that incorporates interfacial thermal resistance, CNT diameter, and particle aspect ratio expressed as:

$$\frac{k_e}{k_m} = 1 + \frac{AR^* f}{3} \frac{\frac{k_f}{k_m}}{f + 2 \frac{a_k}{d} \frac{k_f}{k_m}}, \quad (5a)$$

where,  $a_k$  is the Kapitza radius, defined as:

$$a_k = R_k k_m. \quad (5b)$$

$R_k$  denotes the Kapitza resistance, while  $k_m$ ,  $k_f$ , and  $k_e$  represent the thermal conductivities of the polymer matrix, CNTs and the nanocomposite, respectively,  $f$  is the volume fraction of the CNTs in the nanocomposite,  $AR$  is the aspect ratio of the CNTs, and  $d$  is the nanotube diameter. The Kapitza resistance refers to the interfacial thermal resistance at the matrix-particle interface. This resistance arises from the mismatch in phonon spectra between the inclusions and the surrounding matrix and plays a critical role in determining the overall thermal transport behavior of the composites.

This model assumes completely isolated particles and is most suitable for highly dispersed systems with low filler concentrations. To overcome this limitation, Xue et al. [40] developed a more comprehensive model for evaluating the effective thermal conductivity of CNT-based composites. Their model accounts for the effect of Kapitza resistance, nanotube length and diameter, as well as the concentrations of the nanofillers:

$$9(1-f) \frac{k_e - k_m}{2k_e + k_m} + f \left[ \frac{k_e - k_{33}^c}{k_e + 0.14 \frac{d}{l} (k_{33}^c - k_e)} + 4 \frac{k_e - k_{11}^c}{2k_e + \frac{1}{2} (k_{11}^c - k_e)} \right] = 0, \quad (6a)$$

where,

$$k_{11}^c = \frac{k_f}{1 + \frac{2R_k k_f}{d}}; k_{33}^c = \frac{k_f}{1 + \frac{2R_k k_f}{l}} \quad (6b)$$

The models proposed by Nan et al. and Xue et al. were not directly employed in this study, as they do not account for the influence of porosity. To incorporate the effect of porosity, the approach proposed by Chu et al. [41] was adopted, which evaluates the effective thermal conductivity of a matrix containing embedded pores, as follows:

$$k_m^{eff} = k_m \frac{1 - f_{void}}{1 + 0.5f_{void}} \quad (7)$$

$f_{void}^*$  is the effective fraction of pores, defined as:

$$f_{void}^* = \frac{f_{void}}{1 - f}, \quad (8)$$

where  $f$  denotes the volume fraction of nanofillers, and  $f_{void}$  represents the volume fraction of the pores (porosity), which was estimated from the ratio of the theoretical to measured tablet densities. The resulting effective matrix thermal conductivity,  $k_m^{eff}$ , then replaced  $k_m$  in the Nan et al. and Xue et al. models to calculate the effective thermal conductivity of the porous composite while accounting for the effect of interfacial thermal resistance, aspect ratio, and the filler concentration. In this study, these models were evaluated against the experimental results and subsequently used to back-estimate the interfacial thermal resistance.

