

Bio-based poly (glycerol-itaconic acid)/PEG/APP as form stable and flame-retardant phase change materials

Guang-Zhong Yin,^a Xiao-Mei Yang,^b Jose Hobson,^a Alba Marta López,^a De-Yi Wang^{a,*}

a IMDEA Materials Institute, C/Eric Kandel, 2, 28906 Getafe, Madrid, Spain

b State Key Laboratory of Biobased Fiber Manufacturing Technology, China Textile Academy, Beijing 100025, China

AUTHOR INFORMATION

Corresponding Author

*Tel: +34 91 549 34 22, fax: +34 91 550 30 47; Email: deyi.wang@imdea.org

Abstract

With the improvement of people's living level, smart home and comfortable life put forward novel and highly scientific requirements for building materials and home environment. Environmental protection, renewability, processing convenience and use safety (non-toxic/fire safety) are all core indicators that need to be considered in an all-round way in the process of material design. In this work, we used a simple and efficient green process by blending ammonium polyphosphate (APP) and poly (glycerol-itaconic acid) loaded polyethylene glycol (PEG) to prepare fire safe phase change materials (PCMs). The flame retardancy, phase change performance and thermal response behavior (including form stability, thermal conductivity, cycle stability, and latent heat *etc.*) were systematically characterized. The results showed that limiting oxygen index (LOI) increased significantly with the increase of APP content. Typically, when the filling amount of APP reached 15 wt.%, the LOI value increased from 21.6% to 28.7%, vertical testing reached UL-94 V0 rating and the pHRR decreased by 36.15%. The as-prepared PCMs show excellent form stability, and the enthalpy of phase change keeps higher than 70 J g⁻¹, which is at the high level as that of same

kinds of PCMs. Notably, due to its high preparation efficiency for PCM fabrication and the profiles of all bio-based supporting matrix, solvent-free pathway, mild curing temperature, and fire safety, it is expected to be effectively applied in building for the thermal regulation.

Keywords: Flame retardant, Solvent free, Energy storage materials, Bio-based

1. Introduction

Phase change materials (PCMs) have been widely applied in devices heat regulation for photovoltaic panels, [1] building construction energy saving [2] and solar energy harvesting and storage,[3] due to their large latent heat and proper thermal profiles, such as low extent of supercooling, adjustable phase transition temperature, and good chemical stability. However, the flammability of the organic PCMs, which may lead to fire risks during processing, storage and application of the thermal energy storage materials, which is the main obstacles restraining the organic PCMs from widely practical application [4]. To solve this problem, flame retardants (FRs) are usually used to improve the fire safety. For example, Li et al. [5] mixed intumescent flame retardant (IFR) with paraffin and polypropylene. With 30% of IFR loading, the limiting oxygen index (LOI) improved remarkably to 32.8%. The peak of heat release rate (pHRR) of the PCM was reduced to 135.9 kW m^{-2} from 1189.7 kW m^{-2} , which showed an excellent fire safety. More recently, lots of work focus on the thermal regulation for the battery module. [6], [7] For example, a novel flame-retarded PCMs composed by paraffin, expanded graphite, ammonium polyphosphate (APP), red phosphorus and epoxy resin has been proposed for battery module. [8] The results show that the fire retardant PCMs shown significant cooling and temperature balancing advantages for battery module, leading to a 44.7% reduction rate of the peak temperature. It shows

that the development of new multi-functional PCM has practical significance of the times to a certain extent.

On the other hand, the climate neutrality, aimed by the EU to be reached by 2050, cannot be achieved without a significant change in the manufacturing sector. Reduction of its pollution and waste and increase of its reprocessing potential is necessary to achieve a true circular and sustainable economy. The replacement of fossil raw materials by bio-based ones is crucial for the green transition of manufacturing industries. [9, 10] Therefore, fully bio-based poly (glycerol-itaconic acid) (PGI) was selected as the supporter materials for the fabrication of form-stable PCMs. Furthermore, it is convenient to prepare a flame-retardant composite by blending method. As a commercially available and eco-friendly FR, APP possessed high contents of phosphorus and nitrogen, and had been recognized as an effective FR to solve the fire safety problem. [11-15] In this study, we will synthesize the PGI prepolymer mixing with PEG by a convenient method, and then add APP as flame retardant modifier and Dibenzoyl peroxide (BPO) initiator to prepare bio-based PGI/PEG/APP flame retardant phase change system. It is expected that the obtained PCMs can be applied in the field of fire safe building for energy conservation based on the convenient fabrication nature and high performance in both phase transition process and fire safety.

