Investigating the Effect of Crystallizability and Glass Transition Temperature of Supporting Materials for Preparing High Enthalpy Electrospun Poly(lactic acid)/Poly(ethylene glycol) Phase Change Fibers

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Abstract

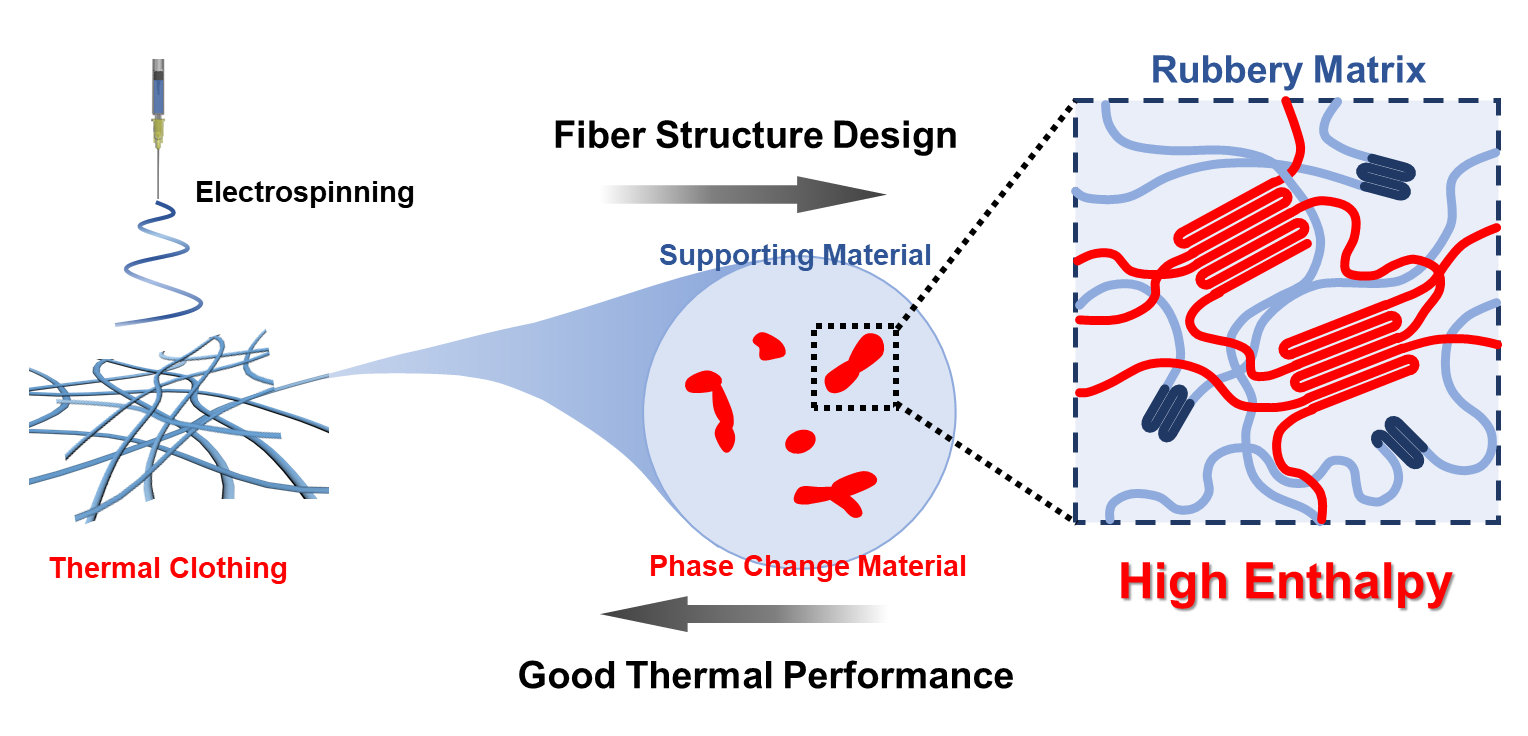
Form-stable phase change fibers (PCFs) that are composed of stable supporting material (as polymer matrix) and phase change material (PCM, as working ingredient) have become novel smart materials, being widely applied in energy storage, thermal regulation and the biomedical field. However, the inherent limitation of PCFs is the restriction of the supporting material on the crystallization of the PCM, which results in low phase change enthalpy (Δ*H*). Here, six different types of PCF comprised of poly(lactic acid) (PLA, as supporting material) and poly(ethylene glycol) (PEG, as PCM) have been fabricated. Their morphology, phase change performance and structural transitions during phase change have been extensively studied. We reveal that the crystallizability and glass transition temperature of PLA have a dominating influence on Δ*H*. In the optimum system, PLA/PEG PCFs can achieve up to 104 J/g Δ*H* which is close to the theoretical value of pristine PEG. This high-performance PCF also exhibits only 2.5% Δ*H* loss after 100 thermal cycles and good ability in thermal energy storage and thermal regulation. This work provides a promising form-stable PCF and introduces a new strategy towards developing high Δ*H* PCFs by selecting suitable supporting materials.

# Keywords

Phase change fibers, High phase change enthalpy, Structural transition, Thermal energy storage, Thermal regulation

1. Introduction

Over the last two decades, phase change fibers (PCFs) have been extensively studied as smart materials, since they not only inherit the thermoactive properties of phase change materials (PCMs) but also endow the PCM with stable form, flexibility and controllable micro-to-nanoscale fibrous structures [1-4]. They have been applied in general thermal storage and regulation (such as thermal regulating textiles [5-8] and electronic device protection [9], such as battery protection [10]), and even in the biomedical field (controlled drug delivery systems [11-13] and cancer therapy [14]).

As a convenient and versatile method, electrospinning techniques have been extensively developed for this field [4, 15-17], since form-stable PCFs can be readily fabricated from a solution containing solid-liquid PCMs and supporting materials [18-21]. During electrospinning, supporting materials can form a three-dimensional fibrous cage (or matrix) to “support and restrict” the melted PCM from flow loss, which would eventually lead to leakage. Therefore, the entire PCF can be rendered stable (no leakage) when phase changing. Many researchers have fabricated advanced form-stable PCFs using electrospinning [22, 23]. The influence of PCF composition, PCM type and ratio [24, 25], additives [26, 27], post treatment (annealing [28], crosslinking [29]) and consequent structures [30] (fiber structure, domain distribution) on electrospun PCF performance (such as phase change enthalpy, Δ*H* [24-31], mechanical properties [29], thermal conductivity [26, 27] and stability [26, 27, 32]) have been studied. 

**Figure 1.** Using a rubbery polymer as supporting material to enhance the enthalpy of electrospun PCFs.

Among the various features of PCFs, Δ*H* is one of the most important parameters that influences their properties [33]. However, the introduction of supporting materials can limit the crystallization of PCMs and cause a decrease in Δ*H*. The interaction between the PCM and supporting material (such as hydrogen bonding [34]) can restrict the molecular motion of the PCM. Supporting materials can also act as a diluent and hinder the chain folding of the PCM during crystallization [35]. As Table 1 shows, the experimental phase change enthalpy (Δ*H*) of encapsulated PCM is typically lower than the theoretical phase change enthalpy (Δ*H*T) of bulk PCM. This phenomenon is called *confined crystallization* [28, 36, 37]. Different types of supporting material exhibit varying degrees of confinement on PCM crystallization. For example, as seen in Table 1, CA, PAN and nylon-6,6 were all used as supporting materials to encapsulate poly(ethylene glycol) (PEG) resulting in a varied effect on the crystallization, with a nylon-6,6 fibrous matrix exhibiting the lowest confinement on PEG crystallization (/ = 95%). Looking at previously reported PCFs [4] we observe that, in many cases, PCFs made up of semi-crystalline supporting materials with lower glass transition temperature (*T*g) than the melting temperature (*T*m) of the PCM usually exhibited a high Δ*H* value, close to Δ*H*T, although this was not explicitly stated nor explored. Based on this finding, we propose two hypotheses to significantly advance the field of PCFs: (1) Will a supporting material with a lower *T*g than the *T*m of encapsulated PCM (*i.e.*, rubbery state supporting material) be beneficial for obtaining high PCFs? (2) Will a semi-crystalline supporting material induce the crystallization of PCM? [38]

**Table 1.** Experimental crystallization (Δ*H*c) and melting (Δ*H*m) enthalpies, and theoretical crystallization (Δ*H*c-T) and melting (Δ*H*m-T) enthalpies of reported PCFs.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No. | Supporting material/ PCM |  |  | % |  |  | % | Ref. |
| 1 | CA/PEG | 65.8 | 83.9 | 78 | 86.0 | 88.7 | 97 | [39] |
| 2 | PAN/PEG | 52.4 | 73.45 | 71 | 44.0 | 82.0 | 54 | [40] |
| 3 | PAN/LA-SA | / | / | / | 53.1 | 67.6 | 79 | [41] |
| 4 | CA/PEG | 46.8 | 73.5 | 64 | 39.5 | 82.0 | 48 | [42] |
| 5 | PA6/LA | 57.1 | 86.6 | 66 | 70.4 | 86.1 | 81 | [43] |
| 6 | PET/LA | 81.1 | 90.1 | 90 | 87.5 | 92.4 | 95 | [44] |
| 7 | PET/GMS | 53.2 | 57.4 | 93 | 57.1 | 57.6 | 99 | [45] |
| 8 | PS/LA | 143.0 | 144.2 | 99 | 141.3 | 148.2 | 95 | [46] |
| 9 | Nylon-6,6/PEG | 86.0 | 91.0 | 95 | 85.4 | 106.8 | 80 | [47] |
| 10 | PVA/Erythritol | 151.4 | 151.4 | 100 | 196.7 | 204.4 | 96 | [48] |
| Definition of theoretical phase change enthalpy (J/g):  (of PCF) = (of PCM) × PCM weight ratio (within PCFs)  (of PCF) = (of PCM) × PCM weight ratio (within PCFs)  CA - cellulose acetate; PEG - poly(ethylene glycol); PAN - polyacrylonitrile; LA - lauric acid; SA - stearic acid; PA6 - polyamide-6; PET - poly(ethylene terephthalate); GMS - glyceryl monostearate; PS - polystyrene; PVA - poly(vinyl alcohol) | | | | | | | | |

Therefore, in this work, six PCFs consisting of poly(lactic acid) (PLA, as supporting material) and PEG (as PCM) were prepared to thoroughly explore our hypotheses. Fiber morphology, phase change performance, crystal structure, shape stability and thermal regulating ability were assessed. The results indicated that both the crystallizability and *T*g of PLA () dramatically influenced the phase change performance of PEG. Δ*H* could be promoted by selecting a suitable supporting material. The most promising support matrix was shown to be semi-crystalline PLA with flexible, or rubbery, amorphous regions ( < operating temperature of PCM) as it provided structural integrity, whilst having weaker confinement on PEG crystallization, resulting in higher Δ*H*.

