



Thermal Properties of Alternative Phase Change Materials for Solar Thermal Applications

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ABSTRACT

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Phase change materials (PCMs) with a solid-solid phase transition are receiving increasing attention as promising materials for thermal energy storage (TES) systems. Unlike the more well-known and widespread solid-liquid PCMs, they generally have negligible volume change during phase transition, no contamination, and long cyclic life. Among the most studied solid-solid PCMs, a group of organic materials known as plastic crystals and their mixtures seem to show energy storage properties suitable for solar thermal systems at low-medium temperatures (80-150°C). In this study, to deeply analyze their suitability for these applications, the thermophysical properties and thermal stability of two promising plastic crystals, pentaerythritol (PE) and pentaglycerine (PG), and their mixture are reviewed. The phase transition properties of these two pure substances were also assessed in this study through differential scanning calorimetry (DSC). The experimental measurements showed good agreement with the data collected from literature. The analysis showed that various properties and characteristics of these materials should be further investigated since a limited number of studies related to their properties is available. However, if their drawbacks are adequately addressed, the studied plastic crystals seem suitable for TES applications.

1. INTRODUCTION

Thermal energy storage (TES) based on phase change materials (PCMs) is considered one of the most attractive techniques to store energy from renewable energy sources or waste heat from industrial applications [1]. PCMs are a broad group of materials able to store and retrieve a large amount of thermal energy in small temperature ranges since the stored energy corresponds to the latent heat involved in their phase transitions. Among the four phase transition processes that can occur in a PCM (i.e., solid-solid, solid-liquid, solid-gas, and liquid-gas), the materials comprising a transition between solid phases and from solid to liquid phase are the most suitable to be used in actual applications [1, 2].

In recent years, many solid-liquid PCMs and their eutectic mixtures have been broadly analyzed for various TES applications, such as solar energy, building sector, cold storage, and industrial sector [3-7]. The materials with solid-liquid phase transition properties suitable for the TES systems are classified into three main categories: organic, inorganic, and eutectic PCMs. However, each group has specific advantages and drawbacks that could hinder their use in different applications [1, 8]. Some of the main ones are high volume expansion, liquid leakage during multiple phase-change cycles,

and phase segregation.

Consequently, PCMs with a solid-solid phase transition have been receiving increasing attention as promising alternatives since they have different advantages, such as negligible volume change during phase transition, no contamination, and long cyclic life [9, 10]. Another advantage of the solid-solid PCMs (S-S PCMs) is their possible direct use in TES systems without the need for encapsulation or heat exchangers [11].

The S-S PCMs can be divided into three main families: organic, inorganic, and hybrid materials. The organic S-S PCMs comprise polyalcohols, polymeric and organic-salt-based materials. This family's phase transition temperatures and enthalpies range between 25 to 185°C and 15 and 270 kJ kg⁻¹, respectively [10]. The family of inorganic S-S PCMs is mainly composed of ceramic-based materials, having phase transition temperature and enthalpy ranges of 30-120°C and 25-70 kJ kg⁻¹, respectively [10], and metallics and metal alloys, which are characterized by high phase transition temperatures (600-1000°C) [9]. Finally, hybrid S-S PCMs include perovskites and organometallic-based materials obtained by appropriately combining the first two families.

Among the organic S-S PCMs, polyalcohols are well-known and widely studied materials that seem suitable for low

and medium-temperature TES systems, such as those used in solar thermal applications. Their solid phase transition temperatures are from 43 to 187°C, while their transition enthalpies are generally higher than other S-S PCMs [10]. Polyalcohols are also known as "plastic crystals" (PCs) since they undergo reversible solid phase transformations from low-temperature layered (or chained) structures (α -phase) to partially disordered ones, which form the plastic phase (γ -phase) [10, 12]. Some of the most studied PCs are as follows [12]: pentaerythritol (PE), pentaglycerine (PG), neopentylglycol (NPG), 2-amino-2-methyl-1,3-propanediol (AMPL), and tris(hydroxyl methyl)aminomethane (TAM or TRIS). AMPL and TAM are amine derived from polyalcohols [12]. Moreover, the mixtures of PCs are considered promising S-S PCMs with phase transition properties adjusted for specific TES systems [12-14]. In particular, some of these mixtures are characterized by non-isothermal continuous phase transitions in temperature ranges specific for each composition. Examples are PE+PG+NPG ternary mixture and its binary subsystems that can be used in TES applications that do not exclusively need conventional isothermal phase transitions, such as different solar thermal systems [15].

Several studies regarding the phase transition properties and crystallographic properties of PCs and their mixtures have been carried out for many years [10, 16-20]. However, to the best of our knowledge, fundamental features to evaluate their actual use in TES applications (e.g., thermophysical properties, thermal stability, cycling stability, cost analysis) were not deeply analyzed. This could be due to the research on the use of solid-solid PCMs in actual TES applications, which still is at an early stage, and further studies are necessary [10]. In this regard, few works about the performance of PCs in TES systems for specific applications were found in the literature. Some of the analyzed applications are solar drying [21], solar cooking [22, 23], solar industrial process heat [24], and heat recovery [25, 26].

