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TOWARD RELIABLE SOLID-SOLID PHASE CHANGE MATERIALS FOR THERMAL ENERGY STORAGE: POLYMER FIBRILLAR NETWORK-REINFORCED ORGANIC PLASTIC CRYSTALS

Summary

Reliable thermal energy storage (TES) is essential for improving the stability and efficiency of solar thermal systems, particularly in low-to-medium temperature applications such as hot water supply and low-pressure steam generation. Solid-Solid Phase Change Materials (PCMs) are attractive candidates due to their leakage-free operation, additive stability, and design flexibility. However, their practical implementation is often limited by insufficient mechanical robustness and poor processability, which hinder large-scale integration into functional TES units.

This work proposes a novel approach to enhance the structural reliability of solid-solid PCMs for mid-to-low temperature solar thermal applications. Polytetrafluoroethylene (PTFE) is employed as a fibrillating binder to reinforce organic plastic crystals (OPCs), specifically pentaglycerine (PG) and pentaerythritol (PE), through a scalable shear-induced processing route followed by compaction. The resulting composites exhibit improved mechanical integrity and structural stability while preserving their latent heat storage capability.

Keywords: Thermal Energy Storage (TES), Organic Plastic Crystals (OPCs), Pentaglycerine (PG), Pentaerythritol (PE), Solid-Solid Phase Change Materials (PCMs), Polytetrafluoroethylene (PTFE), Fibrillation.

Field of application for the findings: Thermal Energy Storage

Addressed audience: Materials scientists and energy researchers focused on phase change materials, polymer composites, and mid-to-low temperature thermal energy storage systems.

1. Introduction

Global energy demand has risen due to population growth, with industries consuming 66% of energy for process heat, 77% of which is derived from nonrenewable sources (Payá et al., 2024). This highlights the urgent need for sustainable solutions to reduce fossil fuel reliance and decarbonize industrial heating. In this context, thermal energy storage (TES) is essential to improve efficiency and enable integration of reliable renewable thermal sources.

PCMs are attractive TES candidates due to their ability to store and release large amounts of thermal energy at nearly constant temperature. Among them, solid-solid PCMs have gained increasing attention because of their low corrosiveness, small volumetric changes, long service life, and intrinsic leakage-free behavior, eliminating the need for complex encapsulation systems (Das et al., 2020; Serrano et al., 2021). OPCs including pentaglycerine (PG) and pentaerythritol (PE), constitute a particularly promising subgroup. These cost-effective materials exhibit high latent heat storage capacities and transition temperatures suitable for low-to-medium solar thermal applications (Little et al., 2024; Tomassetti et al., 2023). PG and PE display solid-solid transitions at ~80 °C and ~185 °C, with enthalpies of ~175 J g^{-1} and ~300 J g^{-1}, respectively(Serrano et al., 2021). Their isomorphous crystal structures further enable solid-solution formation across a wide compositional range, allowing tunable thermophysical properties (Fallahi et al., 2017).

Despite the advantages, the practical integration of OPCs into TES systems remains limited by their intrinsic mechanical fragility, including brittleness and insufficient shape stability(Das et al., 2020; Shi et al., 2021). These mechanical limitations restrict processability and compromise structural integrity in compact storage units, where cracking or collapse must be avoided. Improving mechanical robustness without sacrificing latent heat capacity therefore remains a key challenge for their deployment in solar-driven TES systems.
Herein, PTFE is introduced for the first time as a fibrillating reinforcing additive for OPCs operating at demanding temperatures up to 210 °C. Through shear-induced fibrillation, PTFE forms a continuous network within the OPC matrix, enabling mechanically stable and structurally robust composites while preserving

phase change functionality. This strategy advances the development of durable solid-solid PCMs for compact TES modules supporting solar heat management and steam-based process applications.

2. Experimental

PG or PE powders were first homogenized by hand grinding followed by ball milling for 15 min in a Spex mixer mill (Spex SamplePrep) using stainless-steel vials and balls under mild conditions (BPR = 2).

For composite preparation, PG or PE was mixed with 5 wt.% PTFE and kneaded in a mortar for 5 min under shear, forming a dough-like mass. The material was then biaxially rolled and compacted into pellets using a VICE handheld tablet press with a cylindrical cavity of 12 mm diameter under uniaxial pressure for 30 s.

3. Results and Discussion

The application of shear force to the OPC/PTFE powder mixture leads to the formation of a homogeneous and continuous dough-like mass. This evolution is facilitated by the properties of PTFE, including its high ability to fibrillate under minimal shear due to its low interfacial shear strength (Zhang et al., 2021). The resulting microstructure shown in **Fig.1**. reveals that PTFE fibrils are evenly distributed throughout the matrix. At higher magnification, distinct spherical PTFE particles can be observed, indicating incomplete fibrillation in certain regions. Interestingly, the presence of non-fibrillated domains may be beneficial for TES applications, as they could enhance mechanical resilience under operational stresses.

