

Article

Selection of PEG-Matrix Combinations to Achieve High Performance Form-Stable Phase Change Materials for Building Applications

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Abstract: The construction sector's pursuit of sustainability, driven by growing concerns about climate change and resource depletion, requires innovative solutions to reduce the energy consumption necessary to ensure thermal comfort in buildings. The introduction of phase change materials (PCMs) in construction elements represents an effective solution to these problems. PCMs are, in fact, able to regulate internal temperature by storing and releasing thermal energy during their phase transitions. In particular, polyethylene glycol (PEG)-based organic PCMs offer high heat storage capacity, compatibility with building materials, and minimal environmental impact. They are often used in building applications incorporated in an inert matrix, using the "form-stable method". This article critically examines various matrices proposed in the existing literature to realize PEG-based PCMs, with the aim of analyzing their influence on the final characteristics of any PCM. In addition, an attempt to correlate the quantity of PEG with the heat stored and released by the PCM is presented, using a linear regression model applied to groups of matrices of the same chemical nature. The results of these analyses would, in fact, provide useful indications for an optimal choice of the PEG/matrix system capable of responding to specific application needs, particularly in the building sector.

Keywords: phase change materials (PCMs); polyethylene glycol (PEG); form-stable method; inert matrix; thermal energy storage (TES); heat storage capacity; internal cladding for buildings



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1. Introduction

Across the globe, escalating concerns regarding climate change, rising greenhouse gas emissions, and the depletion of finite resources have underscored a critical need for innovative solutions in various sectors to reduce energy needs. The construction sector, in particular, is characterized by high energy consumption for heating and cooling buildings to maintain adequate internal thermal conditions and, therefore, to ensure occupant comfort [1]. In the pursuit of sustainable and energy-efficient building projects, the integration of innovative materials has become essential. Among these new materials, phase change materials (PCMs) have emerged as versatile systems capable of thermoregulating the internal environment of buildings [2]. PCMs are compounds capable of storing and releasing significant quantities of thermal energy during their phase transitions, thus mitigating indoor temperature fluctuations [3]. This feature makes them strategic in improving interior comfort, reducing energy consumption, and promoting environmental sustainability in the construction sector. Their integration into building envelopes, insulation, and energy storage systems allows structures to dynamically adapt to changing external conditions, thereby reducing dependence on conventional heating, ventilation, and air conditioning (HVAC) systems [4].

When a PCM is applied in a building, its selection must respect specific criteria in order to choose the one most suitable for the environmental conditions. PCMs are, in fact, classified based on various criteria, including their composition, the phase transition

temperature range, and the energy storage/release mechanisms. As for the composition, we can distinguish between (i) organic PCMs derived from organic compounds such as paraffin, fatty acids, and bio-based materials, which typically show a high heat storage capacity; (ii) inorganic PCMs consisting of inorganic compounds such as salts, metals, and eutectics, with the latter offering greater thermal conductivity [5–7].

Organic PCMs have proven to be particularly suitable for construction applications for several reasons, particularly:

1. Their high heat storage capacity allows them to store and release more thermal energy during phase transitions, enabling effective indoor temperature regulation.
2. The high compatibility of organic PCMs with common building materials minimizes unwanted interactions between these materials, ensuring the durability of the integrated system.
3. Compared with inorganic PCMs, organic PCMs do not cause corrosion in building materials, thus improving the overall longevity of the construction.
4. Flexibility in the formulation and encapsulation methods of organic PCMs allows for tailored designs that meet specific project requirements.
5. Finally, organic PCMs can be produced from renewable resources or compounds with low environmental impact, contributing to sustainability in construction.

Among the wide range of organic compounds used to produce PCMs, polyethylene glycol (PEG) is an excellent candidate, thanks to its mix of optimal properties. PEG-based PCMs are widely used in many fields to produce thermal energy storage (TES) systems, such as construction, photovoltaic panels, and textile applications [8,9]. In the field of the energy efficiency of buildings, it is possible to choose the most favorable PEG (in terms of phase change temperature range) for the climate that characterizes the area where the building is located. In fact, different grades of PEG are available (i.e., with different molecular weights); they are characterized by a wide range of phase transition intervals during heating and cooling processes. By appropriately selecting the PEG, it is therefore possible to create a PCM suitable for a specific environmental climate. This characteristic of PEG, combined with its compatibility with different construction materials, places PEG among the most suitable materials for the development of high-energy efficiency systems [10].

The interest in PEG is confirmed by the large and growing number of research publications focused on the use of this polymer to create PCMs for different applications, as shown in Figure 1.

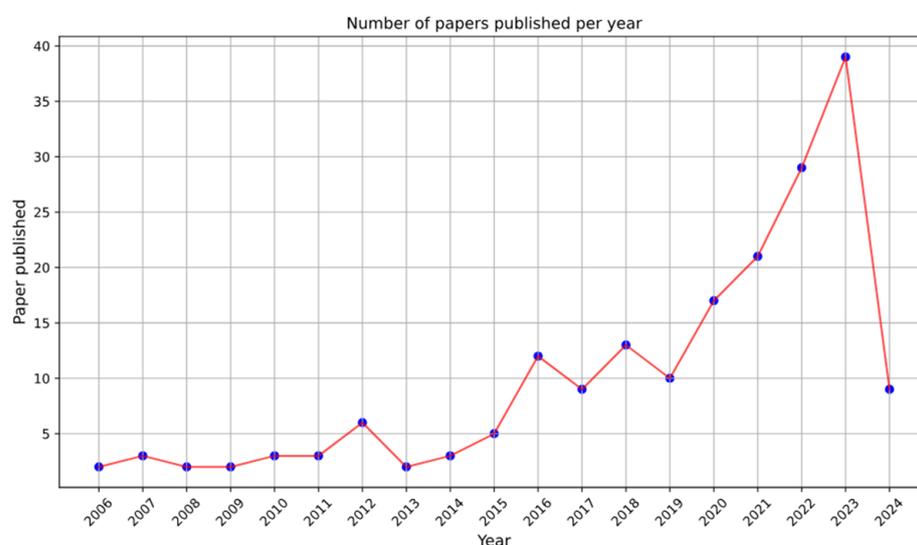


Figure 1. Research papers published from 2006 to the present on PEG polymers used to produce PCMs. (Source: data from Scopus Database, 18 January 2024).

Analysis of the current literature reveals that the use of PEG to make PCMs is not limited to building applications; it is also used to produce thermal energy storage components for general purposes. However, most of the articles concern the integration of PEG within buildings [11].

The most widely used technique to produce a PEG-based PCM is referred to as “form-stable”. This method allows the stabilization of PEG in liquid form within a solid inert matrix to avoid the dispersion of the polymer during its phase transition. Different materials can be used as an inert matrix, and the matrix composition and its structure can have a significant influence on the final characteristics of the PCM, as shown in this paper.

The objective of this paper is, in fact, to analyze the different matrices that have been proposed in the literature to create PEG-based PCMs to highlight their influence on the final performance of PCMs and to guide choices based on the application. The type of matrix and the quantity of PEG contained in it have therefore been correlated with the latent heat developed by each PCM; the results of this correlation could, in fact, offer a valuable tool to select the most suitable PEG/matrix pair to produce a PCM that meets specific requirements, particularly those relating to building applications.

2. Properties and Characteristics of Polyethylene Glycol

Polyethylene glycol is a versatile polymer composed of repeating ethylene glycol units. It is employed in a wide range of diverse applications due to its unique chemical and physical properties [8]. PEG polymers are highly soluble in water, especially low molecular weight grades, and are fully biocompatible (i.e., they are biologically inert and non-toxic). Thanks to these characteristics, they are widely used in biomedical applications such as drug delivery systems, tissue engineering, and medical devices [12]. Furthermore, PEG finds applications in different industrial processes as a lubricant, plasticizer, solvent, and surfactant [13].

As already mentioned, PEG is available in different molecular weights, to be able to respond to specific requirements depending on the application. The molecular weight value, in fact, influences properties such as solubility, viscosity, and range of phase change temperatures. Finally, PEG exhibits good thermal stability within certain temperature ranges, making it suitable for applications where heat resistance is essential.

2.1. Features of PEG as Phase Change Material

The characteristics of polyethylene glycol make this polymer an excellent candidate for producing PCMs. To give some examples, it has been proposed for the preservation of fresh food; PEG-based PCMs can maintain a constant temperature during food transportation and storage, ensuring optimal conditions for perishable goods [14,15]. In the textile industry, PEG-based fabrics have been proposed to ensure the thermal comfort of clothing, being able to regulate the body temperature by storing or releasing heat based on external conditions [16]. Several studies have been conducted using PEG in asphalt mixtures to limit their temperature sensitivity; PEG can help limit deformations in the asphalt due to high/low temperatures and make it more resistant to temperature changes [17]. In energy storage systems, PEG-based PCMs have been extensively studied for different applications, thanks to their great ability to absorb and release heat in electronic devices [18]. Finally, the phase transitions (solid/liquid) of some grades of PEG occur at temperatures in line with human comfort in buildings.

Referring to applications of PCMs in buildings, PEG offers unique advantages.

- Since PEG is available in a wide range of molecular weights corresponding to different melting/solidification temperature ranges, it is possible to select the most suitable PEG for the building where the PCM will be integrated, in terms of geographical position and climatic conditions.
- Offering high latent heat, PEG-based PCMs can store great amounts of thermal energy during phase transition.

- Providing good compatibility with common building materials, PEG can be incorporated into various components, such as insulation materials, wall panels, or other building elements, without significantly altering their integrity.
- Its use, finally, greatly contributes to reducing the need for traditional heating and cooling devices, the presence of which may not be permitted due to, for example, the artistic or historical constraints of the building.

According to the current literature, however, there are some drawbacks to using PEG as PCM in construction elements, such as low thermal conductivity and potential leakage. PEG-based PCMs, in fact, like other organic PCMs, possess a lower thermal conductivity compared with some inorganic PCM alternatives. This can influence the rate at which heat is transferred, affecting the overall efficiency of thermal energy storage and release. The thermal conductivity of PEG ranges between 0.1 and 0.4 W/m·K, depending on its grade, when measured at room temperature. In addition, PEG can exhibit some degree of leakage over extended periods of use or under certain conditions, affecting the long-term reliability and stability of PCMs in building materials [19,20].

An in-depth knowledge of the thermal characteristics of PEG of different grades, including melting and solidification temperatures and relative enthalpies, is critical for the proper selection and use of PEG-based PCMs in building applications. Table 1 presents a list of the thermal properties (melting/solidification temperatures and enthalpies, thermal conductivity) of PEG of different grades often used to produce PCMs.

Table 1. Thermal properties measured on PEG polymers of different molecular weights (MW). (T_m: melting point; ΔH_m: melting enthalpy; T_c: crystallization point; ΔH_c: crystallization enthalpy).

PEG Mw (g·mol ⁻¹)	Heating Process		Cooling Process		Thermal Conductivity (W/m·K)	Ref.
	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)		
PEG400	3.2–3.7	91.4–98.8	–23.4–24.0	85.0–98.9	0.19	[8,21,22]
PEG600	9.9–21.3	137.0–148.5	6.2–6.5	129.8–146.3	0.19	[8,21,23,24]
PEG800	21.8–32.4	133.6–187.3	17.6–21.7	126.6–130.3	0.26	[21,25,26]
PEG1000	32.4–42.8	113.6–153.0	21.5–30.7	115.4–155.0	0.28	[21,27–30]
PEG1500	46.9–49.5	170.3–196.6	31.6–39.7	167.3–188.2	0.30	[21,31–33]
PEG2000	46.5–56.1	170.3–193.7	19.2–39.7	151.1–178.6	0.31	[21,31,34,35]
PEG3000	50.4–56.6	144.9–186.5	23.0–43.2	143.8–160.9	0.33	[21,36,37]
PEG4000	54.5–59.6	181.4–205.7	33.3–40.1	171.8–199.0	0.33	[29,38–42]
PEG5000	60.1–62.2	172.4–204.7	34.2–40.6	168.7–203.2	0.33	[8,29,43]
PEG6000	53.0–63.0	168.6–190.1	36.2–46.8	163.6–187.1	0.34	[29,44–48]
PEG8000	50.9–60.4	113.5–173.0	37.5–47.6	110.3–161.8	0.33	[29,49–51]
PEG10000	52.8–66.6	112.3–189.2	38.1–43.9	109.5–178.3	0.33	[29,49,52–54]
PEG20000	57.5–68.0	163.1–189.8	33.6–44.9	114.9–171.5	0.32	[29,45,55]

As expected, as the molecular weight of PEG increases, the melting and crystallization temperatures and the enthalpy increase. The same trend is also followed by thermal conductivity. However, the thermal properties reach almost constant values for PEG with medium/high molecular weight. It should be emphasized, however, that the thermal data reported in different papers for each grade of PEG present wide variability. The causes can be different; examples include different instruments being used for the measurements, purity differing for specific PEGs, etc.