This study reviews the main characteristics of PE and PG and their mixture to evaluate if they can be suitable for various solar thermal applications at low-medium temperatures (80-150°C). In particular, the literature studies reporting the following characteristics of the mixture and their pure components are analyzed: phase transition properties, thermophysical properties, and thermal and cycling stability analyses. Measurements of the phase transition properties performed using differential scanning calorimetry (DSC) are also reported to confirm the accuracy of the literature data.

2. MATERIALS AND METHODS

2.1 Features of S-S PCMs analyzed in this study

It is well-known that, in general, the following criteria should be considered to select PCMs suitable for practical TES applications [27, 28]:

- Phase change temperatures within the operating conditions and high latent heats.
- High storage density to build compact TES systems.
- High specific heat to effectively exploit also the sensible heat.
- High thermal conductivity to have good TES charge/discharge.

- High density to minimize the size of the TES system.
- Small volume changes during phase transition to reduce the containment issues.
- Limited supercooling to achieve effective heat release in a narrow temperature range.
- High chemical stability, no chemical decomposition, and non-corrosiveness.
- High long-term or cycling stability to have a long lifetime of the TES system without degradation.
- Non-toxic, non-flammable, and non-explosive materials.
- Cost-effectiveness and availability in large quantities.

Besides the essential phase transition properties, it is evident that the accurate knowledge of other thermophysical properties (e.g., density, specific heat, and thermal conductivity) is important during the PCMs' selection. Moreover, analyses of the thermal, chemical, and cycling stability of the PCMs are fundamental to assessing if they are suitable for specific applications [29, 30]. Thermal and chemical stabilities are usually evaluated by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR), respectively. The TGA allows the determination of the thermal decomposition of the material within the operating temperatures. Instead, the cycling stability is evaluated by carrying out many consecutive thermal cycles of heating and cooling to evaluate if the PCMs show thermal performance deterioration and/or degradation. Finally, another critical factor for assessing the suitability of PCMs is their degree of safety and health hazard that should comply with the specific measures for each application.

Consequently, to properly evaluate their possible use in actual TES systems, studies related to the phase transition properties, thermophysical properties, and thermal and cycling stability of the PE+PG mixtures and the pure substances are reviewed and analyzed in this work.

2.2 Materials

The studied samples of pentaerythritol (PE), CAS number 115-77-5, and pentaglycerine (PG), CAS number 77-85-0, were purchased from Thermo Fisher Scientific Inc. The purity of PE and PG are 98% and 97%, respectively. The CAS number is a unique identification number assigned by the assigned by the Chemical Abstracts Service, a division of the American Chemical Society, to every uniquely identifiable substance.

An analysis of their degree of health hazard was reported by Benson et al. [31]. It was stated that PE was considered non-toxic by conventional industrial hygiene standards, while PG caused only slight skin irritation on rabbits and was considered non-hazardous. This analysis is confirmed by the safety and health hazard rating of PE and PG available in the National Fire Protection Association (NFPA) 704 diamond standard [32], shown in Table 1. Considering that the degree of hazard reported in this standard ranges between 0 (minimal hazard) and 4 (severe hazard), the health hazard of PE is 0, which means that it presents no health hazard. Instead, the value of PG is 2, meaning that intense or continued exposure could cause skin and respiratory irritation. Therefore, this material can still be considered suitable for TES applications if it is suitably used. Regarding their fire hazard rating, their value is

1, meaning they require considerable ignition preheating. Finally, while PE usually is stable, PG can become unstable at high temperatures and pressures.

Table 1. Safety and health hazard rating of the studied plastic crystals reported in the NFPA 704 diamond standard [32].

The degree of hazard reported in this standard ranges between 0 (minimal hazard) and 4 (severe hazard)

PCs	Health hazard	Fire hazard	Instability - reactivity
PE	0	1	0
PG	2	1	1

2.3 Methods

DSC analysis has been performed to obtain the onset temperature and the enthalpy related to the solid-solid phase transition for PE and PG. The heat flow of both substances has been recorded in heating and cooling scans as a function of temperature in the ranges 25 - 230°C and 25 - 130°C for PE and PG, respectively.

The measurements were done by means of a Seiko EXSTAR 6000 calorimeter at a scan rate of 10°C min⁻¹, under a nitrogen flow rate of 50 mL min⁻¹.

3. RESULTS AND DISCUSSION

3.1 Phase transition properties

This section presents the S-S phase transition temperatures and enthalpies for PE and PG and their mixture collected from the literature. In particular, the experimental data provided by DSC in the heating and cooling scans were selected. Moreover, at this stage of this work, preliminary DSC measurements performed on the pure components are also reported and compared with the literature data.

Table 2 shows the phase transition temperatures in the heating ($T_{t,h}$) and cooling ($T_{t,c}$) scans for PE and PG reported in different literature studies, together with their enthalpies of S-S phase transitions ($\Delta H_{t,h}$ and $\Delta H_{t,c}$). When available in the original works, both the onset and peak temperatures of the DSC peaks were selected and reported in the table.

