Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Synergistic Polymer-Gelator Design enables Stable Phase Change Materials

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1. Experimental Part

Synthesis of PLLA-g-Gelator

DMDBS (50 mg) and PLLA-*g*-MAH (50 mg) were dissolved in hot DMS (900 mg) in a glass vial and heated to 200 °C for 30 minutes. The reaction conditions were chosen to closely resemble those typically used in the preparation of stabilized PCM. After the reaction, the mixture was cooled to room temperature, and the DMS was replaced with methanol. The resulting solid was collected by filtration. The solid was then partially dissolved in dichloromethane (to solubilize the PLLA fraction) and filtered using a syringe filter. Finally, the PLLA-*g*-Gelator product was precipitated by adding the solution to methanol, yielding a white polymer.

Leakage tests

The prepared stabilized PCM material was reshaped into tablets (d = 5 mm, h = 3 mm) by re-melting at 200 °C in a silicone mold, followed by controlled cooling. The obtained tablets were weighed and placed on a paper filter ($d = 35\ mm$), which was then positioned in a temperature-controlled oven set to 40 °C. After one hour, the samples were removed and re-weighed. The extent of leakage was determined from the mass loss, providing a direct measure of the PCM released during the melting process.

Sample preparation for SEM analysis

Stabilized PCM (1 g) was prepared in glass vials via thermally induced phase separation. Upon cooling to room temperature, each sample was covered with 10 mL of methanol to extract residual DMS. The methanol was periodically replaced with fresh solvent over a two-day purification period. Afterward, the samples were air-dried for three days at ambient conditions without vacuum. For SEM analysis, representative fragments were carefully collected from the dried material.

Recycling of PCM with alcoholic extraction

Stabilized PCM (500 mg) was finely ground using a mortar and pestle to obtain a homogeneous powder. This powder was dispersed in 5 mL of methanol and stirred at room temperature for 1 h to selectively dissolve DMS. The undissolved components (PLLA and gelator) were removed by filtration. The resulting clear methanol solution was cooled to -20 °C to induce recrystallization of DMS. After decanting the methanol, the recovered compound was dried under vacuum at 50 °C until a constant mass was achieved.

Proton Nuclear Magnetic Resonance (^{1}H NMR)

The chemical structure of samples was analyzed by ^{1}H NMR in $CDCl_3$ using a Bruker AV III 300MHz Spectrometer. As for the NMR titration experiments, ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker AV III HD 600MHz Spectrometer. The spectra were evaluated using MestreNova software by MestreLab Research (version 14.2.3).

Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR of the materials and stabilized PCMs was carried out using a Nicolet iS10 FTIR Spectrometer (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA) equipped with a Golden Gate diamond ATR unit. Spectra were recorded in the range of 3500 cm^{-1} to 750 cm^{-1} with a resolution of 4 cm^{-1}.

2. NMR titration of PLLA and Gelator

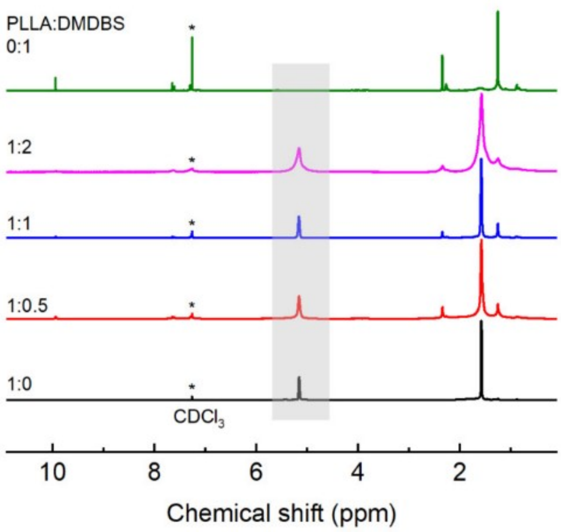
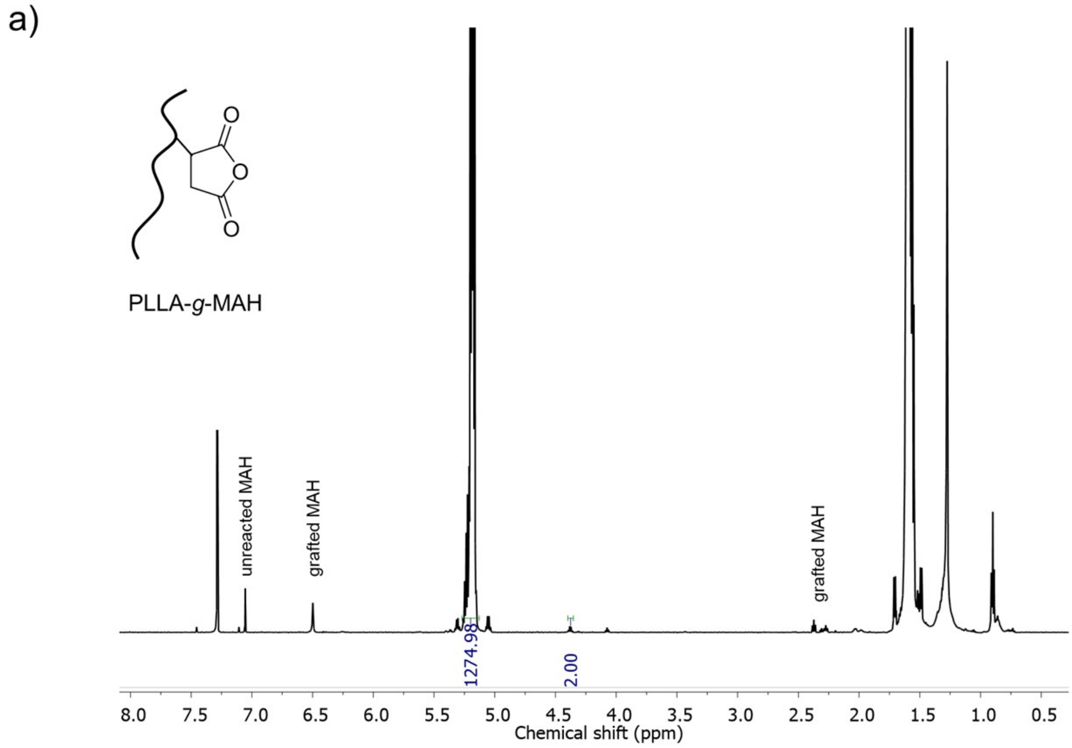


Figure S1. ^{1}H NMR of PLLA and Gelator in different molar concentration.

