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Research Article

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ABSTRACT

In this study, PEG-600/Silica- Alumina composites were developed as shape-stable phase change materials (PCMs) by using ultrasonic-assisted wet impregnation and vacuum impregnation methods to investigate the effects of the preparation method on their thermal performance and structural properties. The comparative evaluation highlights the role of synthesis route on pore-level PEG confinement and phase-change behavior. The mesoporous Si–Al support, with a surface area of $475 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.78 \text{ cm}^3 \text{ g}^{-1}$, provided an efficient porous framework for PEG loading. Nitrogen adsorption analyses showed significant decreases in surface area and pore size after impregnation, particularly for composites prepared by the vacuum impregnation method, indicating more effective pore utilization. Differential scanning calorimetry (DSC) revealed that the composite prepared with vacuum impregnation method (VPCM2) exhibited a melting temperature of $20.96 \text{ }^\circ\text{C}$ and latent heat of 93.62 J g^{-1} , values close to those of pure PEG and indicative of preserved phase-change reversibility under thermal analysis conditions. FTIR and SEM analyses confirmed effective physical confinement, interfacial compatibility, and uniform PEG dispersion within the Si–Al framework, contributing to the enhanced structural integrity and leakage resistance. Overall, the results demonstrate that vacuum impregnation provides superior pore filling, improved phase-change efficiency and thermal response, and enhanced thermal reliability compared to ultrasonic-assisted wet impregnation for medium-temperature thermal energy storage applications. From a processing perspective, vacuum impregnation enables higher PEG utilization, which is beneficial for thermally efficient composite design.

Keywords: Shape-stable phase change materials; silica–alumina composites; PEG-600; impregnation strategies; low-temperature thermal energy storage.

1. INTRODUCTION

With the growing global energy demand and limited availability of conventional resources, efficient and economical energy utilization has become an urgent necessity. The rapid increase in global energy consumption and climate-induced temperature fluctuations further emphasize the need for advanced thermal management solutions. In particular, the integration of efficient thermal energy storage systems is considered essential for improving energy sustainability and reducing greenhouse gas emissions, as highlighted by recent International Energy Agency reports [1]. Among various energy management strategies, latent heat thermal energy storage (LHTES) systems based on phase change materials (PCMs) have attracted significant attention because PCMs can store and release large amounts of heat during phase transitions while maintaining relatively stable temperatures, thereby reducing heat loss and decreasing the required storage volume [2–6]. In this context, understanding the thermal behavior and phase-transition characteristics of storage materials is essential for optimizing heat storage efficiency and operational reliability.

PCMs have been extensively applied in diverse fields such as building energy conservation, solar heating and cooling systems, thermal-regulating textiles, temperature-controlled greenhouses, and air-conditioning systems [7–11]. Their application is also expanding into electronic thermal management and advanced thermal energy storage systems due to their high latent heat, stable phase reversibility, and operational reliability [12–14]. Across these applications, the thermal response, phase stability, and heat-flow characteristics of PCMs play a decisive role in determining system performance.

According to their phase-transition behavior, PCMs can be classified into four main groups: gas–liquid PCMs, solid–liquid PCMs, solid–gas PCMs, and solid–solid PCMs. Among these categories, solid–liquid PCMs are the most widely used due to their high latent heat capacity, nearly constant phase-transition temperature, minimal volume changes during

melting/solidification, and excellent thermal reliability, making them highly suitable for thermal energy storage applications. Additionally, PCMs can be further divided into organic, inorganic, and eutectic types [15-17]. Organic PCMs are particularly attractive for thermal energy storage due to their excellent chemical stability, negligible supercooling, low vapor pressure, non-corrosive nature, and reliable phase-change repeatability over long-term cycling. Their thermal transitions, heat-flow behavior, and phase-change kinetics can be effectively investigated using calorimetric and thermoanalytical techniques. Their safety, environmental compatibility, and wide range of adjustable melting temperatures further increase their suitability for diverse thermal management applications. Commonly used organic PCMs for thermal energy storage applications include paraffin wax (PW), fatty acids such as stearic acid (SA), palmitic acid (PA), and polyethylene glycol (PEG) [18-23].

PEG is one of the most promising organic PCMs because of its high energy storage capacity, chemical stability, non-toxicity, and cost-effectiveness. PEG-600 is especially suitable for medium-temperature thermal energy storage because its melting range (approximately 17–25 °C) aligns well with low-grade heating and cooling applications. This temperature range allows detailed calorimetric investigation of melting–crystallization behavior, supercooling tendency, and latent heat evolution under confined conditions. In addition, PEG-600 exhibits high latent heat, excellent chemical stability, minimal supercooling, and low volatility, making it an effective and safe organic PCM for repeated phase-change cycling. Its molecular weight provides a favorable balance between thermal storage capacity and manageable viscosity in the molten state, which facilitates efficient infiltration into porous matrices [24–26]. However, when PEG approaches its melting point, it undergoes a solid-to-liquid transition accompanied by an increase in molecular mobility. These phenomena are directly reflected in changes in phase-transition temperatures, peak

