

# Polylactic acid/polyethylene glycol blend fibres prepared via melt electrospinning: effect of polyethylene glycol content

Tayebe Nazari, Hamid Garmabi

Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran 15875-4413, Iran  
E-mail: garmabi@aut.ac.ir

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Polylactic acid (PLA) was blended with polyethylene glycol (PEG) and spun via a melt-electrospinning system. The effect of PEG content on the PLA melt and the thermal behaviour of the blend was studied using dynamic rheometry and differential scanning calorimetry, respectively. By fitting a rheological model, parameters such as zero-shear viscosity and the relaxation time of polymer chains were obtained. A substantial reduction of zero-shear viscosity and relaxation time by increasing the PEG content from 0 to 30 wt% was observed. Crystallisation peaks shifted to lower temperatures and the crystallinity level increased in PLA/PEG blends against PEG concentration. The results revealed enhanced polymer chain mobility because of the plasticising effect of PEG. Continuous microfibrils were obtained by electrospinning of PLA/PEG blends. While neat PLA was not spinnable at the spinning temperature of 200°C, PLA/PEG blends were easily spun and the lowest fibre diameters of 3–6 µm were achieved with 30% PEG loading, at an applied voltage of 70 kV.

**1. Introduction:** Since the 1990s, electrospinning of polymeric fluids has been known as a fascinating method of nanofibre production [1–3]. It can be categorised into solution and melt electrospinning when the target fluid is a polymer solution and a melt, respectively. However, polymer melts rarely produce nanofibres [4].

In melt electrospinning, it is necessary to assemble a heating element as well as a high voltage supplier, a nozzle and a collecting plate. For the first time, Larrondo and Manely [5] tried to spin polypropylene (PP) and polyethylene (PE) melts in the electrostatic field. After about one decade, different polymers were melt spun such as poly(ethylene terephthalate) [6], PP [7–12], PLA [11, 13, 14], poly(ethylene-co-vinyl alcohol) [15], nylon 6 [16], polycaprolactone [17], low-density PE [18] and polyurethane [19, 20]. In melt electrospinning, the lack of solvents, especially toxic ones, offers no complementary process like ventilation. The resulting fibres may also be of unlimited use for medical and bio-related applications. In addition to being cost effective and environmentally benign, the process can be easily applied to polymers that are difficult to dissolve in any given solvent and to multi-component polymer systems. Although the process leads to the production of microfibrils, its advantages have attracted attention to melt electrospinning rather than to solution electrospinning. Using these ready-to-use products, it was possible to deposit the bio-fibres onto cells directly [21].

Owing to the high viscosity, low surface charge density and fast solidification of polymer melts which suppress the whipping motion, microfibrils will be commonly formed in melt electrospinning. Adjusting the material parameters such as viscosity/molecular weight, tacticity and polarity, as well as the processing parameters (temperature, voltage, distance and feeding rate), can thin the produced fibre.

Decreasing the viscosity or molecular weight reduces the fibre diameter [9, 22]. The higher tacticity of the polymer chain causes the polymer chains to be closely packed and thus decreases the average fibre diameter. Kadomae *et al.* [8] showed that increasing the amount of isotactic PP reduced the fibre diameter. Zhou *et al.* [13] studied the effect of processing parameters on melt electrospinning and obtained sub-micron fibres of PLA (~800 nm) in the optimised processing condition. They showed that increasing the electrical field strength, nozzle temperature, spinning temperature (more than  $T_g$ ) and lowering the nozzle diameter and flow rate decrease the fibre diameter. However, the polymer degradation

temperature, residence time of the polymer melt in the nozzle, and the chain scission through very small nozzles must be considered.