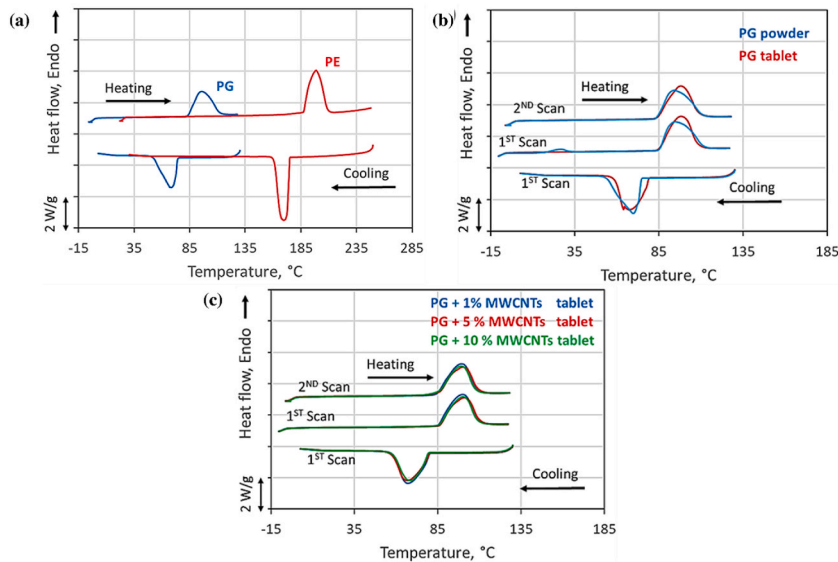
### 3. Results and discussions

#### 3.1. Differential scanning calorimetry

##### 3.1.1. Powders

Initially, DSC was employed to characterize the solid-solid and solid-liquid phase transition temperatures of pure PE and PG powders as shown in Figure S1 (a) and Figure S2 (a), respectively. Distinct peaks in the heat flow rate ( $dQ/|dT| = 0$ ) curve during heating indicate first-order structural phase transitions. These peaks correspond to the solid-solid transition temperatures ( $T_{ss}$ ) of 199.0 °C for PE and 95.0 °C for PG. Similarly, tighter (sharper) peaks in the curve represent the melting temperatures ( $T_m$ ), measured at 266.8 °C for PE and 207.6 °C for PG. The latent heat of solid-solid transition ( $\Delta H$ ), determined by integrating the corresponding peaks after the baseline correction, was 279.99 kJ/kg for PE and 183.22 kJ/kg for PG. Similarly, the latent heat of fusion was calculated by integrating the areas under the melting peaks, which corresponds to the enthalpy absorbed during the solid-liquid transition, resulting in values of 27.44 kJ/kg for PE and 33.81 kJ/kg for PG.

To further investigate the thermal behaviour within the solid-solid phase transition region, multiple DSC scans were conducted on both neat PE and PG powders. The experimental procedure included three heating scans and two cooling scans as shown in Figure S1



**Fig. 4.** Comparison of DSC curves of (a) PE and PG powders, (b) PG powder and tablet and (c) PG/MWCNTs composite PCMs during solid-solid phase transition.

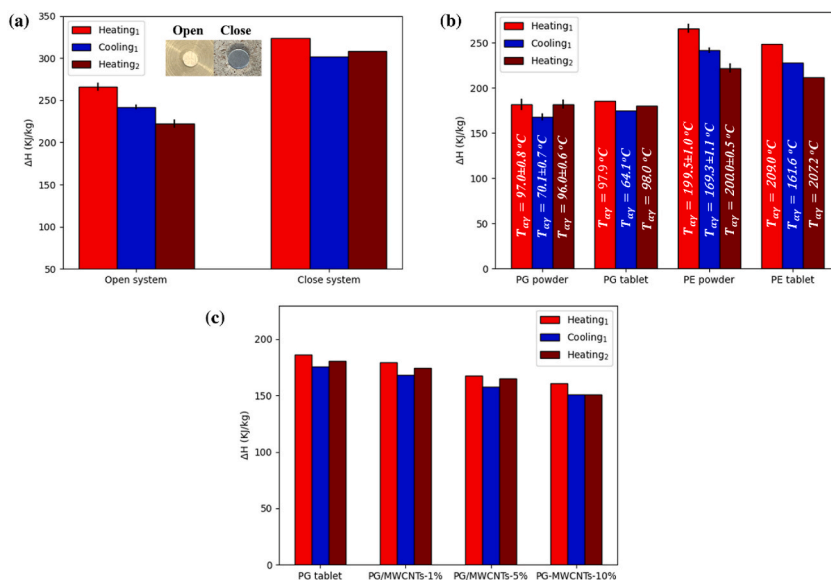
(b) and Figure S2 (b). Analysis of the PE data revealed an average phase transition temperature of  $199.5 \pm 1.0$  °C during the first heating scan, accompanied by a latent heat of  $266 \pm 5$  kJ/kg. The subsequent heating scan exhibited a slightly higher average transition temperature of  $200.0 \pm 0.5$  °C with a corresponding latent heat of  $222 \pm 5$  kJ/kg. These values are comparable to those reported in the literature for heating, where the phase transition temperature and latent heat range from 182 to 192 °C and from 240 to 290 kJ/kg, respectively [28,42–45]. Conversely, the first cooling scan for PE yielded a lower average transition temperature of  $169.3 \pm 1.1$  °C with a latent heat of  $242 \pm 3$  kJ/kg. Literature values reported for cooling indicate phase transition temperatures in the ranges of 162 – 178 °C and latent heat of 238–269 kJ/kg, which are consistent with present results [28,42–45]. Similar trends were observed for PG. During the first heating scan, PG exhibited an average transition temperature of  $97.0 \pm 0.8$  °C and a latent heat of  $182 \pm 6$  kJ/kg. The second heating scan for PG presented a comparable average transition temperature of  $96.0 \pm 0.6$  °C, accompanied by a latent heat of  $182 \pm 5$  kJ/kg. In the first cooling scan, PG showed an average transition temperature of  $70.1 \pm 0.7$  °C with a latent heat of  $168 \pm 4$  kJ/kg. For comparison, literature values report transition temperatures and latent heats for PG of approximately 86 °C and 166–170 kJ/kg during heating, and 76 °C and 162–159 kJ/kg during cooling, respectively [1,32]. A comprehensive comparison of the thermal behaviour of PE and PG powders during the second heating scan is illustrated in Fig. 4 (a). Only the second heating scan is presented here, as it eliminates moisture effects and provides a more accurate representation of the intrinsic thermal behaviour of the materials.