3. NMRs of PLLA-*g*-MAH and PLLA-*g*-Gelator



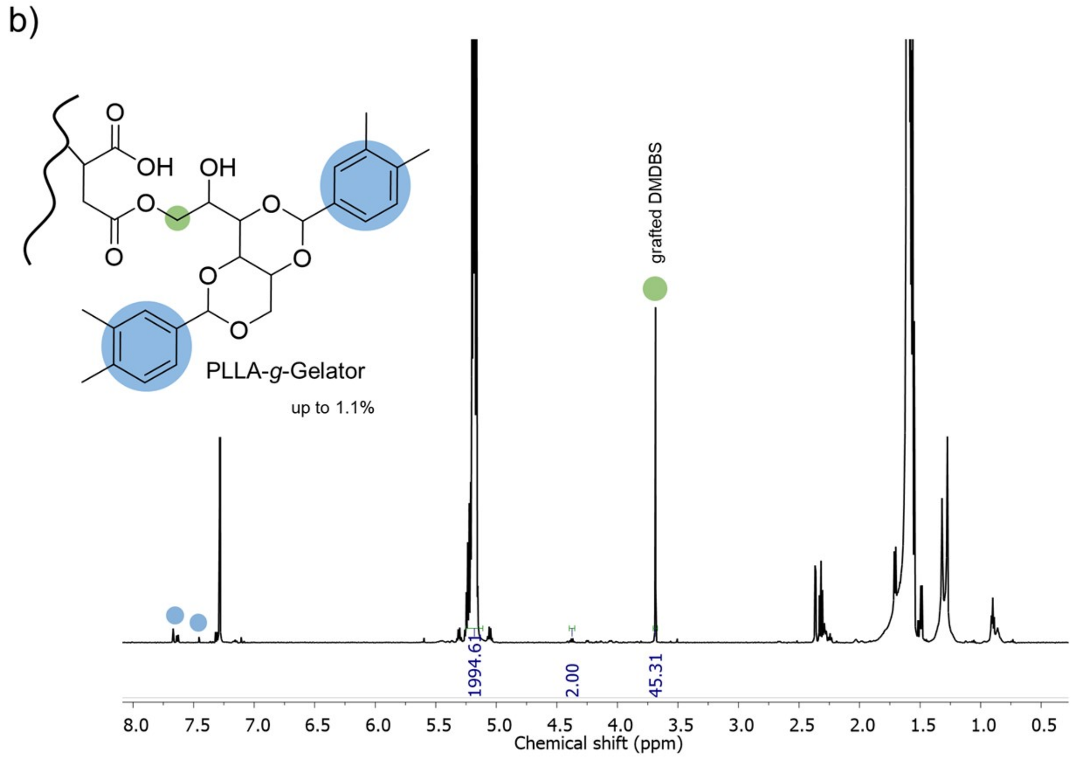


Figure S2. ^{1}H NMR of Scona PLLA-*g*-MAH (a) and of PLLA-*g*-Gelator (b).

4. FTIR of PLLA-*g*-MAH and PLLA-*g*-Gelator

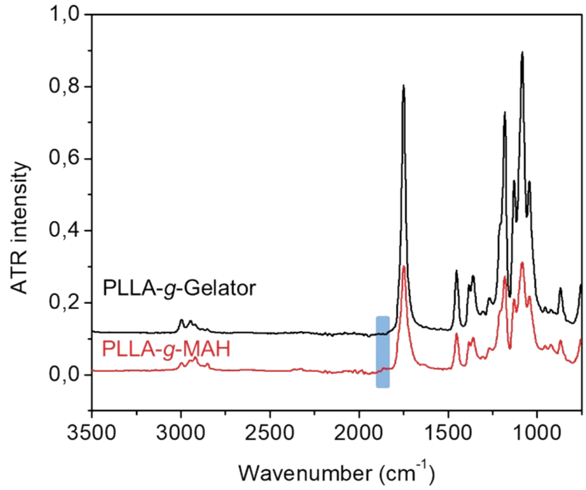


Figure S3. FTIR spectra of PLLA-*g*-MAH and PLLA-*g*-Gelator.