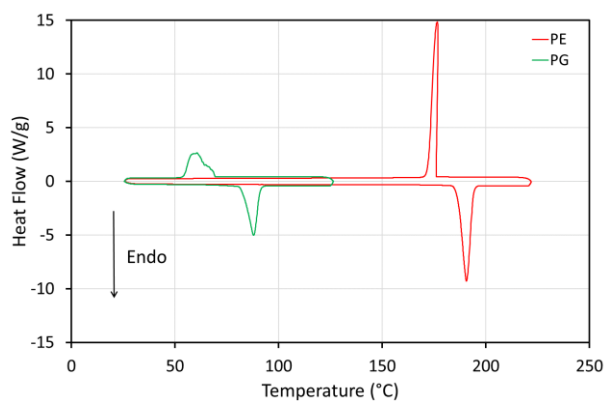


Figure 1. DSC thermograms of PE and PG

The measurements carried out in this work on pure PE and PG samples are shown in Figure 1 and the S-S transition properties are reported in Table 2. The results are comparable with those of literature. While the values of the phase

transition temperatures are in good agreement with that of the literature, the measured enthalpies of S-S phase transitions are slightly lower than the literature data. These differences can be due to the different conditions and samples used in the measurements.

From Table 2, it can be observed that various measurements of $T_{t,h}$ and $\Delta H_{t,h}$ for PE and PG were found. While the measured $T_{t,h}$ of both PCs are generally concentrated in a small range, a higher discrepancy of the $\Delta H_{t,h}$ values is evident. Their differences can be related to the purity of the samples or the accuracy of the measurement setup and procedure. Only a limited number of works report also the values of $T_{t,c}$ and $\Delta H_{t,c}$. However, the measurements of $T_{t,c}$ showed that PE and PG were affected by supercooling (i.e., the release of the enthalpy of phase transition during the cooling occurs at a temperature lower than the phase transition temperature during the heating). Although the values of $T_{t,c}$ were not provided, the supercooling of the studied PCs was also evident in the measurements reported by Benson et al. [31]. They pointed out that it can be related to transformation kinetics and depends on the heating and cooling scan rates. The authors tested different nucleating agents that effectively decreased the degree of supercooling for the studied samples.

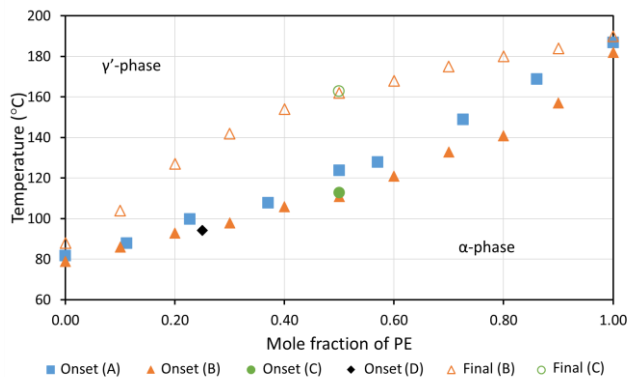
Currently, no well-established theory can explain the supercooling of the PCs, but it seems related to the high degree of directional disorder and mobility of the molecules in the plastic phase [12]. However, since their supercooling could hinder the use of PE and PG as PCMs, specific methods to reduce their supercooling degree should be applied.

Finally, it is worth pointing out that the two PCs have the following melting point temperatures [33]: 256-266°C for PE and 195-203°C for PG. However, they cannot be considered potential solid-liquid PCMs for high-temperature applications due to their low melting enthalpy (22-51 J g⁻¹ for PE and 38-45 J g⁻¹ for PG) [33].

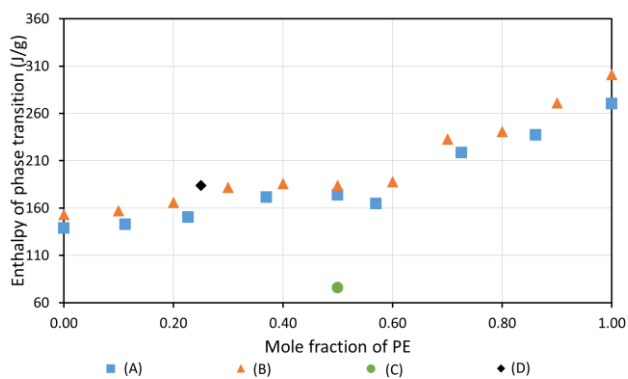
Table 2. S-S phase transition properties of PE and PG

PCs	$T_{t,h}$ (°C)	$T_{t,c}$ (°C)	$\Delta H_{t,h}$ (J g ⁻¹)	$\Delta H_{t,c}$ (J g ⁻¹)	Ref.
PE	182 ¹ -183 ²	-	303	-	[16]
	186	170	287	-	[34]
	187	-	270	-	[31]
	187	-	269	-	[17]
	181 ¹ -188 ²	-	250-323	-	[33]
	182	167	301	298	[18]
	185	-	340	-	[19]
	187	-	289	-	[35]
	184	162-166	245	221	[36]
	188	-	316	-	[15]
	181 ¹ -188 ²	168-169	251	239	[37]
	181 ¹ -188 ²	164-166	264	239	[38, 39]
	181 ¹ -188 ²	168-169	264	239	[25, 26]
	186	162	277	268	[20]
	183	-	232	-	[40]
185	175	290	281	[41]	
186	176	255	242	this work	
PG	81	-	193	-	[16]
	82	-	139	-	[31]
	82	-	174	-	[17]
	81 ¹ -86 ²	-	158-200	-	[33]
	79	66	153	148	[18]
	81	-	161.3	-	[15]
	79 ¹ -86 ²	-	157	-	[42]
	83 ¹ -86 ²	77-75	166	159	[43]
	82	70	146	132	This work

Notes: 1. Onset temperature. 2. Peak temperature.