Referring to the use of PCMs for the regulation of the indoor temperature of buildings, the selection of the most suitable PEG is carried out based on its phase transition tem-

peratures, which must be in line with the human comfort temperature range of typically between 20 and 25 °C [56]. With this in mind, we can conclude that PEG grades with either very low or very high molecular weights cannot be used in these applications because their phase change temperatures deviate significantly from the comfort temperature range. Consequently, the choice must fall on the grade of PEG with moderate molecular weights (i.e., approximately from 800 to 4000 g/mol). This is also confirmed by the large number of experimental studies using PEG in this range of molecular weights, as shown in Figure 2.

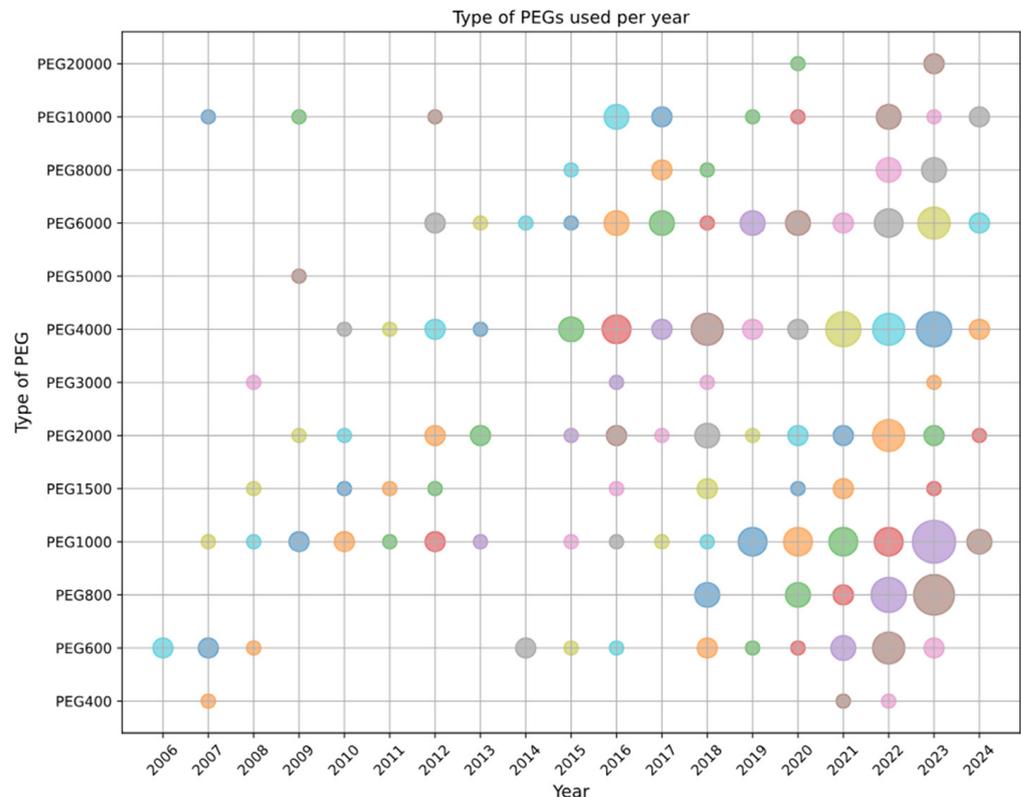


Figure 2. Research papers published from 2006 to the present on PEG of different molecular weights used in building applications. The size of the “bubble” corresponds to the number of papers published in a specific year on a certain PEG. (Source: data from Scopus Database, 18 January 2024).

3. Application of PEG as PCM in Buildings

Over the past two decades, the utilization of PEG as a phase change material incorporated in buildings had a remarkable increase. The integration of a PCM within building materials can occur through various methods, each with some advantages and disadvantages:

- *Direct Mixing.* PCM can be dispersed directly into the binder during the process of production of the building material. This method is applied to materials such as mortars, cement, plaster, or plasterboard, to increase their heat storage capacity. Although this technique appears to be the simplest, fastest, and cheapest one, the PCM can interfere with the hydration process and kinetic reaction, slowing down the reaction rate, and causing a severe reduction of the final mechanical properties of the material. The mentioned phenomena have been observed also when different procedures are used to introduce PEG into building materials; however, these phenomena are more marked with the direct incorporation of PEG [57].
- *Microencapsulation.* The PCM can be encapsulated within tiny capsules. The microcapsules containing the PCM are then dispersed in building materials such as concrete, plaster, or gypsum [5]. This method allows for the controlled absorption/release of thermal energy. However, it is reported that PEG is poorly suited for encapsulation methods [58].

- *Macroencapsulation.* In this case, larger containers enclose the PCM that is dispersed within the building material. Macroencapsulation makes greater quantities of PCM available; the capsules are often integrated into walls, ceilings, or floors. However, (i) macrocapsules can cause structure stiffness when incorporated into building materials; (ii) their size can take up too much volume in the structure; (iii) although the macroencapsulation technique is less expensive than the microencapsulation, it is still more expensive than other methods [59].
- *Form-stable or impregnation method.* PCM can be introduced and stabilized in a porous matrix. In the case of PEG, a physical link between the polymer and the matrix is obtained through the association of soft segments of PEG with the stiff segments of the matrix. Different techniques (i.e., blending, soaking, adsorbing) can be employed to force the soft PEG segments within a rigid polymeric or an inorganic porous matrix [60]. This is the most widely used method, as it offers numerous advantages: (i) its cost-effectiveness and ease of implementation; (ii) the possibility to limit PEG leakage during its phase transition; (iii) the form-stable technique provides stability to the PCM, reducing the risk of degradation or alteration during its handling, transportation, and integration into building materials. In addition, this method allows for tuning the properties of the PCM by appropriately choosing the chemical composition of the matrix. In fact, by selecting different matrices, it is possible to modify the mechanical resistance, thermal conductivity, and other characteristics of the PCMs to adapt them to application needs. All of the mentioned advantages make the form-stable method the most attractive approach to producing a PEG-based PCM.

4. PEG-Based Form-Stable PCMs

Several experimental studies have examined the use of PEG of different grades in form-stable PCMs, proposing diverse porous supports acting as matrices able to prevent leakage and maintain the PCM's stability during PEG phase transitions. It is expected, therefore, that the PCMs obtained with this technique will have greater durability and reliability. Figure 3 schematically shows a porous matrix that includes a PCM and how this later changes its physical state as the external temperature varies, absorbing and releasing energy.

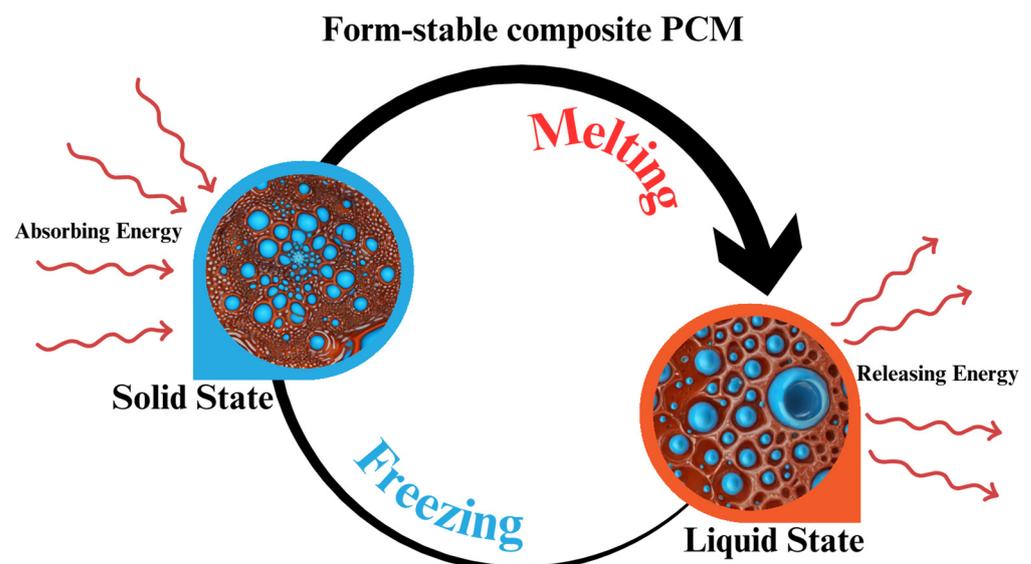


Figure 3. Diagram of a composite form-stable PCM that changes state, from solid to liquid and vice versa, as the external temperature varies.

The most common proposed matrices are based on natural or systemic polymers, carbon-based materials, and inorganic porous materials. Each of these supports has differ-

ent characteristics, offers advantages, and presents drawbacks, which are presented and analyzed in the following paragraphs.

4.1. PEG-Based PCMs with a Polymer Matrix

In this section, works focused on PCMs in which PEG has been integrated into different polymeric matrices, or used in copolymers, are presented. The thermal characteristics of the PCMs found in the reviewed literature are summarized in Table 2.

The authors of the papers [31,61] tried to overcome the typical problems of PEG (i.e., losses during melting, undercooling, and water solubility) by confining it in an epoxy resin matrix. Furthermore, aluminum powder was added to the resulting composite material to increase its thermal conductivity. The produced PCMs were based on different grades of PEG, namely PEG1000, PEG1500, PEG2000 [31], and PEG6000 [61]. The results of both studies demonstrated that the incorporation of a PEG into an epoxy matrix reduces its heat capacity compared with each pure PEG. On the other hand, the final PCMs maintain a sufficiently high enthalpy value, which, as expected, is strictly correlated to the PEG grade (see the melting and crystallization enthalpies of each pure PEG reported in Table 1). These PCM composites, consequently, can still be used as effective systems to thermoregulate the internal environments of buildings.

PEG-based PCMs with a thermosetting matrix of polycarbonate diol (PCD) and polyarylpolyethylene isocyanate have been proposed [49]. DSC (differential scanning calorimetry) measurements confirmed the ability of PEG8000 and PEG10000, included in the thermosetting matrix, to store and release heat during their phase transitions. High latent heat and an adequate phase change temperature range are among the advantages of these PCMs.

In a different study [62], PEG has been integrated into rigid PU foams to obtain insulating materials that, at the same time, have high thermal capacity. Three grades of PEG (i.e., 600, 1000, and 1500) were used to produce PCMs with different phase transition temperature ranges suitable for diverse applications. A high heat absorption/release capacity of PU foams in which PEG is included was assessed using DSC tests, along with good leak resistance characteristics. Finally, simulation experiments carried out on concrete walls containing the PCM showed a good thermal capacity of this material.

The investigation presented in [63] focused on the synthesis of PEG4000-polyurethane copolymers, analyzing their potential use as form-stable PCM. The produced copolymers had phase change temperatures close to ambient temperature, with a high heat capacity. The presence of urethane bonds in the copolymer influences the behavior of the PCM during its phase changes, altering the melting and crystallization temperatures of pure PEG.