5. Cloud point measurement of generation 1

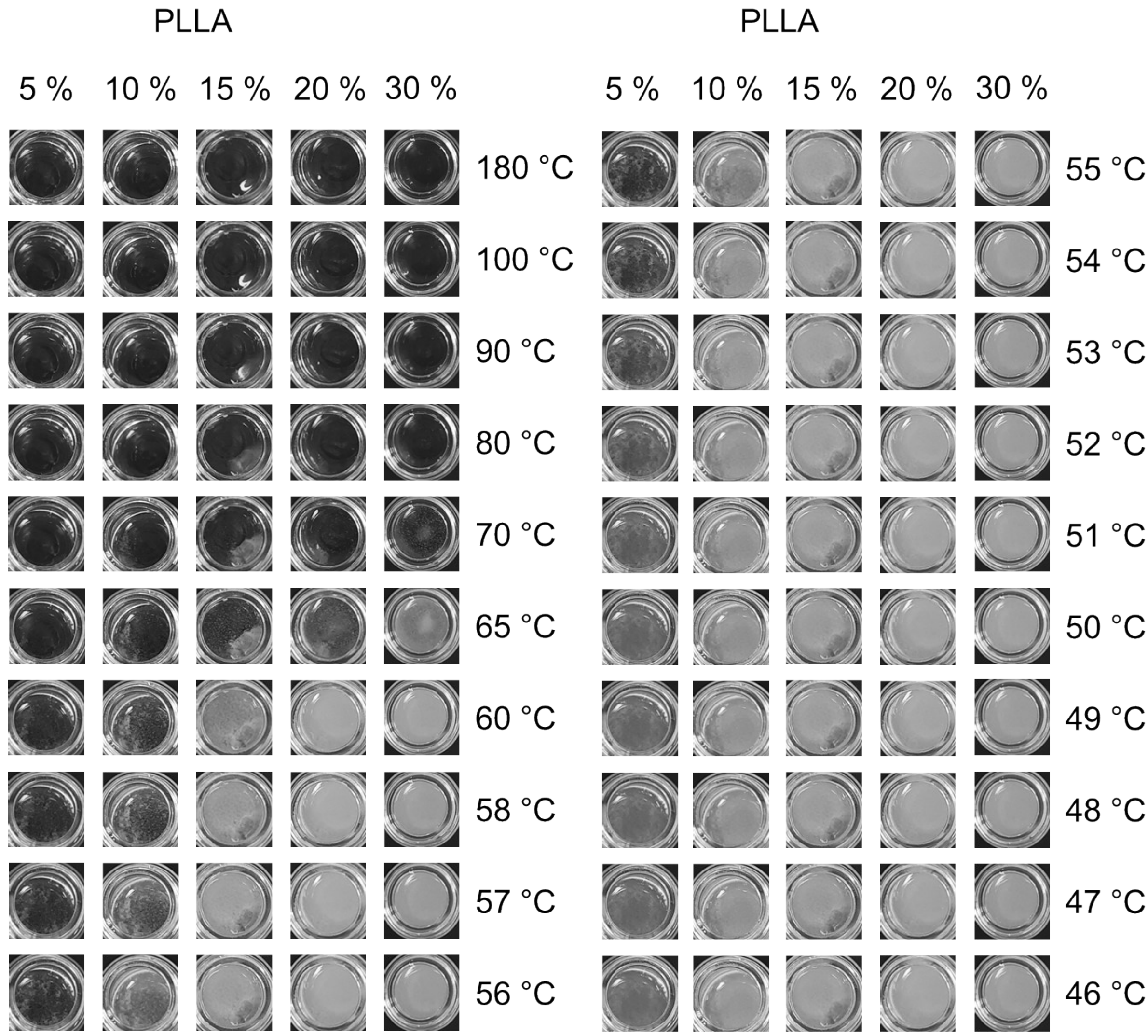


Figure S4. Phase separation of generation 1 with different PLLA contents of 5, 10, 20 and 30 m% (from left to right) during cooling from 180 °C to 46 °C.

6. Cloud point measurement of generation 2

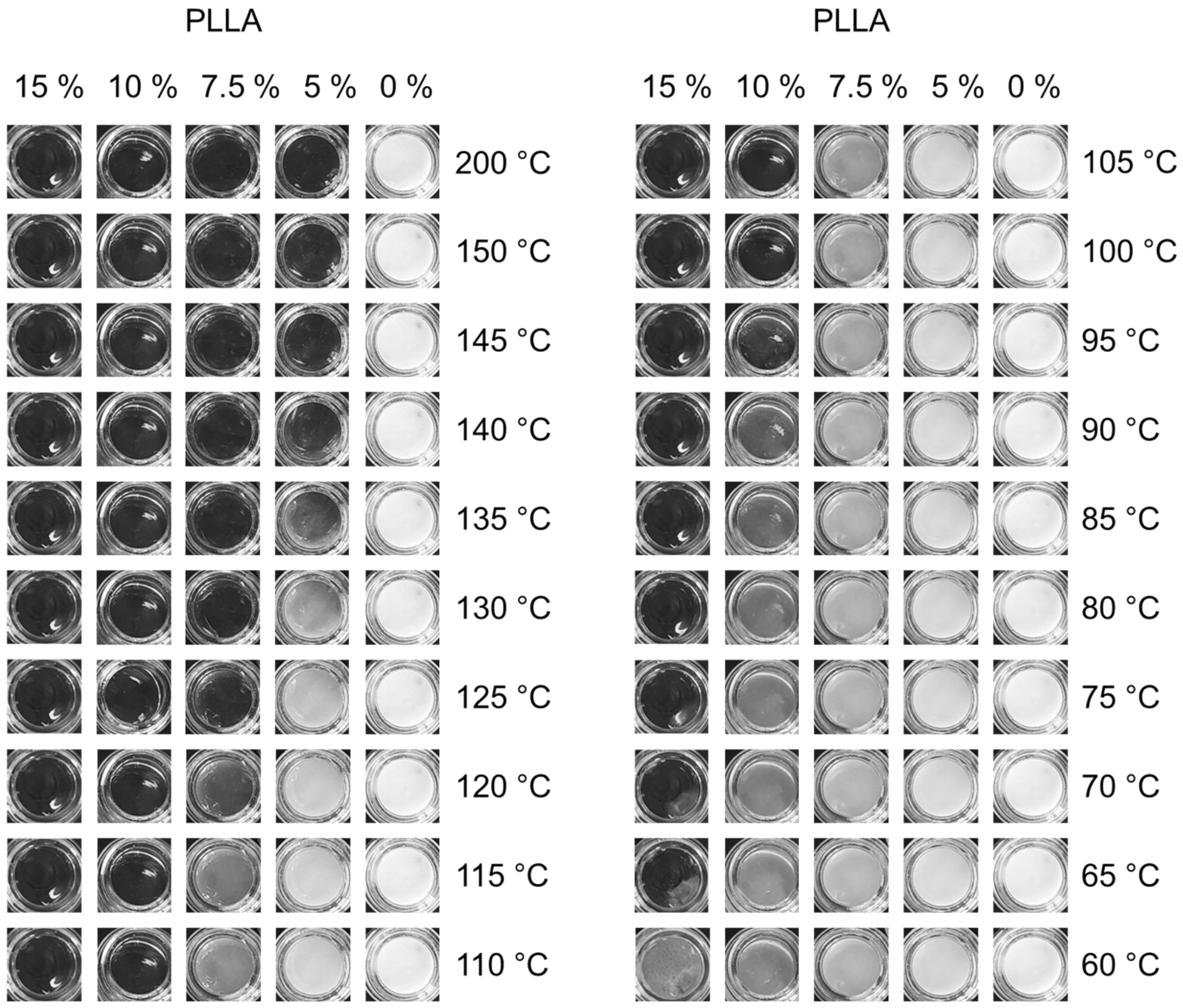


Figure S5. Phase separation of generation 2 with different PLLA contents of 15, 10, 7.5, 5 and 0 m% (from left to right) during cooling from 200 °C to 60 °C.