2. Materials and methods

2.1 Materials

The following chemicals were used as supplied without further purification. Three forms of PLA: poly(L-lactic acid) (L-PLA), poly(D-lactic acid) (D-PLA), and random copolymer of L-lactic acid and D-lactic acid (D,L-PLA) were obtained from Jinan Daigang Bio-engineering Co., Ltd. China (see PLA type and weight-average molecular weight (*M*w) in Supporting Information (SI), Table S1). PEG of varying *M*w (6k, 1k and 0.6k g/mol) were bought from Petroliam National Berhad, Malaysia. Dichloromethane (DCM) was analytical grade and purchased from Aladdin.

2.2 Fibers Preparation

2.2.1 PLA solutions

8 wt% PLA solutions (SI, Table S1) were prepared by dissolving PLA (L-PLA, D-PLA or D,L-PLA) in DCM (stirred for 24 h at room temperature).

2.2.2 PLA/PEG solutions

PLA was firstly dissolved in DCM to form the primary PLA solution (see PLA wt.% in Table S1) as described above. An equal weight of PEG (*M*w = 6k, 1k or 0.6k g/mol) was added into the PLA solution to form PLA/PEG (1:1 wt./wt.) solution, which was stirred for 24 h at room temperature.

2.2.3 Electrospinning

The prepared solution (PLA or PLA/PEG) was loaded into a syringe to fabricate the corresponding electrospun fibers. Fibers were collected on an aluminum plate at room temperature and humidity ~65%. The needle and collector were connected with positive and negative voltages, respectively. The solution supply rates and applied voltages are listed in the Supporting Information, Table S1. Electrospun fibers were dried in the air at room temperature for 48 hours to remove residual solvent for the further use.

2.3 Characterization

Scanning electron microscopy (SEM) was performed on a Phenom Pro G3 (Phenom, Holland). Samples were sputtered with a layer of platinum for 120 seconds (Q150T ES PLUS, Quorum, U.K.).

Differential scanning calorimetry (DSC) was performed on a DSC 2500 (TA Instruments, USA). A hole was stabbed in the aluminum sample pan to balance pressure during heating. To assess phase change performance, samples were firstly maintained at 100 °C for 5 minutes to eliminate thermal and processing history. Subsequently, they were cooled down to -20 °C before being heated to 100 °C. All temperature ramps were performed at 10 °C/min. Samples were held for 5 minutes between each temperature ramp to establish thermal equilibrium. values were obtained by heating PLA powder to melt (200 °C for L-PLA, D-PLA and 100 °C for D,L-PLA), cooling to -20 °C and heating back to 100 °C at a rate of 20 °C/min. The values were recorded during the final heating ramp.

The thermal cycling test was performed by heating and cooling PCFs for 100 cycles. PCFs were firstly heated to 100 °C, held for 10 min to establish equilibrium, then thermally cycled between -20 to 100 °C at 10 °C/min in the DSC.

Time-resolved wide-angle X-ray scattering (WAXS) was undertaken on a HomeLab instrument (Rigaku, Japan) with a copper target Kα X-ray with 0.154 nm wavelength. Sample-to-detector distance was approximately 70 mm and calibrated with the diffraction pattern of silicon powder. The pixel size of the detector (Hypix-6000) was 100 μm × 100 μm. Fibers were packed between two pieces of aluminum foil and then placed on the hot stage (LTSE420, Linkam, U.K.). The applied temperature program was identical to the DSC tests. 2D WAXS patterns were collected every 15 seconds with 10 seconds exposure time.

Thermal regulating tests were performed on a hot stage (LTSE420, Linkam, U.K.). Approximately 0.5 g of the fibers were wrapped in 20 × 15 mm aluminum foil and pressed against the hot stage for full surface contact. Thermocouples were respectively wrapped within aluminum foil to measure the temperature of the environment and the fibers. The temperature was collected every second by a digital thermometer (TA612C, Suzhou TeAnSi Electronics Co., Ltd, China). Hot stage and fibers were cooled down and heated up at a rate of 20 °C/min around the phase change temperature (namely, working temperature) of PCFs to measure the fiber capability for stabilizing temperature during the rapid fluctuation of temperature.

PEG leakage tests were performed on a hot stage (LTSE420, Linkam, U.K.) based on protocols reported elsewhere [33, 34, 49]. Approximately 0.1 g of sample (pristine PEG, PLA fibers and PLA/PEG PCFs) was placed on filter paper and heated from 25 °C to 100 °C at a rate of 10 °C/min, and then maintained at 100 °C for 10 minutes. Digital photographic images of the samples were recorded before and after heating.

3. Results and discussion

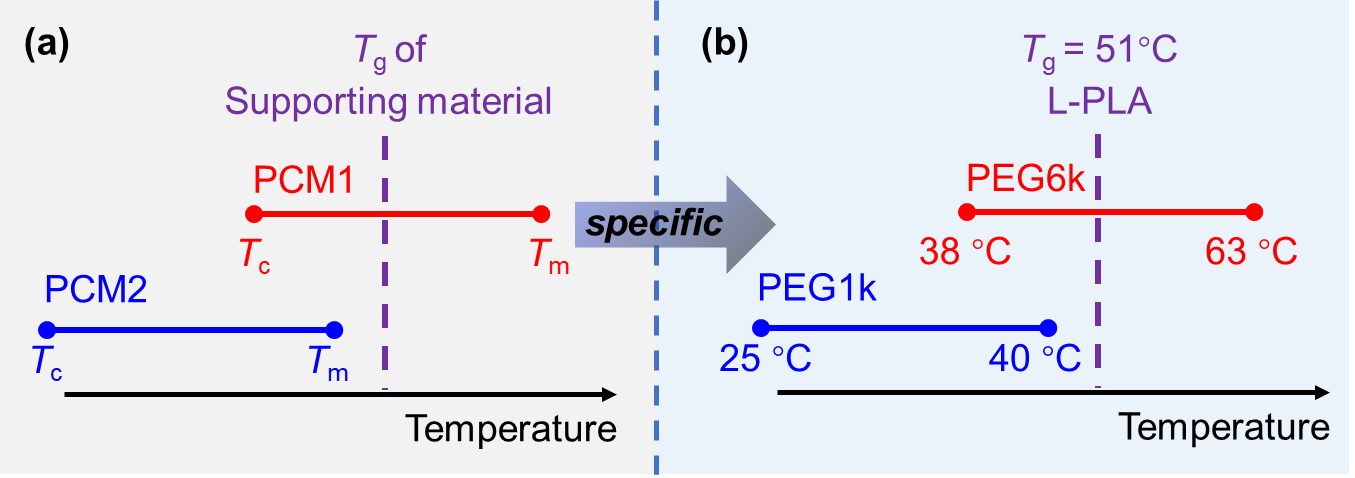
Six different PLA/PEG PCFs (illustrated in Table 2) were prepared. The effect of *T*g and crystallizability of the supporting material (PLA) on the phase change performance of PCM (PEG) are studied in Sections 3.1 and 3.2, respectively. The PEG used in this study are named as PEG0.6k, PEG1k and PEG6k according to their *M*w.

**Table 2.** Electrospun PLA and PLA/PEG (1:1 wt.) fibers created in this study.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| No. | PCFs | PLA type | | PEG type |
| 1 | L-PLA/PEG6k | Semi-crystalline | Rubbery statea | PEG *T*m > PLA *T*g |
| 2 | L-PLA/PEG1k | Semi-crystalline | Glassy stateb | PEG *T*m < PLA *T*g |
| 3 | D-PLA/PEG6k | Semi-crystalline | Rubbery state | PEG *T*m > PLA *T*g |
| 4 | D-PLA/PEG1k | Semi-crystalline | Glassy state | PEG *T*m < PLA *T*g |
| 5 | D,L-PLA/PEG6k | Amorphous | Rubbery state | PEG *T*m > PLA *T*g |
| 6 | D,L-PLA/PEG0.6k | Amorphous | Glassy state | PEG *T*m < PLA *T*g |
| a Glassy-to-rubbery transition of the PLA matrix occurs during PEG phase changing when PEG *T*m > PLA *T*g  b PEG phase changes within glassy PLA matrix when PEG *T*m < PLA *T*g | | | | |