The authors of the study reported in [64] analyzed the copolymerization processes capable of tuning the transition temperature (T_t) of PEG1000 with a polymer matrix (based on methyl ether methacrylate) for use in building applications. Polarized optical microscopy analysis and X-ray techniques proved that there is a relationship between the composition of the copolymer, the crystal structure, and T_t . This work provided a new approach to producing polymeric solid-solid PCM with a tunable T_t for TES applications.

The development of thermoplastic solid-solid PEG-PCMs based on polybutylene terephthalate (PBT) and adipic acid is described in [65]. The addition of adipic acid can prevent the leakage of PEG6000 during its phase change, ensuring stability to PCMs with high PEG content. Thermal analysis of these PCMs revealed thermal degradation temperatures greater than 200 °C and high thermal capacity.

The development of a PCM composed of an aerogel matrix of polyvinyl alcohol and reduced graphene oxide (PVA-rGO) able to incorporate PEG6000 through vacuum impregnation is reported in [48]. Aerogels are materials characterized by low density, high porosity, and an extensive surface area, ideal for incorporating PEG. In fact, a significant amount of PEG, up to approximately 97% by weight, was integrated into the PVA-rGO aerogel matrix. Figure 4a shows the surface morphology of PVA aerogel, while Figure 4b,c show the surface morphology of the PVA aerogel with the incorporation of GO and rGO,

respectively. The introduction of GO creates a network of interconnected pores. With the inclusion of rGO, this porous structure is more evident. A vacuum impregnation process was performed with PEG: in Figure 4d–f, it is shown that the PEG polymer was well included in the porous aerogel, confirming good compatibility among the different phases.

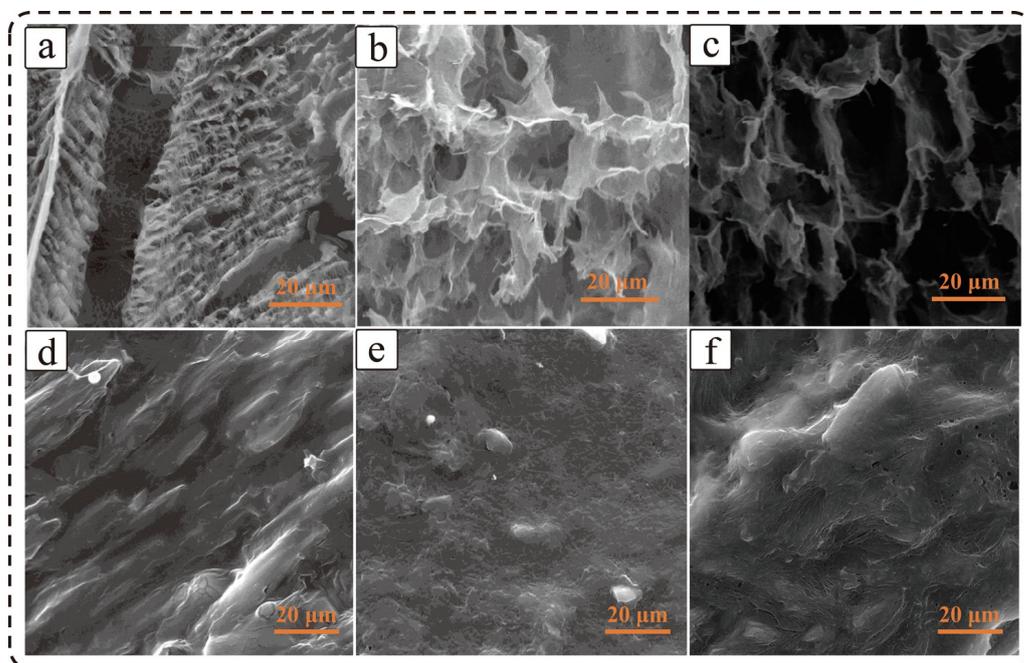


Figure 4. Surface characterization of the developed aerogel: (a) PVA; (b) PVA-GO; (c) PVA-rGO; (d) PVA/PEG; (e) PVA-GO/PEG; (f) PVA-rGO/PEG. Reprinted from [48], with permission from Elsevier (5 February 2024).

A novel strategy employing a self-template method was proposed in [45] to fabricate form-stable PCMs inspired by the structures of orange and pomegranate. The structure obtained allowed exceptional PEG load values using PEG20000 as a template to create a cross-linked polymer. The resulting PEG-PCMs display a high phase change enthalpy (around 190 J/g), close to that of pure PEG20000, with excellent thermal stability.

Table 2. Thermal characteristics (relating only to the PCM component) of different PEG-based PCMs with a polymer matrix. The amount of PEG in each PCM is also reported. (T_m: melting point; ΔH_m: melting enthalpy; T_c: crystallization point; ΔH_c: crystallization enthalpy).

PEG	Matrix	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)	Amount of PEG (% wt.)	Ref.
1000	Epoxy resin	34.9	92.7	31.6	89.8	70.0	[31,61]
1500		45.8	108.5	38.8	103.4		
2000		52.6	116.2	37.9	107.8		
6000		58.0	115.0	44.2	113.6		
8000	Polyaryl polymethylene isocyanate and polycarbonatediol	50.9	113.5	39.7	110.3	-	[49]
10000		52.8	112.3	39.7	109.5	-	

Table 2. Cont.

PEG	Matrix	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)	Amount of PEG (% wt.)	Ref.
600	Polyurethane foam	18.1	62.3	-	-	44.0	[62]
1000		37.8	76.7	-	-	49.0	
1500		49.6	138.1	-	-	53.0	
600–1000–1500		17.0–31.0–42.4	72.4	-	-	38.0	
4000	4,4'-Diphenylmethane di-isocyanate	51.1	144.1	33.0	117.5	90.0	[63]
4000	Polyvinyl alcohol	44.5	132.3	27.2	115.6	80.0	
		49.7	107.1	31.2	93.3	60.0	
		47.0	105.5	31.1	65.3	40.0	
1000	Triethylene glycol methyl ether methacrylate	35.2	108.0	-	-	-	[64]
		33.5	101.0	-	-	-	
		30.6	95.0	-	-	-	
		25.3	75.0	-	-	-	
6000	Polybutylene terephthalate and adipic acid	45.6	136.8	33.4	110.1	91.0	[65]
6000	Polyvinyl alcohol	59.0	144.6	46.2	132.7	94.5	[48]
6000	Polyvinyl alcohol and graphene oxide	59.1	153.9	47.4	150.6	97.2	
6000	Polyvinyl alcohol and reduced graphene oxide	59.6	155.5	49.0	149.9	96.9	
20000	Carboxylic acid	60.2	188.8	46.3	167.8	90.0	[45]

The data reported in Table 2 confirm that there is a correlation between the enthalpies of PCM and the molecular weight of PEG; i.e., the greater the molecular weight of PEG, the greater the enthalpy developed by the corresponding PCM. Furthermore, with the same grade and content of PEG, it is not clear whether, and to what extent, the type of polymer matrix influences the enthalpy of each PCM. It must be underlined, however, that the enthalpy measured on the PEG-based PCM is attributable to the PEG phase alone (i.e., the polymer matrix does not contribute in any way). In fact, in the case of adopting matrices based on amorphous polymers (i.e., thermosetting resins or non-crystalline thermoplastic polymers), this occurrence is expected. On the other hand, in the case of matrices based on semicrystalline thermoplastic polymers (e.g., polybutylene terephthalate or polyvinyl alcohol), the phase transition temperatures of the matrices are much higher than the melting/crystallization temperature ranges of any grade of PEG. Further discussion on the influence of the type of polymer matrix is given in Section 5.

4.2. PEG-Based PCMs with a Natural Organic Matrix

The use of natural organic materials (such as cellulose, wood, or waste produced by the food industry or agricultural processes) as matrices for form-stable PCMs has been widely explored in recent years as a totally eco-sustainable solution for reducing the energy consumption of buildings. Organic natural materials are widely available and are renewable resources. The exploitation of waste materials from various processes allows also the reduction of the costs of their treatment/disposal, offering a further advantage for the environment. In addition, some of these materials possess discrete thermal properties, such as conductivity and heat capacity, which can complement the thermal performance of

encapsulated PCMs, improving the heat accumulation and release capabilities of the final composite material. They are often available at relatively low costs compared with synthetic matrices, making them advantageous for building applications where large volumes of materials are required. They are mostly biodegradable, which leads to a low environmental impact at the end of their use. More generally, compared with synthetic materials, natural organic matrices pose fewer health risks during production, use, and disposal, allowing for a safer environment also for workers [66]. As for PEG-based PCMs, natural organic matrices have good compatibility with PEG, providing an excellent medium to encapsulate and stabilize it. The thermal properties of some PEG-based PCMs, produced starting from an organic natural matrix, are listed in Table 3.

Cellulose-graft-polyethylene glycol copolymers have been proposed as solid-solid PCMs, demonstrating good thermal storage capacity and offering phase transitions in the temperature range of 40–60 °C [43]. Setting the molecular weight of the copolymer and the PEG1000, PEG2000, and PEG5000 contents allows for control of the phase transition temperatures and enthalpy. If expanded graphite (EG) is incorporated into the PCM, it is possible to increase its thermal conductivity without causing any leakage, the best results being observed at 5% wt. EG.

The microwave-assisted technique has allowed for the development of form-stabilized mixtures of PEG8000 and cellulose acetate (CA), proposed as PCM in [67]. Different compositions of PEG/CA mixtures were tested until a PEG incorporation equal to 96.5% by weight was obtained without any loss during the transition process. Spectroscopic analysis revealed the absence of chemical bonds between PEG and CA, suggesting that their interaction occurred through secondary bonds, such as hydrogen bonds and polar interactions. The PCMs exhibited a maximum heat storage capacity of 155 J/g, coupled with excellent thermal stability.

The authors of the study reported in [68] created PCM composites by integrating PEG2000 and Fe₃O₄ nanoparticles into a cellulose skeleton. The resulting PCMs exhibited a high thermal capacity and thermal stability after repeated solid-liquid cycles, withstanding strong pressures without leakage, even above the melting point of PEG. The integration of Fe₃O₄ nanoparticles (NPs) remarkably enhanced thermal conductivity. Figure 5a schematically illustrates the PCM manufacturing process, and Figure 5b–g shows the morphologies of cellulose matrix, unloaded or when loaded with Fe₃O₄ NPs, containing PEG2000. In Figure 5b, the cellulose hydrogel exhibits a layered structure; this structure plays a crucial role in the encapsulation of molten PEG and serves as an attachment site for Fe₃O₄ NPs. After loading with Fe₃O₄ NPs, the layered structure of the hydrogel remains intact, with these NPs deposited on the cellulose layers (Figure 5c). The interlayers of cellulose hydrogel are filled with PEG (Figure 5d,e). At high magnifications, PEG appeared to be sandwiched in the layered cellulose (Figure 5f), with Fe₃O₄ NPs uniformly dispersed (Figure 5g).

The development of lightweight wood PCM composite into which PEG800 is incorporated is described in [69]. The obtained PCM allowed indoor temperature fluctuations to be significantly reduced through the accumulation of thermal energy.

A novel energy-efficient material was developed in [70], referred to as the DW-EP-PEG system. A transparent energy storage wood (TESW) was obtained by impregnation of delignified wood (DW) with a compound of epoxy resin (EP) and PEG800. The PEG integration in the wood matrix significantly improved the TESW's thermal energy storage without compromising its light transmittance, which remained high and equal to around 81%. The DW-EP-PEG system exhibited also good thermal stability. The porous structure of delignified wood, together with the cross-linked structure, was able to prevent the leakage of PEG during its phase transitions. Finally, the eco-sustainable composite PCM showed complete biodegradability.