7. Cloud point measurement of generation 3

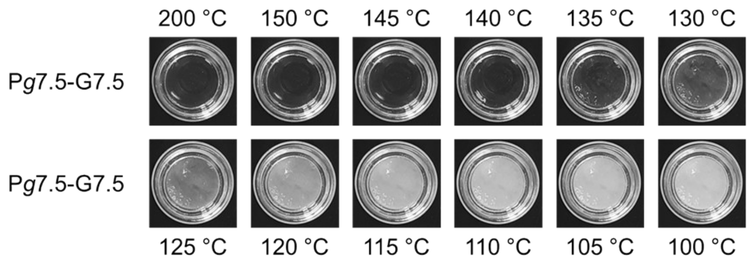


Figure S6. Phase separation of generation 3 with PLLA-*g*-MAH contents of 7.5 m% during cooling from 200 °C to 60 °C.

8. Thermal degradation of gelator DMDBS and inside its PCMs

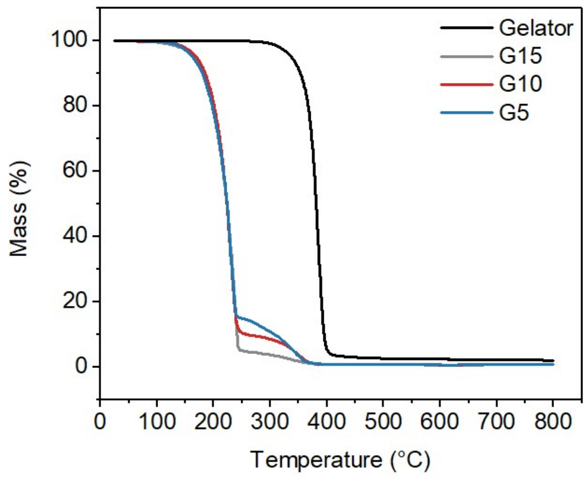


Figure S7. TGA of gelator DMDBS and curves of DMS/DMDBS mixtures with gelator content of 5, 10 and 15 m% as a function of temperature, obtained using a heating rate of 10 K/min and N_2 as a purge gas.

9. Thermal degradation of generation 2 and 3

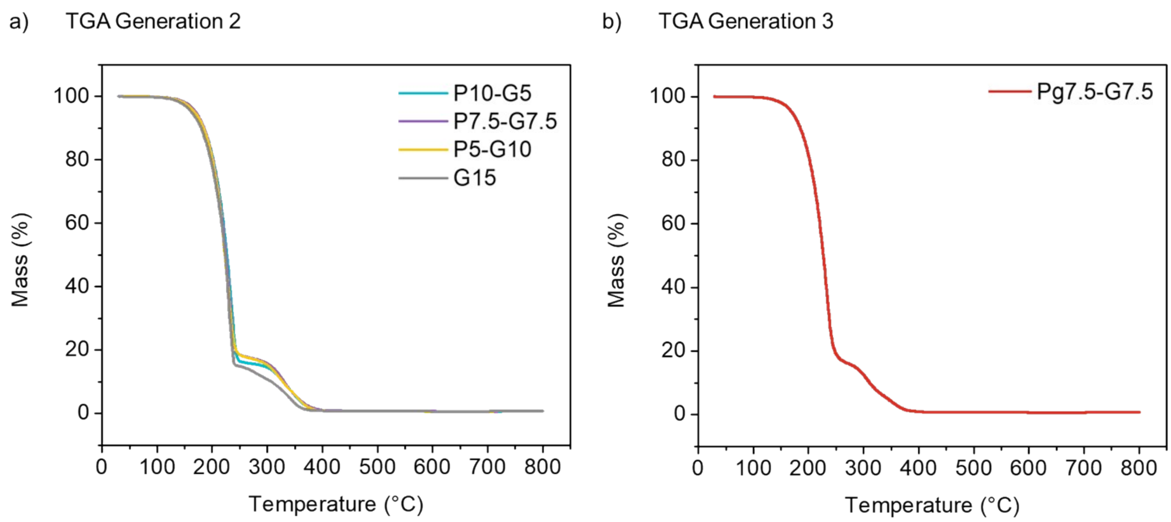


Figure S8. TGA of curves of DMS/PLLA/DMDBS mixtures with gelator content of 5, 7.5 and 10 m% (a) and DMS/PLLA-g-Gelator/DMDBS (b) as a function of temperature, obtained using a heating rate of 10 K/min and N_2 as a purge gas.

10. FTIR spectra for generation 1, 2 and 3

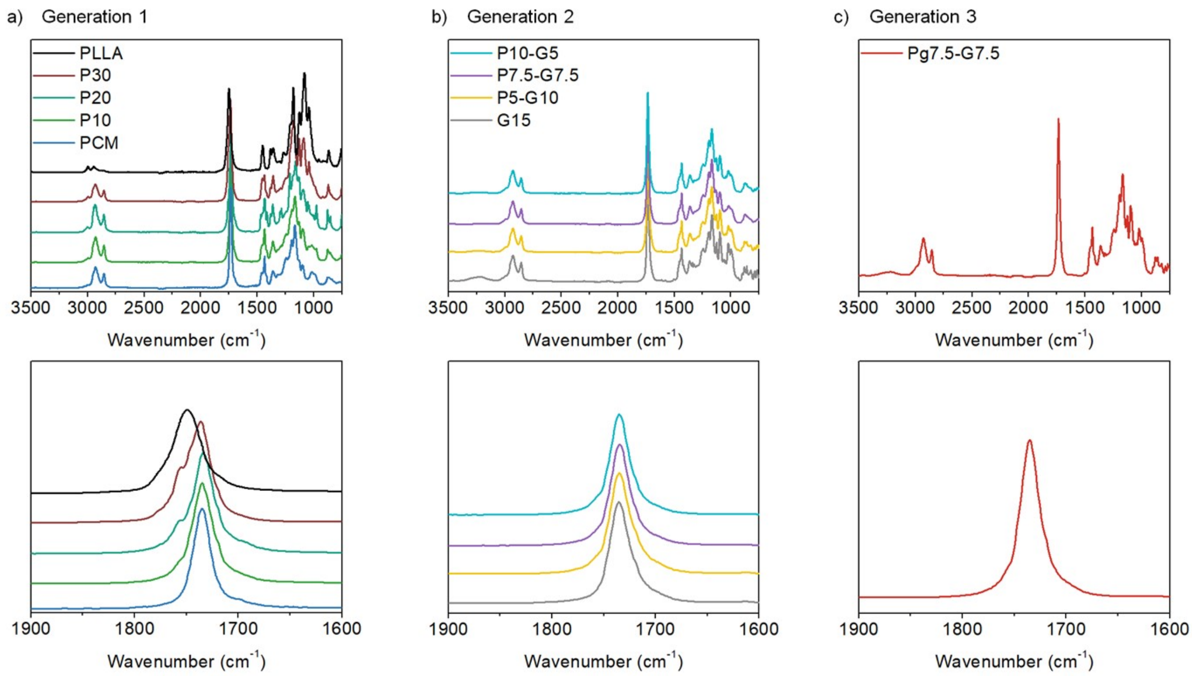


Figure S9. FTIR spectra of DMS and stabilized PCMs with generation 1 (a), generation 2 (b) and generation 3 (c). The lower plots show details in the wavenumber range of 1900 to 1600 cm^{-1}.