3.1 Effect of supporting material *T*g

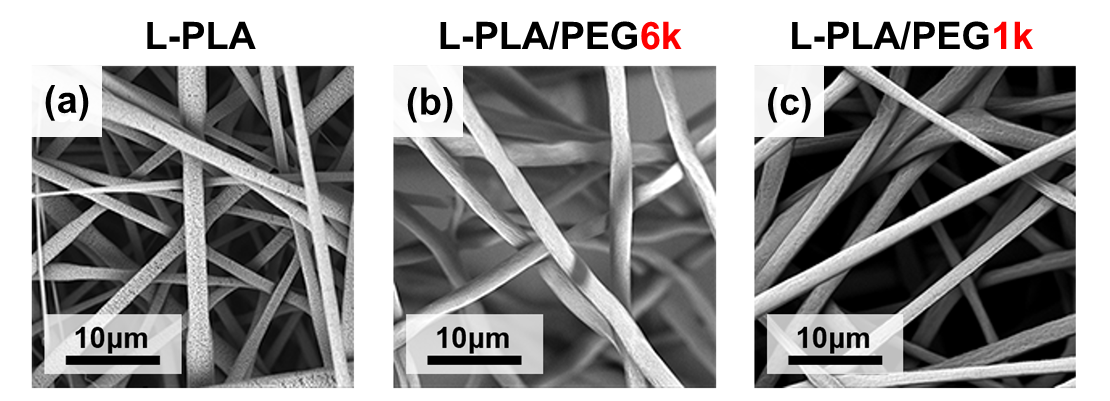
*T*g is the macro-manifestation of segmental chain motion in the polymer chain *i.e.* the flexibility of the macromolecules in the amorphous phase [50]. Ke *et al.* [45], Emilija *et al.* [51] and Samanta *et al.* [28, 52] all reported that within electrospun PCFs, a PCM-rich domain formed within a matrix of supporting material (see fiber structure in Figure 1). Based on these studies, we propose that a flexible matrix formed by rubbery polymer chains (*T*g < PCM *T*m) may confer reduced confinement on PCM crystallization, resulting in higher Δ*H*. Therefore, we designed two types of PCF consisting of the same supporting material, but encapsulating two different types of PCM; one with high phase change temperature (PCM1) and one with low phase change temperature (PCM2) (see Figure 2a). During the phase change of the PCM in PCM1, a glassy-to-rubbery transition of the supporting material would concomitantly occur. In contrast, the supporting material in PCM2 would remain glassy and encapsulate the PCM component throughout the phase change. Consequently, the effect of the *T*g of thesupporting material can be probed in these two systems.



**Figure 2.** (a) The PCFs designed for evaluating the effect of the *T*g value of the supporting material on PCM phase change performance and (b) the specific properties of selected supporting material (L-PLA) and phase change materials (PEG6k and PEG1k). *T*g – glass transition temperature, *T*m – melting temperature, *T*c – crystallization temperature.

PLA is a biodegradable, environmentally friendly polymer that has been exploited in many systems [53-55]. In this part of our study, semi-crystalline L-PLA was selected as supporting material. PEG is a widely used PCM with controllable phase change temperature by adjusting PEG *M*w [25]. Therefore, PEG1k and PEG6k were selected to meet the *T*c and *T*m requirements of the PCM (see Figure 2b). The measured values can be found in the SI, Figure S2. A relatively high ratio (50 wt.%) of PEG was loaded into PLA fibers to avoid frustrated crystallization, which was reported in systems with low PCM ratio (≤ 20%) and shown to dramatically decrease the ΔH value in PCFs [28].

3.1.1 Fiber morphology



**Figure 3.** SEM images of electrospun L-PLA (a), L-PLA/PEG6k (b) and L-PLA/PEG1k (c). L-PLA, where PLA *M*w = 120 kg/mol and the PLA:PEG ratio was 50/50 (w/w) in the PCF blends.

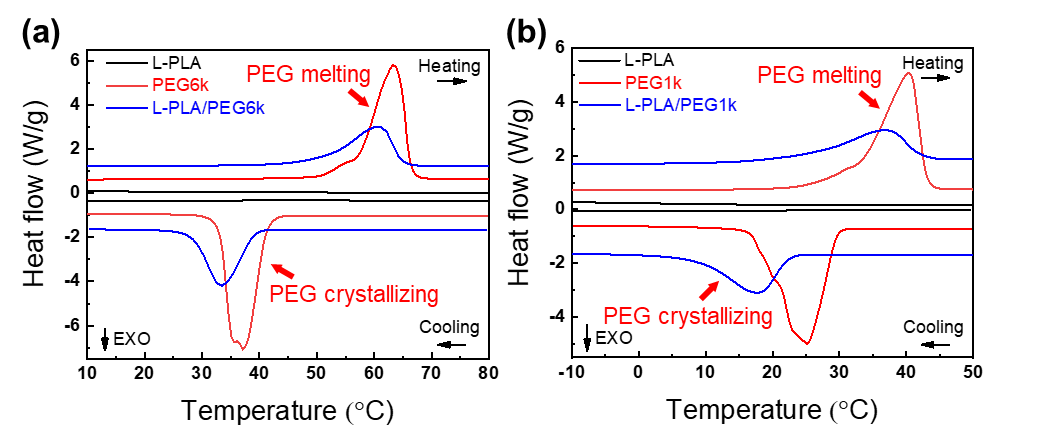
Numerous researchers have shown that the morphology of electrospun fibers is influenced by polymer molecular weight [56, 57]. Thus, L-PLA with varying molecular weight (*M*w = 115, 120 and 315 kg/mol) were used (see SEM images in SI, Figure S1 and corresponding description on selecting suitable PLA *M*w). Considering fiber morphology and electrospinnability, L-PLA *M*w = 120 kg/mol was selected for further studies. As shown in Figure 3, continuous cylindrical L-PLA, L-PLA/PEG6k and L-PLA/PEG1k non-oriented fibers with similar diameter and morphology were successfully electrospun to avoid the potential impact of fiber morphology on PEG phase change performance.

3.1.2 Phase change performance

Δ*H* and phase change temperature are key performance parameters of PCMs. Thus, DSC measurements were performed and results are shown in Figure 4 and Table 3. The *T*c and *T*m values were derived from the peaks of the DSC thermograms and the Δ*H*c and Δ*H*m values were obtained by integrating the corresponding peak areas. Since PEG6k and PEG1k have different Δ*H* values, to directly compare the Δ*H* loss of PEG after being loaded into the PLA matrix, the normalized parameter χ was introduced according to Equation 1:

(Eq. 1)

Where c and m represent crystallizing and melting, is the experimental phase change enthalpy of PLA/PEG fibers, is the theoretical phase change enthalpy of PLA/PEG fibers, is the experimental phase change enthalpy of PEG, and is the mass ratio of PEG within PLA/PEG fibers (wt.%). As aforementioned, was kept at 50% in this study. According to the definition, actually represents the relative crystallinity of PEG encapsulated within the fibers, compared to its bulk state. Higher χ values (closer to 100%) indicate a lower degree of confined crystallization in the PCFs.



**Figure 4.** DSC thermograms of pristine PEG (red lines), L-PLA fibers (black lines) and PLA/PEG PCFs (blue lines): (a) PEG6k and L-PLA/PEG6k; (b) PEG1k and L-PLA/PEG1k.

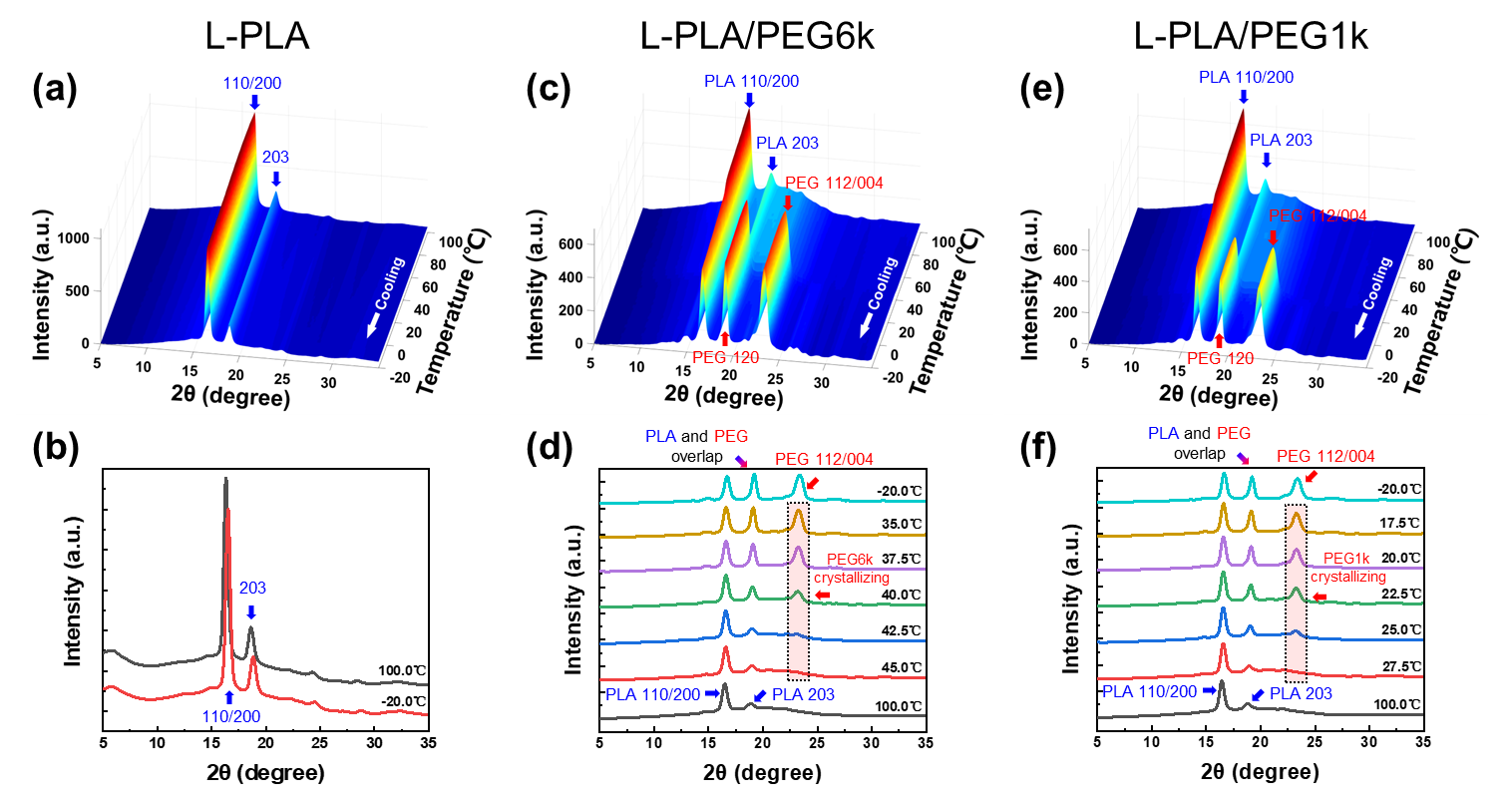
**Table 3.** Phase change performance of pristine PEG6k, PEG1k and L-PLA/PEG6k, L-PLA/PEG1k fibers.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | *T*c (°C) | Δ*H*c (J/g) | (%) | *T*m (°C) | Δ*H*m (J/g) | (%) |
| PEG6k | 37.6 | -208.9 | 100.0 | 63.3 | 201.2 | 100.0 |
| L-PLA/PEG6k | 33.5 | -104.2 | 99.8 | 61.1 | 99.2 | 98.6 |
| PEG1k | 25.1 | -189.6 | 100.0 | 40.5 | 190.1 | 100.0 |
| L-PLA/PEG1k | 18.2 | -70.9 | 74.8 | 36.6 | 75.4 | 79.4 |