In a similar work [71], phase change energy storage wood (PCES-Wood) composites were produced using balsa wood delignified to contain PEG800 and PEG1000, with the addition of carbon black (CB) to improve the thermal conductivity of PCMs. Further grafting of CB with octadecyl isocyanate resulted in an increase in the thermal storage capacity

of the PCMs, denoted as aCB-PCES@Balsa. At 4% aCB content, the composites showed minimal undercooling, with high melting and solidification enthalpies of approximately 100 J/g and 91 J/g, respectively. After 200 cooling/heating cycles, the PCMs maintained high phase change enthalpy values, proving good durability.

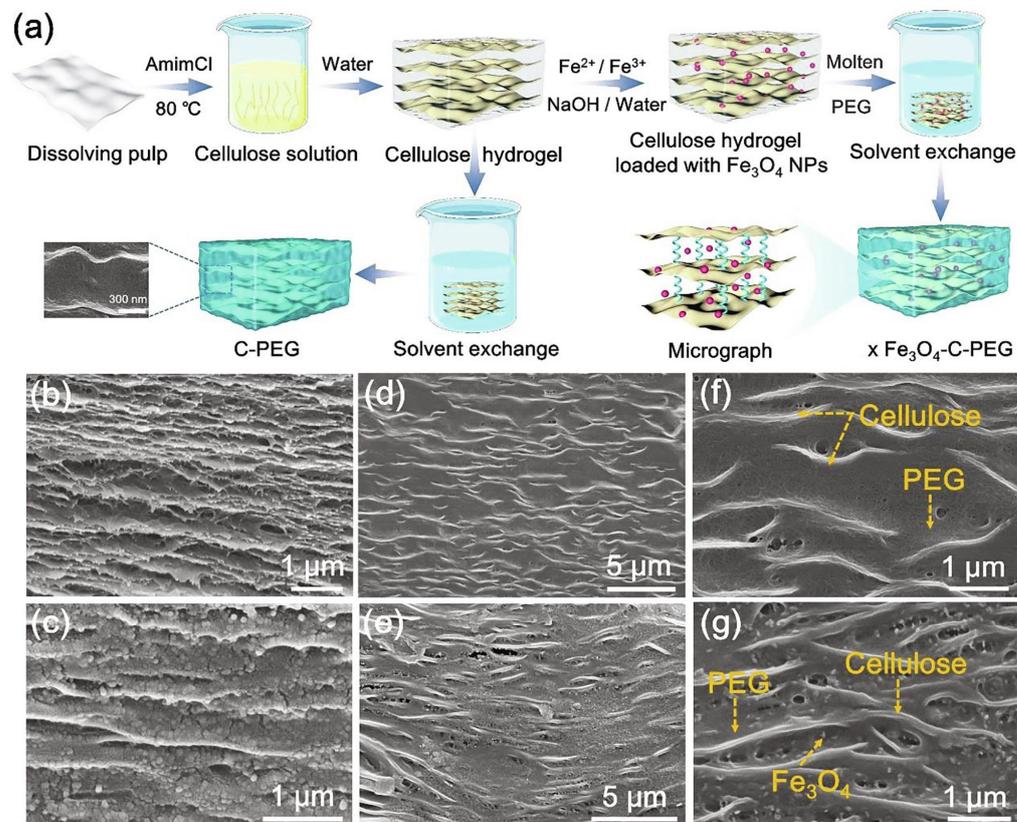


Figure 5. (a) Schematic representation of the process of production of the composite PCM. SEM images of (b) cellulose hydrogel, (c) cellulose hydrogel with embedded Fe_3O_4 NPs, (d) cellulose hydrogel with PEG, (e) 0.2 Fe_3O_4 -cellulose hydrogel with PEG, (f) cellulose hydrogel with PEG at a higher magnification, and (g) 0.2 Fe_3O_4 -cellulose hydrogel-PEG at a higher magnification. Reprinted from [68], with permission from Elsevier (5 February 2024).

The development of eco-friendly energy storage materials, obtained by impregnating a delignified bamboo (DB) porous matrix with PEG800 and PEG1000 to produce DB/PEG PCM composites, was reported in [72]. The PCMs exhibited enthalpies in the range of 72.2–84.3 J/g, according to the grade of PEG, and good stability if subjected to thermal cycles.

Modified rice husk ash (mRHA) was proposed as a natural organic matrix for a form-stable PEG-based PCM [73]. Modification of rice husk ash by ultrasonic acid treatment increased the porous structure of raw RHA (rRHA), allowing deeper penetration of PEG2000 into the pores of the mRHA. Therefore, form-stable PEG/mRHA PCM offers a heat capacity of approximately 119 J/g, almost 21% higher than that measured on the PEG/rRHA system.

The exploitation of waste materials from the food industry is illustrated also in the paper [74]. In this case, activated carbon derived from apricot kernel waste (ACAS) was used as a matrix to contain PEG1000. The highly reactive surface and porous structure of ACAS allowed the impregnation of a high quantity of PEG. The resulting ACAS/PEG PCMs showed phase change enthalpies of up to 193.7 J/g. Furthermore, the ACAS/PEG composites showed thermal conductivities approximately 1.75 times higher than those of pure PEG. The leak-proof feature of these composites ensures them high thermal stability up to 120 °C and after 1200 PEG melt-freeze cycles.

The authors of the study reported in [75] proposed the use of polypyrrole (PPy)-coated agricultural corn straw (CS) as an organic matrix to include PEG2000 in different amounts and produce shape-stable PCMs (CS@PPy-PEGx). The cross-linked structure of the composites allows for a high PEG content in PCMs, approximately 90% by weight, and a thermal conductivity of about 0.22 W/(m·K). The PCM composites showed high thermal stability, even after 100 heating and cooling cycles, and adequate heat capacity. Finally, CS@PPy-PEGx composites showed excellent leak resistance.

In [76], a PCM composite based on coral sand (with 35% porosity) with the inclusion of PEG1000 is reported. The PCM composite showed high chemical and thermal stability even after 500 cycles. PEG losses from the composite were limited due to the inclusion in the coral sand structure. The characteristics of the CS-PCM composite ensure its suitability for construction applications such as in coastal areas characterized by abundant resources of coral sand.

Table 3. Thermal characteristics of different PEG-based PCMs with natural organic matrix. The amount of PEG in each PCM is also reported. (Tm: melting point; ΔHm: melting enthalpy; Tc: crystallization point; ΔHc: crystallization enthalpy).

PEG	Matrix	Tm (°C)	ΔHm (J·g ⁻¹)	Tc (°C)	ΔHc (J·g ⁻¹)	Amount of PEG (% wt.)	Ref.	
5000	Cellulose-graft with expanded graphite	58.9	166.6	37.6	165.3	84.8	[43]	
8000	Cellulose acetate	60.6	155.35	-	-	82.0	[67]	
2000	Cellulose	56.2	177.7	29.1	168.9	98.1		
2000	Cellulose with 0.05% Fe ₃ O ₄	55.8	176.6	28.8	167.7	97.5	[68]	
	Cellulose with 0.1% Fe ₃ O ₄	56.1	175.5	28.4	166.4	96.9		
	Cellulose with 0.15% Fe ₃ O ₄	57.4	173.9	28.5	164.3	96.0		
	Cellulose with 0.2% Fe ₃ O ₄	56.7	172.6	28.8	163.7	95.3		
800	Delignified wood with an epoxy resin	32.2	28.2	21.7	21.5	50.0	[70]	
		32.7	71.7	21.7	46.5	60.0		
		31.3	106.7	22.3	79.7	70.0		
		30.7	134.1	22.2	122.9	80.0		
800–1000	Balsa wood and 0% of carbon black	29.4	119.3	23.6	118.5	-	[71]	
	Balsa wood and 1% of carbon black	28.7	140.3	18.4	133.9	-		
	Balsa wood and 2% of carbon black	27.7	112.8	16.2	89.49	-		
	Balsa wood and 4% of carbon black	23.7	100.3	18.7	91.1	-		
	Balsa wood and 6% of carbon black	40.1	137.00	19.6	135.3	-		
800–1000	Delignified bamboo	28.8–41.6	84.3	7.0	72.2	81.9	[72]	
2000	Rough rice husk ash	55.2	98.7	38.5	88.6	53.1	[73]	
	Modified rice husk ash	55.7	119.3	40.4	107.9	64.6		
1000	Waste apricot kernel shell-derived activated carbon	26.6 *	110.6	28.8 *	112.5	70	[74]	
2000	Corn straw coated by polypyrrole	Corn straw	54.0	143.2	38.1	140.2	90	[75]
			52.1	40.8	29.1	35.6	60	
			52.6	69.5	33.1	65.7	70	
			53.0	105.8	37.0	102.6	85	
			52.7	145.8	37.2	141.5	90	
1000	Coral sand	28.6	43.6	20.5	48.9	-	[76]	

* These values refer to the onset temperatures.

Most of the comments reported when analyzing the results in Table 2 can be repeated for the data summarized in Table 3 (i.e., the enthalpy developed by the PCM is related to the degree of PEG used to make it). Also in this case, the type of natural polymer matrix seems to have some influence on the heat developed by the PCM during its phase change.

In Section 5, further insights are provided on the influence of the type of natural polymer matrix on the enthalpies developed by each PCM.

4.3. PEG-Based PCMs with a Carbon Matrix

The use of a carbon matrix (i.e., graphene, carbon nanotubes, expanded graphite, etc.) as porous support for PCMs can offer several advantages. First, carbon-based materials possess excellent thermal conductivity: when used to produce a PCM, the carbon matrix increases heat transfer, improving the PCM's thermal performance. In addition, carbon matrices can improve the thermal stability and durability of PCMs, reducing the amount of PEG loss and degradation due to repeated thermal cycling. Carbon materials have a high surface area due to their porosity and/or nanoscale structure. The large specific surface area provides more space for encapsulation, with higher PCM contents, resulting in greater energy storage capacity. Furthermore, carbon matrices can also improve the mechanical strength properties of PCMs. A carbon matrix can be adequately modified to be compatible with the active phase of any PCM, ensuring its homogeneous distribution within the matrix and good physical interaction between the phases. Finally, carbon-based materials often possess additional capabilities beyond PCM-supporting function. As an example, some carbon structures show photo-responsive behavior and are, therefore, used also in applications where the phase change is induced by light. The thermal characteristics of PEG-based PCMs with a carbon matrix are shown in Table 4.

Table 4. Thermal characteristics of different PEG-based PCMs with a carbon matrix. The amount of PEG in each PCM is also reported. (Tm: melting point; ΔH_m : melting enthalpy; Tc: crystallization point; ΔH_c : crystallization enthalpy).

PEG	Matrix	Tm (°C)	ΔH_m (J·g ⁻¹)	Tc (°C)	ΔH_c (J·g ⁻¹)	Amount of PEG (% wt.)	Ref.
6000	Single-walled carbon nanotubes	55.3	165.4	43.6	151.6	90.0	[77]
		55.8	169.4	43.3	154.6	92.0	
		56.0	172.4	43.0	157.6	94.0	
		56.3	176.4	42.8	160.6	96.0	
		56.7	179.4	42.7	163.6	98.0	
800	Expanded graphite	30.1	78.06	12.6	81.5	-	[25]
		25.9	98.6	19.1	97.6	-	
		25.8	98.3	18.7	95.0	-	
800	Expanded graphite	22.6 *	97.7	21.9 *	92.9	87.0	[21]
1000		30.2 *	121.9	33.6 *	116.8		
1500		42.7 *	122.9	33.9 *	114.9		
2000		51.6 *	143.8	41.7 *	137.5		
3000		54.6 *	141.6	41.7 *	124.1		
4000	Expanded graphite aerogel	53.8	170.1	37.9	144.7	90.8	[78]
		53.8	166.4	36.0	146.5	90.2	
		53.8	155.2	40.0	134.8	83.7	
		53.4	148.9	36.6	128.5	80.1	

* These values refer to the onset temperatures.