In efforts to reduce the fibre sizes, Zhmayev *et al.* [4] achieved PLA nanofibre (~180 nm) through gas-assisted melt electrospinning. A heated gas stream in the spinning region delayed the polymer melt solidification and provided an additional deformation of fibre other than the electric field. Increasing the polymer melt conductivity by conductive additives such as sodium chloride [23], and decreasing the viscosity by viscosity reducing agents are other strategies to fabricate submicron fibres [22, 24].

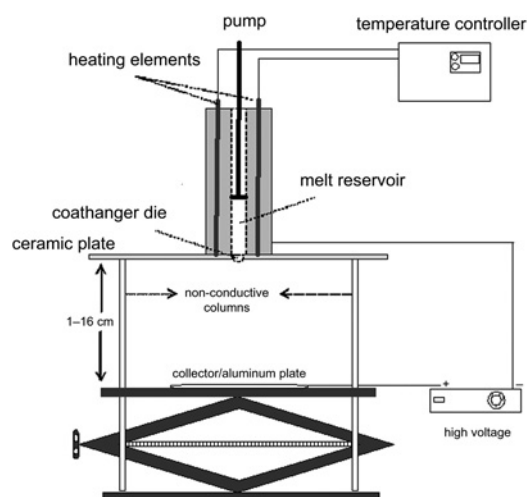
PLA is an eco-friendly bioplastic with superior biocompatibility and processability compared with other biopolymers such as PEG, PCL and so on. It can be processed by injection moulding, film extrusion, blow moulding, thermoforming, fibre spinning and film forming [25]. For the industrial application of PLA, plasticising to improve processability and mechanical properties is inevitable. PEG, as a hydrophilic and biodegradable polymer, is an effective plasticiser for PLA which modifies the toughness, hydrophobicity, cell affinity and degradation rate [25–28]. PLA blended with PEG ensures both consumer and biomedical applications.

In the work reported in this Letter, an attempt was made to thin the PLA fibres obtained from melt electrospinning. For this reason, PLA was plasticised by PEG through melt compounding and then electrospun. The effects of varying PEG content (wt%) on the PLA/PEG melt rheology and the thermal properties have been investigated. Then, the effects of PEG content on the fibre morphology have been studied.

## 2. Experimental

**2.1. Material:** The PLA (6350D-grade) was obtained from Nature Works LLC with a molecular weight at around  $M_n = 116\,000$  g/mol and a polydispersity of 1.9. Polyethylene glycol (PEG), molecular weight 6000 g/mol, was purchased from the Kimiagaran Emrooz Co. of Iran. Irganox 1010 (Ciba Specialty Chemicals Inc., Basel, Switzerland) was applied to thermally stabilise the prepared samples at 0.3 wt%.

**2.2. Preparation:** PLA granules were dried in an oven at 50°C overnight prior to blending. PLA and PEG with composition ratios of 100/0, 90/10, 80/20 and 70/30 were melt blended in a laboratory batch internal mixer (Brabender PL2200, Germany) at 180°C and at a rotor speed of 60 rpm. PLA and Irganox 1010



**Figure 1** Melt-electrospinning setup

were fed into the mixing chamber at first. Afterwards, PEG was fed continuously during the mixing time (7 min). The prepared samples were pelletised using a granulator.

**2.3. Melt-electrospinning:** The equipment used for melt electrospinning is shown in Fig. 1. It is composed of a temperature controller, a high voltage power supply, a heating-assembly, a nozzle, a syringe pump and a collector. The temperature controller (itron 04 Jumo, Germany) was able to control the temperature with an accuracy of  $\pm 1^\circ\text{C}$ . Temperature was measured using a K-type thermocouple. Positive voltage was applied to the collector using a high voltage power supply (Nano Azma, Iran) with a voltage range of 0–100 kV. The heating assembly consisted of a metallic barrel of 1 cm inner diameter, 5 cm outer diameter and 16 cm length placed on the ceramic plate. Heating was produced by three electrical heating elements housed inside the barrel. To reduce the die swell effect, a 0.3 mm coated hanger die was employed as the nozzle. A syringe pump was used to control the polymer melt flow rate. A thin aluminium plate placed on the ironing moving plate ( $30 \times 25$  cm) was used as the collector. The heating assembly and the collector were set on the four non-conductive wooden columns. For melt electrospinning, 5 g of the prepared samples was fed into the barrel. After 10 min preheating at a fixed temperature (200 or  $220^\circ\text{C}$ ), a Taylor cone was formed using a piston and electrospinning was initiated at a voltage of 50 kV. The collection distance was 10 cm and the fibres were collected throughout the first 2 min.