broadening, and enthalpy loss, which can be effectively quantified by thermal analysis techniques. This results in undesirable leakage, diffusion into surrounding structures, and partial mass loss during operation. In addition to liquid leakage, PEG may experience thermal cycling degradation or a gradual reduction in latent heat due to repeated melting–solidification cycles, which undermines its long-term thermal reliability. These drawbacks significantly restrict the direct use of PEG as a standalone PCM, making structural confinement within porous supports essential to maintain shape stability, suppress leakage, and preserve phase-change performance over extended cycling [27–30]. Common strategies for preparing PEG-based composite PCMs include the eutectic blending method, adsorption (impregnation) of PEG into porous matrices, chemical cross-linking via polymerization, and microencapsulation [26]. Among these, the impregnation method using porous supporting materials has gained particular attention. This method primarily utilizes the capillary forces of the porous framework to adsorb the molten PCM into the pore structure, allowing the composite PCM to maintain a stable shape after energy storage. Therefore, it is noteworthy that the performance of such composite PCMs is closely related to the pore structure of the porous materials and the properties of the supporting carrier. Pore size, connectivity, and surface chemistry strongly influence heat-flow characteristics, nucleation behavior, and phase-transition kinetics of confined PEG. Various porous materials have been used for this purpose, such as activated carbon, perlite, silica, molecular sieves, and aerogels, which offer large specific surface areas and well-developed pore structures that allow PEG to be physically confined within the pores through capillary and surface tension effects, thereby preventing leakage during melting [31,32]. In addition, carbon-based supports (e.g., expanded graphite, graphene, carbon nanotubes) and inorganic oxides (e.g., SiO_2 , Al_2O_3) have also been widely employed to enhance the mechanical stability and thermal conductivity of PEG-based composites [23,33–34]. Silica and

alumina materials are highly attractive supporting matrices for organic PCMs due to their well-developed mesoporous structure, high specific surface area, and strong mechanical and thermal stability. The presence of both silica and alumina provides a synergistic pore architecture that enhances capillary absorption and confinement of the molten PCM, effectively preventing leakage during melting. Moreover, silica–alumina surfaces offer favorable chemical compatibility and weak intermolecular interactions with PEG, which help maintain phase-change reversibility while limiting PCM volatilization or structural degradation during cycling [27, 35]. Silica–alumina was selected not only for its high surface area and mesoporosity, but also for its mechanical robustness and chemical stability, making it a representative and scalable inorganic support compared with purely carbon-based matrices. Such characteristics make silica–alumina an ideal platform for systematically investigating confinement-induced changes in the thermal behavior of PEG using calorimetric methods.

Among the various preparation routes for composite PCMs, impregnation-based techniques are widely employed to incorporate organic PCMs such as PEG into porous supports and obtain shape-stable composites. In the vacuum impregnation method, the porous matrix is first evacuated to remove air trapped within the pore structure, after which molten PEG is introduced. When the pressure is restored to ambient conditions, the resulting pressure gradient and strong capillary forces drive the PCM deeply into the mesopores, leading to high loading efficiency and effective pore utilization. This enhanced pore filling directly influences the thermal response of the composite by promoting more uniform heat-flow distribution and well-defined melting–crystallization transitions during calorimetric measurements. This technique has been widely reported to effectively suppress leakage and improve thermal reliability. For example, Lu et al. prepared PEG/carbon black shape-stable composites by vacuum impregnation and observed

enhanced thermal conductivity and stable phase-change performance [36], whereas Liu et al. demonstrated uniform PEG infiltration and reduced leakage in mesoporous carbon–Cu composites prepared via the same method [37].

In addition to vacuum-driven infiltration, PEG can also be incorporated into porous matrices using the wet impregnation method, in which the PCM is dissolved in a suitable solvent to reduce its viscosity and facilitate penetration into the pore network [38]. However, this method may result in lower PCM loading due to solvent evaporation and limited pore saturation. Ultrasonic assistance significantly enhances wet impregnation by inducing acoustic cavitation, during which microbubbles form and collapse violently, generating localized high-pressure, high-velocity microstreaming. However, the non-uniform local energy input and solvent-assisted diffusion may introduce heterogeneous confinement environments, which can manifest as broadened phase-transition peaks and increased supercooling in thermal analysis. These effects remove trapped air from the pore structure, increase surface wettability, and accelerate PEG diffusion into micro- and mesoporous networks. As a result, ultrasonic treatment improves infiltration uniformity and reduces the likelihood of PCM agglomeration during impregnation, making it a promising alternative for preparing composite PCMs despite its less frequent application compared with vacuum impregnation [39–41]. Therefore, comparing vacuum and ultrasonic-assisted impregnation provides a valuable framework for understanding how processing-induced confinement differences govern the thermal behavior and phase-transition kinetics of PEG-based composite PCMs.

Although both vacuum impregnation and ultrasonic-assisted wet impregnation have been individually applied in the preparation of PEG-based composite PCMs, direct comparisons under identical material compositions and pore structures remain limited. In particular, the influence of

impregnation route on pore utilization efficiency, PEG confinement behavior, and phase-transition reversibility in silica–alumina systems has not been systematically investigated. Most previous studies focus on a single impregnation technique or employ carbonaceous or pure silica matrices, which limits mechanistic comparison under controlled structural conditions. Therefore, this study provides a comprehensive comparison of vacuum impregnation and ultrasonic-assisted wet impregnation to clarify their effects on pore structure, chemical characteristics, thermal performance, and leakage behavior. A detailed assessment based on BET, DSC, TGA, FTIR, SEM, and leakage analysis is carried out to identify the most effective synthesis route for producing PEG-600/silica–alumina shape-stable PCMs. Understanding how impregnation route governs PEG confinement and thermal response is essential for the rational design of shape-stable PCMs intended for medium-temperature thermal energy storage, where long-term reliability and leakage resistance are critical for practical implementation. From both thermal-analysis and sustainability perspectives, the selection of impregnation route directly influences material utilization efficiency, processing-related energy consumption, and scalability; however, comparative studies addressing these aspects simultaneously remain scarce.