As shown in Figure 4, L-PLA fibers showed no phase change (black lines) over the temperature range studied and all PCF Δ*H* values were contributed to by PEG. After being encapsulated within the L-PLA matrix, the *T*c and *T*m values of PEG1k and PEG6k were both slightly lower than those of the corresponding bulk polymers. Excitingly, L-PLA/PEG6k fibers exhibited higher (99.8%) than that of L-PLA/PEG1k (74.8%) demonstrating that, as predicted, rubbery L-PLA chains have weaker confinement on PEG crystallization.

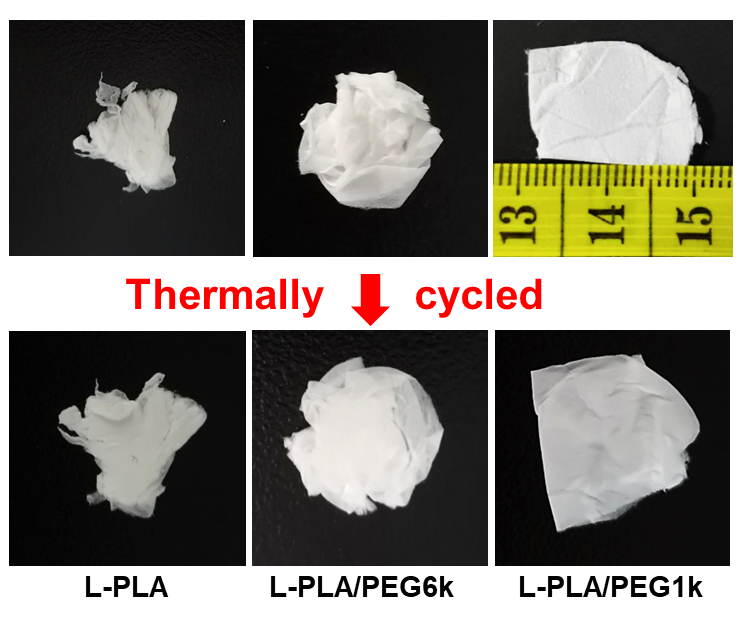
3.1.3 Structural transition

To study the crystalline structure of L-PLA, L-PLA/PEG6k and L-PLA/PEG1k fibers during operation, time-resolved WAXS were undertaken. The WAXS data for the cooling (crystallizing) process of the fibers are illustrated in Figure 5 and the heating (melting) process data are provided in SI, Figure S3.



**Figure 5.** Time-resolved WAXS data of L-PLA (a), L-PLA/PEG6k (c) and L-PLA/PEG1k (e) fibers during cooling. The 1D integrated WAXS profiles of the fibers at 100 °C, -20°C and critical phase change temperatures are illustrated in (b), (d) and (f).

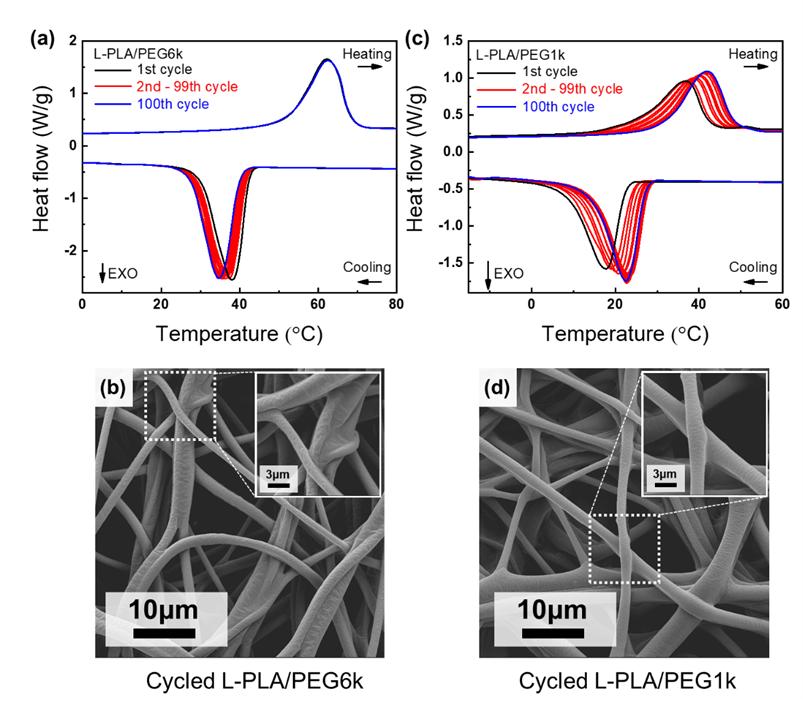
As shown in Figure 5a, the 110/200 and 203 crystalline peaks of PLA [58, 59] at 2θ = 16.3° and 18.8° were observed. During cooling (Figure 5b) and heating (SI, Figure S3a and b) no more peaks were observed and no peaks disappeared, indicating that L-PLA was stable across the entire temperature range of -20 to 100 °C. For the L-PLA/PEG6k fibers, the same PLA crystalline peaks were found and remained unchanged during heating and cooling cycles, again demonstrating the stable crystalline structure of L-PLA as a supporting material for the PCM. The crystallization of PEG6k was identified during cooling (Figure 5c) as the PEG 112/004 crystalline peaks (2θ = 23.3°) [60] appeared when cooled down to 42.5 °C and increased in intensity with further cooling. PEG6k melting can also be observed, as shown by the disappearance of the WAXS peaks in the SI, Figure S3c and d. The onset temperatures of crystallization (42.5 °C) and melting (55 °C) of PEG6k match those derived from DSC. L-PLA/PEG1k exhibited the same structural transition as L-PLA/PEG6k, except for a decrease in phase transition temperature (*i.e.* lower and ). The visual appearance of L-PLA, L-PLA/PEG6k and L-PLA/PEG1k fibers before and after time-resolved WAXS was recorded (Figure 6). Digital photographs show an unchanged fibrous structure after thermal cycles for both of the PCFs. PEG leakage test results reveal that there was no PEG leakage from L-PLA/PEG6k and L-PLA/PEG1k fibers (SI, Figure S7).



**Figure 6.** Digital camera images of as spun (first row) and thermally cycled (second row) L-PLA, L-PLA/PEG6k and L-PLA/PEG1k fibers. The units of the scale bar are centimeters. All samples were prepared in close size.