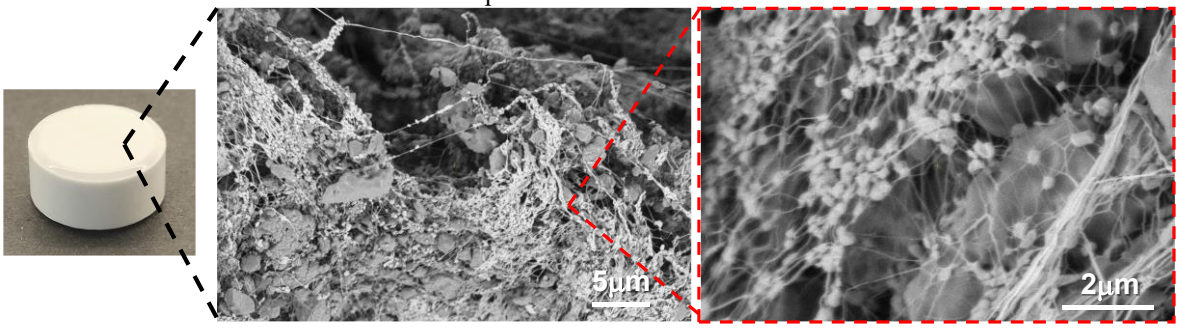

Fig. 1. SEM images along the cross-section of cryogenic fractured PG/PTFE composite with 5 wt.% PTFE at magnifications of 5 000× and 20 000×.

DSC measurements were performed on pure PG and PE and on composites containing 5 wt.% PTFE (**Tab. 1**). The latent heats of pure OPCs agree with literature values(Tomassetti et al., 2023). In the composites, enthalpy decreases proportionally to PTFE content, following the rule of mixtures, confirming that PTFE is thermally compatible and does not alter the intrinsic phase transition. Transition temperatures remain unchanged with ~82 °C for PG and ~186 °C for PE and subcooling of 3.0 °C and 12.9 °C, respectively. PTFE incorporation reduces subcooling to 2.2 °C (PG) and 7.4 °C (PE) at 5 °C min^{-1}, among the lowest values reported. This improvement is attributed to additional structural defects introduced by PTFE, which facilitate nucleation, and to improved densification, enhancing heat transfer and promoting a more uniform phase transition.

Tab. 1. Solid-Solid Phase Transition Properties of pure PG and PE and their respective composites with PTFE (5 wt.%).

Sample	Heating		Cooling	
	T_{onset} (°C)	ΔH (J g^{-1})	T_{onset} (°C)	ΔH (J g^{-1})
PG	**82.5**	**175.7**	**79.5**	**166.5**
PG/PTFE	**82.6**	**162.5**	**80.4**	**155.0**
PE	**186.2**	**285.2**	**173.3**	**278.6**
PE/PTFE	**186.3**	**272.4**	**178.9**	**267.8**

Thermal cycling stability was assessed over 50 heating-cooling cycles (**Fig. 2**). After 25 cycles, pure OPC pellets showed wrinkling, delamination, and deformation, which became severe after 50 cycles. In contrast, PG/PTFE and PE/PTFE composites maintained structural integrity, exhibiting only minor surface roughening. The fibrillated PTFE network acts as a mechanical scaffold, limiting plastic deformation and crack propagation under repeated thermal stress. Although long-term behavior may still be influenced by sublimation, the enhanced mechanical robustness facilitates the application of protective coatings or encapsulation, enabling more durable TES modules.

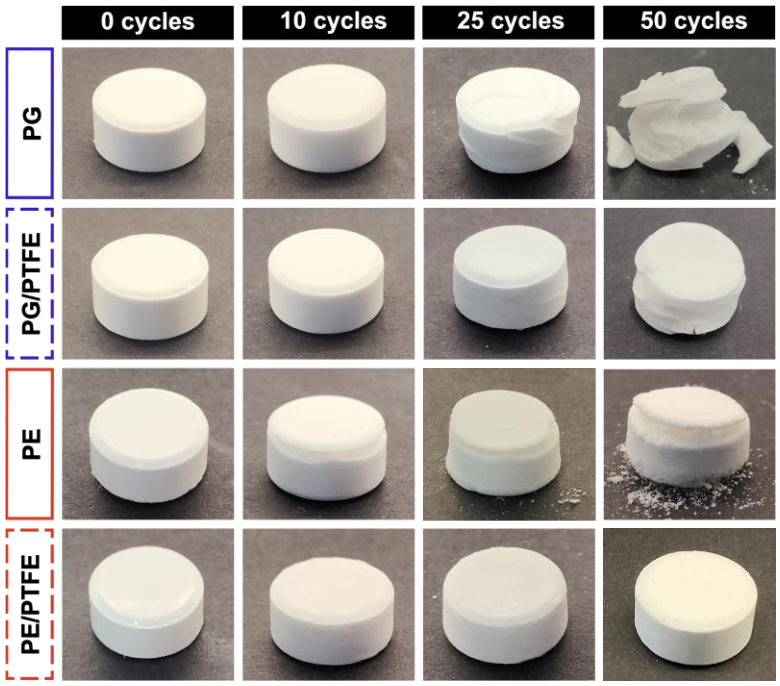

Fig. 2. a Pure PG and PE pellets and their respective composites with PTFE (5 wt.%) after 0, 10, 25 and 50 thermal cycles.

4. References

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