2. Materials and Methods

2.1. Materials

Polyethylene glycol (PEG, MW = 600) was used as the phase change material (PCM) and supplied by Merck KGaA (Germany). The supporting material was silica–alumina (Grade 135), containing approximately 13 wt.% Al₂O₃, obtained from Sigma-Aldrich. Ethanol (>99.5%, Merck) and deionized water were used as solvents throughout the preparation processes.

2.2. Preparation of Shape Stable composite PCMs

PEG-600 was incorporated into the pores of silica–alumina using two different synthesis methods: (i) ultrasonic-assisted wet impregnation and (ii) vacuum impregnation.

The compositions of all prepared samples are listed in Table 1.

Table 1. Compositions of Prepared PCMs

Sample	PEG-600 (wt%)	SiO ₂ –Al ₂ O ₃ (wt%)
UPCM1	%30	%70
UPCM2	%50	%50
VPCM1	%30	%70
VPCM2	%50	%50

Before impregnation, the silica–alumina support was thoroughly washed with deionized water and dried in a vacuum oven at 130 °C for 24 hours to remove residual moisture and impurities.

2.3. Ultrasonic - Assisted Wet Impregnation Method:

A predetermined amount of PEG-600 was heated to 30 °C to reduce its viscosity and ensure efficient impregnation. Since PEG-600 melts at approximately 21 °C, it remained fully liquid during processing. To further decrease viscosity and improve diffusion into the pores, a 1:1 (v/v) mixture of ethanol and deionized water was added to the PEG, and the blend was stirred at 800 rpm for 1 hour at 30 °C.

The silica–alumina powder was then added to the PEG solution, and the resulting suspension was treated in an ultrasonic bath at 30 °C for 1 hour to facilitate penetration of the PEG mixture into the porous framework. Ultrasonic treatment was performed using a bath-type ultrasonic cleaner operating at a fixed frequency of 37 kHz and an output power of 200 W. After ultrasonic treatment, the mixture was heated to 80 °C and stirred for 2 hours to evaporate the solvent. The final product was dried in an oven at 80 °C for 16 hours to ensure complete solvent removal and obtain a shape-stable composite PCM.

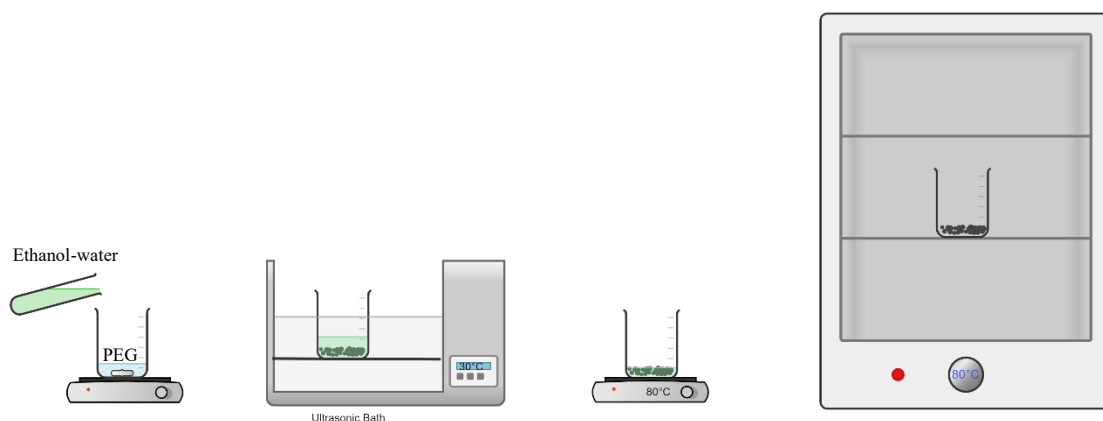


Figure1. Schematic illustration of the ultrasonic-assisted wet impregnation process.

2.4. Vacuum Impregnation Method:

For vacuum impregnation, the dried silica–alumina support was placed inside a vacuum chamber, and preheated PEG-600 was gradually added. A vacuum of ~0.1 bar was applied at 30 °C for 2 hours to remove trapped air from the pore structure. After vacuum application, the chamber was slowly returned to atmospheric pressure, allowing PEG to infiltrate the previously evacuated pores via capillary action. To increase loading efficiency, the vacuum-release cycle was repeated twice.

After impregnation, excess PEG remaining on the surface was carefully removed by blotting the composite with absorbent filter paper, and the final product was cooled to ambient temperature.

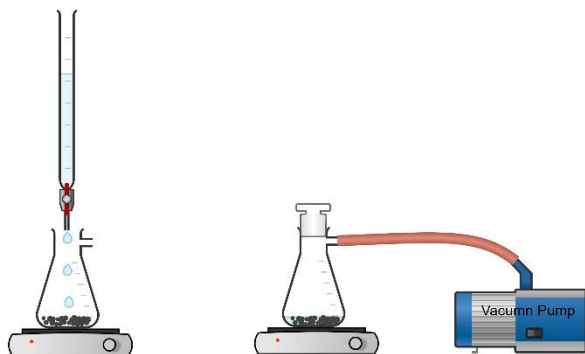


Figure 2. Schematic representation of the vacuum impregnation process.

2.5. Characterization

Textural properties, including specific surface area, total pore volume, and pore size distribution of the Si-Al support and PEG-loaded PCM samples, were determined through nitrogen adsorption-desorption measurements at 77 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the surface area, whereas the Barrett-Joyner-Halenda (BJH) model was applied to evaluate pore size distribution. Textural analysis was employed to correlate pore structure parameters with PEG confinement efficiency and the resulting thermal behavior observed by DSC.