11. Latent heat of stabilized PCMs

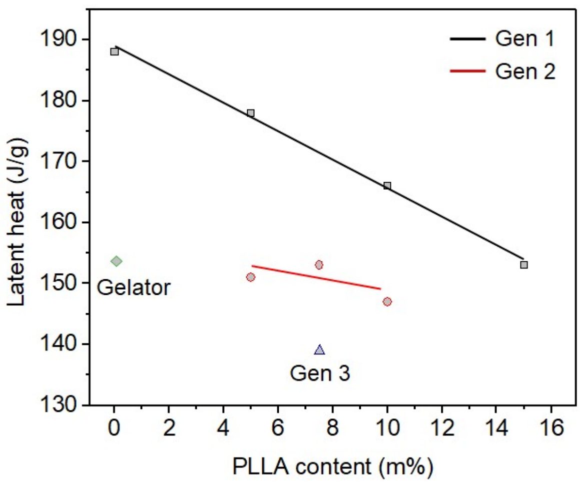


Figure S10. Latent heat of different generation samples as function of PLLA content.

12. Leakage for stabilized PCMs

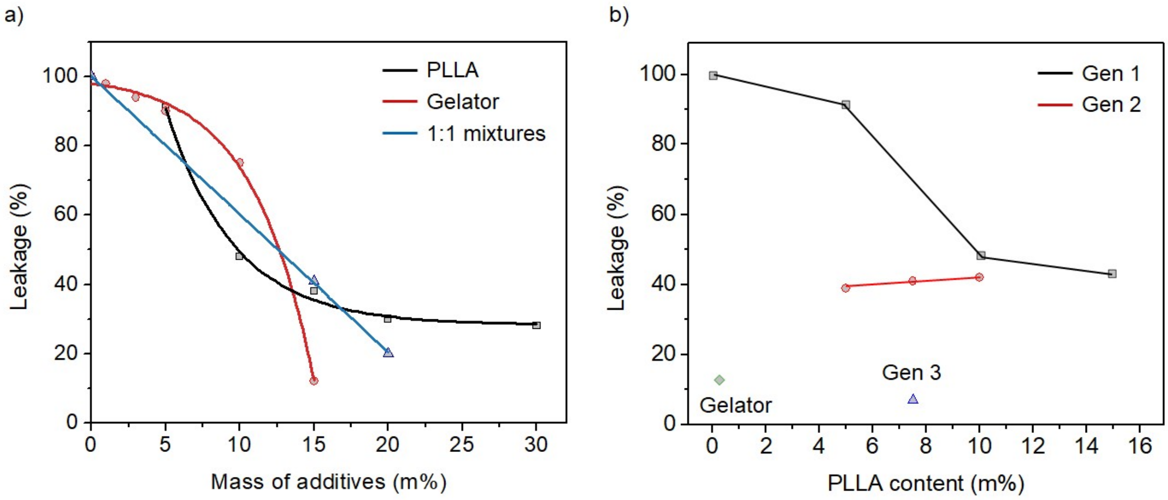


Figure S11. Leakage of stabilized PCM in PLLA (black), gelator (red) and their 1:1 mixtures (blue), used as additives, respectively, as a function of additive mass percentage (a), and leakage of PCM in different generation samples as a function of PLLA content (b).

13. Flory-Huggins Parameters

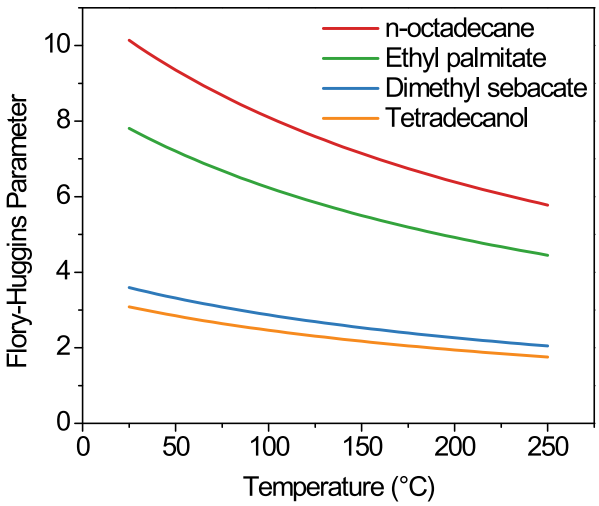


Figure S12. Flory-Huggins parameters of the gelator interaction with *n*-octadecane, ethyl palmitate, dimethyl sebacate and tetradecanol, respectively, as a function of temperature.[3]