2. Results and discussion

2.1 Fabrication of flame retardant PCM composites

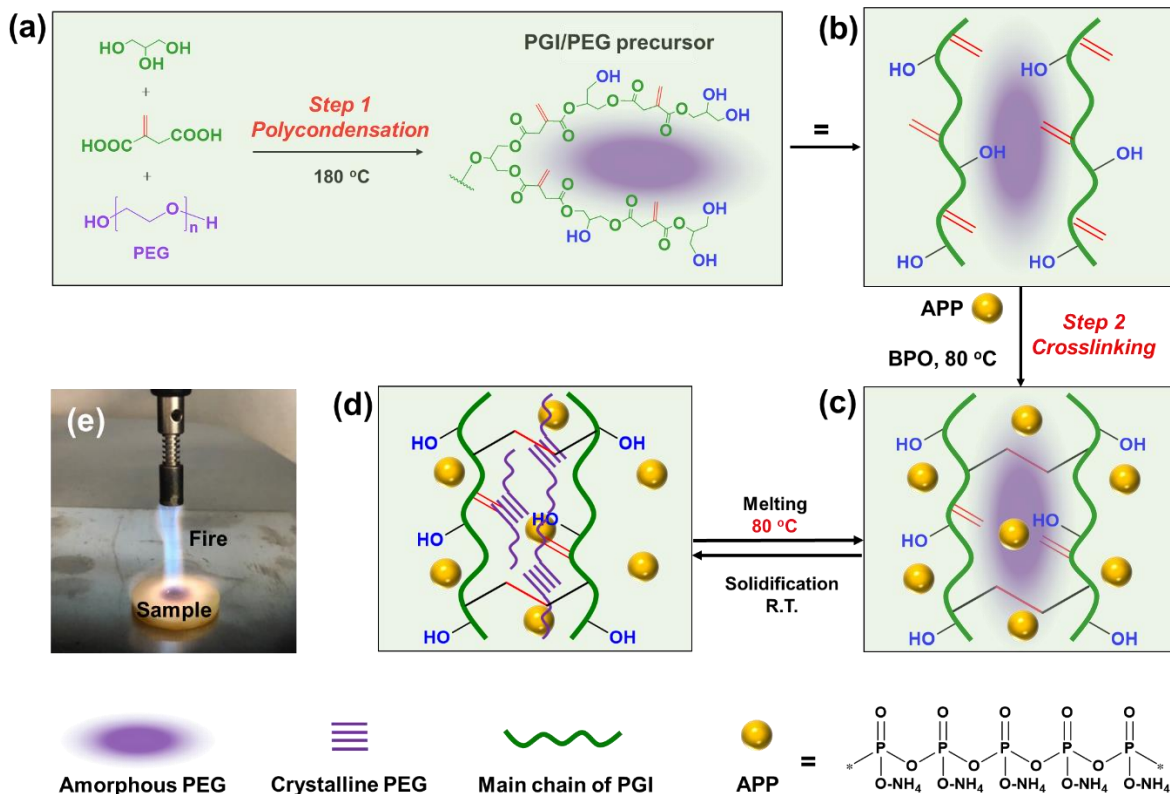


Figure 1. (a) PGI/PEG synthesis by polycondensation, (b) Schematic diagram of the precursor with vinyl and hydroxyl groups, (c) Cross-linked precursor induced by BPO and mixing APP flame retardant at 80 °C, (d) the reversible phase transition illustration and (e) sample (PCM-15%) as a typical example to show the fire resistance.