Differential Scanning Calorimetry (DSC) measurements were performed using a TA Instruments Q20 calorimeter to determine the phase-change temperatures and latent heat values of pure PEG-600 and the composite PCMs. All measurements were conducted under a nitrogen atmosphere at a constant heating and cooling rate of 5 °C·min⁻¹ over the temperature range of 0–60 °C. To eliminate thermal history effects, two consecutive heating-cooling cycles were applied, and the thermal parameters were evaluated from the second heating cycle. Latent heat values were calculated using TA Universal Analysis software, and the PEG incorporation rate into the silica-alumina support was determined using Equation (1):

$$\text{Incorporation rate (\%)} = \frac{\Delta H_{m,PCM}}{\Delta H_{m,PEG}} 100 \quad (\text{Eq. 1})$$

where, $\Delta H_{m,PCM}$ is the heat of fusion of prepared PCM composite and $\Delta H_{m,PEG}$ is the heat of fusion of PEG 600.

The chemical structures were examined using Fourier Transform Infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum 100). Spectra were recorded within the 400–4000 cm^{-1} range at room temperature using KBr pellet technique.

The morphological characteristics of the silica–alumina support and composite samples were examined using scanning electron microscopy (SEM, Thermo Scientific Apreo S).

Thermal stability of the samples was assessed through thermogravimetric analysis (TGA) using a TA Instruments SDT Q600 device. Measurements were performed under nitrogen flow from room temperature to 600 °C at a heating rate of 10 °C·min⁻¹. TGA was employed to assess the thermal stability of PEG under confinement and to verify the absence of premature mass loss related to PEG volatilization or leakage

Leakage resistance of the composite PCMs was evaluated qualitatively by heating the samples above the melting temperature of PEG and visually inspecting possible PCM leakage on filter paper.

3. Results and Discussions

3.1 Textural Properties

The textural properties of the Si–Al support and PEG-loaded composites (UPCM2 and VPCM2), prepared via different impregnation methods, were investigated using nitrogen adsorption–desorption analysis, and the BET results are given in Table 2. The Si–Al support exhibits a well-developed mesoporous structure with a large specific surface area of 475 m² g^{−1} and a high total pore volume of 0.78 cm³ g^{−1}, demonstrating its suitability for PCM encapsulation.

Pore utilization percentage was calculated $\phi = \frac{V_{po}-V_p}{V_{po}} 100$

Table 2. Specifications of Si-Al Support and prepared PCMs

	Si-Al support	UPCM2	VPCM2
BET surface Area (m ² g ^{−1})	475	225	185
BJH Adsorption pore volume (cm ³ g ^{−1})	0.78	0.42	0.39
BJH Adsorption pore width (nm)	5.54	4.5	4.1
ϕ (%)	-	46.1	50

After PEG loading, a noticeable decrease in surface area, pore volume, and average pore diameter is observed for both UPCM2 and VPCM2 samples. The surface area decreased by 52% for UPCM2 and 61% for VPCM2, and the corresponding pore volumes decreased to 0.42 cm³ g^{−1} and 0.39 cm³ g^{−1}, respectively. These reductions suggest effective occupation of the mesoporous network by PEG, which is consistent with physical confinement of PEG within the pores of the Si–Al support. Such decreases are consistent with previous studies on PEG/porous-silica composites and are attributed to pore filling and confinement of PEG within the mesoporous network of support [34,44].

The more significant decline in surface area and pore width observed for VPCM2, together with its higher pore utilization percentage ($\phi = 50\%$), suggests a higher degree of effective pore occupation under vacuum impregnation conditions. This observation is consistent with literature reports indicating that vacuum impregnation can enhance capillary-driven uptake and mitigate air entrapment, improving effective pore utilization [24,44-46]. Overall, while both impregnation methods enable PEG incorporation into the porous framework, vacuum impregnation appears to promote more efficient pore utilization, which may contribute to improved thermal performance of the resulting PCM composites.

3.2 Thermal Properties and Latent Heat Storage Capacities

The melting and crystallization behaviors of pure PEG-600 and the composite PCMs prepared via ultrasonic-assisted wet impregnation (UPCMs) and vacuum impregnation (VPCMs) methods were evaluated using DSC, and the results are summarized in Table 3 and Figure 3a–b.

Table 3. Thermal properties and incorporation ratios of PEG-600 and composite PCMs

PCMs	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_c (J g ⁻¹)	Incorporation (%)
PEG-600	21.68	132.91	11.05	104.11	100.00
UPCM1	17.2	75.88	8.22	50.65	57.09
UPCM2	17.99	91.42	6.65	68.29	68.78
VPCM1	18.25	80.12	14.52	54.6	60.28
VPCM2	20.96	93.62	12.6	85.68	70.44