(a)



(b)

Figure 2. Onset and final phase transition temperatures (a) and enthalpies of phase transition (b) of PE + PG mixtures measured using a DSC in the heating phase. (A) [17], (B) [18], (C) [15], (D) [12]

The literature phase transition properties of the PE+PG mixtures obtained by DSC analyses are shown in Figure 2 as a function of the PE composition. In detail, the phase transition temperatures measured in the heating phase (both onset and final) are shown in Figure 2a, while the enthalpies of phase transition for the heating phase are reported in Figure 2b.

It can be noted in Figure 2 that few studies presenting the phase transition properties of the PE+PG mixture were found in the literature. However, this figure also shows that the properties of the different mixture compositions generally vary within that of the pure components. While a slight discrepancy between the collected onset phase transition temperatures can be noted, the phase transition enthalpies generally agree. Only the enthalpy provided by Singh et al. [15] is lower than the values of the other studies. In addition, Figure 2a shows that the difference between the onset and final phase transition temperatures is also 50°C for some compositions. As pointed out in various literature studies [12, 44], this behavior is ascribable to an isomorphous phase diagram of PE+PG mixture with complete solid miscibility for all compositions, as it can be deduced from Figure 2a. Consequently, the mixture is characterized by continuous S-S phase transitions, and its phase diagram shows temperature ranges (specific for each composition) where the low-temperature α -phase and the plastic γ' -phase coexist.

As the pure PE and PG, their mixtures also show the supercooling drawbacks [12, 18]. However, it was shown that the intermediate compositions had smaller supercooling degrees [18].

3.2 Other thermophysical properties

This section presents the density, specific heat, and thermal conductivity values for PE+PG mixture and its pure components collected from the literature.

Regarding the density, different values measured at room temperature were reported for the pure compounds. For PE, a density of 1.39 g cm⁻³ was given in some works [12, 17], while Bushnell [22] provided a value of 1.107 g cm⁻³. The following values were found for PG: 1.15 g cm⁻³ [42] and 1.22 g cm⁻³ [12, 17]. Instead, only two studies reporting the density of the PE+PG mixture were found in the literature. Benson et al. [17] showed that its density changes with the composition between the values of the pure components (1.39 g cm⁻³ of PE and 1.22 g cm⁻³ of PG). Serrano et al. [12] provided a density of 1.27 g cm⁻³ for the 1:4 M ratio mixture of PE and PG, which is in good agreement with the data reported by Benson et al. [17].

Table 3. Specific heat values (c) for PE, PG, and their mixture available in the literature

PCs	x_{PE}	c (kJ kg ⁻¹ K ⁻¹)	T (°C)	Phase	Ref.
PE	-	1.616	57	α	[17]
	-	1.983	117	α	[17]
	-	2.864	207	γ'	[17]
	-	1.550-3.357	32-177	α	[45]
	-	3.489-3.386	199-212	γ'	[45]
	-	1.372	25	α	[40]
	-	2.781	-	-	[39]
PG	-	1.998	57	α	[17]
	-	2.747	107	γ'	[17]
	-	2.913	137	γ'	[17]
	-	1.633-1.967	32-82	α	[45]
	-	2.705-2.952	102-174	γ'	[45]
	-	1.779	room T	α	[43]
	PE+PG	0.57	1.779	57	α
0.57		2.011	77	α	[17]
0.73		1.745	57	α	[17]
0.73		2.124	107	α	[17]
0.73		2.883	197	γ'	[17]
0.5		1.951	57	α	[17]
0.5		2.263	87	α	[17]
0.5	3.199	177	γ'	[17]	

Table 3 shows the specific heat values for the mixture and its pure components. Various sources reporting the data for the pure components, measured at different temperatures, were found. Although a certain discrepancy between the collected data is evident, the specific heat of the plastic γ' -phase is always higher than that of the α -phase. Instead, the specific heat data for the PE+PG mixture were found in only one study. It can be noted that the values of the different mixture compositions are quite close to that of the pure compounds.

Finally, the values of thermal conductivity for PE, PG and their mixture collected from the literature are reported in Table 4. One data source was found for PG and the mixture, while different values were collected for PE. It is worth noting that, for specific temperatures, the thermal conductivity values of PE reported in various studies vary in quite wide ranges. These differences could be due to the different samples and methods used in the measurements.

However, from Table 4, it can be noted that their thermal conductivity values are generally low. Consequently, this weakness was addressed in different studies that tried to enhance the thermal conductivity of the two PCs by combining

them with materials with high thermal conductivity, such as graphite [42, 43], graphene [40], alumina [26, 38-40], titanium nitride [46], copper nanoparticles [41], indium [25]. The results of these studies showed that an increase of the thermal conductivity of the studied composite PCMs was generally obtained.