3.1.4 Thermal cycling test

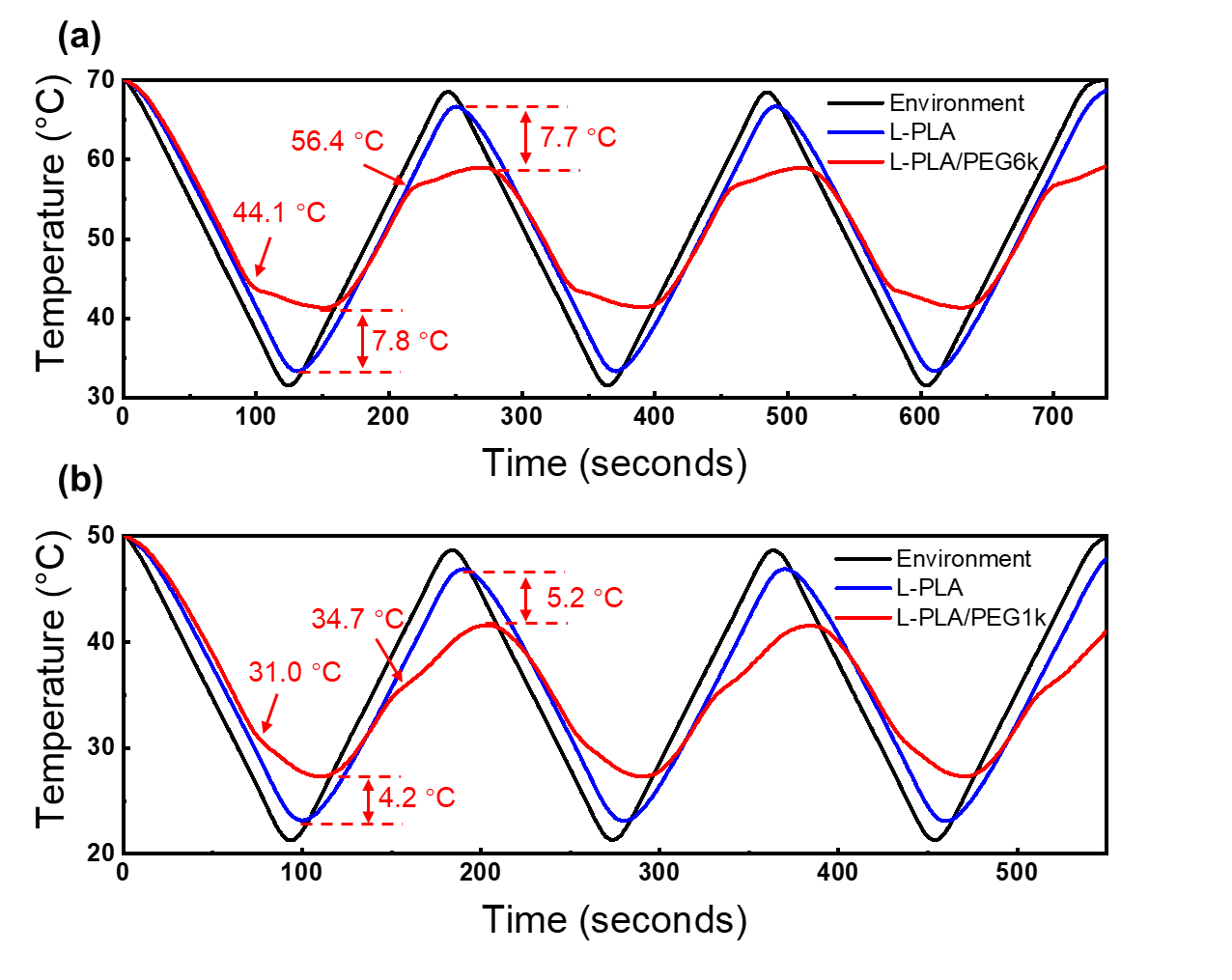
The DSC and WAXS experiments showed that L-PLA was a stable supporting material during the temperature range of the PEG phase change. Furthermore, L-PLA/PEG6k and L-PLA/PEG1k fibers exhibited considerable potential for further application. Therefore, the phase change stability of L-PLA/PEG6k and L-PLA/PEG1k fibers was measured by being thermally cycled 100 times in DSC. The DSC thermograms are shown in Figure 7a and c. Accordingly, the *T*c, *T*m, Δ*H*c and Δ*H*m values were obtained and are provided in the SI, Figure S4. It can be seen that during cycling, decreased slightly from 38.0 °C to 34.5 °C, whereas remained consistent at approximately 62.5 °C. and decreased by only approximately 2.5% from 101.60 J/g and 99.16 J/g to 100.76 J/g and 98.21 J/g, respectively, after 100 cycles. This Δ*H* loss is attributed to leakage of PEG6k that was distributed on the surface of PCFs, which is supported by the SEM image of L-PLA/PEG6k fibers after 100 cycles (Figure 7b) that shows surface fusion at fiber contact points. In contrast to L-PLA/PEG6k fibers, during thermal cycling, (17.8 to 22.7 °C) and (36.8 to 42.0 °C) both increased during the first 10 cycles and then remained constant thereafter. Moreover, and also increased by 5.4 and 3.0 J/g from 64.6 and 68.0 J/g, respectively. These results suggest that there could be PLA and PEG domain rearrangement due to thermal annealing, which results in enhanced crystallization and higher Δ*H*. Generally speaking, L-PLA is an ideal supporting material for encapsulating PEG1k and PEG6k and successfully protects PEG from flow loss, with 97.5% Δ*H* remaining after 100 cycles of phase changing.



**Figure 7.** DSC thermograms (a and c) and SEM images (b and d) of thermally cycled (100 times) L-PLA/PEG6k (a and b) and L-PLA/PEG1k fibers (c and d).

3.1.5 Thermal regulating ability

Thermal energy storage and release is one of the most attractive abilities of PCFs on regulating heat. One particular application of note for PCFs is their use in the stabilization of intra-fibrous temperature [61, 62]. Based on the intended application, the thermal regulating ability can be exploited to serve a specific function, such as buffering intra-fibrous temperature under rapid environmental temperature fluctuations [39, 63] and increasing intra-fibrous temperature hysteresis against ambient temperature change. [64, 65]. Here, a hot stage was used to simulate rapid environmental temperature fluctuations. L-PLA, L-PLA/PEG6k and L-PLA/PEG1k fibers were tested on the hot stage within the PEG6k and PEG1k phase change temperature range, where L-PLA fibers were used as a control.

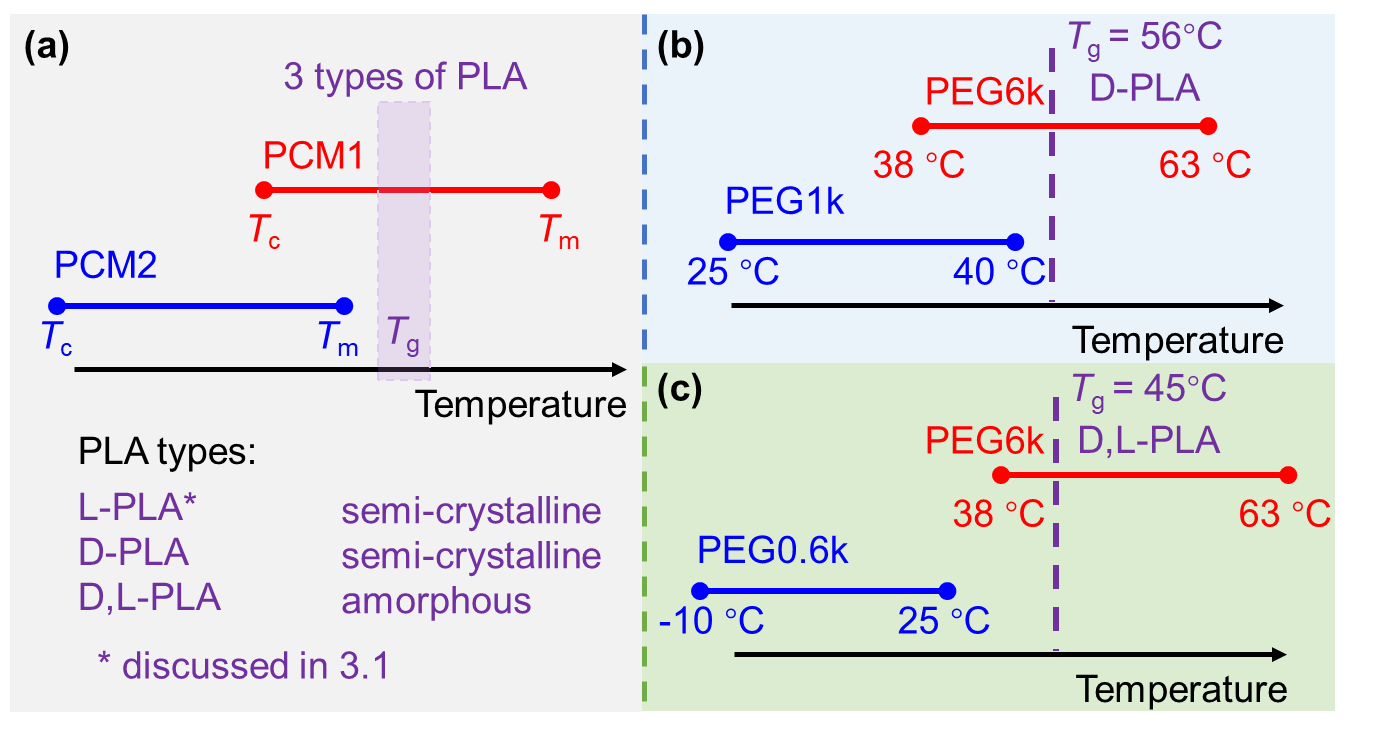


**Figure 8.** Thermal regulation test results of (a) L-PLA/PEG6k and (b) L-PLA/PEG1k fibers (red lines) compared with the temperature of environment (black lines) and pristine L-PLA fibers (blue lines).

As Figure 8 shows, compared with the environmental temperature (that was cycled rapidly over the phase change range, *i.e.* between room temperature and 50 °C or 70 °C for PEG1k and PEG6k, respectively), L-PLA fibers exhibited thermal hysteresis only (due to the low thermal conductivity of polymers). In contrast, L-PLA/PEG6k and L-PLA/PEG1k exhibited both thermal hysteresis and obvious temperature stabilizing effect due to the phase changing of PEG. The critical temperature points have been marked in Figure 8 and they match the onset temperature of the phase change of L-PLA/PEG PCFs from the DSC studies. It can be seen that due to the thermal energy storage and release of PEG, L-PLA/PEG6k fibers achieved 7.7 °C (heating) and 7.8 °C (cooling) maximum temperature difference against environmental temperature fluctuation. L-PLA/PEG1k fibers only achieved 5.2 °C (heating) and 4.2 °C (cooling) maximum temperature difference due to lower Δ*H*. Li *et al.* [63] reported a coaxial PCF consisting of paraffin wax (PW, as PCM) and polyurethane (PU, as supporting material) which exhibited ΔH ~ 90 J/g, which is superior to L-PLA/PEG1k fibers (approximately 90 J/g ΔH) and inferior to D-PLA/PEG1k fibers (approximately 100 J/g ΔH). The PW/PU PCF exhibited 5.8 °C (heating) and 4.7 °C (cooling) maximum temperature difference. This again indicates that a higher ΔH value is the key for better thermal regulating performance.