**2.4. Characterisation:** The surface morphology of the melt-electrospun fibres was characterised by optical microscopy (Leica DMRX, Buffalo Grove, IL, USA). The average fibre diameter  $\pm$  standard deviation was determined through the measurement of about 30 fibres using image analysis software (Image Pro). Rheological measurements were performed by a UDS 200, Paar Physica rheometer with a parallel plate geometry (25 mm diameter and 1 mm gap). Isothermal dynamic frequency sweep experiments were carried out at the strain of 1% and temperature of 180 and  $200^\circ\text{C}$  to study the linear viscoelastic behaviours. Tests were performed under nitrogen atmosphere to avoid any degradation. The thermal properties of the melt-blended samples were analysed by differential scanning calorimetry (Mettler, DSC 220C) with a heating rate of  $10^\circ\text{C}/\text{min}$  in a nitrogen atmosphere at the temperature range of  $25$ – $200^\circ\text{C}$ .

### 3. Result and discussion

**3.1. Melt rheology:** To understand the processing properties of plasticised PLA blends comprehensively, a detailed investigation

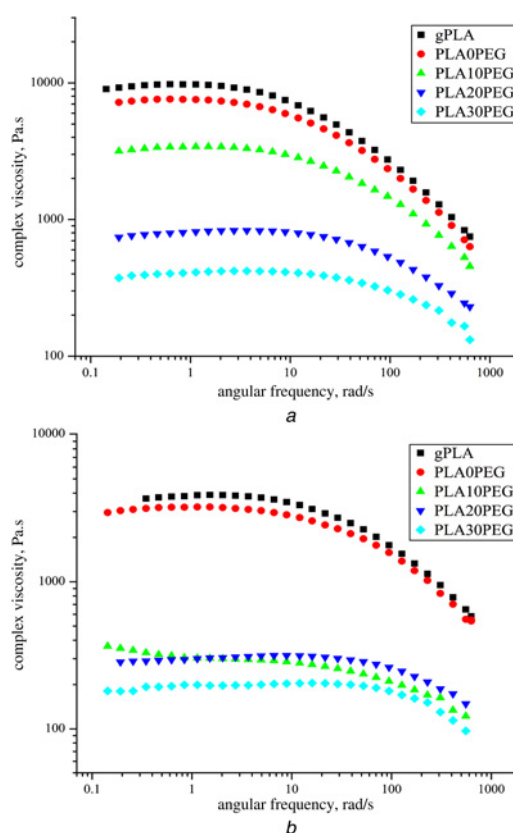
of the melt rheological behaviour of these PLA/PEG blends was required.

Figs. 2a and b represent the frequency dependence of complex viscosity at various PEG concentrations at the melt blending and electrospinning temperatures, 180 and  $200^\circ\text{C}$ , respectively. Since PLA is prone to degradation during high temperature processing, the unprocessed PLA granules (gPLA) data were obtained from dynamic frequency sweep measurement for comparison. It shows a Newtonian plateau at low oscillation frequencies with the zero-shear rate viscosity of about 10,000 and 4000 Pa.s at 180 and  $200^\circ\text{C}$ , respectively. It seems to have a shear thinning behaviour at high oscillation frequencies ( $\sim \omega > 4$  rad/s). On the other hand, the processed PLA (PLA0PEG) also exhibits a non-Newtonian behaviour, but with lower zero-shear rate viscosity values (about 7000 and 3000 Pa.s).