A simple melt-mixing method was employed to produce a PCM containing PEG 6000 with a matrix of single-walled carbon nanotubes (SWCNs) [77]. The resulting PCM nanocomposite showed very high PEG contents (up to 98%) and good thermal stability, with no loss of PEG after more than 400 freeze-melt cycles. The presence of SWCN produces a lowering of the melting point and a raising of the crystallization temperature of the composite, with a significant reduction of undercooling phenomena. Thermal conductivity was also improved, with an increase of 1329% in the solid state and 533% in the liquid state compared with pure PEG. Finally, the nanocomposite showed a high enthalpy value, almost 180 J/g.

A form-stable PCM containing PEG4000 and with expanded graphite (EG) as a matrix was successfully developed via vacuum impregnation [25]. The characteristics of EG matrix, characterized by a mesoporous structure and high absorption capacity, contributed to the excellent sealing characteristics of PEG in the PCM and its remarkable energy storage ability. Thermal analysis assessed the good thermal stability of PCM; moreover, the presence of EG leads to an increase in thermal conductivity.

The development of molecular-bridged expanded graphite (EG)/polyethylene glycol (using different PEG of different grades, i.e., 800, 1000, 1500, 2000, and 3000) PCM composites (referred to as m-EPs) is described in [21]. A titanate coupling agent (i.e., KR-38S) facilitated the creation of stable interactions between EG and PEG, enhancing the thermal properties of the PCM and increasing the decomposition temperature by about 20 °C. The m-EPs showed a low undercooling phenomenon and a great thermal energy storage capacity. Furthermore, this PCM offered ten times higher thermal conductivities than pure PEG, ensuring high heat transfer rates and rapid response to temperature fluctuations.

Expanded graphite-based aerogel (EGA) was employed as a matrix of a PEG4000-based PCM [78]. Due to its low thermal conductivity, EG was integrated with aerogel obtaining an EGA composite characterized by a microporous structure able to include PEG, as shown in Figure 6. In Figure 6g,h, in particular, PEG was able to fill the interconnected pore structure of EGA using a vacuum immersion technique. The EGA/PEG PCM composite provided very high thermal conductivity, equal to 3.74 W/(m·K), with an increase of 1290% compared with pure PEG. The amount of PEG contained in the EGA/PEG PCM was equal to 80%. An economic analysis performed by the authors revealed an energy cost payback period of 1.7 years when applying the EGA/PEG composite.

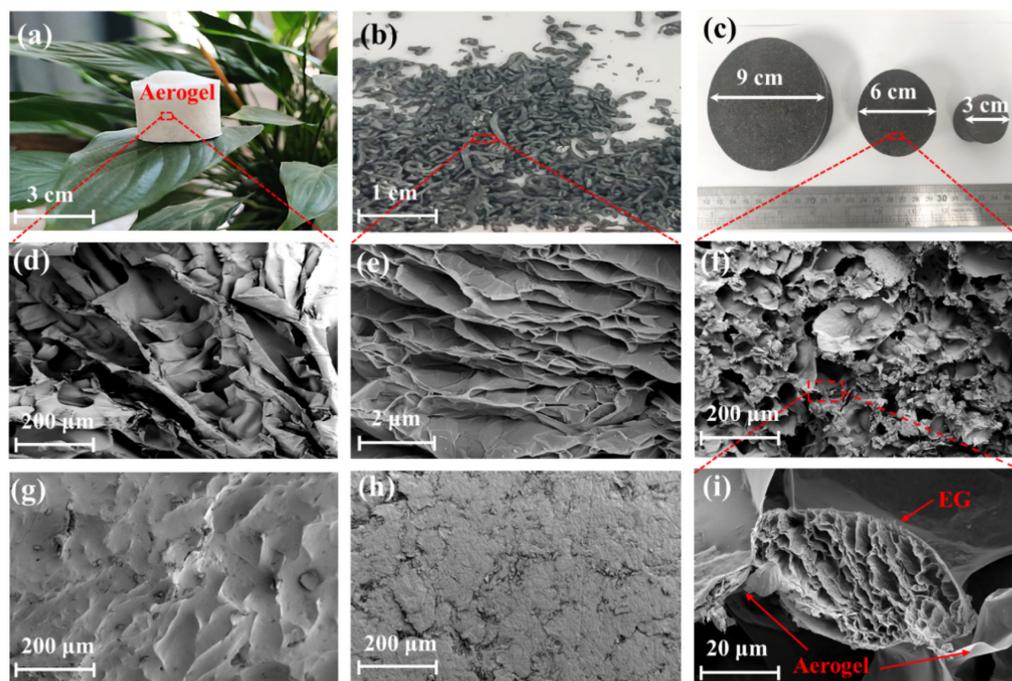


Figure 6. Microstructure of EGA/PEG4000 PCMs: (a) EGA; (b) EG; (c) different shape of EGA; (d) SEM observation of EGA ($\times 50$); (e) SEM observation of EG ($\times 5000$); (f) SEM observation of EGA with SA and borax ($\times 30$); (g) SEM observation of EGA/PCM ($\times 50$); (h) SEM observation of EGA/SA/borax/PCM ($\times 50$); (i) SEM observation ($\times 400$) of image reported in (f). Reprinted from [78], with permission from Elsevier (5 February 2024).

The data reported in Table 4 relating to PCMs with a carbon-based matrix show a trend consistent with what was observed in the previous tables (i.e., an increase in the PEG content in the PCM corresponds to an increase in the developed ΔH). The PEG content included within the porous carbon-based matrices is always very high, generally well above

80% by weight. As already reported, the use of carbon-based matrices (such as single-wall carbon nanotubes [77] or expanded graphite [21,25,78]) allows a substantial increase in the conductivity of the final PCM. This can promote and accelerate the phase change process. Indeed, the areas of the endothermic and exothermic peaks appear significantly narrower than those observed for the respective PEG grades in isolation. Some additional discussion on the influence of carbon-based matrix type on PCM characteristics is in Section 5.

4.4. PEG-Based PCMs with an Inorganic Porous Matrix

Among the different types of support matrices for PCM, inorganic porous materials are undoubtedly the most used. These materials offer several advantages. First, they are characterized by a large specific surface area and interconnected pore structures; both features facilitate the impregnation of the PCM, limiting its leakage, and improve the heat exchange between the PCM and the element in which it is contained. Moreover, some inorganic matrices are able to increase the thermal conductivity of PCM. In addition, they offer good mechanical properties that are then transferred to the PCM composite [60].

The inorganic porous materials employed in form-stable PCMs are lightweight aggregates (LWA), diatomite, perlite, vermiculite, mica, kaolin, and calcium carbonate. Based on their characteristics, costs, availability, and compatibility with PCM, it is possible to select the most suitable inorganic matrix for a given application. Finally, inorganic porous materials are environmentally friendly and can better contribute to the development of sustainable solutions for thermal energy storage.

4.4.1. PEG-Based PCMs with an LWA-Based Porous Matrix

Only a few studies in the literature report lightweight aggregates as an inert support of PEG-based PCMs. The works described in [79–81] demonstrate the substantial ability to integrate PEG within LWAs to produce PCMs for diverse applications in construction technology.

In [79], the inclusion of PEG of different grades (i.e., PEG400, 600, and 1000) in LWA proved to be capable of controlling temperature variations during the curing of concrete, limiting the formation of thermal stress and potentially preventing cracking. In addition, PCMs with low phase transition temperatures in LWAs help to reduce the onset of freeze/thaw cycles, improving durability in the winter season.

The thermal behavior of PCMs composed of PEG1500 included in LWAs was analyzed in [80]. Replacing conventional aggregates with the same ones impregnated with PEG allows for modification of thermal conductivity and heat accumulation capacity. The study showed a substantial increase in heat storage by increasing the LWA-PCM content.

The investigation in [81] highlighted the superior heat retention of hybrid PCM aggregates (i.e., those combining PEG1500 with paraffin) compared with single-type PCM ones (i.e., containing only paraffin), emphasizing the potential of PEG1500-based PCM aggregates in enhancing lightweight concrete's thermal properties.

4.4.2. PEG-Based PCMs with a Silica-Based Porous Matrix

The main results of the investigations conducted on PEG-based PCMs with a porous silica matrix are reported below and their thermal characteristics are listed in Table 5.

The research works presented in [82–85] report the development of PEG-based composite PCMs with different silica-based supports, namely mesoporous calcium silicate (MCS), radial-like mesoporous silica (RMS), graphene-based mesoporous silica sheets (GS), and silica nanosheets (SNSs) modified with Ag nanoparticles (AgNPs) onto Sn²⁺-activated SNSs. These studies confirm that the thermal characteristics and energy storage properties of each PCM depend not only on the grade of PEG but also on the type of silica-based support. In particular, by using PEG1000, 2000, 4000, and 6000 in MCS [82] and PEG4000 in RMS [83], respectively, significant improvements were observed in relation to undercooling phenomena, melting and solidification times, and heat stored in PCM composites compared with their respective pure PEG of different molecular weight. The papers underlined the

versatility of these PCMs, which can be adaptable to different operating temperatures and diverse energy storage systems.

The inclusion of PEG2000 into graphene-based mesoporous silica sheets (GS) [84] and of PEG6000 into silica nanosheets (SNSs) modified with Ag nanoparticles (AgNPs) onto Sn^{2+} -activated SNSs [85], respectively, was found to be effective for producing PCMs. The authors of both studies highlighted the good confinement of PEG in PCMs obtained with these supports thanks to their physical interactions with the polymer, which resulted in improvements in the phase change process, thermal conductivity, and stability of PEG-based PCMs.

The use of silica fume (SF) as an inert matrix for PCMs to support different grades of PEG is reported in [33,40,86,87]. The investigation presented in [40] focused on the development of shape-stabilized PCM composites obtained by impregnating PEG4000 in low-cost SF. The obtained spherical PCM agglomerates allow for better flowability, packability, and enhanced heat transfer. These agglomerates showed a higher heat capacity, both in the solid and liquid phases, and, consequently, superior heat transfer characteristics. Finally, PCM composites offer remarkable thermal stability even after repeated temperature cycles. The SEM images in Figure 7 illustrate the surface characteristics of porous SF and SF/PEG PCM composites at different PEG concentrations. The surface of SF appeared granular and uneven (Figure 7a). With an increasing PEG content within the composite's pores (Figure 7b–d), the SF morphology transformed, adopting a smoother and more cohesive appearance.

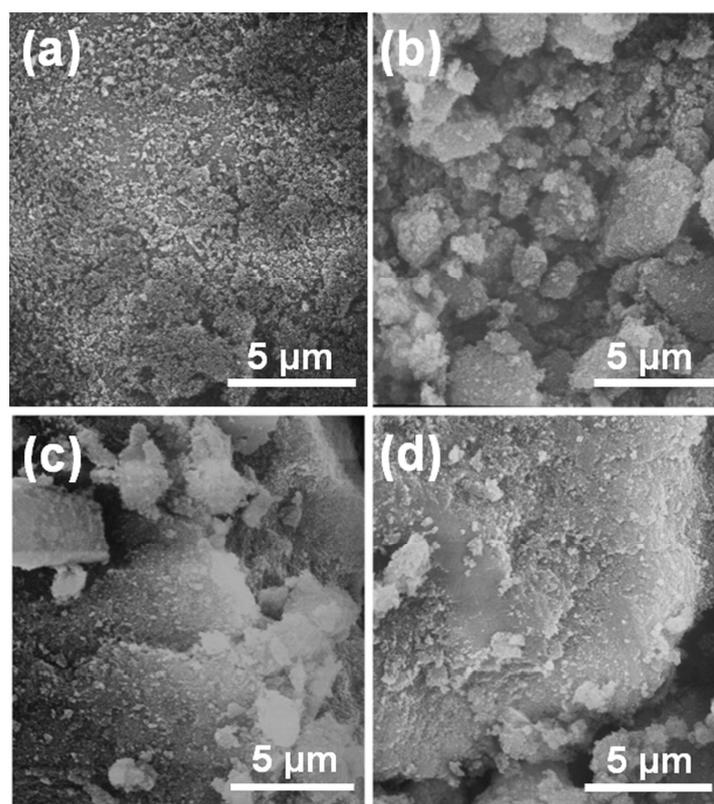


Figure 7. Surface microstructure of (a) porous SF; (b) SF/PEG PCM composite (at 25% wt.); (c) PEG/SF PCM composite (at 50% wt.); (d) PEG/SF PCM composite (at 75% wt.). Reprinted from [40], with permission from Elsevier (5 February 2024).