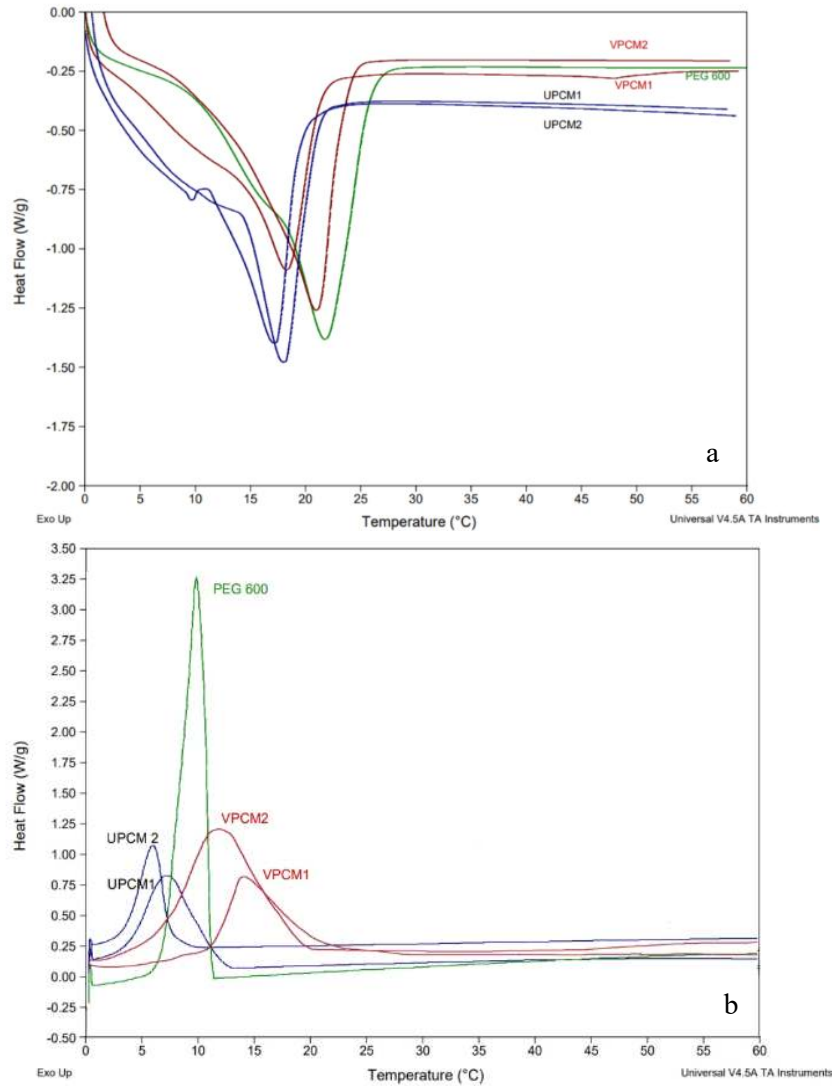


Figure 3. DSC curves of pure PEG 600 and prepared PCM composites a) heating b) cooling cycles

Pure PEG-600 exhibited a sharp melting point at 21.68 °C with a latent heat of 132.91 J g⁻¹ and a crystallization temperature at 11.05 °C. After impregnation into Si-Al support, latent heat of melting (ΔH_m) and latent heat of crystallization (ΔH_c) of all composite samples decreased, which can be attributed to confinement effects within the mesoporous structure. The pore network of the Si-Al support restricts molecular mobility through capillary and surface-interaction forces, inhibiting PEG chain rearrangement and lowering overall phase-change enthalpy [24,25]. The

broadened melting peaks observed in Figure 3a suggest restricted molecular mobility of PEG within the pores and possible partial amorphous behavior for the composites.

Among the composites prepared with 30 wt% PEG, UPCM1 exhibited the lowest latent heat (75.88 J g^{-1}) and incorporation ratio (57.09%). In contrast, VPCM1, containing the same PEG fraction, showed higher latent heat (80.12 J g^{-1}) and an improved incorporation ratio (60.28%), suggesting more efficient PEG uptake under vacuum conditions. A similar trend was observed for the composites prepared with 50 wt% PEG. VPCM2 demonstrated thermal behavior closest to pure PEG, with a melting temperature of $20.96 \text{ }^{\circ}\text{C}$, a high latent heat of 93.62 J g^{-1} , and the highest incorporation ratio (70.44%). Although UPCM2 also contained 50 wt% PEG, it exhibited a lower melting temperature ($17.99 \text{ }^{\circ}\text{C}$), a slightly reduced latent heat (91.42 J g^{-1}), and a lower incorporation ratio (68.78%). The downward shift in melting temperature and broader DSC peaks observed for UPCM2 may be associated with restricted molecular mobility of PEG within the pores, possibly associated with less uniform pore filling or variations in local confinement environments during ultrasonic-assisted wet impregnation.

These results collectively indicate that vacuum impregnation more effectively removes trapped air, enhances capillary-driven infiltration, and promotes uniform PEG distribution throughout the pore network. As a result, VPCM1 and VPCM2 retain phase-transition temperatures and latent heat values closer to pure PEG, demonstrating superior pore utilization and more efficient PCM confinement compared with the ultrasonic-assisted wet impregnation method.

All composite PCMs exhibited significantly lower crystallization temperatures than their melting temperatures, which is attributed to delayed nucleation and restricted segmental motion of PEG molecules within the mesopores [44-46]. The crystallization behavior of the composites (Figure 3b) shows a clear dependence on the impregnation method. UPCM samples exhibit lower