Using the Fox equation for PLA ( $\eta_0 = 5.5 \times 10^{-15} M_w^{3.4}$ ), it is possible to calculate the molecular weight reduction ( $\Delta M_w$ ) because of thermal and shear strain degradation [29]. Accordingly,  $\Delta M_w$  is about  $-8$  and  $-11\%$  at 180 and  $200^\circ\text{C}$ , respectively.

As seen from Figs. 2a and b, increasing the PEG concentrations in all PLA/PEG blends causes great discrepancy in the viscosity of unprocessed PLA and PLA/PEG blends. The values of terminal viscosities (zero-shear viscosity) are considerably decreased. More disentanglement of the PLA chain and increased segmental mobility of the PLA chains because of the plasticising effect of PEG can be deduced. Moreover, by varying the PEG content, a more pronounced Newtonian response with an extended Newtonian plateau compared with unprocessed PLA is observable. Rheological parameters were obtained by fitting the Carreau-Yasuda model as follows [30]

$$\eta = \eta_0 [1 + (\lambda \dot{\gamma})^a]^{(n-1)/a}, \quad a = 2 \quad (1)$$



**Figure 2** Complex viscosity against frequency for unprocessed PLA (gPLA) and PLA/PEG blends at temperatures of 180 and  $200^\circ\text{C}$   
a  $180^\circ\text{C}$   
b  $200^\circ\text{C}$

**Table 1** Rheological parameters PLA and PLA/PEG blends melts

Sample		gPLA	PLA/0 PEG	PLA/10 PEG	PLA/20 PEG	PLA/30 PEG
at 180°C	$\eta_0$ , Pa.s	9534	7436	3342	804	406
	$\lambda$ , s	0.128	0.119	0.073	0.025	0.021
	$N$	0.5	0.5	0.5	0.6	0.6
	$R^2$	0.996	0.996	0.995	0.99	0.981
at 200°C	$\eta_0$ , Pa.s	3796	3125	317	303	196
	$\lambda$ , s	0.061	0.061	0.04	0.01	0.005
	$N$	0.5	0.6	0.6	0.6	0.5
	$R^2$	0.995	0.991	0.943	0.979	0.94

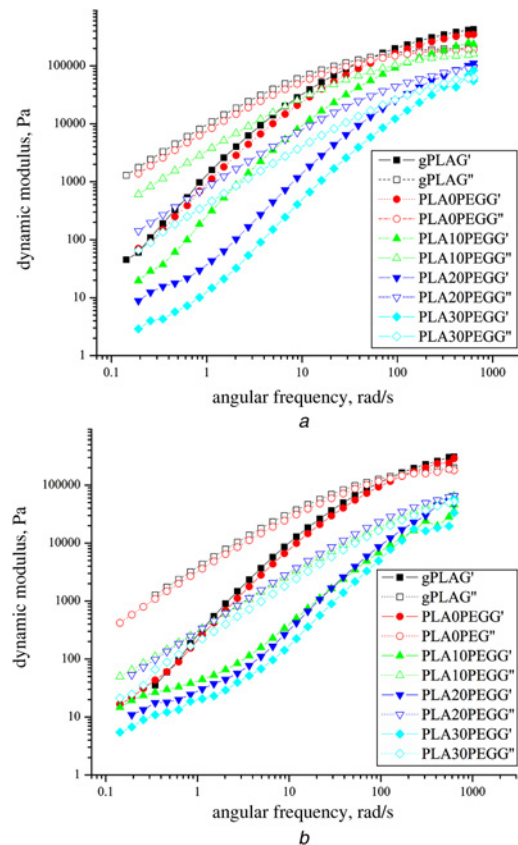
where  $\eta_0$  represents the zero-shear rate viscosity (Pa.s),  $\lambda$  represents the characteristic relaxation time (s) that approximately corresponded to the reciprocal of frequency for the onset of shear thinning and  $n$  characterises the slope of the line over the shear thinning region in the logarithmic plot. The calculated parameters are summarised in Table 1. The Carreau-Yasuda model fits the data well with the correlation coefficient ( $R^2$ ) being more than 0.94. As shown in Table 1, the incorporation of PEG led to a decrease the value of  $\lambda$  and  $\eta_0$ . This demonstrates that adding more PEG content into PLA could decrease the relaxation time, increase the chain mobility and the chain disentanglement. Owing to an unnoticeable difference between the  $n$  values in the PLA/PEG blends, the same tendency of shear thinning over the pseudoplastic region is implied. Sungsanit *et al.* [31] reported the rheological parameters of L-PLA/PEG blends by fitting the modified cross-model. They showed that by varying the PEG content in the range of 0–20 wt% at 180°C,  $\lambda$  and  $n$  decreased from 0.1 to 0.01 and 0.09, respectively.