3.2 Effect of supporting material crystallizability

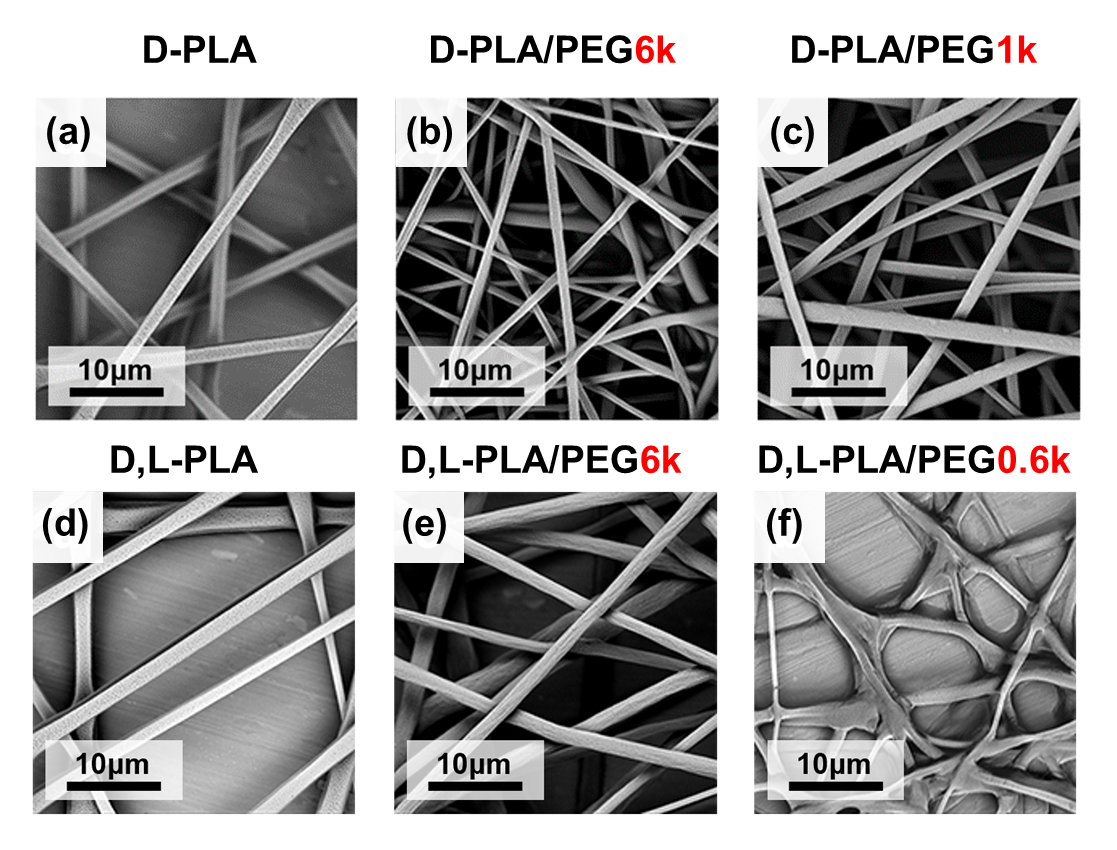
The results discussed in Section 3.1 using L-PLA/PEG1k and L-PLA/PEG6k fibers show the effect of glass transition temperature control, demonstrating that a supporting matrix comprising flexible PLA chains (*T*g below operating temperature) promotes an increase in the Δ*H* value of the PCF. In this section, the effect of the crystallizability of the supporting material on Δ*H* is studied. For this study, PLA is an ideal candidate for the supporting material due to the two optical isomers of lactic acid, namely Levo- (L-) and Dextro (D-). As a consequence of this chirality, three types of PLA with different crystallizability can be obtained: L-PLA, D-PLA (both semi-crystalline) and D,L-PLA (amorphous). In the work presented in Section 3.1, semi-crystalline L-PLA was used as the supporting material. As shown in Figure 9a, semi-crystalline D-PLA and amorphous D,L-PLA were also used to encapsulate PEG and the corresponding PCF phase change performance and structure were studied and compare to the L-PLA-based system.



**Figure 9.** PLA/PEG PCFs designed to evaluate the effect of PLA crystallizability on PCF Δ*H* value (a). The specific properties of selected supporting material for (b) D-PLA and (c) D,L-PLA) with their corresponding phase change materials (PEG6k, PEG1k and PEG0.6k). *T*g – glass transition temperature, *T*m – melting temperature, *T*c – crystallization temperature.

It should be noted that PEG6k and PEG1k were chosen as PCM1 and PCM2 to fabricate D-PLA/PEG1k and D-PLA/PEG6k fibers (Table 2 and Figure 9b). However, due to the molecular irregularity of D,L-PLA, (45.1 °C) is lower than (56.3 °C). The offset melting temperature of PEG1k (44.7 °C) is too close to and is too high, therefore PEG1k is not a suitable PCM2 candidate to be encapsulated within a D,L-PLA matrix. Consequently, PEG0.6k (with lower phase change temperature) was selected as PCM2 to prepare D,L-PLA/PEG0.6k fibers for further study (Figure 9c).

3.2.1 Fiber morphology

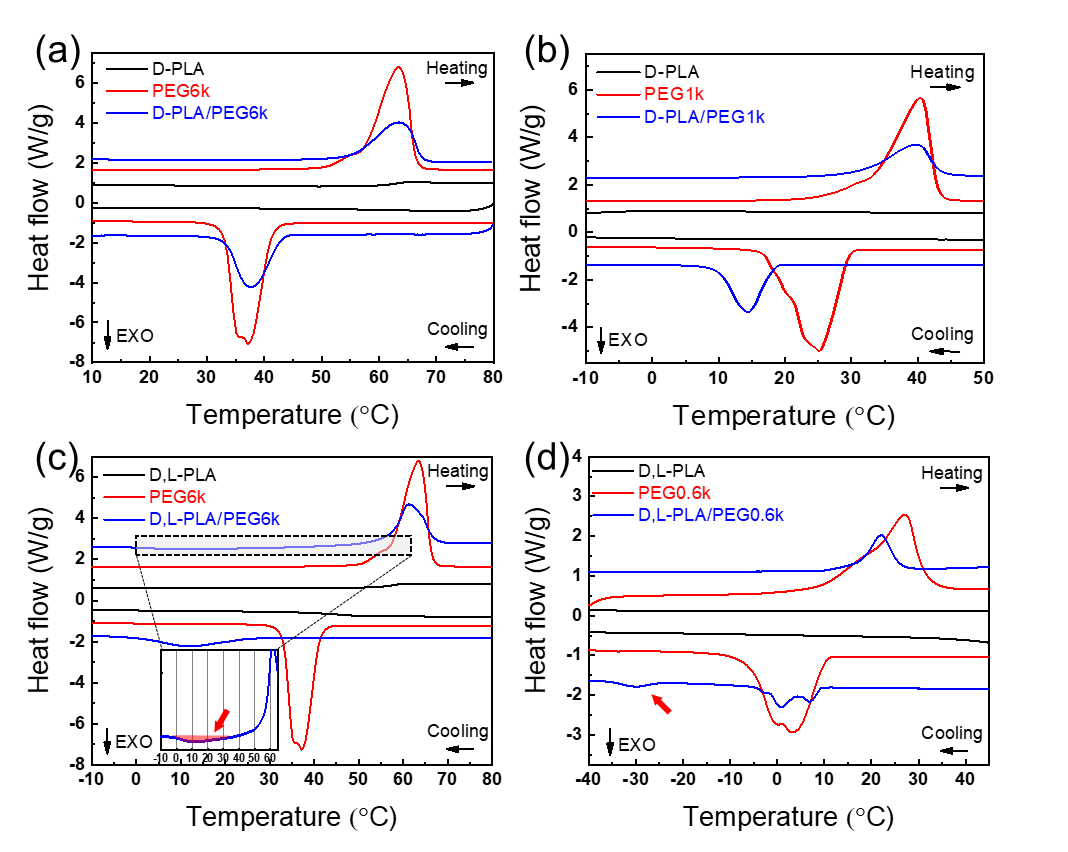


**Figure 10.** SEM images of electrospun D-PLA (a), D-PLA/PEG6k (b), D-PLA/PEG1k (c), D,L-PLA (d), D,L -PLA/PEG6k (e) and D,L -PLA/PEG0.6k (f) fibers. D-PLA *M*w = 100 kg/mol. D,L-PLA *M*w = 100 kg/mol and the PLA:PEG ratio was 50/50 (w/w) in the PCF blends.

Figure 10 shows that D-PLA, D,L-PLA and corresponding PCFs have a similar morphology to L-PLA/PEG6k and L-PLA/PEG1k PCFs. However, the melted structure shown in Figure 10f is attributed to a heating effect of the electron radiation source in SEM, as (45.1 °C) and the melting temperature of PEG0.6k (about 15 °C) are low.

3.2.2 Phase change performance

Thermal behavior of the prepared fibers was measured by DSC as shown in Figure 11 and the key parameters are listed in Table 4.



**Figure 11.** DSC thermograms of pristine PEG (red lines), PLA fibers (black lines) and PLA/PEG PCFs (blue lines): (a) D-PLA/PEG6k; (b) D-PLA/PEG1k; (c) D,L-PLA/PEG6k; (d) D,L-PLA/PEG0.6k.

As shown in Figure 11, D-PLA and D,L-PLA fibers showed no phase change (black lines) across the temperature range studied. After being encapsulated within a D-PLA matrix, the *T*c and *T*m values of PEG1k and PEG6k were close to those of the corresponding bulk polymers. D-PLA/PEG6k fibers exhibited higher (95.1%) than D-PLA/PEG1k (66.9%). This result was similar to the PCFs composed of L-PLA (see Section 3.1.2). All findings herein demonstrate that flexible, or rubbery PLA chains (*T*g < ) inferred less confinement on PEG crystallization.

**Table 4.** Phase change performance of pristine PEG6k, PEG1k, PEG0.6k and D-PLA/PEG6k, D-PLA/PEG1k, D,L-PLA/PEG6k D,L-PLA/PEG0.6k fibers.