Table 4. Thermal conductivity values (λ) for PE, PG, and their mixture reported in the literature

PCs	x_{PE}	λ ($W m^{-1} K^{-1}$)	T ($^{\circ}C$)	Phase	Ref.
PE	-	0.66-0.53	30-180	α	[20]
	-	0.23-0.20	186-220	γ'	[20]
	-	0.71-0.57	30-140	α	[41]
	-	0.106	-	-	[37, 39]
	-	0.112	40-95	α	[25]
	-	0.108	95-150	α	[25]
PG	-	0.232	room T	α	[43]
	PE+PG	0.25	0.395	21	α

3.3 Thermal, chemical, and cycling stability analyses

Regarding thermal stability, only studies reporting TGA measurements for PE were found [26, 34, 39, 46, 47]. In different studies of Venkitaraj and co-authors [26, 39, 47], it was shown that the analyzed samples had almost negligible weight loss up to 240 $^{\circ}C$, while the final degradation temperature was 350 $^{\circ}C$. The TG curves reported by Luo et al. [46] seem to agree with that of Venkitaraj and co-authors [26, 39, 47]. Instead, the TG behaviors presented by Sakamoto et al. [34] show that weight loss of PE began at lower temperatures than 240 $^{\circ}C$.

It is also worth pointing out that, since PCs have high vapor pressures, they could sublime at high temperatures [34]. For this reason, the samples studied in different works [14, 17, 33, 34] were sealed in aluminum crucibles to prevent sublimation. However, it was shown that, at temperatures close to their S-S phase transition, the sublimation of PCs should occur only under vacuum conditions [12, 48]. However, additional investigations are necessary to understand if this phenomenon could happen in working conditions for TES applications at low-medium temperatures.

For cycling stability, different works studying PE samples were recently published in the literature [25, 26, 39, 46, 47], while the studies concerning PG and their mixture are limited [18, 43]. The results of these studies generally proved that the cycled samples had a limited reduction of the enthalpies of phase transitions and good thermal and chemical stability. For PE, Venkitaraj et al. [25] showed that its enthalpies of phase transitions decreased by about 10% after 500 repeated heating and cooling cycles. In contrast, the change of the phase transition temperatures was negligible. In the other works, the enthalpies of phase transitions of PE decreased by less than 10% since the samples were subjected to a limited number of thermal cycles (less than 500). Moreover, in some works [26, 38, 39, 47], it was demonstrated that the thermal conductivity and specific heat of PE only slightly changed due to thermal cycles. As concern PG, Zhang et al. [43] showed that its enthalpies of phase transitions decreased by about 1% after 100 cycles, the change of the phase transition temperatures was negligible.

4. CONCLUSIONS

This work reviewed the main thermophysical properties of two promising organic S-S PCMs, namely pentaerythritol (PE) and pentaglycerine (PG), and their mixture to evaluate if they can be really used in low-medium temperature TES applications. To this end, the studies reporting their thermal and cycling stability were also analyzed.

The collected information shows that these materials could be suitable PCMs for different TES applications given their good degree of safety, high enthalpy of S-S phase transition, and quite good cycling stability. In particular, considering its non-isothermal continuous phase transitions in temperature ranges specific for each composition, the PE+PG mixture can be a potential PCM for applications that do not exclusively need conventional isothermal phase transitions.

The DSC measurements performed in this work on both pure substances demonstrated comparable results with the literature data.

However, apart from the phase transition properties, very few experimental data for other thermophysical properties and thermal and cycling stability analyses are available in the literature. This is especially true for the mixture for which no study evaluating its thermal stability was found. Therefore, additional studies about these aspects should be carried out to deeply understand the possibility of developing TES systems based on these materials for actual applications.

Finally, it is worth pointing out that, despite the limited number of available literatures works, the studied S-S PCMs showed some issues, such as supercooling and low thermal conductivity, that could hinder their use in various TES systems. Consequently, in addition to the studies already presented in the literature, further research on specific techniques to solve supercooling and increase their thermal conductivity should be addressed. For example, a possibility to overcome these issues could be the development of composite or shape stabilized PCMs based on the studied materials.

REFERENCES

- [1] Nazir, H., Batool, M., Bolivar Osorio, F.J., Isaza-Ruiz, M., Xu, X., Vignarooban, K., Phelan, P., Inamuddin, Kannan, A.M. (2019). Recent developments in phase change materials for energy storage applications: A review. *International Journal of Heat and Mass Transfer*, 129: 491-523. <https://doi.org/10.1016/j.ijheatmasstransfer.2018.09.126>
- [2] Pielichowska, K., Pielichowski, K. (2014). Phase change materials for thermal energy storage. *Progress in Materials Science*, 65: 67-123. <https://doi.org/10.1016/j.pmatsci.2014.03.005>
- [3] Alva, G., Liu, L., Huang, X., Fang, G. (2017). Thermal energy storage materials and systems for solar energy applications. *Renewable and Sustainable Energy Reviews*, 68: 693-706. <https://doi.org/10.1016/j.rser.2016.10.021>
- [4] Cabeza, L.F., Castell, A., Barreneche, C., De Gracia, A., Fernández, A.I. (2011). Materials used as PCM in thermal energy storage in buildings: A review. *Renewable and Sustainable Energy Reviews*, 15(3): 1675-1695. <https://doi.org/10.1016/j.rser.2010.11.018>
- [5] Jaguemont, J., Omar, N., den Bossche, P., Mierlo, J.