The PCM composites preparation pathway here is solvent free and highly efficient, which is conducive to the practical applications in the area of building construction. **Table S1** listed the preparation parameters in details. **Figure 1a** shows the PGI/PEG synthesis (Step 1). Concretely, Itaconic acid, Glycerol and PEG were heated together under N₂ protection, generating a viscous oil. ¹³C Nuclear magnetic resonance (¹³C NMR) and Fourier transform infrared spectroscopy (FTIR) were provided in **Figure S1-S2** to confirm the successful obtaining of the PGI

precursor/PEG blending. With the mixture of BPO (0.5 wt.%), and APP with vary contents as flame retardant, the entire system was heated and an integrated solid-state material after vinyl cross-linking (**Figure 1b** and **1c**) was obtained. **Figure 1d** shows the microstructure of PCM after solidification. In addition, sample PCM-15% was used as a typical example to show the fire resistance (**Figure 1e**). The detailed fire safety performance will be investigated in section 2.2.

The FTIR curves of the PCMs were carried out and presented in **Figure 2a**. All the PCM shows the typical peaks at $\sim 3450\text{ cm}^{-1}$ for terminal -OH groups, 2870 cm^{-1} for $-\text{CH}_2-$, and $\sim 1720\text{ cm}^{-1}$ for $-(\text{C}=\text{O})-$. $I_{\text{C}=\text{O}}$ is the relative intensity of $-(\text{C}=\text{O})-$. It is selected as the internal standard of FTIR analysis. The $I_{\text{vinyl}}/I_{\text{C}=\text{O}}$ is the intensity ratio of vinyl characteristic signal ($\sim 1640\text{ cm}^{-1}$) and peak C=O. As it can be seen (Figure S2), the $I_{\text{vinyl}}/I_{\text{C}=\text{O}}$ for PGI-0 (before curing) and PGI-0 (after curing) are 0.434 and 0.319, respectively. The significant decrease of Vinyl group intensity indicated the crosslinking occurred among the vinyl under the action of BPO initiator.[16] There was no significant difference in FTIR curves (**Figure 2a**) among the APP modified PCMs samples because of the blending nature and good compatibility between APP and the PCM matrix. **Figure 2b** presents the X-ray diffraction (XRD) curves of the PEG and all the PCMs. The XRD curve of pure APP is shown in **Figure S3**, which shows two obvious signals at $2\theta=14.8^\circ$ and 15.7° . The other main peaks appeared at $2\theta\sim 19^\circ$ (120) and $\sim 23^\circ$ (032), which are assigned to be the signal of PEG. The diffraction peak position of PCMs composite are similar to those of PEG and all the FTIR curves are also similar, indicating that the encapsulation of PEG and blending of APP does not influence PEG respective crystal morphology and the intra-molecular interaction significantly, thus ensuring that the composite materials have relative high phase change enthalpies (see Section 2.3).