14. Morphology of stabilized PCM samples by SEM

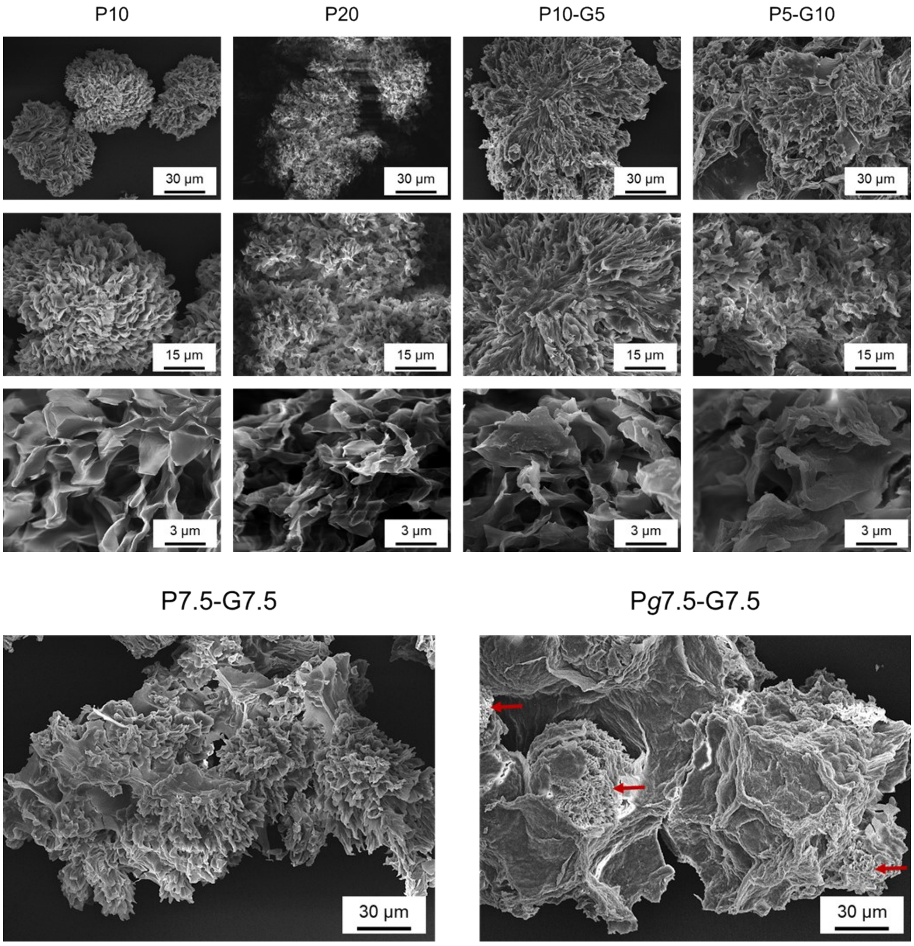


Figure S13. SEM micrographs of samples containing PLLA and/or gelator after extraction with methanol, followed by drying for three days at ambient conditions without vacuum. The red arrows mark spherulite structures beneath the gelator fibrils.

15. Fibril morphology by SEM

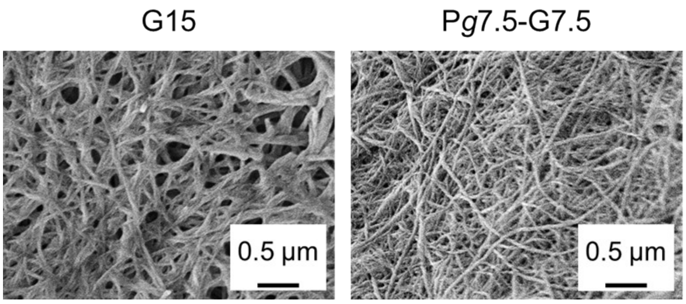


Figure S14. SEM micrographs for fibril structures in G15 and P*g*7.5-G7.5.

16. Pore size of the scaffolds

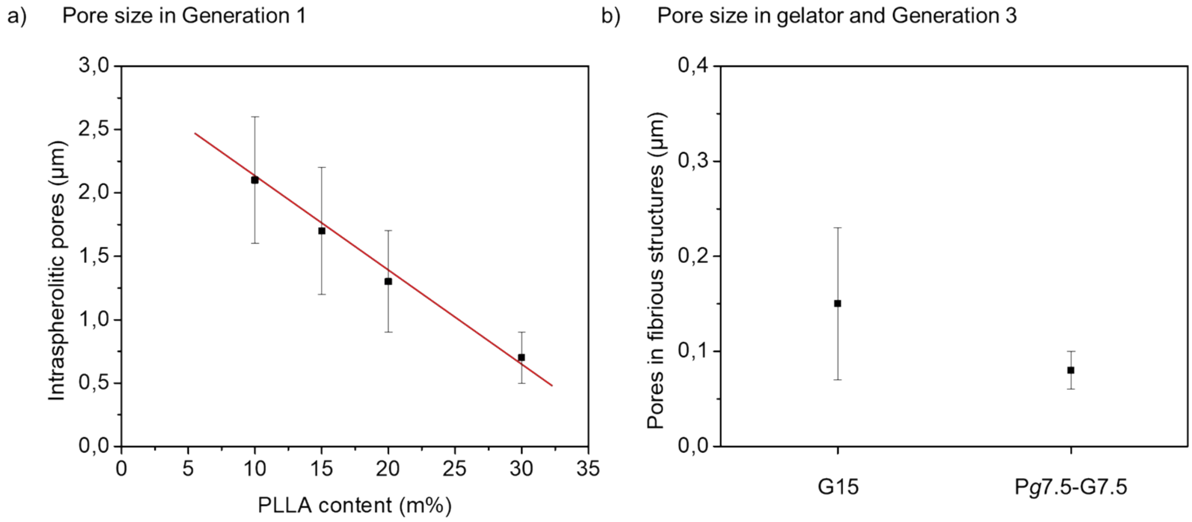


Figure S15. Intraspherulitic pore size of generation 1 sample as function of PLLA content (a) and pore size of G15 and P*g*7.5-G7.5 (b).