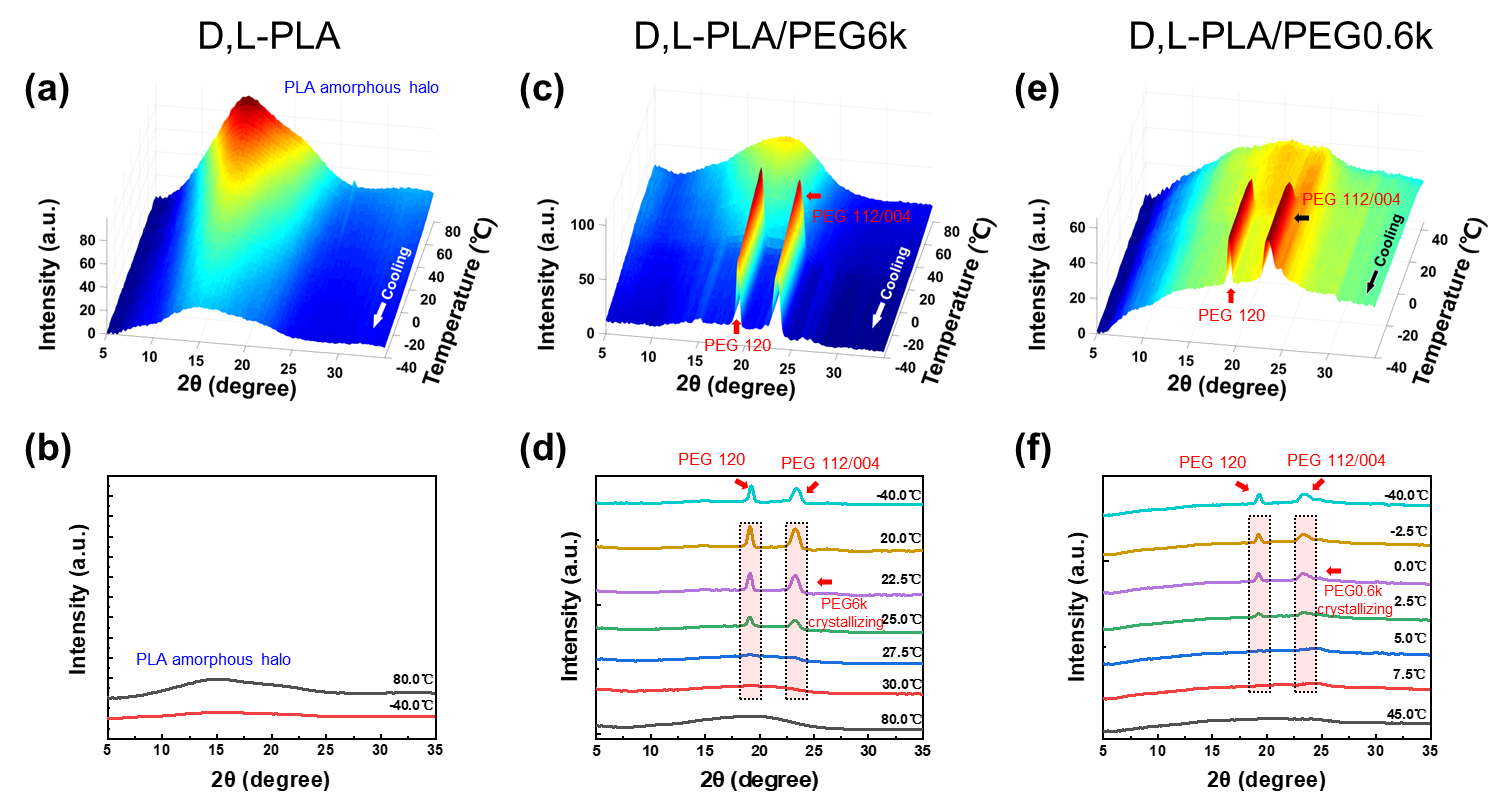
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | *T*c (°C) | Δ*H*c (J/g) | *χ*c (%) | *T*m (°C) | Δ*H*m (J/g) | *χ*m (%) |
| PEG6k | 37.6 | -208.9 | 100.0 | 63.3 | 201.2 | 100.0 |
| D-PLA/PEG6k | 37.5 | -99.3 | 95.1 | 63.2 | 100.3 | 99.7 |
| D,L-PLA/PEG6k | 11.2 | -44.7 | 42.8 | 61.4 | 84.6 | 84.1 |
|  | 13.7a | -9.8a | 9.7a |  |  |  |
| PEG1k | 25.1 | -189.6 | 100.0 | 40.5 | 190.1 | 100.0 |
| D-PLA/PEG1k | 14.5 | -63.4 | 66.9 | 39.6 | 64.1 | 67.4 |
| PEG0.6k | 3.0 | -132.6 | 100.0 | 27.2 | 146.7 | 100.0 |
| D,L-PLA/PEG0.6k | 0.7 | -23.8 | 42.7 | 22.1 | 36.1 | 49.3 |
|  | -30.3 | -4.5 |  |  |  |
| a Cold crystallization during heating | | | | | | |

D,L-PLA/PEG6k and D,L-PLA/PEG0.6k exhibited completely different phase change performance. The crystallization peak of PEG6k within D,L-PLA/PEG6k fibers was much broader than that of pristine PEG6k (Figure 11c) and decreased to only 42.8%. Moreover, cold crystallization of PEG6k was observed at about 15 °C during heating (enlarged area in Figure 11c), implying that the crystallization of PEG6k was severely confined by the D,L-PLA matrix. The phase change performance of D,L-PLA/PEG0.6k fibers was also significantly different from that of the PEG0.6k polymer. Within D,L-PLA/PEG0.6k fibers, the crystallization behavior of PEG0.6k can be divided into two parts. One part is at approximately 0 °C (close to its bulk state), and the other at -30 °C (red arrow in Figure 11d), which was reported to be caused by PEG homogeneous nucleation [52]. Furthermore, of D,L-PLA/PEG0.6k fibers was only 42.7%. Comparing the phase change performance of PCFs consisting of semi-crystalline L-PLA (discussed in Section 3.1.2), semi-crystalline D-PLA and amorphous D,L-PLA, it can be seen that amorphous D,L-PLA is not a suitable supporting material, as it largely confines PEG crystallization.

PEG0.6k exhibited low within the D,L-PLA matrix (*i.e.* D,L-PLA/PEG0.6k PCFs). In an attempt to verify the effect of the crystallizability of PLA, PEG0.6k was also encapsulated within L-PLA and D-PLA matrices to form L-PLA/PEG0.6k and D-PLA/PEG0.6k PCFs as control groups. Their DSC thermograms are shown in the Supporting Information, Figure S9 with key parameters listed in Table S2. The results suggest that the low value of D,L-PLA/PEG0.6k PCFs could be caused by the melting of the D,L-PLA matrix (see detailed discussion in SI).

3.2.3 Structural transition

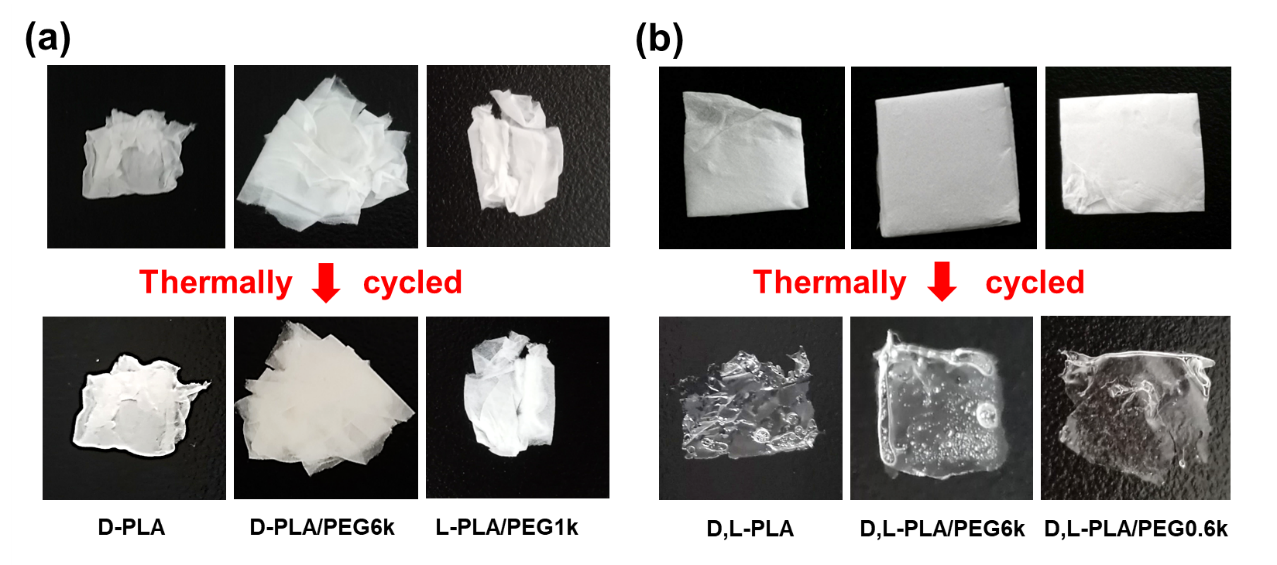
From the results obtained thus far, it appears that the significant differences in phase change performance of D-PLA/PEG and D,L-PLA/PEG PCFs is due to the crystallizability of PLA and its impact on PEG crystallization. Therefore, time-resolved WAXS studies were undertaken to probe the crystalline structure in the PCFs. D-PLA fibers and D-PLA/PEG PCFs had similar structural transition to L-PLA fibers and L-PLA/PEG PCFs (see the SI, Figures S5 and S6 and associated discussion). The WAXS data of D,L-PLA fibers and D,L-PLA/PEG PCFs are shown in Figure 12 (cooling) and SI, Figure S7 (heating).



**Figure 12.** Time-resolved WAXS data of D,L-PLA (a), D,L -PLA/PEG6k (c) and D,L -PLA/PEG0.6k (e) fibers during cooling and associated 1D integrated WAXS profiles at critical phase change temperatures in (b), (d) and (f), respectively.

D,L-PLA is an amorphous polymer. Thus, Figure 12a and SI, Figure S7a show an amorphous halo of D,L-PLA. It can be seen that the shape of this halo changed with temperature indicating a structural change within the amorphous D,L-PLA during heating and cooling. The WAXS data of D,L-PLA/PEG6k and D,L-PLA/PEG0.6k PCFs also showed that there was no PLA crystalline peak. Within the D,L-PLA matrix, the crystallization and melting of PEG6k and PEG0.6k can be followed by tracking the appearance and disappearance of PEG 120 and 112/004 crystalline peaks. The *T*c and *T*m values of PEG6k and PEG0.6k match those measured from DSC.