Figs. 3a and b demonstrate the corresponding storage and loss modulus of these blends. As expected, the dynamic modulus of PLA decreased with increasing the plasticiser loading at all frequencies. These results indicate that the flexibility and extensibility of PLA could be improved through incorporation of PEG [31]. At low frequencies,  $G'(\omega)$  of all blends exhibited a shoulder which moved towards medium frequencies at higher temperature (200°C) and became more pronounced. This behaviour was attributed to a super-slow relaxation process, typically considered as being an indication of discrete phase deformation–relaxation in the immiscible blends [32].

**3.2. DSC analysis:** The effects of PEG loading on the thermal behaviour of PLA studied by differential scanning calorimetry (DSC) are presented in Fig. 4 and Table 2 during the second heating scan. The neat PLA displays a glass transition temperature ( $T_g$ ) at 60°C, an exothermic peak of cold crystallisation  $T_{cc}$  at 128°C, and an endothermic melting peak centred at 153°C. The slight difference between the crystallisation and melting enthalpy for neat PLA (Table 2) indicates an amorphous morphology for it.

For PLA/PEG blends, cold crystallisation peaks shift to lower temperatures and crystallinity degrees increases against PEG concentration. However, the melting temperature of PLA was not affected by the addition of PEG. Increasing the motion ability of the PLA chains and an easier rearrangement of polymer chains to crystallise can be inferred from the DSC results. Indeed, the higher the amount of PEG, the higher the motion, the lower the  $T_{cc}$  of PLA and the higher the crystallinity degree [26–28, 33]. These DSC results verify the rheological observations of plasticised PLA/PEG blends.

**3.3. Fibre morphology:** The optical microscopy images of electrospun PLA and PLA/10 wt% PEG fibres at the spinning temperature of 220°C are shown in Figs. 5a and b. It is clear that the PLA/PEG fibres are thinner than the PLA fibres.



**Figure 3** Dynamic modulus [storage ( $G'$ ) and loss ( $G''$ )] against frequency for unprocessed PLA (gPLA) and PLA/PEG blends at temperatures of 180 and 200°C  
a 180°C  
b 200°C

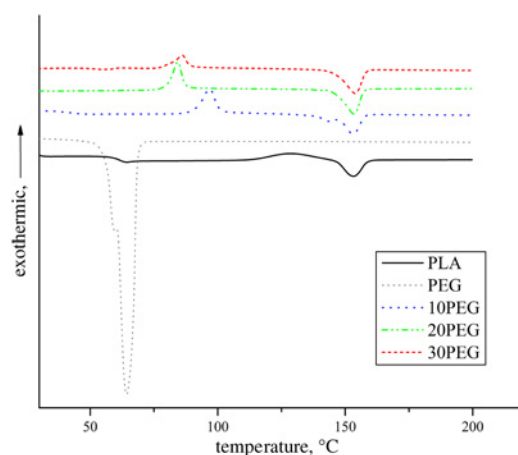
**Table 2** PLA, PEG and PLA/PEG cold crystallisation data