- (2018). Phase-change materials (PCM) for automotive applications: A review. *Applied Thermal Engineering*, 132: 308-320. <https://doi.org/10.1016/j.applthermaleng.2017.12.097>
- [6] Andreozzi, A., Buonomo, B., Ercole, D., Manca, O. (2017). Phase change materials (PCMs) in a honeycomb system for solar energy applications. *International Journal of Heat and Technology*, 35(SP1): S472-S477. <https://doi.org/10.18280/ijht.35Sp0164>
- [7] Abdulhussein, M.A., Hashem, A.L. (2021). Experimental study of the thermal behavior of perforated bricks wall integrated with PCM. *International Journal of Heat and Technology*, 39(6): 1917-1922. <https://doi.org/10.18280/ijht.390628>
- [8] Tomassetti, S., Aquilanti, A., Muciaccia, P.F., Coccia, G., Mankel, C., Koenders, E.A.B., Di Nicola, G. (2022). A review on thermophysical properties and thermal stability of sugar alcohols as phase change materials. *Journal of Energy Storage*, 55: 105456. <https://doi.org/10.1016/j.est.2022.105456>
- [9] Fallahi, A., Guldentops, G., Tao, M., Granados-Focil, S., Van Dessel, S. (2017). Review on solid-solid phase change materials for thermal energy storage: Molecular structure and thermal properties. *Applied Thermal Engineering*, 127: 1427-1441. <https://doi.org/10.1016/j.applthermaleng.2017.08.161>
- [10] Usman, A., Xiong, F., Aftab, W., Qin, M., Zou, R. (2022). Emerging solid-to-solid phase-change materials for thermal-energy harvesting, storage, and utilization. *Advanced Materials*, 34(41): 2202457. <https://doi.org/10.1002/adma.202202457>
- [11] Serrano, A., Garrido, I., Santos, S., Duran, M., Dauvergne, J.L., Carmona, M., Del Barrio, E.P. (2022). Effect of processing on microstructure and mechanical properties of pentaglycerine based solid-solid phase change materials. *Journal of Energy Storage*, 55: 105677. <https://doi.org/10.1016/j.est.2022.105677>
- [12] Serrano, A., Duran, M., Dauvergne, J.L., Doppii, S., Del Barrio, E.P. (2021). Tailored transition temperature plastic crystals with enhanced thermal energy storage capacity. *Solar Energy Materials and Solar Cells*, 220: 110848. <https://doi.org/10.1016/j.solmat.2020.110848>
- [13] Chandra, D., Chellappa, R., Chien, W.M. (2005). Thermodynamic assessment of binary solid-state thermal storage materials. *Journal of Physics and Chemistry of Solids*, 66(2-4): 235-240. <https://doi.org/10.1016/j.jpcs.2004.08.047>
- [14] Gao, W., Lin, W., Liu, T., Xia, C. (2007). An experimental study on the heat storage performances of polyalcohols NPG, TAM, PE, and AMPD and their mixtures as solid-solid phase-change materials for solar energy applications. *International Journal of Green Energy*, 4(3): 301-311. <https://doi.org/10.1080/15435070701332112>
- [15] Singh, H., Talekar, A., Chien, W.M., Shi, R., Chandra, D., Mishra, A., Tirumala, M., Nelson, D.J. (2015). Continuous solid-state phase transitions in energy storage materials with orientational disorder-computational and experimental approach. *Energy*, 91: 334-349. <https://doi.org/10.1016/j.energy.2015.07.130>
- [16] Murrill, E., Breed, L. (1970). Solid—solid phase transitions determined by differential scanning calorimetry: Part I. Tetrahedral substances. *Thermochimica Acta*, 1(3): 239-246. [https://doi.org/10.1016/0040-6031\(70\)80027-2](https://doi.org/10.1016/0040-6031(70)80027-2)