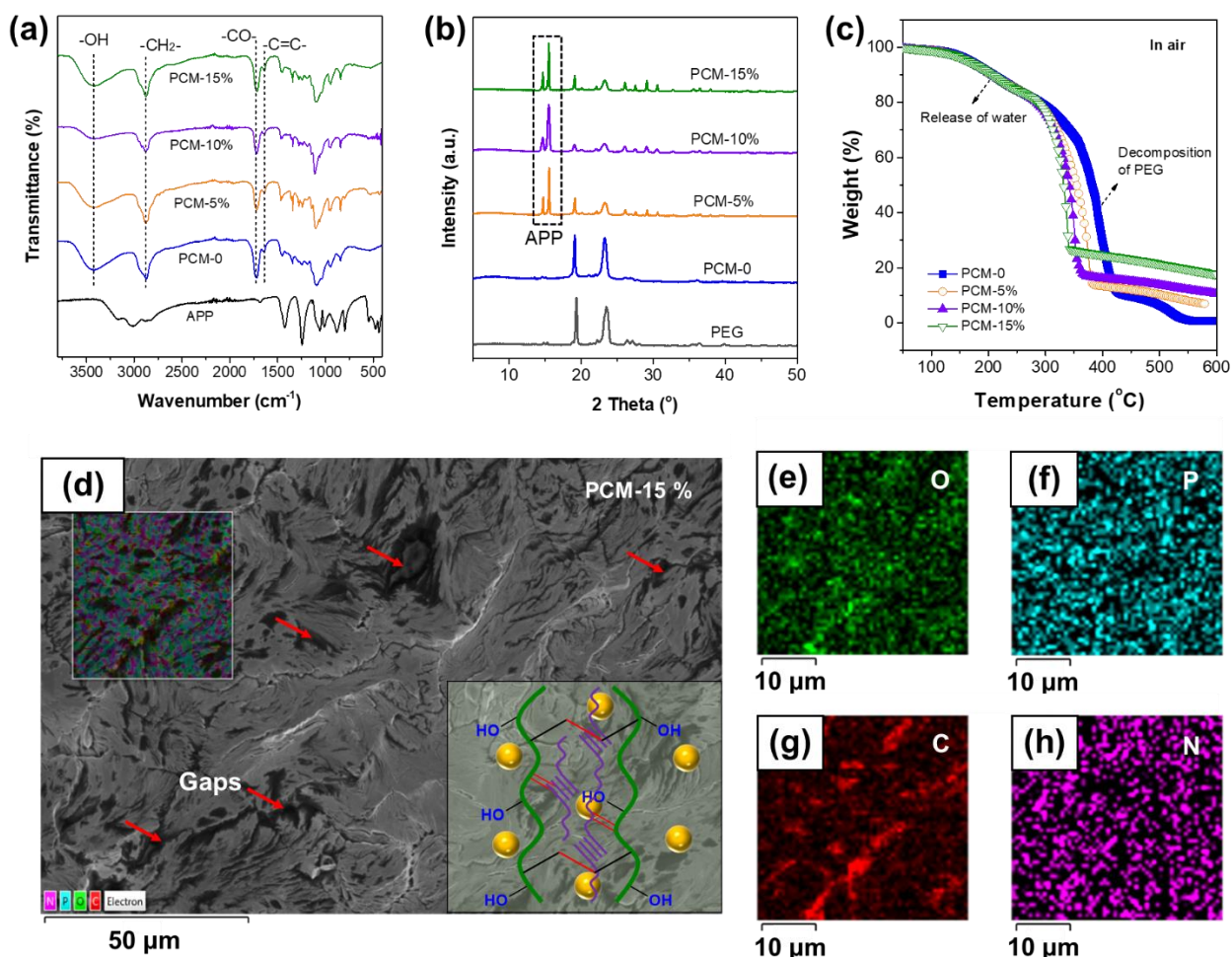


Figure 2. (a) FTIR spectra of APP, PCM-0, and the APP modified samples, (b) XRD patterns of PEG, and all the PCMs, (c) Thermo Gravimetric Analyzer (TGA) curves of all the PCMs, (d) scanning electron microscope (SEM) image of sample PCM-15% as a typical example (Note: Because the density of the crystalline region is higher than that of the amorphous region. The polymer precursor crosslinked to form a dense and shape-stable PCM, and then the material will undergo the transformation from low density (melting state) to local high density (crystalline region) in a specific space when cooling down. While the volume remains unchanged, the formation of internal crystal region will inevitably derive many discontinuous intervals, which are

manifested as gaps in the SEM image), and the Energy Dispersive X-Ray Spectroscopy (EDX) mapping of element of (e) O, (f) P, (g) C and (h) N, respectively.

Figure 2c shows the TGA curves of the PCM samples. The thermal weight loss of the PCMs is mainly divided into two stages. We assigned that the weight loss in the first stage near 200 °C mainly comes from the intermolecular dehydration and release of water. The second stage is the pyrolysis loss of PEG. It is found that the addition of APP will give rise to the earlier the decomposition of the material and the higher the char residue. The specific pyrolysis behavior index parameters are listed in **Table S2**. As a typical example, PCM-15% was selected for the APP dispersion test (**Figure 2d**). It is found that the APP has good compatibility and is easy to be well dispersed in the PCMs. Therefore, no significant aggradation was formed in the composites. Moreover, the uniform EDX profiles (**Figure 2e-h**) directly proved the good dispersion of APP in PCM matrix.