Activated silica fume (ASF) was also proposed as an inert matrix able to reduce the leakage of PEG1500 from PCM [86]. ASF-PCM displayed good mechanical properties when applied as a coating on rubberized concrete (RC), influencing also its thermal conductivity. The ASF-based PCM showed limited heat storage losses during hot/cold cycles.

Shape-stabilized (SS)-PCM, used for masonry wall finishes, was developed by integrating PEG600 into silica fume [33]. The integration of SS-PCM into cement mortars modified its mechanical properties and significantly reduced temperature fluctuations in the wall. The study also correlated the ambient temperatures of different cities in Iran and the thermal performance of the PCM, proving its effectiveness.

Form-stable-latent heat storage materials (FS-LHSMs) were developed using raw silica fume (RSF) as a matrix with PEG600 [87]. Carbon nanofibers (CNFs), carbon nanotubes (CNTs), and graphene nanoplatelets (GNPs) were added to improve the thermal conductivity. The obtained FS-LHSMs displayed, in addition, good stability and improved durability, preventing the leakage of PEG with a content of 40% by weight.

Several works analyzed PEG-based PCMs with SiO₂ as a matrix. In [88], PCM composed of PEG2000 and SiO₂ was developed through the sol-gel method. PEG and SiO₂ matrix formed a core-shell structure that maintained a solid form even well beyond the melting point of PEG. The addition of graphite is able to increase the thermal conductivity of PCM up to 0.558 W m⁻¹ K⁻¹.

The sol-gel method was also used in [89] to stabilize SiO₂/PEG800 in a porous structure of modified wood. The results of the study showed a very high heat accumulation capacity and exceptional dimensional stability, with the modified wood being capable of preventing the leakage of PEG during phase transitions. This system can be suitable for applications in exterior walls, roofs, or floor thermal insulation panels.

PEG6000/SiO₂ PCM was proposed also to enhance the fire resistance in building structures [90]. This composite, when introduced in a mortar, was able to absorb the additional heat developed during a fire. It was found that 15% wt. SiO₂ content is required to keep the composite undamaged (i.e., avoiding leakage).

A PEG4000/SiO₂ composite was produced in [39] using waste oil shale ash as a matrix (i.e., ss-CPCM). The resulting composite offers excellent thermal stability, reduced supercooling, and shorter melting and solidification times compared with pure PEG. These findings suggest that the ss-CPCM PCM could be employed as thermal energy storage material, especially in climates characterized by hot summers.

The authors of the study reported in [28] analyzed concrete blocks integrated with a form-stable PEG1000/SiO₂ PCM. An optimal thermal performance of the blocks was achieved with the addition of 7.5% wt. PCM, with reduced temperature fluctuations and improved mechanical strength.

In a similar study [91], PEG1000-SiO₂ was integrated in bricks. The PCM-saturated bricks displayed an improved thermal energy storage capacity, capable of guaranteeing optimal indoor temperatures even in extreme outdoor conditions.

A shell material with good heat storage capacity, based on PEG2000-nanoSiO₂ (SSHS FSPCM), is illustrated in [92]. A 9 °C reduction of the indoor temperature during the heating phase was achieved using this PCM.

Table 5. Thermal characteristics of different PEG-based PCMs with a silica-based porous matrix. The amount of PEG in each PCM is also reported. (T_m: melting point; ΔH_m: melting enthalpy; T_c: crystallization point; ΔH_c: crystallization enthalpy).

PEG	Matrix	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)	Amount of PEG (% wt.)	Ref.
1000	Mesoporous calcium silicate	58.0	28.6	41.1	21.1	40.0	[82]
2000		58.4	65.8	41.5	52.9	50.0	
4000		58.3	104.6	43.3	89.8	60.0	
6000		57.0	122.1	44.1	106.8	70.0	
4000	Radial-like mesoporous silica	57.8	121.7	46.4	104.4	70.0	[83]
2000	Graphene-based mesoporous silica sheets	49.2	136.3	-	-	80.0	[84]

Table 5. Cont.

PEG	Matrix	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)	Amount of PEG (% wt.)	Ref.
6000	Silica nanosheets	57.8	114.8	43.5	104.6	-	[85]
	Silica nanosheets with Sn ²⁺	57.9	114.7	44.0	104.1	-	
	Silica nanosheets with Sn ²⁺ and Ag nanoparticles	58.0	113.9	44.3	103.8	66.1	
4000	Silica fume	56.9	169.7	24.1	159.6	75.0	[40]
		56.0	120.5	17.6	107.3	50.0	
		55.7	101.0	15.3	79.6	25.0	
600	Silica fume	19.6	71.6	13.7	74.1	-	[33]
600	Raw silica fume	14.2	56.1	9.0	53.3	40.0	[87]
	Raw silica fume with carbon nanofiber	15.2	56.1	8.1	54.2		
		15.1	55.3	8.2	54.1		
	Raw silica fume with carbon nanotube	14.0	55.2	9.2	53.5		
		13.8	55.7	8.9	53.5		
	Raw silica fume with graphene nanoplatelet	15.0	55.0	10.0	54.1		
		14.9	55.1	10.0	53.1		
2000	SiO ₂	57.4	128.4	-	-	80.0	[88]
800	SiO ₂	25.6	14.1	16.0	11.6	70.0	[89]
		25.8	25.4	17.3	21.9	80.0	
		25.3	39.4	17.7	33.4	90.0	
6000	SiO ₂	65.6	133.4	-	-	80.0	[90]
		58.9	79.4	-	-	60.0	
4000	SiO ₂	58.09	151.8	42.3	141.0	80.0	[39]
1000	SiO ₂	36.8	113.6	21.5	115.4	80.0	[28]
1000	SiO ₂	29.7	143.0	40.0	117.2	86.7	[92]

As for the matrices of a different chemical nature analyzed previously, also in this case the ΔH of the PCM generally rises as the PEG content increases. On the other hand, a decrease of the enthalpies was observed in some cases and explained in terms of delay of the PEG crystallization process [83,85]; the movement and arrangement of the PEG molecular chains were somewhat limited in nanopores and mesopores, resulting in a decrease in the extension of the crystalline regions. Once again, the type of matrix and its structure influence the phase change enthalpy of the PCM; further aspects are discussed in Section 5.

4.4.3. PEG-Based PCMs with Other Mineral Porous Matrices

Diatomite, bentonite, pumice, vermiculite, mica, expanded perlite, natural clay, kaolin, and calcium carbonate are the most widely used mineral porous materials to produce form-stable PCMs. The main thermal characteristics of PEG-based PCMs with different inorganic porous matrices are reported in Table 6.

To the best of our knowledge, the paper reported in [93] is the first in which a form-stable PCM was produced by vacuum impregnation of PEG in a diatomite matrix. The composite PCM showed promising thermal properties, retaining up to 50% of PEG1000 within the diatomite pores without any loss of molten PEG. The addition of EG allowed for increased thermal conductivity in the PCM. Subsequently, other works in which diatomite is used as a matrix for PEG-based PCMs were published, as in [94], where PEG4000 was incorporated into a diatomite matrix decorated with Ag nanoparticles. Carbon nanotubes (CNTs) were proposed to enhance the thermal performance of PEG600-based PCM with raw diatomite as a matrix [95]. In both investigations, remarkable improvements in ther-

mal properties were achieved in terms of thermal conductivity and heat storage capacity compared with their respective reference PCMs.

Bentonite is another mineral porous material commonly used to incorporate PEG to create form-stable PCMs. The work reported in [96] reports the use of PEG600 included in bentonite clay. DSC measurements demonstrated that the obtained PCM had adequate phase change temperatures and thermal storage ability; its thermal conductivity was improved by the addition of expanded graphite. Scanning electron microscopy analysis revealed a homogeneous dispersion of PEG within the bentonite matrix, while FTIR investigations revealed that only physical interactions (i.e., capillary forces) are established between the components, favoring the retention of PEG in the matrix.

Pumice has been proposed as a cheap and efficient support material to make a PCM including PEG600 [23]. The developed leak-proof PCM, when incorporated into mortars based on ordinary cement (OC), was able to maintain indoor temperatures in a more comfortable range compared with environments plastered with OC only.

An innovative approach was proposed in [97] to modify the surface of attapulgite (ATP) using hydrochloric acid (H-ATP) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (N-ATP) to improve the thermal performance of a PEG2000-based form-stable composite (FSCPCM). The proposed procedure was effective for changing the pore structure of attapulgite, facilitating the crystallization of PEG within the pores, obtaining a PEG/N-ATP FSCPCM. Figure 8 shows how the morphology of attapulgite changes based on the treatments used, and how PEG integrates into these modified and unmodified matrices. The raw attapulgite appears in the form of fibers (Figure 8a) that disappear when PEG is added (Figure 8d). H-ATP still appears in fiber form (Figure 8b) while, upon the addition of PEG, these fibers become more homogeneous (Figure 8e). The same occurs in the case of N-ATP (Figure 8c), whose surface appears smoother upon the addition of PEG (Figure 8f). These differences show how the PEG is dispersed within the matrix.

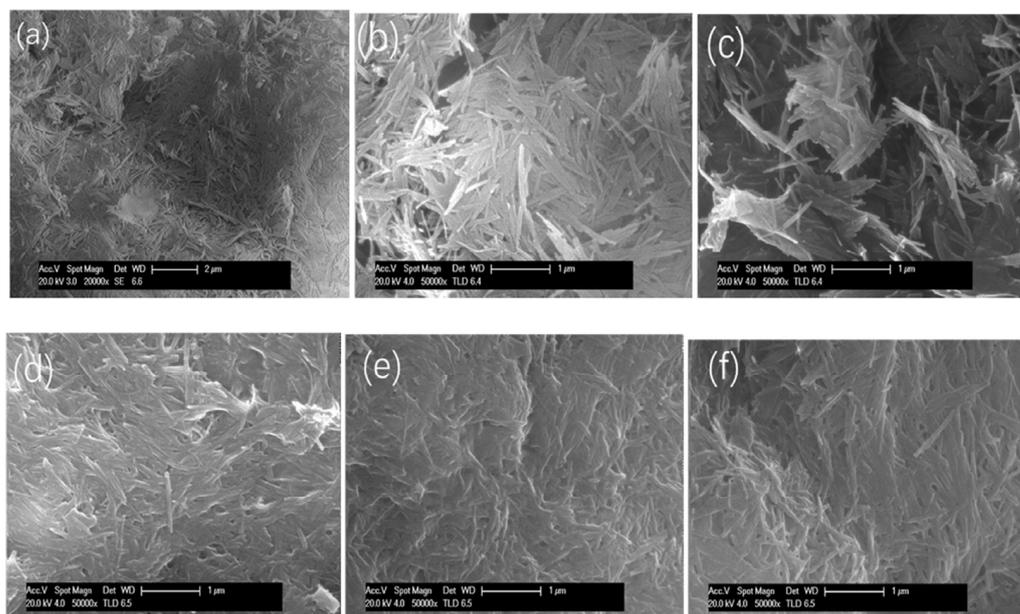


Figure 8. Microstructure of modified and unmodified attapulgite and its integration with PEG: (a) raw ATP; (b) H-ATP; (c) N-ATP; (d) raw ATP with PEG; (e) H-ATP with PEG; (f) N-ATP with PEG. Reprinted from [97], with permission from Elsevier (5 February 2024).