To evaluate potential sample degradation during the DSC scans, mass loss measurements were conducted after multiple scans. PE exhibited a substantial average mass loss of 38%, while negligible mass loss was observed for PG. Mass measurements taken during subsequent scans of PE revealed decreases of 20% for both the first and second scans, and 24% for the third scan. To address the significant mass loss in PE, DSC measurements were conducted using a crucible with a lid, resulting in a reduction of mass loss to 13%. The decrease in mass loss indicates that the phenomenon is mainly attributable to PE sublimation, which may still occur despite the covered configuration because of minor peripheral gaps between the crucible and the lid. This behaviour is commonly observed in certain solid-solid transition materials and has been documented in previous studies [46]. This mitigation strategy resulted in a minimal change in the phase transition temperature but led to a notable increase in the measured latent heat of the phase transition compared to the open system (see Fig. 5 (a)).

### 3.1.2. Tablets

To investigate the influence of sample morphology, tablets with a thickness of 1 mm were fabricated for both PE and PG using a cold pressing technique. For the PG tablets, the phase transition temperature and latent heat exhibited minimal change compared to the powder measurements. In contrast, PE tablets displayed an increase in the phase transition temperature and a decrease in the latent heat relative to the PE powder as shown in Fig. 5 (b). Similar to powder form, PE tablets experienced an average mass loss of 13%, while the PG tablets maintained their mass. Furthermore, the determination of subcooling in phase change materials is not standardized in the literature and two commonly used approaches are reported: (i) peak temperature based and (ii) onset temperature based. In the present study, both approaches are retained to ensure meaningful comparison with the previously published values, as different materials in the literature adopt different criteria.

The subcooling effect using peak temperature approach increased for both materials in the tablet form (see Fig. 6 (a)). In PG, the subcooling effect increased from 26.9 °C (powder) to 33.8 °C (tablet), and for PE, it increased from 30.2 °C (powder) to 47.4 °C (tablet).



**Fig. 5.** Comparison of latent heat of (a) PE powder measured with an open crucible and with a lidded crucible, (b) neat PG powder, PG tablet, PE powder and PE tablet and (c) PG/MWCNTs composite PCM tablets obtained from multi-DSC scans.

Detailed experimental results are provided in Supplementary Note 2. The reported subcooling degree for PE powder using peak temperatures is approximately 24 °C [28]. In contrast, direct comparison with reported subcooling values for PG is limited, as the literature reports subcooling temperatures based on onset temperatures rather than peak temperatures. Using onset temperature, the subcooling temperatures of pure PG in powder and tablet forms were determined to be 7.14 °C and 3.15 °C, respectively. These values are in good agreement with previously reported subcooling ranges for PG powder (6–13 °C) [1,32,47] and PG tablets (3–5 °C) produced using ball milling followed by pressing [3,47].