2.2 Fire safety

Fire safety of PCMs was investigated via limiting oxygen index (LOI), UL-94 and CONE calorimeter. The corresponding data are all listed in **Table S2**. UL-94 test revealed that PCM-5% and PCM-10% performed no rating, which are the same as PCM-0 (**Figure 3a**). Notably, PCM-15% passed UL-94 V-0 rating with self-extinguishing performance (**Figure 3b**), which indicated that proper amount of APP suppressed fire spread of PCMs significantly. Combustion image of PCM-5% and PCM-10% were provided in **Figure S5**. LOI investigation (**Figure 3 (c)**) demonstrated that the addition of 15 wt. % APP significantly increased LOI value of PCM matrix. Typically, the LOI increased from 21.6 % from PCM-0 to 28.7 % for PCM-15%.

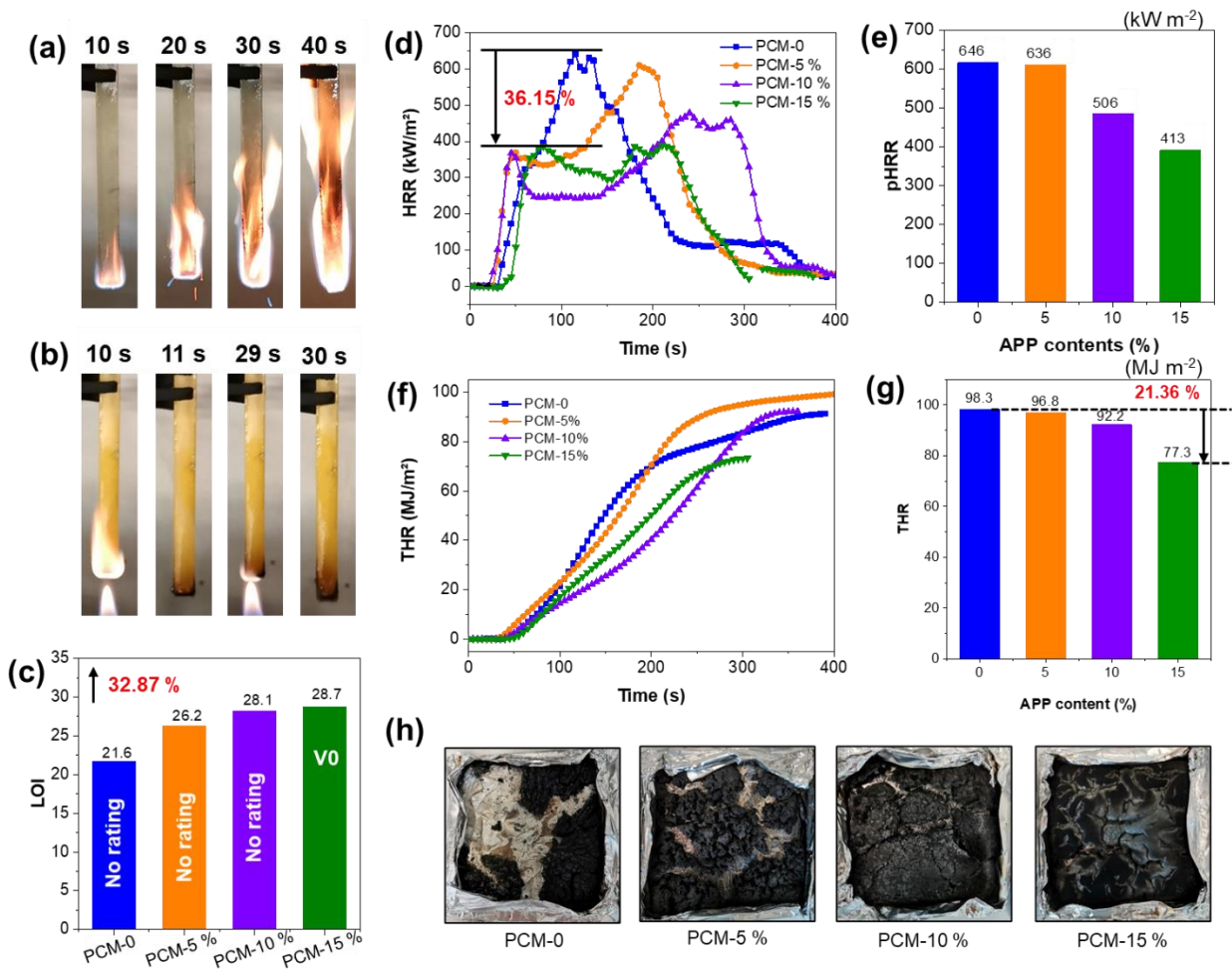


Figure 3. (a) Digital photos of UL-94 test for sample PCM-0, (b) Digital photos of UL-94 test for sample PCM-15%, (c) LOI values of the samples (the LOI value increased by 32.87% for PCM-15%), (d) heat release rate (HRR) curves, (e) peak of HRR (pHRR) values, (f) THR curves, (g) THR values based on the THR curves, and (h) char images of the four samples after CONE tests.

CONE test was carried out for the four PCMs. The HRR and total heat release (THR) are displayed in **Figure 3d** and **3f**. The corresponding values are listed in **Figure 3e** and **3g**. As shown in **Figure 3d**, neat PCM-0 showed a sharp pHRR at 646 kW/m^2 . After APP modification, the pHRR

decreased distinctly to 636 kW m^{-2} , 506 kW m^{-2} and 413 kW m^{-2} for PCM-5%, PCM-10% and PCM-15%, respectively. In contrast to PCM-0 with a continuously rising HRR, the curves of modified PCMs showed an obvious decrease before reaching the main peak, which may be due to the formation of carbonaceous layers during combustion and