A notable increase in phase change enthalpy was achieved in the FSCPCM PEG/N-ATP composite compared with the reference, i.e., PEG/raw attapulgite. The new PCM had good long-term stability, adequate thermal energy storage capabilities, and satisfactory thermal conductivity. Also, in this case, the modified composite incorporated into the

cement mortar showed a higher heat storage capacity than the mortar containing the unmodified PEG/raw attapulgite.

The research reported in [98] illustrated the development of a form-stable composite, indicated with PCE-CPCM, obtained by incorporating PEG2000 with carbon nanotubes in an expanded vermiculite (EVM) matrix. A synergy between the characteristics of vermiculite and CNTs produced a PCM with high heat transfer and storage capabilities. The modified structure of EVM contributed to the shape stability of the PCE-CPCM, characterized by a PEG content between 78% and 82% by weight. The addition of CNTs also improved the heat transfer efficiency of the PCM, resulting in a thermal conductivity of 0.5148 W/(m·K). Finally, PCE-CPCM showed excellent chemical and thermal stability.

Mica, composed of sheets of aluminum silicate that form a layered structure, is not conventionally considered a porous material. However, some treatments can create diffuse porosity in it. A modified mica (Md) was, for example, used as a support matrix for PEG-based PCMs [99]. The authors of the study did not specify the degree of employed PEG. Through extensive characterization, the developed Md/EG/PEG composite was found to offer remarkable heat stability and improved thermal performance. Furthermore, the introduction of EG in the PCM significantly increased thermal conductivity (by nearly 110%) and substantially increased phase change enthalpy.

Several authors have used expanded perlite (EP), a light material with good thermal properties, as a porous support to create PEG-based PCM. In [44], a PEG6000/EP PCM (PEPC), was produced. The composite presented a highly porous structure composed of micropores, ideal for adsorbing molten PEG. A satisfactory thermal conductivity (0.479 W/(m·K)) was found for PEPC PCM. The improvement of thermal characteristics of PCMs composed of carbon-modified expanded perlite (EPC) and PEG4000 was investigated in [100]. Through an in situ carbonization and vacuum impregnation process, it was possible to increase the amount of PEG incorporated in the modified EPC micropores. The thermal conductivity of EPC/PEG PCM reached 0.521 W/(m·K), nearly 1.3 times that of pure PEG. The development of a PCM based on EP with the inclusion of PEG6000 blended with industrial byproducts is presented in [47]. If carbon nanotubes were incorporated into the EP/PEG system (0.5% by weight), a thermal conductivity of 0.453 W/(m·K) was achieved. Furthermore, the developed composite showed superior energy storage/release capabilities, minimizing supercooling and maintaining stability even after 200 heating and cooling cycles. The porous structure of the expanded perlite matrix, in fact, was able to prevent PEG leakage. PCM composites with a shell-core structure formed by EP and wood powder/high-density polyethylene (WF/HDPE) matrix including PEG800 (i.e., E-shell PCM) were developed in [101]. The innovative E-shell PCM exhibited high phase transition enthalpy and excellent thermal stability.

Clay is another example of a sustainable porous inert matrix able to retain PEG to make PCMs for use as aggregates in mortars or concrete. It is a naturally abundant material and can contribute to the energy efficiency of buildings thanks to its thermal properties. The research reported in [102] aimed to develop composite PCMs based on PEG600 and natural clay. SEM and FTIR analyses showed a homogeneous confinement of PEG600 within the inert PCM matrix. Furthermore, PCM remains stable even following thermal cycling. Thermal tests performed on PEG600/natural clay cubes have shown that it is possible to significantly reduce the temperature inside building elements during an external temperature rise. PEG600/expanded clay aggregates (ECA), combined with Alccofine1203 (which is a mineral additive), were employed as PCM to be applied in concrete [103]. A very limited PEG leakage from this PCM was observed even when it was aged at 40 °C for 6 h. The addition of Alccofine1203 also contains the reduction of the mechanical properties, in compressive and flexural mode, of the cement.

Kaolin and calcium carbonate have been proposed in numerous papers as matrices for PCMs used in building applications. Form-stable PCMs (Kb-CPCMs) were produced using vacuum impregnation to incorporate PEG600 into kaolin [104]. The obtained PCM composites offer phase change temperatures and enthalpies suitable for indoor temperature

regulation. The addition of expanded graphite in the Kb-CPCMs resulted in an increase in their thermal conductivity. In another work [105], PEG1000 was enclosed into acid-modified halloysite (i.e., a type of kaolin) to obtain a PCM with enhanced thermal performance. The modification increased the amount of PEG included in the halloysite-based PCM, with an additional increase in thermal conductivity.

Referring to investigations focused on calcium carbonate matrices, in [106], PEG6000 was incorporated into a Sr²⁺-doped BaCO₃ matrix to obtain a shape-stabilized PCM composite. This system exhibited exceptional thermal characteristics and stability. In another study [30], the development of a form-stable PCM based on PEG1000 embedded into flakes of waste Lecce stone (LS), byproducts of the processing of this very porous stone, was investigated for possible applications in different mortars. Further investigations, reported in [107–110], analyzed different compositions of PEG800-based and PEG1000-based PCMs within LS, in order to identify the PCM composition giving rise to the best performance when included in mortars based on different binders (aerial and hydraulic limes, gypsum, and cement). In [111–113], the thermal performance of PEG800/LS and PEG1000/LS PCMs was assessed, taking as reference two different climate zones (i.e., Mediterranean and continental Europe); the produced PCMs proved to be particularly effective in reducing temperature fluctuations in hot seasons.

Table 6. Thermal characteristics of different PEG-based PCMs with a mineral porous matrix. The amount of PEG in each PCM is also reported. (T_m: melting point; ΔH_m: melting enthalpy; T_c: crystallization point; ΔH_c: crystallization enthalpy).

PEG	Matrix	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)	Amount of PEG (%wt.)	Ref.
1000	Diatomite	27.7	87.1	32.2	82.2	50.0	[93]
600	Diatomite and 1% CNTs	7.9	51.4	6.9	53.2	41.0	[95]
	Diatomite and 2% CNTs	7.3	53.8	8.2	57.9	42.8	
	Diatomite and 3% CNTs	6.9	55.9	8.1	59.8	44.5	
	Diatomite and 4% CNTs	7.2	62.9	8.8	69.5	50.7	
600	Bentonite	4.0	56.7	10.3	55.1	43.0	[96]
600	Pumice	8.8 *	98.4	13.9 *	96.1	56.0	[23]
2000	Modified attapulgite	45.2	38.7	35.7	35.2	25.0	[97]
		45.2	54.8	36.2	51.1	35.0	
		45.8	75.6	36.2	70.8	45.0	
2000	Expanded vermiculite with 1.59 CNTs	41.9	19.4	11.8	46.2	77.8	[98]
	Expanded vermiculite with 3.30 CNTs	42.8	25.6	16.2	58.1	79.3	
	Expanded vermiculite with 5.20 CNTs	45.1	45.1	21.1	77.5	81.5	
	Expanded vermiculite with 7.09 CNTs	48.0	83.9	27.3	104.2	81.5	
-	Mica	57.7	91.8	42.4	91.9	53.6	
-	Decorated mica (Md)	57.9	99.6	45.9	99.4	57.2	[99]
-	Md with expanded graphite	57.7	136.3	46.4	132.6	76.7	
6000	Expanded perlite	58.4	145.1	46.3	137.3	70.1	[44]
	Expanded perlite with carbon layer	55.2	134.9	46.7	129.3	66.4	
4000	Expanded perlite	56.8	139.9	41.3	132.1	73.4	[100]
	Carbon-modified expanded perlite	57.5	127.8	41.3	122.0	73.9	
6000	Expanded perlite	59.5	150.7	41.4	134.6	79.5	
6000	Expanded perlite with 0.5% CNTs	61.6	132.1	41.2	118.5	69.7	[47]
	Expanded perlite with 1% CNTs	61.8	121.9	39.2	109.2	64.2	
800	Untreated expanded perlite	23.8	101.2	12.8	97.2	65.0	[101]
	Treated expanded perlite	28.2	136.4	21.6	123.2	85.0	
600	Gypsum	10.6	24.2	15.8	21.6	18.0	[102]
	Natural clay	10.9	28.8	16.3	26.0	22.0	

Table 6. Cont.

PEG	Matrix	T _m (°C)	ΔH _m (J·g ⁻¹)	T _c (°C)	ΔH _c (J·g ⁻¹)	Amount of PEG (%wt.)	Ref.
600	Kaolin	5.2	32.8	−15.4	29.8	20.0	[104]
1000	Acid-modified halloysite and graphene	38.4	83.0	27.2	82.2	55.0	[105]
6000	5% of SrBaCO ₃	60.2	148.8	39.1	145.0	78.5	[106]
	10% of SrBaCO ₃	60.3	141.8	39.9	139.2	74.8	
	15% of SrBaCO ₃	60.1	124.1	37.4	121.5	65.5	
1000	Lecce stone	39.3	27.7	19.4	26.2	23.0	[30]
800		12.7	28.3	9.3	28.1	23.0	[108,109]

* These values refer to the onset temperatures.

Even in the case of composite PCMs with porous mineral matrices, an increase in phase change enthalpies is observed for increasing PEG contents, although with some exceptions. For instance, the data reported in [89,98] appear to be “outliers”, since a high PEG content does not correspond to a high heat developed during melting and crystallization. Generally speaking, weak physical interactions (i.e., hydrogen bonds, capillary forces, surface adsorption) develop between PEG and the porous mineral support. As a consequence, the matrix appears to have only a limited influence on the thermal properties of the PCM. These aspects are also discussed in Section 5.

5. Statistical Analysis and Discussion

Once all the thermal data relating to PEG-based PCMs made with different matrices had been collected, we tried to correlate the ΔH measured in each PCM with the amount of PEG included in it. For the sake of brevity, only the enthalpies measured during the melting phase were analyzed. This analysis could be very useful for choosing which PCM to use in a specific application. Furthermore, it is also very important to understand if there is an effect due to the type (in terms of composition and chemical nature) of the matrix composing the PEG-based PCM. For this purpose, it was decided to divide and analyze the data separately based on the nature of the PCM matrix (i.e., organic, both synthetic and natural, matrices; data reported in Tables 2 and 3), carbon-based matrices (data reported in Table 4), silica-based porous matrices (data reported in Table 5), and other mineral porous matrices (data reported in Table 6). Furthermore, taking into account that, as already underlined, the order of magnitude of the enthalpies of PEG with medium/high molecular weights is approximately the same, only data relating to PEG with a molecular weight equal to or greater than 800 were taken into consideration. The linear regression method was then applied to the data divided on the basis of the nature of the PCM matrix.

The enthalpies developed by form-stable PCMs having a synthetic or natural polymeric matrix, as a function of the PEG content (in terms of weight percentage), are reported in Figure 9 (data from Tables 2 and 3), along with linear fitting of the data.

A coefficient of correlation (R^2) of about 0.59 indicates that the correlation between analyzed data is not high. In fact, even visually, it is clear that the ΔH data appear scattered around the regression line. This observation suggests that the type of matrix (i.e., different composition and/or structure of the polymer matrix, synthetic or natural polymer) can have a certain influence on the enthalpy developed by the PCM during the melting/crystallization of PEG. As a consequence, there is no linear relationship between ΔH and PEG content that applies exactly to all PCMs analyzed. For example, (physical) interactions between PEG and the polymer matrix can favor/hinder the crystallization of PEG; moreover, restricted movements of PEG chains due to crosslinks of thermosetting matrices or to the rigid segments of thermoplastic crystalline polymers, cellulose skeleton, or wood structure, can hamper crystallization. As already observed when commenting on the discrepancies in the data reported in Table 1, there may be additional causes to justify some differences in thermal data (different instruments, same grade of PEG but with

different purity). The slope of the linear relationship reported in Figure 3 (i.e., m equal to 1.7471) represents the rate at which the enthalpy (on average) varies as the percentage of PEG increases. A slope around 1.8 indicates that, as expected, ΔH on average increases as PEG% increases. The growth rate, on the other hand, depends on the composition of the individual polymer matrix of the PCM, as can be inferred from the dispersion of the data.