17. Temperature measurement during heating and cooling

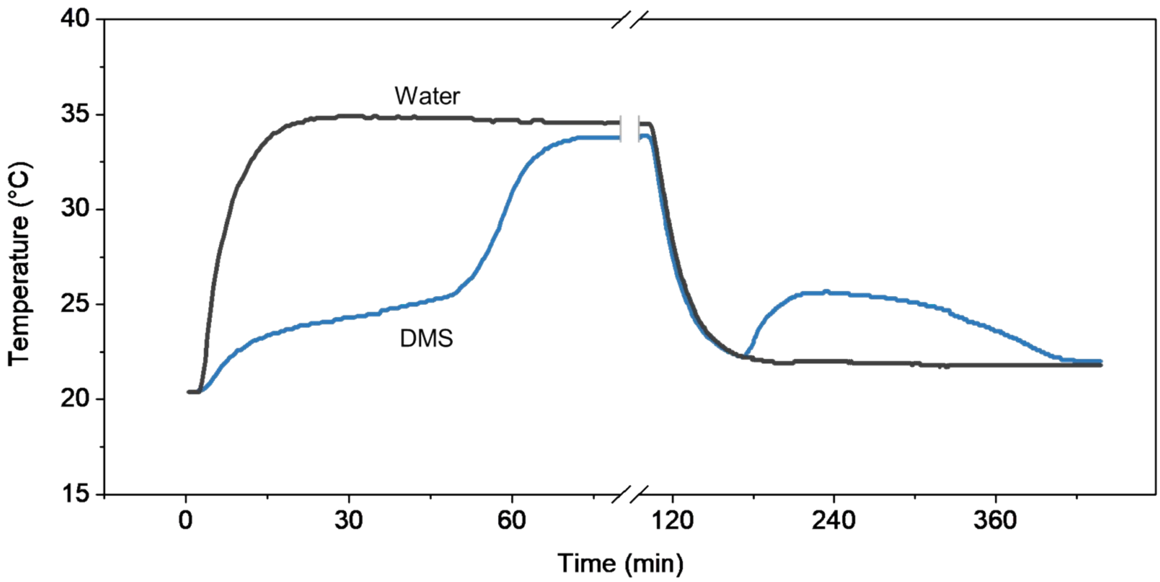


Figure S16. Direct temperature measurement of neat DMS in comparison to water (both inside glass vials on a 40 °C heating plate and cooled back to room temperature).

18. DSC for recycled sample of generation 3

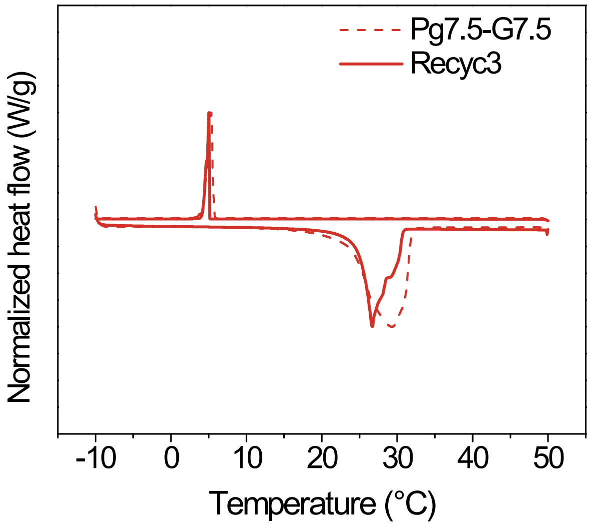


Figure S17. DSC melting and cooling curves of stabilized PCM (heating and cooling rate at 2 °C/min) inside the recycled generation 3, compared to P*g*7.5-G7.5. The melting and freezing peaks were normalized by dividing the measured intensities by their respective minimum and maximum values.

19. Property comparison of stabilized PCMs

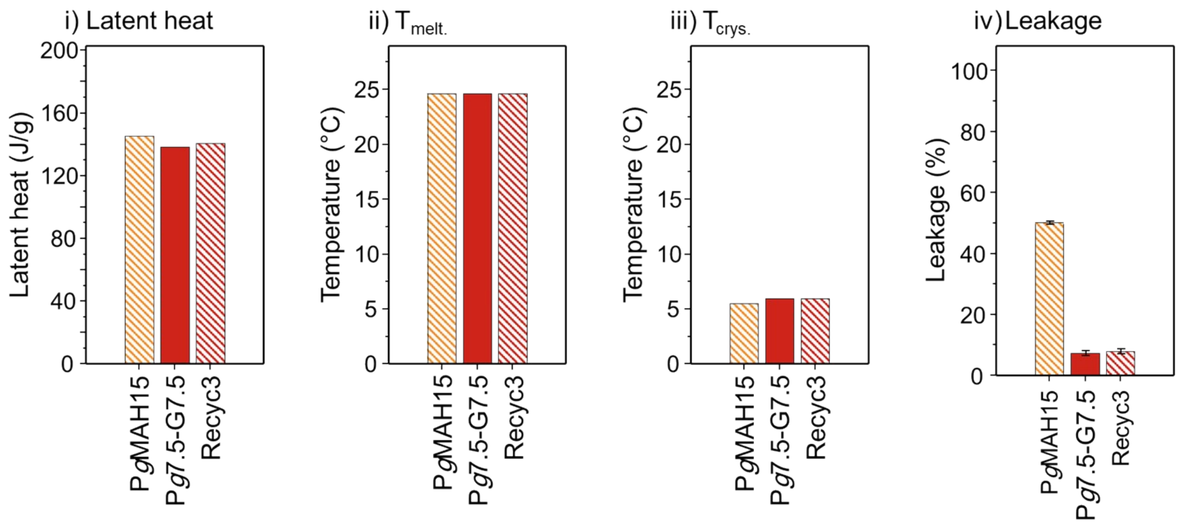


Figure S18. Properties of stabilized PCM with 15 m% P*g*MAH15, P*g*7.5-G7.5 and recycled Gen 3: Latent heat (i), melting temperature (ii), crystallization temperature (iii) and leakage (iv).

20. Storage modulus during cooling

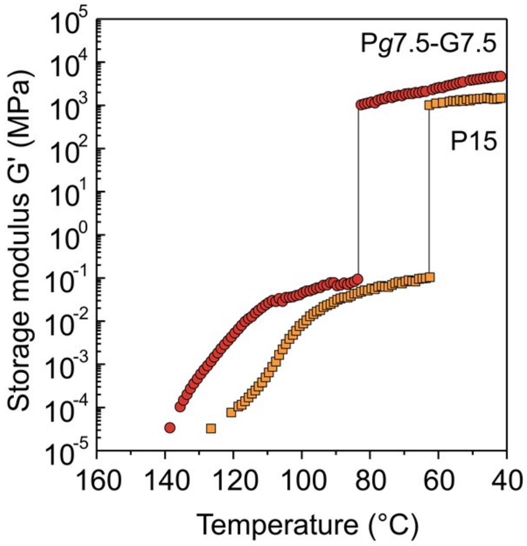


Figure S19. Storage moduli *G'* of P15 and P*g*7.5-G7.5 during cooling at the rate of 5 °C/min.