The visual appearance of D-PLA, L-PLA fibers and corresponding PCFs were recorded both before and after time-resolved WAXS during the thermal sweeps (Figure 13). It can be seen that a PLA matrix formed from semi-crystalline D-PLA remained stable, while the D,L-PLA fibrous matrix melted and fused into a transparent film. This fusion is attributed to the lack of PLA crystals in D,L-PLA. In contrast, L-PLA and D-PLA are semi-crystalline polymers and when heated over *T*g (but lower than *T*m, 179 °C [66]), the PLA crystals could act as physical crosslinks to encapsulate and stabilize the highly mobile amorphous phase. As Figure 11c and d shows, the fused D,L-PLA matrix dramatically confines the crystallization of PEG and results in low Δ*H*c.

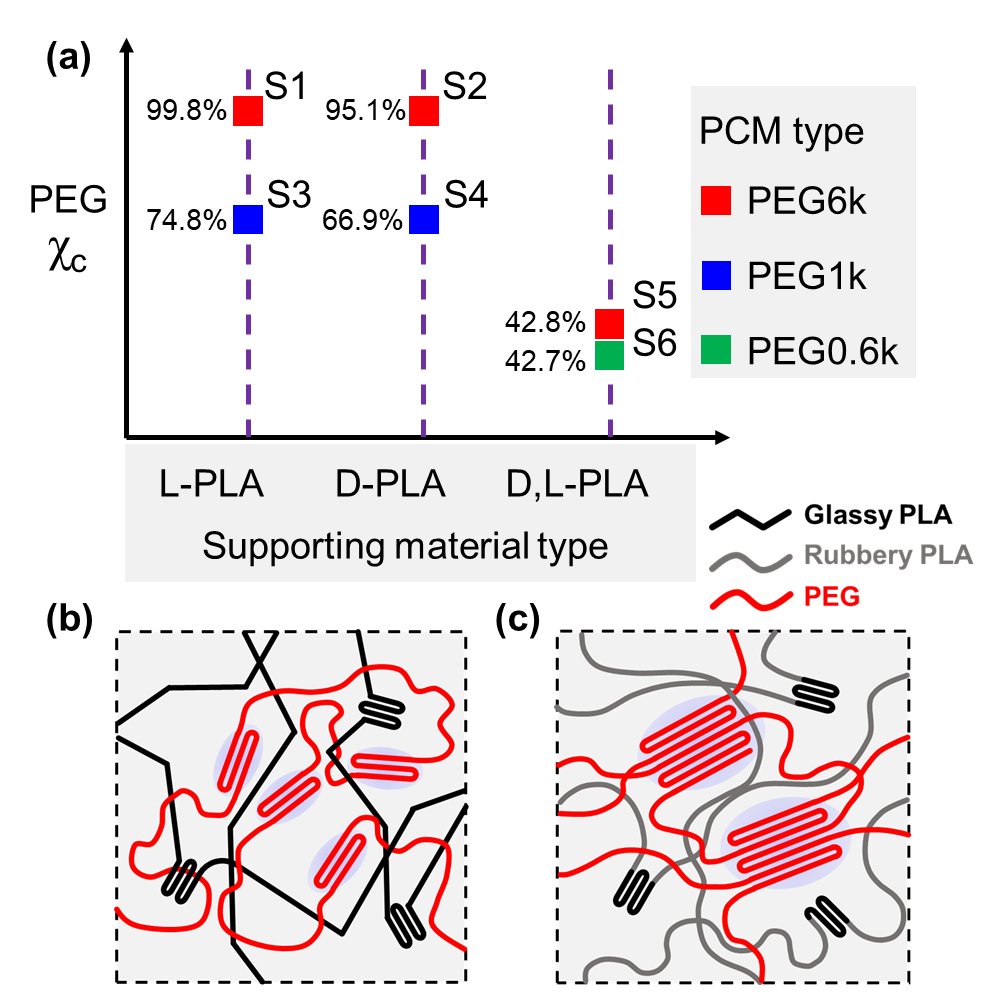


**Figure 13.** Digital camera images of as spun (first row) and thermally cycled (second row) (a) D-PLA, D-PLA/PEG6k, D-PLA/PEG1k fibers and (b) D,L-PLA, D,L-PLA/PEG6k, D,L-PLA/PEG0.6k fibers.

3.3 Mechanism hypothesis

In this study, in order to verify our two hypotheses, six PLA/PEG PCFs were fabricated by selecting various PEG *M*w and PLA types. We investigated the relative crystallinity, , when PEG was encapsulated within rubbery, glassy, semi-crystalline and amorphous PLA fibrous matrices, as summarized in Figure 14a.

As proposed, a rubbery fibrous PLA matrix (where < ) conferred weaker confinement than a glassy matrix ( > ) on PEG crystallization (Figure 14a). This is attributed to the glassy PLA chains forming a rigid network with interpenetrating PEG chains within the PLA/PEG fibers, hindering the chain folding of PEG and confining PEG crystallization (Figure 14b) [67]. Samanta *et al.* [28] studied an electrospun PCF and discovered that microphase separation occurred by annealing PCF over due to incompatibility between supporting material (polystyrene, PS) and PCM (PEG). The system formed by PLA and PEG in our study have also been shown to be physically incompatible [68]. Therefore, to some extent, the chain entanglement of rubbery PLA and PEG may be minimized due to the enthalpic driving force of their physical incompatibility and, thus, result in better PEG crystallization (Figure 14c)*.*



**Figure 14.** (a) The relative crystallinity (χc)of various *M*w PEG encapsulated in different PLA matrices: S1, S2 for semi-crystalline and rubbery PLA matrix; S3, S4 for semi-crystalline and glassy PLA matrix; S5 for amorphous and rubbery PLA matrix; S6 for amorphous and glassy PLA matrix. (b) Glassy PLA matrix showed stronger confinement than rubbery matrix (c) on PEG crystallization.

Initially, it was believed that semi-crystalline supporting materials may induce the crystallization of PCM, but our experimental findings did not support this concept. Surprisingly, it was shown that PLA crystallinity was the key to stabilize the fibrous structure. PLA crystals appear to provide physical crosslinks within the fibers and prevent the macroscopic motion of amorphous PLA chains when PLA/PEG PCFs are operating above the . In contrast, as Figure 13b and Figure 11c and d show, a physically fused PLA fibrous matrix (observed in the non-crystalline D,L-PLA-containing systems) severely confines the crystallization of PEG.

Chen *et al.* [34] attempted to enhance Δ*H* by increasing PEG content.An enthalpy of 107.6 J/g was successfully obtained at 80 wt.% PEG ratio by introducing stronger hydrogen bonding in supporting material*.* While, in this study, by controlling the molecular arrangement of supporting material, a Δ*H* valueof 104.2 J/g can also be achieved (Table 5, L-PLA/PEG6k). This value is comparably superioramong reported PCFs at 50 wt.% PCM ratio.

**Table 5.** Crystallization (Δ*H*c) and melting (Δ*H*m) enthalpies of some reported PCFs with approximately 50% PCM ratio.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| No. | Supporting material/ PCM | (J/g) | (J/g) | PCM (wt.%) | Ref. |
| 1 | PAN/paraffin | 57.42 | 58.74 | 50 | [35] |
| 2 | PAN/MP-LA | 84.50 | 88.51 | 50 | [69] |
| 3 | PET/MES | 88.03 | 90.43 | 50 | [70] |
| 4 | PA6/PEG | / | ~95 | 50 | [71] |
| 5 | PVA/PEG | 70.50 | 72.30 | 50 | [62] |
| 6 | PAN/ butyl stearate | 55.10 | 55.10 | 45 | [72] |
| 7 | PAN/ ethyl palmitate | 95.37 | 95.37 | 55 | [72] |
| 8 | PVA/PEG | 73.43 | 59.31 | 50 | [73] |
| 9 | PVP/PEG | 51.0 | 101.1 | 50 | [74] |
| 10 | Copolyamide/ionic liquid | 57.60 | 67.67 | 47.5 | [75] |
| 11 | L-PLA/PEG6k | 104.2 | 100.6 | 50 | This work |
| 12 | L-PLA/PEG1k | 70.91 | 75.44 | 50 | This work |
| PAN - polyacrylonitrile; MP - methyl palmitate; LA - lauric acid; PET - poly(ethylene terephthalate); MES - methyl stearate; PA6 - polyamide-6; PVA - poly(vinyl alcohol); PVP - polyvinylpyrrolidone. | | | | | |

Semi-crystalline polymers with rubbery amorphous regions (*T*g < operating temperature) appear to provide an ideal supporting material for preparing high Δ*H* PCFs. On one hand, the crystalline regions of the supporting material stabilize the fibrous structure of the PCFs, whilst on the other hand, the rubbery amorphous domains bring about higher Δ*H*.

4. Conclusions

As one of the most important parameters of PCFs, the phase change enthalpy (Δ*H*) of encapsulated PCMs have been reported to be significantly influenced by the supporting materials in which they are housed*.* Therefore, the present study was designed to investigate the effects of crystallizability and *T*g of supporting materials to enhance the Δ*H* value of PCFs. Six different PLA/PEG PCFs were successfully electrospun for our in-depth study. PLA and PEG were selected for their biocompatibility and biodegradability. PEG was encapsulated within rubbery or glassy, and semi-crystalline or amorphous PLA fibrous matrices. The findings of this study indicate that semi-crystalline PLA with rubbery amorphous regions (*T*g < operating temperature) could help to promote the crystallization of encapsulated PEG. Among all PCFs prepared, the representative L-PLA/PEG6k fibers showed a very high Δ*H* (~100 J/g) at 50 wt.% PCM and 97.5% Δ*H* remained after 100 thermal cycles. L-PLA/PEG6k fibers can stabilize their intra-fibrous temperature and achieve a maximum of 7.8 ℃ temperature difference against environmental temperature fluctuations. These novel L-PLA/PEG6k fibers can be considered as promising form-stable PCFs for application in many fields, such as thermal energy storage, thermal regulation, smart textiles, controlled drug delivery and cancer thermal therapy. We believe that the strategy of selecting semi-crystalline polymers with flexible amorphous regions may inspire researchers to find suitable supporting materials and undertake further studies to fully exploit this strategy for advancing PCF technology.

Data Availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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