DSC analysis was also employed to investigate the phase transition behaviour and latent heat of the PG/MWCNTs composite tablets with nominal thickness of 1 mm. To quantify the thermal behaviour within the solid-solid phase transition region, multiple DSC scans were performed, including two heating scans and one cooling scan, as shown in Fig. 4 (b) and 4 (c). The DSC curves for the PG/MWCNTs composite tablets closely resemble those for pure PG, indicating that the incorporation of MWCNTs has minimal influence on the phase transition temperature and latent heat of the composites compared to pure PG. All curves display a sharp peak indicative of a solid-solid phase transition for both PG/MWCNTs composite tablets and pure PG in powder and tablet forms. However, a slight shift in the peak temperature for the composites, relative to pure PG, suggests a minor influence of MWCNTs. Furthermore, the integrated area under the DSC curves for the composites is reduced compared to pure PG. This reduction can be attributed to the decreased mass fraction of PG in the composite material, leading to a corresponding decrease in the overall total latent heat storage capacity. Similar behaviour has been reported in the literature for PG, where the latent heat decreases with increasing nanofiller content in both powder and pressed tablet forms [1,3,32].

Analysis of the DSC curves for neat PG tablets revealed a phase transition temperature of 97.98 °C during the first heating scan, with a latent heat of 186.3 kJ/kg. The subsequent heating scan recorded a transition temperature of 98.0 °C and a latent heat of 180.3 kJ/kg. In contrast, the first cooling scan showed a transition temperature of 64.12 °C and a latent heat of 175.6 kJ/kg. Reported literature values for pressed PG tablets indicate a transition temperature of approximately 80 °C and a latent heat of about 175 kJ/kg [3]. Similar trends were observed for PG/MWCNTs composite tablets. Specifically, the first heating scan for PG/MWCNTs-1% exhibited a comparable transition temperature of 99.6 °C and a latent heat of 179.5 kJ/kg. The second heating scan for PG/MWCNTs-1% showed a transition temperature of 98.9 °C with a latent heat of 174.2 kJ/kg. The first cooling scan for PG/MWCNTs-1% resulted in a transition temperature of 67.0 °C and a latent heat of 168.0 kJ/kg. For the PG/MWCNTs-5% tablet, the first heating scan revealed a phase transition temperature of 100.78 °C with a latent heat of 167.7 kJ/kg. The second heating scan recorded a transition temperature of 99.9 °C and a latent heat of 164.9 kJ/kg. The first cooling scan for PG/MWCNTs-5% produced a transition temperature of 66.6 °C and a latent heat of 157.5 kJ/kg. In the case of PG/MWCNTs-10%, the first heating scan resulted in a transition temperature of 100.0 °C and a latent heat of 160.4 kJ/kg. The second heating scan exhibited a transition temperature of 99.0 °C with a latent heat of 144.3 kJ/kg. The first cooling scan for PG/MWCNTs-10% indicated a transition temperature of 68.4 °C and a latent heat of 150.7 kJ/kg. Since MWCNTs do not undergo a solid-solid phase transition, they do not contribute to the latent heat storage capacity of the PG/MWCNTs composite tablets. Consequently, the latent heat of the composite tablets is inherently lower compared to pure PG, both in powder and tablet form. This trend is further corroborated by the decreasing trend in latent heat with increasing MWCNTs content observed in all DSC scans, as shown in Fig. 5 (c).