- [17] Benson, D.K., Burrows, R.W., Webb, J.D. (1986). Solid state phase transitions in pentaerythritol and related polyhydric alcohols. *Solar Energy Materials*, 13(2): 133-152. [https://doi.org/10.1016/0165-1633\(86\)90040-7](https://doi.org/10.1016/0165-1633(86)90040-7)
- [18] Barrio, M., Font, J., Muntasell, J., Navarro, J., Tamarit, J.L. (1988). Applicability for heat storage of binary systems of neopentylglycol, pentaglycerine and pentaerythritol: A comparative analysis. *Solar Energy Materials*, 18(1-2): 109-115. [https://doi.org/10.1016/0165-1633\(88\)90051-2](https://doi.org/10.1016/0165-1633(88)90051-2)
- [19] Wang, X., Lu, E., Lin, W., Liu, T., Shi, Z., Tang, R., Wang, C. (2000). Heat storage performance of the binary systems neopentyl glycol/pentaerythritol and neopentyl glycol/trihydroxy methyl-aminomethane as solid-solid phase change materials. *Energy Conversion and Management*, 41(2): 129-134. [https://doi.org/10.1016/S0196-8904\(99\)00097-7](https://doi.org/10.1016/S0196-8904(99)00097-7)
- [20] Feng, B., Tu, J., Sun, J.W., Fan, L.W., Zeng, Y. (2019). A molecular dynamics study of the effects of crystalline structure transition on the thermal conductivity of pentaerythritol as a solid-solid phase change material. *International Journal of Heat and Mass Transfer*, 141: 789-798. <https://doi.org/10.1016/j.ijheatmasstransfer.2019.07.017>
- [21] Gao, W.F., Lin, W.X., Liu, T., Li, M. (2017). An experimental study on the application of polyalcohol solid-solid phase change materials in solar drying with cross-corrugated solar air collectors. *IOP Conference Series: Earth and Environmental Science*, 93(1): 12075. <https://doi.org/10.1088/1755-1315/93/1/012075>
- [22] NKhonjera, L., Kuboth, M., König-Haagen, A., John, G., King'onde, C., Brüggemann, D., Bello-Ochende, T. (2016). Experimental investigation of a finned pentaerythritol-based heat storage unit for solar cooking at 150-200°C. *Energy Procedia*, 93: 160-167. <https://doi.org/10.1016/j.egypro.2016.07.165>
- [23] Bushnell, D.L. (1988). Performance studies of a solar energy storing heat exchanger. *Solar Energy*, 41(6): 503-512. [https://doi.org/10.1016/0038-092X\(88\)90053-9](https://doi.org/10.1016/0038-092X(88)90053-9)
- [24] Biencinto, M., Bayón, R., González, L., Christodoulaki, R., Rojas, E. (2021). Integration of a parabolic-trough solar field with solid-solid latent storage in an industrial process with different temperature levels. *Applied Thermal Engineering*, 184: 116263. <https://doi.org/10.1016/j.applthermaleng.2020.116263>
- [25] Venkitaraj, K.P., Suresh, S., Praveen, B. (2019). Energy storage performance of pentaerythritol blended with indium in exhaust heat recovery application. *Thermochimica Acta*, 680: 178343. <https://doi.org/10.1016/j.tca.2019.178343>
- [26] Venkitaraj, K.P., Suresh, S., Venugopal, A. (2018). Experimental study on the thermal performance of nano enhanced pentaerythritol in IC engine exhaust heat recovery application. *Applied Thermal Engineering*, 137: 461-474. <https://doi.org/10.1016/j.applthermaleng.2018.03.062>
- [27] Abhat, A. (1983). Low temperature latent heat thermal energy storage: heat storage materials. *Solar Energy*, 30(4): 313-332. [https://doi.org/10.1016/0038-092X\(83\)90186-X](https://doi.org/10.1016/0038-092X(83)90186-X)
- [28] Agyenim, F., Hewitt, N., Eames, P., Smyth, M. (2010). A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy

- storage systems (LHTESS). *Renewable and Sustainable Energy Reviews*, 14(2): 615-628. <https://doi.org/10.1016/j.rser.2009.10.015>
- [29] Rathgeber, C., Hiebler, S., Bayón, R., et al. (2020). Experimental devices to investigate the long-term stability of phase change materials under application conditions. *Applied Sciences*, 10(22): 7968. <https://doi.org/10.3390/app10227968>
- [30] Ferrer, G., Solé, A., Barreneche, C., Martorell, I., Cabeza, L.F. (2015). Review on the methodology used in thermal stability characterization of phase change materials. *Renewable and Sustainable Energy Reviews*, 50: 665-685. <https://doi.org/10.1016/j.rser.2015.04.187>
- [31] Benson, D.K., Webb, J.D., Burrows, R.W., McFadden, J., Christensen, C. (1985). *Materials research for passive solar systems: Solid-state phase-change materials*. United States: N. p., 1985. Web. <https://doi.org/10.2172/5923397>
- [32] National Fire Protection Association. (2017). NFPA 704, Standard system for the identification of the hazards of materials for emergency response. National Fire Protection Association.
- [33] Font, J., Muntasell, J., Navarro, J., Tamarit, J.L., Lloveras, J. (1987). Calorimetric study of the mixtures PE/NPG and PG/NPG. *Solar Energy Materials*, 15(4): 299-310. [https://doi.org/10.1016/0165-1633\(87\)90045-1](https://doi.org/10.1016/0165-1633(87)90045-1)
- [34] Sakamoto, R., Kamimoto, M., Takahashi, Y., Abe, Y., Kanari, K., Ozawa, T. (1984). Investigation of latent heat-thermal energy storage materials. III. Thermoanalytical evaluation of pentaerythritol. *Thermochimica Acta*, 77(1-3): 241-249. [https://doi.org/10.1016/0040-6031\(84\)87063-X](https://doi.org/10.1016/0040-6031(84)87063-X)
- [35] Yan, Q., Liang, C. (2008). The thermal storage performance of monobasic, binary and triatomic polyalcohols systems. *Solar Energy*, 82(7): 656-662. <https://doi.org/10.1016/j.solener.2007.12.008>
- [36] Hu, P., Zhao, P.P., Jin, Y., Chen, Z.S. (2014). Experimental study on solid--solid phase change properties of pentaerythritol (PE)/nano-AlN composite for thermal storage. *Solar Energy*, 102: 91-97. <https://doi.org/10.1016/j.solener.2014.01.018>
- [37] Venkataraj, K.P., Suresh, S. (2017). Experimental study on thermal and chemical stability of pentaerythritol blended with low melting alloy as possible PCM for latent heat storage. *Experimental Thermal and Fluid Science*, 88: 73-87. <https://doi.org/10.1016/j.expthermflusci.2017.05.018>
- [38] Venkataraj, K.P., Suresh, S., Praveen, B. (2019). Experimental charging and discharging performance of alumina enhanced pentaerythritol using a shell and tube TES system. *Sustainable Cities and Society*, 51: 101767. <https://doi.org/10.1016/j.scs.2019.101767>
- [39] Venkataraj, K.P., Suresh, S., Praveen, B., Venugopal, A., Nair, S.C. (2017). Pentaerythritol with alumina nano additives for thermal energy storage applications. *Journal of Energy Storage*, 13: 359-377. <https://doi.org/10.1016/j.est.2017.08.002>
- [40] Liu, T., Yang, Q., Gong, X., Wang, L., Yao, E., Zou, H. (2021). Investigation on thermal conductivities of pentaerythritol-graphene composites for thermal energy storage. *Heat and Mass Transfer*, 57(12): 1909-1919. <https://doi.org/10.1007/s00231-021-03076-z>
- [41] Mani, D., Saranprabhu, M.K., Rajan, K.S. (2021). Intensification of thermal energy storage using copper-pentaerythritol nanocomposites for renewable energy utilization. *Renewable Energy*, 163: 625-634. <https://doi.org/10.1016/j.renene.2020.08.119>
- [42] Johnson, D.J., Ervin, J.S., Hanchak, M., Patnaik, S.S., Hu, X. (2015). Graphite foam infused with pentaglycerine for solid-state thermal energy storage. *Journal of Thermophysics and Heat Transfer*, 29(1): 55-64. <https://doi.org/10.2514/1.T4484>
- [43] Zhang, N., Song, Y., Du, Y., Yuan, Y., Xiao, G., Gui, Y. (2018). A novel solid--solid phase change material: Pentaglycerine/expanded graphite composite PCMs. *Advanced Engineering Materials*, 20(10): 1800237. <https://doi.org/10.1002/adem.201800237>
- [44] Mishra, A., Talekar, A., Chandra, D., Chien, W.M. (2012). Ternary phase diagram calculations of pentaerythritol--pentaglycerine--neopentylglycol system. *Thermochimica Acta*, 535: 17-26. <https://doi.org/10.1016/j.tca.2012.02.009>
- [45] Chandra, D., Chien, W.M., Gandikotta, V., Lindle, D.W. (2002). Heat capacities of "plastic crystal" solid state thermal energy storage materials. *De Gruyter (O)*, 216(12): 1433. <https://doi.org/10.1524/zpch.2002.216.12.1433>
- [46] Luo, R., Wang, L., Yu, W., Shao, F., Shen, H., Xie, H. (2023). High energy storage density titanium nitride-pentaerythritol solid--solid composite phase change materials for light-thermal-electric conversion. *Applied Energy*, 331: 120377. <https://doi.org/10.1016/j.apenergy.2022.120377>
- [47] Venkataraj, K.P., Suresh, S. (2018). Experimental study on the thermal storage performance and non-isothermal crystallization kinetics of pentaerythritol blended with low melting metal. *Thermochimica Acta*, 662: 75-89. <https://doi.org/10.1016/j.tca.2018.02.007>
- [48] Font, J., Muntasell, J. (1995). Comparative study on solid crystalline-plastic-vapour equilibrium in plastic crystals from pentaerythritol series. *Journal of Materials Chemistry*, 5(8): 1137-1140. <https://doi.org/10.1039/JM9950501137>

NOMENCLATURE

Latin symbols

c	Specific heat, $\text{kJ kg}^{-1} \text{K}^{-1}$
T	Temperature, $^{\circ}\text{C}$
x	Mole fraction

Greek symbols

ΔH	Enthalpy, J g^{-1}
λ	Thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$

Subscripts

c	Cooling
h	Heating
PE	Pentaerythritol
t	Phase transition

Acronyms

AMPL	2-amino-2-methyl-1,3-propanediol
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DSC	Differential scanning calorimetry	PG	Pentaglycerine
FTIR	Fourier transform infrared spectroscopy	S-S	Solid-solid
NFPA	National Fire Protection Association	TAM/TRIS	Tris(hydroxyl methyl)aminomethane
NPG	Neopentylglycol	TES	Thermal energy storage
PCM	Phase change material	TGA	Thermogravimetric analysis
PE	Pentaerythritol		