21. FTIR after alcoholic extraction

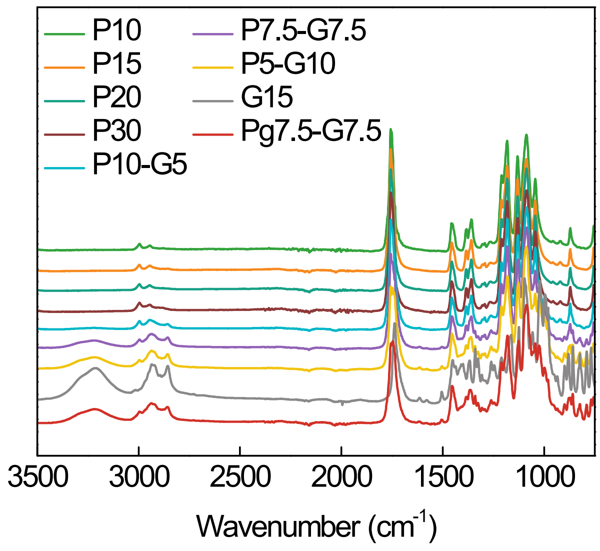


Figure S20. FTIR of different stabilized PCM samples after extraction with methanol, followed by drying for three days at ambient conditions without vacuum.

22. Organic gelators as stabilizer for solid-liquid PCMs in recent publications

Table S1. Organic gelators as stabilizer for solid-liquid PCMs in recent publications.

Gelator	**PCM**	**PCM content**	**Ref**
MDBS	Paraffin	94 m%	[1]
DMDBS	1-tetradecanol	88-97 m%	[2]
DMDBS	n-octadecane ethyl palmitate 1-octadecanol 1-tetradecanol	97 m%	[3]
Gm	Paraffin	90-99.5 m%	[4]
Gn	n-octadecane		[5]
HSA- and Mil MT-800	CrodaTherm 29-SO-(GD)	96-99.7 m%	[6]
DMDBS	1-octadecanol / EG	83-97 m%	[7]
Gelator / Polymer	**PCM**	**PCM content**	**Ref**
TBPMN / PO	Paraffin PEG	95-98 m%	[8]
DBS / UHMWPE	Paraffin		[9]

1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS), 1,3:2,4-di-*O*-*p*-methyl benzylidene-D-sorbitol (MDBS) and 1,3:2,4-di-*O*-*m*,*p*-dimethylbenzylidene-D-sorbitol (DMDBS), 12-hydroxystearic acid (HSA), 1,2,3-tridesoxy-4,6:5,7-bis-*O*-[(4-propylphenyl) methylene]-nonitol (TBPMN).

23. Solubility parameters

23.1. Solubility parameter Gelator DMDBS

Table S2. Calculation of solubility parameters by Fedors method for the gelator DMDBS.

Fedors Method							
Groups	$-CH_3$	$-CH_2-$	-CH<	-O-	-OH	Ph	5-Ring
N_i	4	2	6	4	2	2	2
E_i (J/mol)	4710	4940	3430	3350	29800	31940	1050
V_i (cm³/mol)	33.5	16.1	-1.0	3.8	10.0	33.4	16.0
Sum	$E = \Sigma E_i N_i = 188280$ $V = \Sigma V_i N_i = 294.2$						
δ ($J^{0.5}/cm^{1.5}$)	$\delta = (E/V)^{0.5} =$ **25.3**						

23.2. Solubility parameter PCM Dimethyl sebacate

Table S3. Calculation of solubility parameters by Fedors method for the PCM dimethyl sebacate.

Fedors Method			
Groups	$-CH_3$	$-CH_2-$	$-CO_2-$
N_i	2	8	2
E_i (J/mol)	4710	4940	18000
V_i (cm³/mol)	33.5	16.1	18.0
Sum	$E = \Sigma E_i N_i = 84940$ $V = \Sigma V_i N_i = 231.8$		
δ ($J^{0.5}/cm^{1.5}$)	$\delta = (E/V)^{0.5} =$ **19.1**		

24. Enthalpy of PLLA during TIPS

Table S4. Crystallization enthalpy of PLLA during TIPS.

	PLLA (m%)	ΔH_{crys} (J/g)	Norm. ΔH_{crys} (J/g)
	100	38.6	38.6
P10	10	3.2	32.1
P15	15	5.4	35.9
P20	20	7.3	36.6
P30	30	9.7	32.2
P5-G10	5	1.3	26.0
P7.5-G7.5	7.5	2.4	32.5
P10-G5	10	3.2	32.2
P*g*7.5-G7.5	7.5	3.7	49.3

25. Gel content of selected stabilized PCMs in DCM

Table S5. Gel content of stabilized PCM samples.

	Residue of complete PCM (m%)	Residue Error (m%)	Residue of stabilization agents (m%)	Residue Error (m%)
P15	0	-	0	-
P7.5-G7.5	5.9	±0.8	39	±5
P*g*7.5-G7.5	4.8	±0.9	32	±6
G15	8.1	±1.0	54	±10

26. Thermal properties of stabilized PCMs

Table S6. Thermal parameters of stabilized PCM samples.

	Leakage (%)	Leakage Error (%)	Melting Latent heat (J/g)	Latent heat error (J/g)	Freezing Latent heat (J/g)	Latent heat error (J/g)	Melting Temp. (°C)	Freezing Temp. (°C)	PCM (m%)
P5	91		176.3	±0.6	179.7	±0.6	26	10	95
P10	48		164.7	±1.2	166.3	±0.6	26	5	90
P15	40	±2.1	152.3	±0.6	153.3	±0.6	26	3	85
P20	30		143.3	±0.6	145.0	±1.0	27	5	80
P30	28		113.7	±0.6	104.3	±1.2	25	5	70
P10-G5	42		147.3	±0.6	146.7	±0.6	24	12	85
P7.5-G7.5	41	±2.1	153.0	±0.0	151.3	±1.2	25	10	85
P5-G10	39		147.3	±1.2	147.7	±0.6	25	12	85
G15	12	±0.7	154.0	±0.0	151.3	±1.2	26	19	85
P*g*7.5-G7.5	7	±1.4	138.3	±0.6	137.3	±0.6	24	7	85
P*g*MAH15	50	±0.7	144.3	±0.8	144.1	±1.4	24	6	85
Recycled Gen3	8	±1.4	139.9	±0.6	140.1	±1.0	24	7	85

27. References

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