Analysis of the DSC heating curves indicated that MWCNTs have a minimal effect on the phase transition temperature of PG. However, the cooling curves suggest that MWCNTs might exert a nucleating effect at lower concentrations. The PG powder exhibited a subcooling degree of 26.90 °C, while the PG tablet showed an increased subcooling degree of 33.86 °C. For the PG/MWCNTs composites, the subcooling degrees were 32.60 °C, 34.28 °C, and 31.60 °C for the 1%, 5%, and 10% MWCNT concentrations, respectively, as illustrated in Fig. 6 (b). In addition, the subcooling effect reduced by approximately 2.20 °C in the PG/MWCNT-10% as compared to the neat PG tablet. These subcooling degrees were calculated using the difference between the peak temperatures of the heating and cooling DSC curves. When the subcooling degree was alternatively determined using onset temperatures, values in the range of 2–3 °C were obtained for all PG/MWCNTs composites, which is consistent with onset-based subcooling values reported in the literature [3].

Supercooling is defined as the difference between the equilibrium phase transition temperature and the onset crystallization temperature observed in the DSC cooling curve. In this study, the supercooling degree of the neat phase change materials (PE and PG) and the PG/MWCNT composites were found to be approximately 20 °C based on DSC analysis consistent with previous study [48]. The incorporation of MWCNTs is expected to influence the crystallization behaviour by providing heterogeneous nucleation sites, which

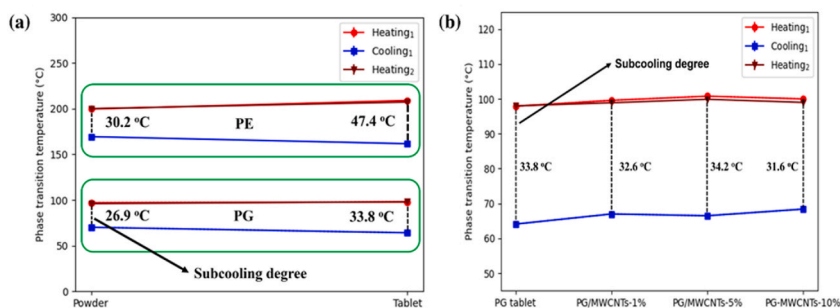


Fig. 6. Comparisons of the phase change temperature for (a) PG and PE and (b) for PG/MWCNTs composite PCM tablets.

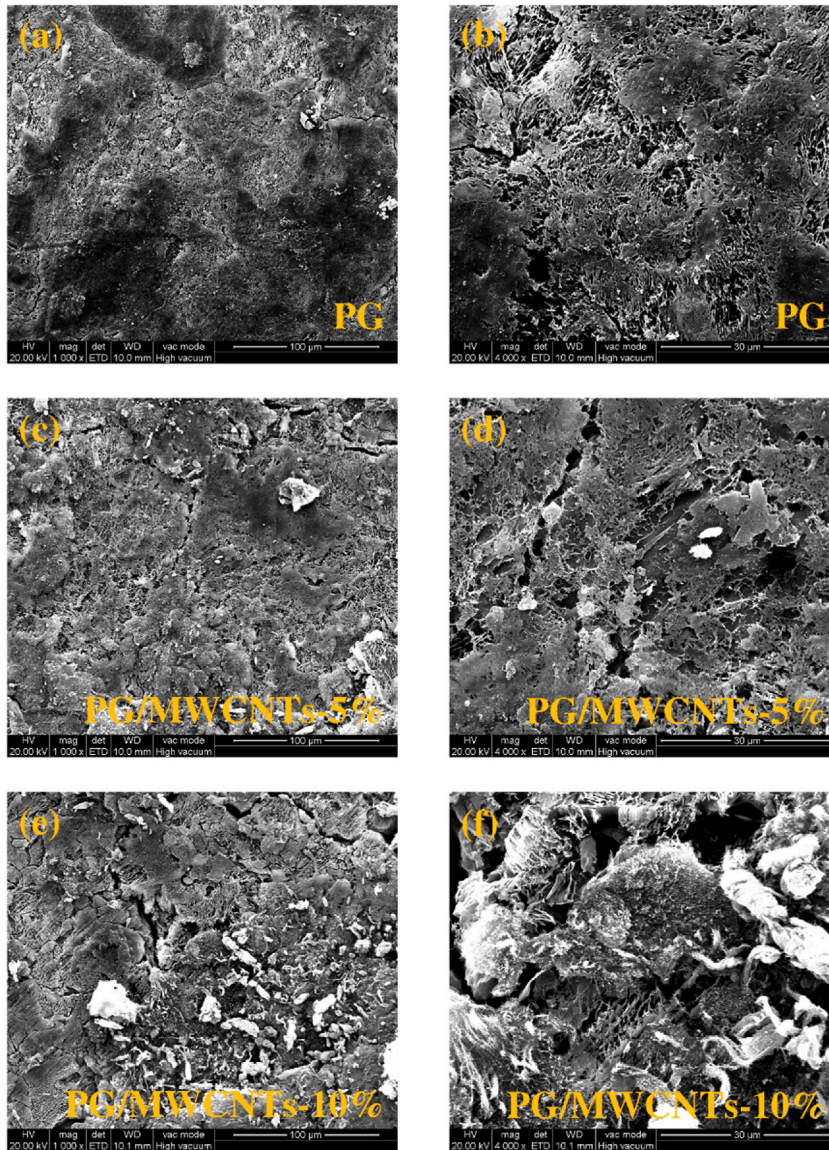
generally promotes crystallization and can help reduce the supercooling of phase change materials. However, in the present system, the measured supercooling remains similar, indicating that the addition level of MWCNTs did not change the crystallization.