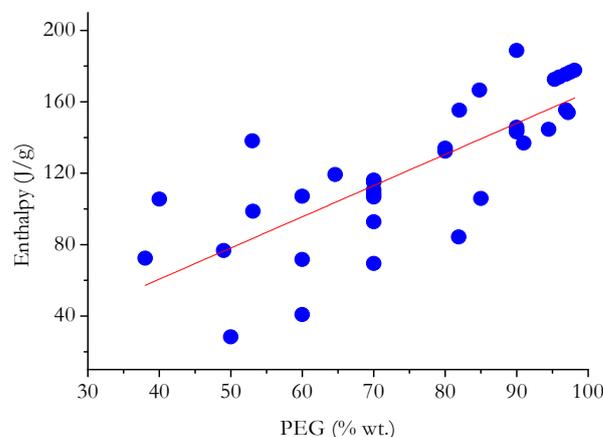


Figure 9. Data and linear fitting relative to the enthalpy developed on melting by each PEG-based PCM, with a polymer (synthetic and natural) matrix, vs. the amount (in weight percentage) of PEG in the PCM. Parameters of the fitting: $R^2 = 0.58844$, $m = 1.7471$, $q = -9.24499$.

The values of ΔH of form-stable PCMs with a carbon matrix versus PEG content (% wt.) are shown in Figure 10 (data from Table 4). The linear relationship of the data is also shown. For easier comparison, the diagrams have been drawn using the same scale. In this case, to have a fitting correlation coefficient greater than 0.5, it was necessary to eliminate three points relating to PCM having an expanded graphite matrix with PEG of lower molecular weights. In fact, using all the points gives an R^2 equal to 0.31052. The residual data used for fitting are few and concentrated at high percentages of PEG, since, as already underlined, carbon-based matrices are able to contain large quantities of PEG. Despite the removal of three data points, the correlation coefficient (R^2) of the fitting remains modest. Keeping this in mind, it is possible to observe that the enthalpy developed by PCMs with a carbon-based matrix depends more significantly on PEG content compared with PCMs with a polymer-based matrix. In fact, the slope equal to 2.09396 is somewhat greater than that reported in Figure 9. Bearing in mind what has just been underlined, no further considerations can be made.

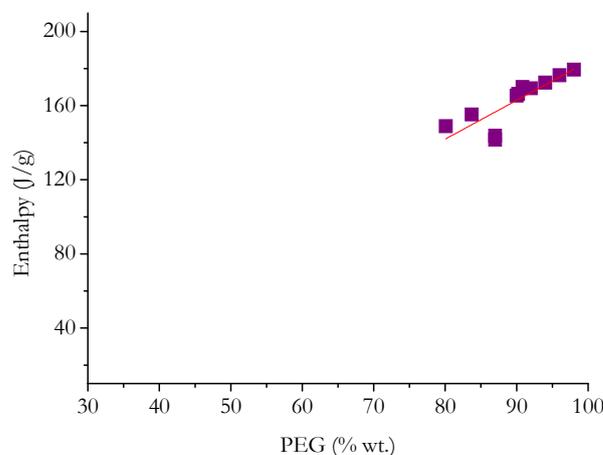


Figure 10. Data and linear fitting relative to the enthalpy developed on melting by each PEG-based PCM, with a carbon-based matrix, vs. the amount (in weight percentage) of PEG in the PCM. Parameters of the fitting: $R^2 = 0.66667$, $m = 2.09396$, $q = -25.59131$.

The enthalpy values found for form-stable PCMs with a silica-based porous matrix as a function of the PEG content (% wt.), with the linear relationship correlating the data, are shown in Figure 11 (data from Table 5). In this case, even eliminating three data points from the analysis (i.e., those relative to PEG800, significantly out of trend), the R^2 value remains just under 0.5. The confirmation of the limited correlation of the data is also visual; the points in Figure 11 appear, in fact, to be quite widespread. As already observed in Section 4.4.2, the energy stored in each PCM depends appreciably also on the type of siliceous support, due to different effects of the support and interactions between PEG and matrix. Despite this, it is still evident that enthalpy has an increasing trend as the % PEG content increases (slope equal to 1.38067), as in the case of PCMs with different matrices.

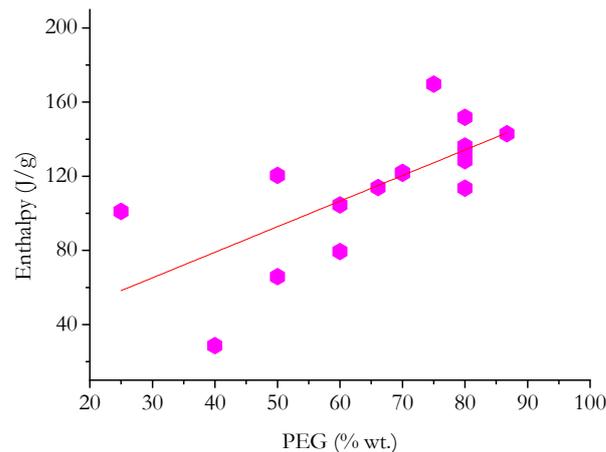


Figure 11. Data and linear fitting relative to the enthalpy developed on melting by each PEG-based PCM, with a silica-based porous matrix, vs. the amount (in weight percentage) of PEG in the PCM. Parameters of the fitting: $R^2 = 0.44385$, $m = 1.38067$, $q = 23.76451$.

Finally, the values of ΔH found for form-stable PCMs with a mineral (non-siliceous) porous matrix versus the PEG content (in terms of weight percentage) are presented in Figure 12 (data from Table 6). The linear relationship of the data is shown in the same figure.

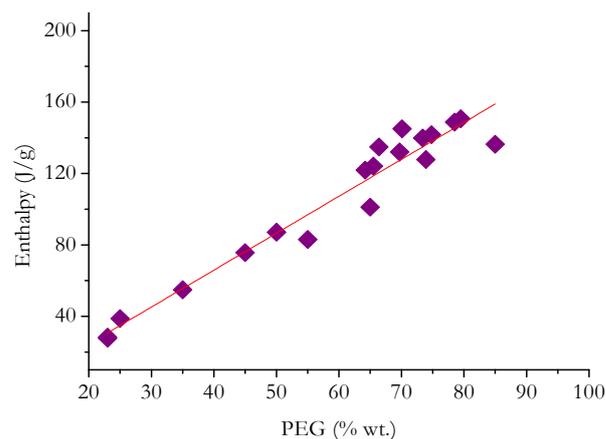


Figure 12. Data and linear fitting relative to the enthalpy on melting developed by each PEG-based PCM, with a mineral non-siliceous porous matrix, vs. the amount (in weight percentage) of PEG in the PCM. Parameters of the fitting: $R^2 = 9.4406$, $m = 2.06969$, $q = -16.96255$.

The data reported in Figure 12 suggests that the ΔH of PCMs having a non-siliceous mineral matrix is essentially a function of the PEG content, increasing significantly with it (slope greater than 2); that is, the composition and structure of the mineral-based matrix have a minimal influence on the heat developed/absorbed by the PCM during its phase

transition, as can also be deduced from a correlation coefficient close to 10 ($R^2 = 9.4406$). This observation suggests that no strong interactions occur between PEG and the mineral matrix, as already highlighted in Section 4.4.3. It must be taken into account, however, that to obtain good correlation in this case as well, three data points have been eliminated (related to PEG2000)—the same data previously identified as “outliers”. On the other hand, the data on which the correlation was carried out are still abundant and they appear sufficient to prove that, in this case, a clear trend exists.

To conclude the discussion, we reported the ΔH developed by PCMs with different matrices, but all obtained with PEG1000 versus the content of this polymer, to check whether a trend of some kind can be identified. As anticipated in Section 2.1, the PCMs most suitable for applications in buildings are those based on PEG with moderate molecular weights, thanks to their phase change temperatures (shown in Table 1), which are compatible with human comfort temperatures. Among the different grades, PEG1000 is probably the most suitable candidate for these applications. The enthalpy of melting, shown with different colors in Figure 13 depending on the nature of the matrix, generally increases as PEG content increases, as expected. It is evident that there is a certain influence of the nature of the matrix on the ΔH , because the different data do not align on a straight line. On the other hand, this is what has already been highlighted in the analysis just reported. Finally, the data are few and quite widespread, so it is not possible to conclude which matrix provides the best thermal properties.

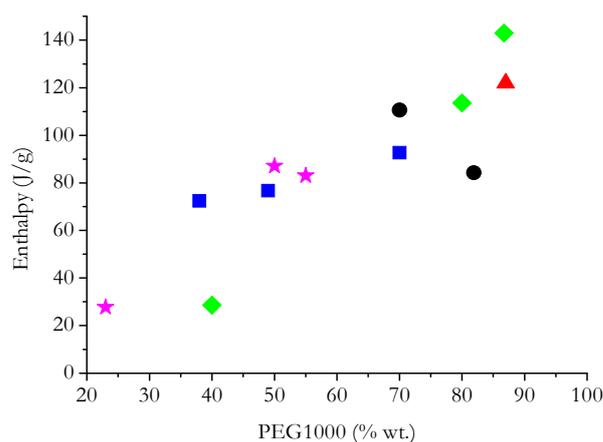


Figure 13. Data relative to the enthalpy developed on melting by each PEG1000-based PCM with different porous matrices, vs. the amount (in weight percentage) of PEG1000 in the PCM. (Type of matrix: blue squares = synthetic polymers; black circles = natural polymers; red triangle = carbon-based material; green rhombuses = silica-based materials; fuchsia stars = other minerals).

6. Conclusions

PEG polymer has been widely used to make form-stable PCMs for building applications and beyond, thanks to a mix of favorable properties and the possibility of selecting the most appropriate phase change interval as a function of the molecular weight. In the literature, matrices of different natures have been tested to contain PEG in form-stable PCMs; in this work, the different matrices were reviewed with the aim of identifying the PEG/matrix pair that best responds to a specific application. The study also aimed to detect if there is a correlation between phase change enthalpy and the content of PEG depending on the type of matrix. The analysis carried out allowed the following conclusions to be drawn.

- In general, ΔH increases with PEG content (in terms of weight percentage) for PEG grades with comparable thermal characteristics.
- By separately analyzing PCMs having matrices of a specific nature, it is possible to deduce that the enthalpy developed by PCMs with carbon-based or mineral non-siliceous porous matrices depends greatly on the PEG content compared with PCMs with polymer-based or siliceous matrices.

- Even sorting the matrices based on their chemical nature, it is not possible to find linear relationships that precisely fit the heat developed during the phase change and the PEG content in each PCM. This suggests that, in most cases, the nature of the matrix has a diverse effect on the ΔH measured during the phase change. This may depend on physical interactions that are established between PEG and the matrix; difficulty for PEG to crystallize in the pores of the matrix; and limits in the crystallization of PEG due to the presence of cross-links/crystalline macromolecules of the polymer matrix.
- While the selection of the PEG grade is made based on the thermal fluctuations that must be reduced, the choice of the matrix must also be made based on the final expected characteristics of the PCM. For instance, to increase the low thermal conductivity of PEG, carbon-based matrices can be used. To ensure optimal PCM performance that is maintained over time, it is necessary to use a matrix that allows the stabilization of the PEG inside the support. The PCM must not significantly compromise the mechanical properties or weight of the element in which it is inserted, for example, if it is added to mortars.
- Keeping sustainability in mind, the choice of the matrix must also be made based on its availability onsite, limiting fuel resources and costs for its transportation and favoring the exploitation of byproducts from other industries, according to the principles of circular economy.
- Finally, the choice of the optimal PEG/matrix couple must also be made based on the quantity of PCM that can be included in the building component; for example, the percentage that can be added to a mortar.

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