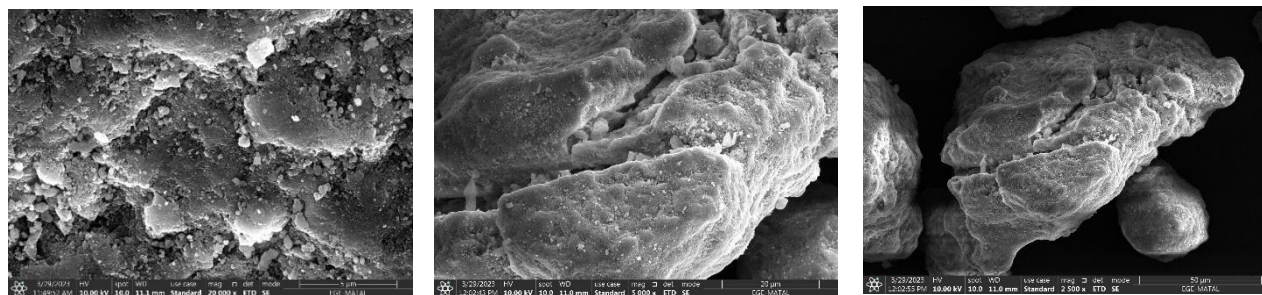
crystallization temperatures, indicating enhanced supercooling and restricted molecular mobility. The lower crystallization temperatures observed in UPCM samples may be associated with less uniform pore filling or limited nucleation site availability, rather than a complete suppression of crystallization. This trend is consistent with previous studies reporting similar T_c depression in PEG confined within mesoporous silica matrices. [24,32]. In contrast, VPCM1 and especially VPCM2 show crystallization peaks closer to pure PEG, indicating reduced supercooling and more efficient PEG crystallization. This improvement is attributed to vacuum impregnation, which enhances pore accessibility by removing air from the pore network and promoting homogeneous PEG distribution. In recent PCM composite studies, the role of vacuum-assisted infiltration in improving nucleation and reducing supercooling has been similarly highlighted [25,32].

Overall, DSC results clearly demonstrate that vacuum impregnation better preserves the intrinsic phase change characteristics of PEG, resulting in higher latent heat, narrower peak shifts, and more distinct thermal transitions. Among all prepared composites VPCM2 emerges as the most promising candidate for thermal energy storage applications due to its excellent thermal response and high PEG incorporation efficiency.

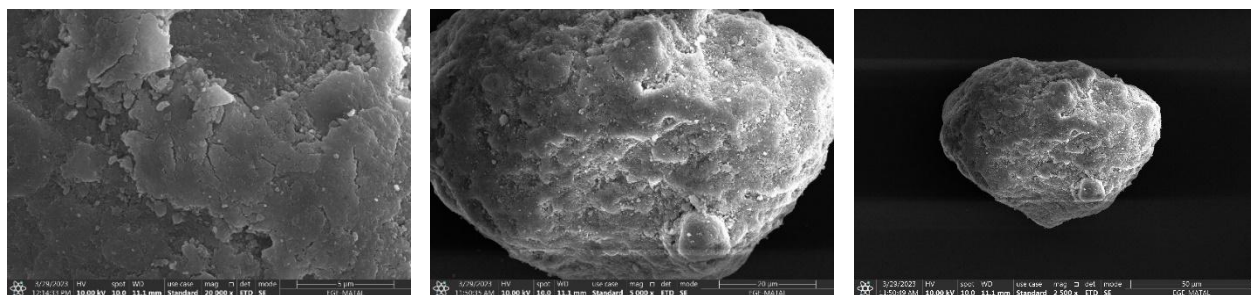
Higher incorporation efficiency achieved via vacuum impregnation implies more effective use of PCM content per unit mass of composite, which is beneficial for reducing material demand in practical thermal energy storage applications.

3.3 Morphological and Chemical Structure Analysis

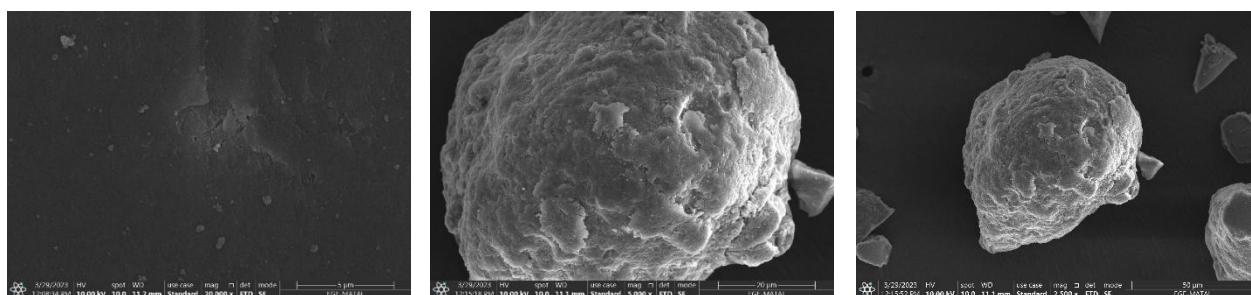
The SEM images of the Si–Al support, UPCM2, and VPCM2 composites were given in Figure 4.



a) Si-Al support



b) prepared PCM composites of UPCM2



c) prepared PCM composites of VPCM2

Figure 4. SEM images of (a) Si–Al support, (b) UPCM2, and (c) VPCM2 at different magnifications (scale bars: 5, 20, and 50 μm), showing overall particle morphology and surface-level PEG coverage.

In Figure 4a, the Si–Al support exhibits a rough, heterogeneous, and highly porous surface with granular texture, which provides a large surface area suitable for PEG impregnation. In Figures 4b and 4c, the PEG-loaded composites prepared by ultrasonic-assisted wet impregnation and vacuum impregnation, respectively, display more rounded particle morphologies and relatively smoother surfaces compared to Si–Al support, indicating surface coverage by PEG.

The composite prepared by the vacuum impregnation method (VPCM2) exhibits a more compact and uniformly smooth surface, suggesting a more homogeneous PEG distribution and more effective coverage of the support structure. In contrast, UPCM2 shows a slightly less uniform surface, with partial exposure of the underlying support, which may be associated with less complete infiltration during ultrasonic-assisted wet impregnation.