### 3.2. Morphology

Fig. 7 depicts the SEM images of uniaxially compressed pristine PG and PG/MWCNTs composite tablets at different magnifications. The images reveal a uniformly structured morphology. At a magnification of 4000 $\times$ , the samples reveal minimal significant defects, although small voids, characteristic of compaction process, are present as slight porosities within the final samples. Microstructure analysis indicates that PG and MWCNTs are thoroughly and uniformly distributed. EDS elemental analysis mapping of the neat PG and PG/MWCNTs composite tablets was performed using EDAX, with detailed results provided in Fig. S3.

### 3.3. Thermal conductivity

The thermal conductivities of the fabricated pure PG and PG/MWCNTs composite tablets were measured experimentally and compared with the results from numerical models (see Fig. 8). The measured thermal conductivity at the room temperature of the pure



**Fig. 7.** SEM images for (a) PG at magnification of 1000 $\times$ , (b) PG at magnification of 4000 $\times$ , (c) PG-MWCNTs-5% at magnification of 1000 $\times$ , (d) PG-MWCNTs-5% at magnification of 4000 $\times$ , (e) PG-MWCNTs-10% at magnification of 1000 $\times$  and (f) PG-MWCNTs-10% at magnification of 4000 $\times$ .

PG tablet was 0.364 W/mK, which is consistent with previously reported value ( $\sim 0.3$  W/mK) for pressed PG prepared using a ball-milling process [3], whereas the thermal conductivity of PG powder was lower ( $\sim 0.23$  W/mK) [1,32]. Interestingly, the addition of MWCNTs resulted in a decrease in thermal conductivity. This trend contradicts the typical behaviour observed in composite materials, where thermal conductivity generally increases with increasing filler content [25–27]. For PG/MWCNTs composites containing 1 wt%, 5 wt%, and 10 wt% MWCNTs, the measured thermal conductivities at room temperature were 0.270, 0.267, and 0.269 W/mK, respectively. These values represent reductions of 25.6%, 26.5%, and 26.0% respectively, compared to the pure PG tablet. This unexpected decrease in thermal conductivity is attributed to the porosity introduced during the tablet fabrication process via uniaxial pressing. The presence of pores disrupts the continuity of the solid matrix and introduces thermal barriers, thereby hindering phonon transport and reducing the overall thermal conductivity of the composites. To account for the effect of porosity, numerical models were employed (Section 2.4).