can slow down the oxygen and volatiles transmission. No sharp pHRRs were observed for PCM-15%, indicating the formed char layers were robust enough to protect the underlying PCM matrix. Additionally, the THR of the PCMs was gradually reduced with the increasing of APP loading. Like the TGA results, an increased char residue was observed for modified PCM, which was in accordance with the enhanced char forming ability that observed during CONE test (**Figure 3h**). To sufficiently show the char forming enhancement, the top and side view of char residue of PCM-15% after CONE test are shown in **Figure S6**. Herein, it can be concluded that APP particles showed a high flame retardant improvement in the PCMs.

2.3 Phase change performances of the PCMs

Figure 4a shows the Differential Scanning Calorimeter (DSC) curves of the PCMs. The corresponding melting enthalpies are shown in **Figure 4b** and listed in **Table S3**. It is found that with increase the APP contents, the latent heat decreased. Fortunately, when APP content researched 15 wt.%, the melting enthalpy keeps higher than 70 J g^{-1} , which is relative high value in the same kind of PCMs. [17-19] The crystallinity was calculated and shown in **Table S3**. Typically, the crystallinity of PCM-0, PCM-5%, PCM-10% and PCM-15% are 65.13%, 60.98%, 62.05 % and 60.43%, respectively. The slightly decrease of crystallinity was probably due to the impurity effect of APP on PEG crystallization. For their form stability tests, the PCMs were put in an $80 \text{ }^\circ\text{C}$ oven for 2 h, and then the PCMs were taken out and photographed. As shown in **Figure**

4c, all the PCMs were only softened and remained in a solid-state without shape change. These results indicated the PCMs could perform excellent form stability.