Overall, the SEM images confirm that PEG was successfully impregnated in both preparation methods, but they also show that vacuum impregnation achieves more complete pore filling and a more uniform PEG distribution. This observation is consistent with the BET results, which indicate greater reductions in surface area and pore volume for VPCM2.

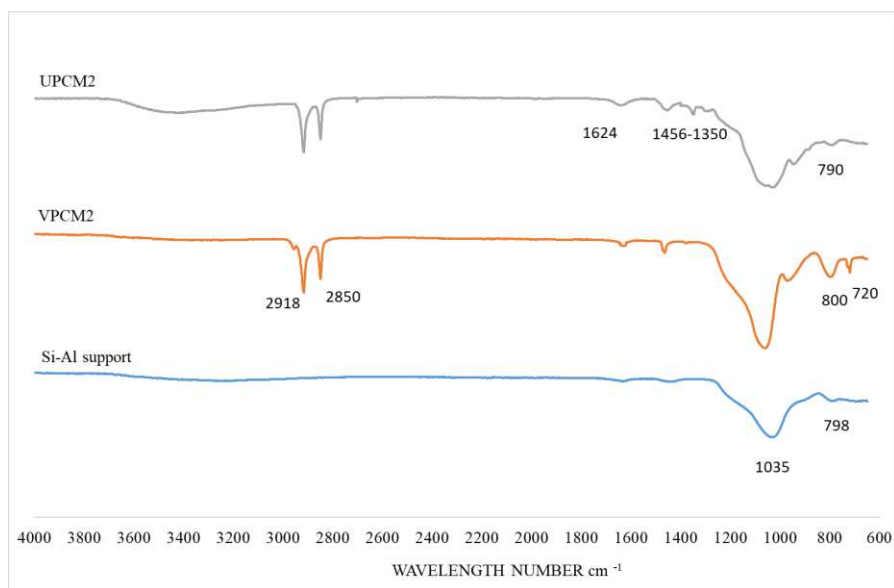


Figure 5 . FTIR Spectrum of Si-Al Support, prepared UPCM2 and VPCM2

FTIR spectra of the Si-Al support, UPCM2, and VPCM2 are shown in Figure 5. The spectrum of the Si-Al support displays a strong absorption band at 1035 cm^{-1} , attributed to the asymmetric stretching vibrations of Si-O-Si or Si-O-Al bonds, confirming the typical structure of the silica-alumina matrix. A smaller peak at 798 cm^{-1} also corresponds to Si-O bending vibrations. Both PCM composites display new absorption bands at 2918 and 2850 cm^{-1} , corresponding to C-H stretching vibrations of $\text{-CH}_2\text{-}$ groups, confirming the presence of PEG. The bands observed around 800 cm^{-1} and 720 cm^{-1} may also correspond to C-H bending vibrations of the polymer chain. A weak band at approximately 1624 cm^{-1} may correspond to -OH bending, possibly due to residual moisture or traces of ethanol-water solvent used during synthesis. These results confirm the successful incorporation of PEG into the Si-Al matrix without significant chemical interaction or structural degradation.

Additionally, no significant peak shifts were observed in the characteristic PEG bands—particularly the O-H stretching region ($\sim 3450\text{ cm}^{-1}$) and the C-O-C stretching region ($\sim 1100\text{ cm}^{-1}$). The Si-O-Si / Si-O-Al band of the support also remained at $\sim 1035\text{ cm}^{-1}$ after PEG loading.

The absence of noticeable wavenumber shifts indicates that PEG is predominantly physically confined within the mesoporous silica–alumina network rather than chemically bonded to the support surface. This finding aligns with previous studies reporting predominantly physical PEG–matrix interactions in mesoporous silica and silica–alumina systems, where confinement occurs without chemical modification of PEG [18,27].

3.4 Thermal Stability and PEG Loading (TGA Analysis)

TGA curves of the Si–Al support, UPCM2, and VPCM2 are shown in Figure 6. Si–Al support shows virtually no weight loss up to 600 °C, confirming its high thermal stability and purely inorganic nature. In contrast, both PEG-loaded composites (VPCM2 and UPCM2 composites) show significant weight loss between 200 °C and 350 °C, which is attributed to thermal decomposition and volatilization of PEG embedded within the silica–alumina matrix. The total weight loss for both samples is about 45 %, indicating substantial PEG loading. The slightly higher residual weight of UPCM2 compared to VPCM2 at elevated temperatures. This difference may be associated with variations in PEG distribution within the porous structure or differences in PEG–support interactions arising from the impregnation route. Importantly, no additional low-temperature weight loss stages were detected, suggesting the absence of free or weakly bound PEG on the composite surface. These results confirm that PEG is effectively confined within the silica–alumina framework and that both composite PCMs exhibit sufficient thermal stability for medium-temperature thermal energy storage applications.