For the numerical models, the thermal conductivity of the MWCNTs was assumed to be 3000 W/mK, a typical value in the literature for the MWCNTs [49]. In the modified ME-I model, the thermal conductivity of air was taken as 0.026 W/mK under ambient conditions. The key difference among the models lies in how they treat interfacial effects and porosity. The modified ME-I model explicitly accounts for porosity by representing the voids as air-filled regions but neglects interfacial thermal resistance. In contrast, the Nan et al. and Xue et al. models incorporate thermal boundary resistance at the filler-matrix interface, allowing them to capture interfacial effects more accurately in the composites. The results obtained from all the numerical models exhibited a consistent trend with the experimental data, showing a reduction in the thermal conductivity with increasing MWCNTs content. This decrease is attributed to the profound influence of porosity in the composite tablets compared with the pure PG tablets. However, the Nan et al. and Xue et al. models show stronger decrease in thermal conductivity than the modified ME-I model primarily due to the inclusion of interfacial thermal resistance. From the numerical fitting, the interfacial thermal resistance between PG and MWCNTs was estimated to be  $1.0 \times 10^{-5}$  m<sup>2</sup>K/W. The considered thermal properties and porosity data are summarized in Table S6.

It should be noted that the numerical models used in this study are based on the assumptions of uniformly dispersed fillers and constant thermal conductivity of the MWCNTs. In real composite systems, MWCNT orientation, agglomeration, aspect ratio variation, and nonhomogeneous voids significantly affect thermal transport behaviour. These factors were not considered in the present work because the composites were prepared via cold pressing, and reliable quantitative parameters for the PG-MWCNTs composite are not currently available in the literature. Therefore, the numerical models are intended to provide qualitative trends rather than quantitative predictions of thermal conductivity.

#### 4. Conclusion

This study presents experimental, case-based investigations of novel solid-solid PCMs with enhanced thermal performance for low to high temperature thermal energy storage applications. The summarizing radar plot in Fig. 9 facilitates the targeted design and selection of SS-PCMs for specific applications. DSC scans were initially conducted to identify both solid-solid and solid-liquid transitions. Furthermore, multiple DSC analyses were performed within solid-solid phase transition region of both materials (PE and PG). To assess the potential degradation of PE, a comparison between an open crucible and a lidded crucible was conducted, revealing an increase in latent heat in the crucible with lid. Additionally, the influence of sample morphology was explored by fabricating 1 mm thick tablets of both PE and PG using a cold pressing technique. This process led to an observed increase in the subcooling effect in the tablets compared to the corresponding powders. The enhanced subcooling is likely associated with the compact geometry of the tablets, which restricts crystal nucleation and limits heat dissipation during phase transition.

To address the limitations posed by low thermal conductivity in solid-solid PCMs, MWCNTs were introduced into PG to potentially

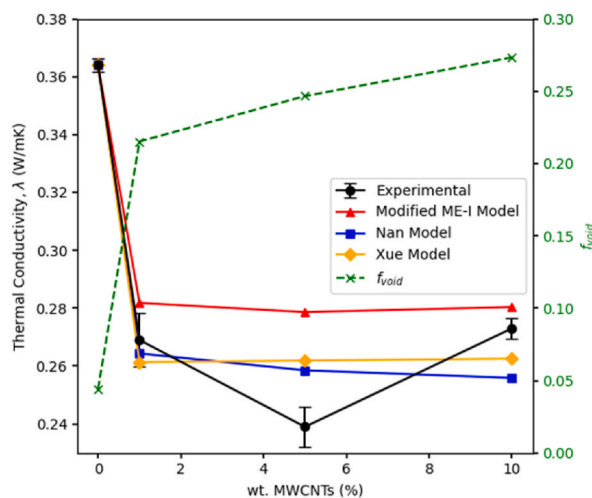
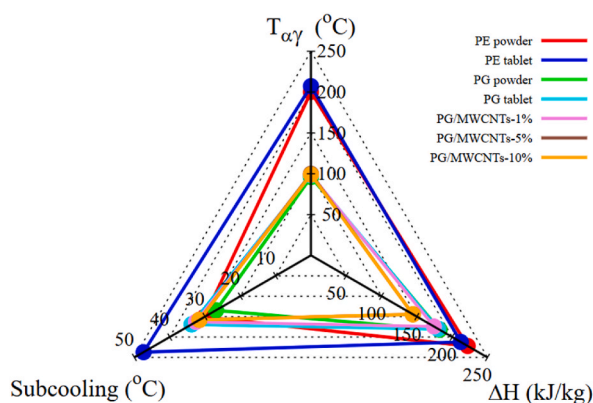


Fig. 8. Thermal conductivity (experiments vs. models) and porosity (experiments) values as a function of the wt.% of MWCNTs in PG tablets.