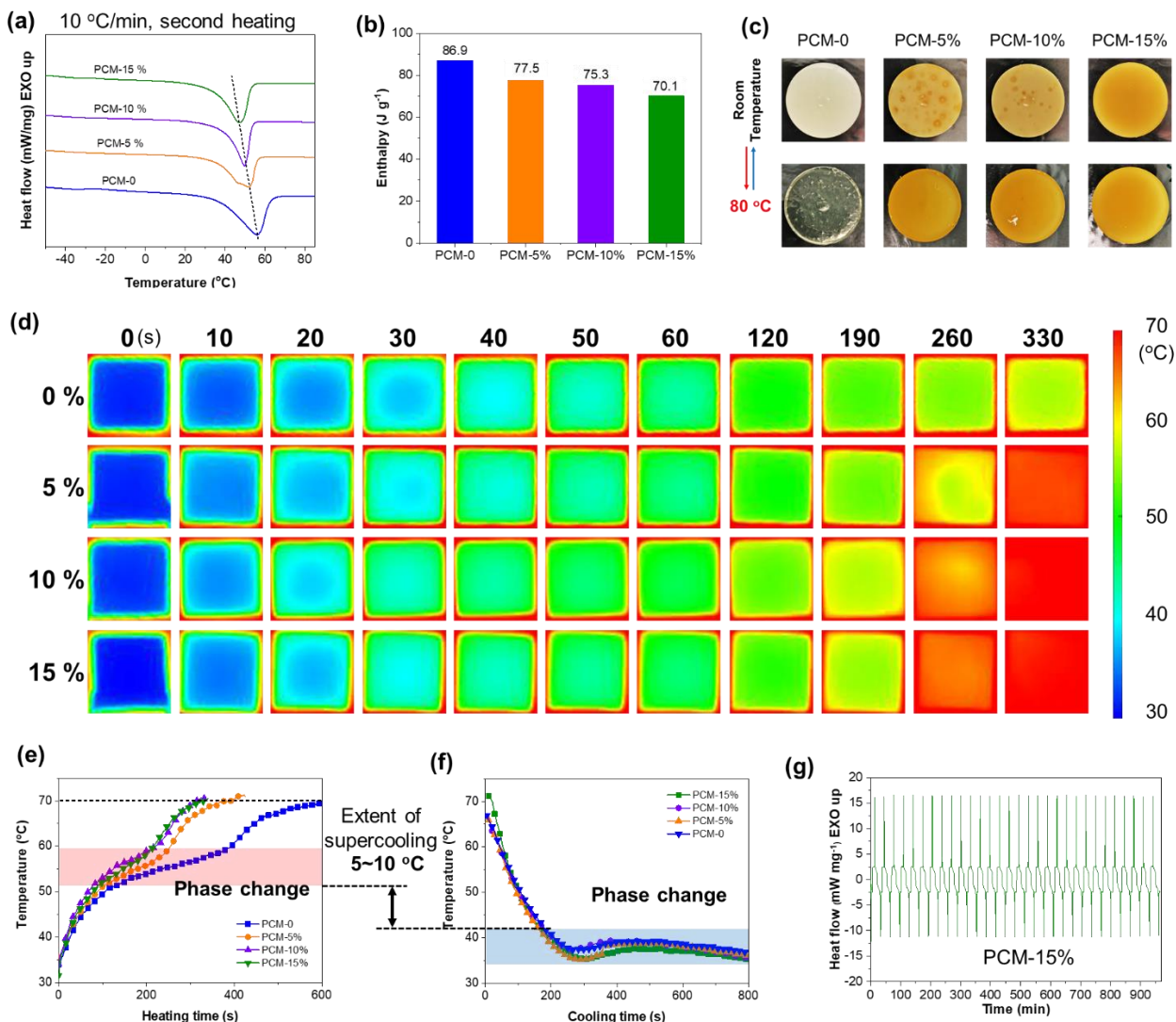


Figure 4. (a) Melting enthalpies of PCM-0 and PCMs with different APP contents, (for completing the information, DSC curve of PEG6k was provided in Figure S7) (b) the melting enthalpy (ΔH_m) obtained by DSC tests, (c) form stability test results, (d) heat response (IR Images) of the four samples, (e) heating and (f) cooling curves of the four samples, and (g) DSC cycle curves of PCM-15%.

The extent of supercooling (ΔT , °C) was calculated according to the equation below: [20]

$$\Delta T = T_{m,onset} - T_{s,onset} \quad (1)$$

The ΔT of the PCMs is calculated and listed in **Table S3**. Concretely, the ΔT of sample PCM-0, PCM-5%, PCM-10% and PCM-15% are 13.21 °C, 5.90 °C, 10.01 °C and 3.86 °C, respectively, which is in good agreement with the results (with value of 5~10 °C) obtained by the heating and cooling response curves (**Figure 4e** and **4f**). The percentage of heat lose (η , %) was calculated via equation 2: [21]

$$\eta = \frac{\Delta H_m - \Delta H_s}{\Delta H_m} \times 100 \% \quad (2)$$

where, ΔH_m and ΔH_s are the melting enthalpy and solidification enthalpy of the PCMs, respectively. As shown in **Table S3** and **Figure 4b**, the PCMs exhibited an enthalpy of (70.11~86.93 J g⁻¹). Furthermore, the η (<3.8 %) for the PCMs are also calculated and listed in **Table S3**.