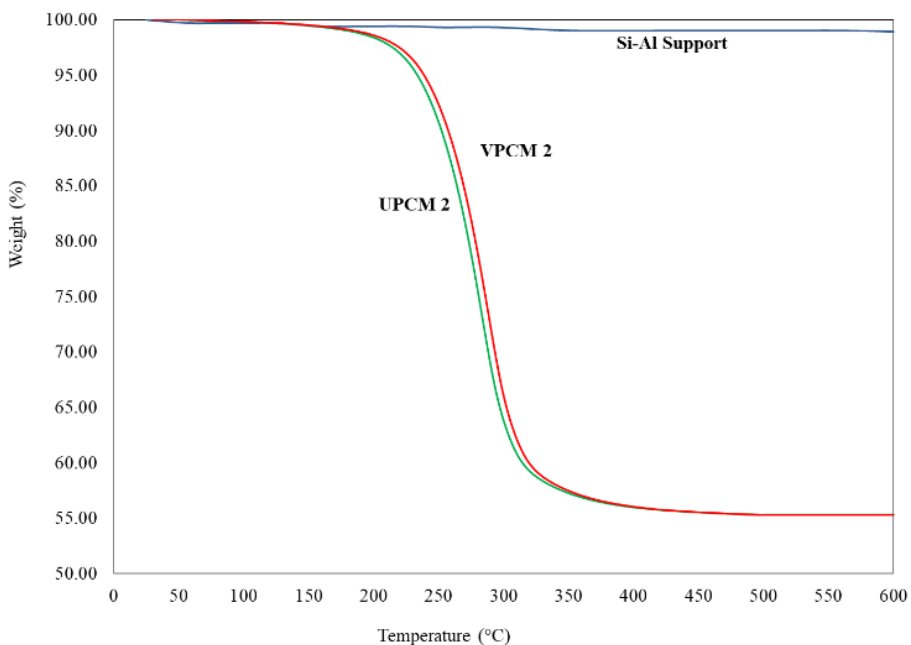


Figure 6. TGA curves of Si-A support, prepared UPCM2 and VPCM2

3.5 Leaching Tests

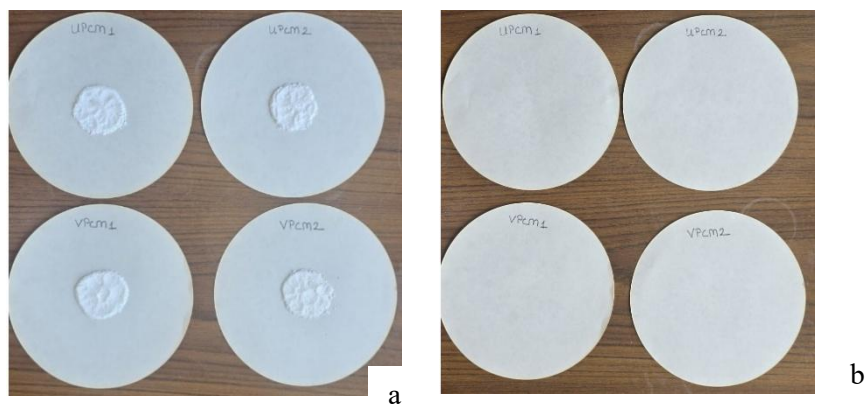


Figure 7. Images of the leakage test of the composite PCMs

A qualitative leaching test was conducted to evaluate the stability and immobilization efficiency of PEG within the silica–alumina support matrix of the prepared PCMs. As shown in Figure 7a, each composite PCM samples were initially placed onto filter paper and subsequently heated in an oven at 40 °C, which is above the melting temperature of PEG-600, for 1 hour. After cooling to

room temperature, the filter papers were visually inspected for signs of leakage. Although qualitative in nature, the leakage test provides a rapid and widely accepted screening method for assessing shape stability in PEG-based composite PCMs.

As seen in Figure 7b, no visible oil stains or melted PEG residues were observed on the filter papers for any of the composite samples, indicating that PEG was effectively immobilized within the porous matrix. The absence of leakage traces is commonly accepted as evidence of successful shape stabilization in form-stable PCM systems, as reported in previous studies [27,29].

In addition, the leakage results are further supported by the thermal and structural characterization data. TGA analysis revealed no early-stage mass loss attributable to PEG leakage, while BET results confirmed substantial pore filling without indications of PEG migration to the external surface. Taken together, these findings demonstrate that both UPCM and VPCM formulations exhibit excellent encapsulation stability under melting conditions, confirming the effectiveness of the silica–alumina support in suppressing PEG leakage. Leakage suppression is particularly relevant for sustainable building-integrated thermal storage, as it minimizes maintenance requirements and extends service lifetime.

4. Conclusion

In this study, PEG-600/silica–alumina composites were successfully fabricated using vacuum impregnation and ultrasonic-assisted wet impregnation, enabling a systematic evaluation of how the synthesis route influences the structural and thermal behavior of shape-stable PCMs. Both preparation methods ensured effective confinement of PEG within the mesoporous Si–Al framework. However, vacuum impregnation consistently resulted in superior pore utilization, higher PEG incorporation ratios, and phase-transition properties closer to those of pure PEG. BET, DSC, SEM, and TGA analyses collectively demonstrated how impregnation route governs pore

accessibility, PEG confinement, and the resulting phase-change thermodynamics, confirming that vacuum-prepared composites exhibit more uniform PEG distribution and more efficient phase-change performance. Importantly, this work provides a direct comparison between vacuum impregnation and ultrasonic-assisted wet impregnation for PEG–silica–alumina systems, a topic that has been scarcely addressed in the existing literature. The results demonstrate that the impregnation route is a key parameter governing pore accessibility, PEG confinement behavior, and thermal response. Although long-term thermal cycling stability was not investigated in this study, the strong agreement among leakage tests, TGA stability, and structural characterization indicates stable thermal confinement under repeated melting conditions, suggesting promising durability for future thermal cycling applications.

Overall, these findings highlight vacuum impregnation as a highly effective strategy for preparing stable and high-performance PEG-based composite PCMs suitable for medium-temperature thermal energy storage. Future studies may focus on long-term thermal cycling experiments and advanced thermal analysis to quantify degradation kinetics, as well as exploring thermally conductive yet sustainable additives to further enhance system efficiency.

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