**Fig. 9.** Radar plot for the key performance parameters (phase transition temperature, latent heat and subcooling degree) for SS-PCMs and their composites.

enhance its thermal properties. PG/MWCNTs composite tablets were fabricated with MWCNT concentrations of 1%, 5%, and 10% by employing a simple and scalable method involving manual mixing followed by uniaxial cold pressing. The phase change behaviour of these composites was investigated using DSC. The results indicated that all PG/MWCNTs composites experienced a solid-solid phase transition at approximately 99 °C during heating scans. However, the incorporation of MWCNTs led to a slight increase in the phase change temperature during cooling scans compared to the neat PG tablet. Furthermore, the subcooling effect was observed to decrease by approximately 2.2 °C for the 10 wt% MWCNT composite relative to the neat PG, suggesting that the addition of MWCNTs improves nucleation efficiency. Concurrently, there was a reduction in the latent heat storage capacity with increasing MWCNTs content, since they do not undergo phase change for the considered temperatures. SEM was employed for morphological characterization revealing a uniform and homogeneous distribution of PG and MWCNTs within the composites.

In addition, thermal conductivity measurements of both neat PG and PG/MWCNTs composite tablets revealed a decrease in thermal conductivity with the addition of MWCNTs. This reduction is primarily attributed to the porosity introduced during uniaxial pressing, which disrupts the continuity of the solid matrix and introduces thermal barriers that hinder phonon transport. These findings are further supported by numerical modelling. Overall, MWCNTs are commonly incorporated into composites to enhance thermal conductivity. In the present study, their addition did not lead to an increase in thermal conductivity due to the porosity introduced during uniaxial cold pressing. Despite this reduction, the fabricated PG/MWCNT composites exhibited several important advantages including reduced subcooling and improved form stability, while maintaining a high latent heat exceeding 150 kJ/kg. These properties indicate excellent thermal energy storage capacity, surpassing that of many polymer-based solid-solid PCMs. This study focuses on solid-solid phase transitions, and long-term stability was not directly assessed. Nevertheless, previous work by Zhang et al. [32] demonstrated that the phase transition temperature and latent heat of plastic crystal-based SS-PCMs change only slightly even after 100 cycles, suggesting that these materials can maintain good thermal stability even after repeated cycles.

Future work will focus on optimizing MWCNTs content and developing fabrication strategies, aiming to reduce porosity through composite densification or surface functionalization of the nanotubes, thereby enhancing both thermal conductivity and latent heat retention for practical applications. From an industrial perspective, scalability and cost considerations associated with the use of MWCNTs must also be addressed. Although MWCNTs contribute significantly to form stability, their relatively high cost and challenges related to large-scale dispersion and processing may limit widespread adoption. Approaches such as minimizing nanotube loading, employing hybrid filler systems or using alternative conductive materials could help balance performance and improve economic feasibility. In addition, the feasibility of hybrid PE/PG-based systems will be explored. Such blends may exploit the high latent heat of PE with the superior thermal stability of PG. This approach could yield an improved balance between energy storage capacity and long-term cycling stability.

#### CRediT authorship contribution statement

**Atta Muhammad:** Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Visualization, Writing – original draft. **Leandro Iorio:** Data curation, Formal analysis, Methodology, Visualization, Writing – original draft. **Elena Campagnoli:** Formal analysis, Investigation, Methodology, Resources, Writing – review & editing. **Valter Giaretto:** Resources, Supervision, Validation, Writing – review & editing. **Matteo Morciano:** Supervision, Validation, Writing – review & editing. **Eliodoro Chiavazzo:** Conceptualization, Methodology, Supervision, Validation, Writing – review & editing. **Fabrizio Quadri:** Conceptualization, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing. **Matteo Fasano:** Conceptualization, Formal analysis, Methodology, Project administration, Supervision, Validation, Writing – review & editing.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Atta Muhammad reports financial support was provided by Higher Education Commission Pakistan. The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.csite.2026.108265>.

## Data availability

Data will be made available on request.

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