The thermal conductivity (TC) is a primary factor for the practical application. [22] The measured TC of PCM-0 is 0.28±0.03 W m⁻¹ K⁻¹. Due to the improved TC of the APP modified PCMs (0.31±0.04 W m⁻¹ K⁻¹, 0.36±0.02 W m⁻¹ K⁻¹, 0.38±0.04 W m⁻¹ K⁻¹ for PCM-5%, PCM-10% and PCM-15%, respectively), the heat diffusion in the PCMs is accelerated. The surface temperature variations of the four PCMs with different heating times were recorded by an IR cameral. As shown in **Figure 4d**, the color of samples with APP changes quicker than that of PCM-0, indicating that APP can slightly enhance the heat transfer rate of PCMs. **Figure 4e** and **4f** shows the temperature-time plots of all the four samples during the heating and cooling process, respectively. The surface temperature of PCM-APP is higher than that of PCM-0 at the same time.

The PCMs had good cycle performance (**Figure 4g**) because the main PCM parameters maintained unchanged (**Table S3**). Solvent free two-steps method with high formation efficiency were used to fabricate the PCM composites with APP as the flame retardant. The $T_{m, onset}$ of the PCMs was 30.02~41.92 °C, which is a comfortable transition temperature range for human being. In a word, the PCMs had good potential for application in building constructions for the thermal regulation and energy conservation.

Some preparation methods, PCM key parameters in some other reports are listed in **Table 1**. There are few articles on the fire safety of PCM. To our best of knowledge, the flame retardant safety of biomass has not been reported. In **Table 1**, we listed some core indexes of form stable PCM of biomass matrix. Through comparison, we found that the significant progress of this work is reflected in: (1) efficient molding, (2) high enthalpy of phase change (3) excellent flame retardant performance. Therefore, the material is expected to be applied in the field of energy saving and temperature control of fire safety building materials.

Table 1. Thermal properties of as-prepared composite PCMs and recently PCM composites

Year	PCMs	Bio-based		Latent heat (J g ⁻¹)	LOI increase (%)	pHRR decrease (%)	References
		supporter	FR				
2019	Bio-char/Paraffin	Yes	-	25.2-92.1	-	-	[23]
2019	Bio-waste/Nature soy-wax or Golden soy-wax	Yes	-	19.4-21.1	-	-	[24]
2020	Oilseed straw or Miscanthus straw/n-dodecane or 1-dodecanol	Yes	--	54.1-90.5	-	-	[25]

2010	HDPE/Paraffin	No	Expanded graphite	68.3-81.5	N/A	-62.04%	[26]
2010	HDPE/Paraffin	No	Chlorinated paraffin	49.6-70.1	N/A	-61.20%	[27]
2008	HDPE/Paraffin	No	APP/Zinc Borate	78.8-91.2	N/A	-68.44%	[28]
2021	PGI/PEG	Yes	APP	70.1-86.9	+21.36%	-36.15%	This work

3. Conclusion

In this work, APP was selected as flame retardant to modify PGI/PEG by a simple and efficient green process to prepare fire safe phase change materials. The flame retardancy, phase change performance and thermal response behavior were systematically characterized. The results showed that LOI increased significantly with the increase of APP content. When the filling amount of APP was 15 wt.%, UL-94 reached grade V0 and the pHRR decreased by 36.15%. Phase change materials show excellent form stability, and the enthalpy of phase change is 70.1-86.9 J g⁻¹, which is at the same level as that of similar materials. Notably, it was found that the significant progress of this work is reflected in: (1) green and efficient fabrication and convenient molding, (2) high phase change enthalpy (3) excellent flame retardant performance. Therefore, the material is expected to be applied in the field of energy saving and temperature control of fire safe building materials.

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