Sample	$T_{cc}$ , °C	$T_m$ , °C	$\Delta H_c$ , Jg <sup>-1</sup>	$\Delta H_m$ , Jg <sup>-1</sup>	$X_c$ , %
PLA	128	153	13.74	-12.83	0
PEG	—	62	—	-195.61	—
PLA/10 PEG	97	153	23.34	-26.93	4.3
PLA/20 PEG	84.5	153	19.04	-26.32	9.7
PLA/30 PEG	86	153.5	11.19	-23.95	19.5

$T_m$  is the melt temperature of PLA;  $T_{cc}$  is the cold crystallisation temperature of PLA;  $\Delta H_m$  is the heat of melting of PLA; and  $\Delta H_c$  is the heat of cold crystallisation of PLA. Crystallinity ( $X_c$ ) (%) was calculated by  $((\Delta H_m - \Delta H_c)/\Phi_{PLA}/93.6) \times 100$  [27].

The measured average fibre diameters are  $d_{PLA} = 25 \pm 5 \mu\text{m}$  and  $d_{PLA/10PEG} = 9.7 \pm 3 \mu\text{m}$ . To limit PLA thermal degradation, fibre spinning at lower temperatures is preferred. Therefore, melt electrospinning of PLA/PEG blends was carried out at 200°C. Unfortunately, the neat PLA was not spinnable because of high viscosity ( $\eta_0 = 3125$  Pa.s). Figs. 6a–d exhibit the PLA/PEG fibres obtained at the spinning temperature of 200°C. The measured average fibre diameters are  $d_{PLA/10PEG} = 11.5 \pm 1.5 \mu\text{m}$ ,  $d_{PLA/20PEG} = 9.4 \pm 1.2 \mu\text{m}$  and  $d_{PLA/30PEG} = 5.9 \pm 1.7 \mu\text{m}$ . By increasing the PEG concentration from 10 to 30 wt%, a clear reduction of fibre diameter is achieved. Actually, easily spinnable PLA fibres could be prepared by incorporation of PEG as a viscosity reducing and extensibility increasing agent. Consequently, adding the PEG increased the chain mobility, decreased the  $\eta_0$ , and led to lowering the fibre diameter. Fig. 6d shows the PLA/30 PEG

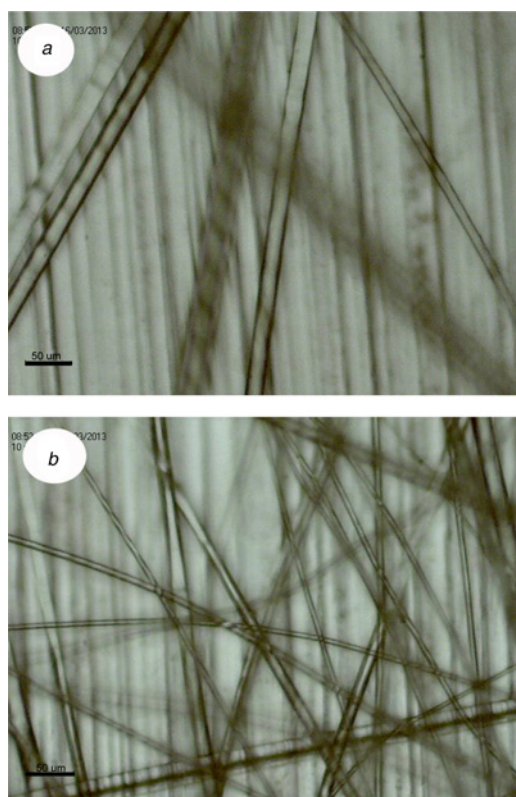




**Figure 4** DSC thermograms of PLA, PEG and PLA/PEG blends during the second heating

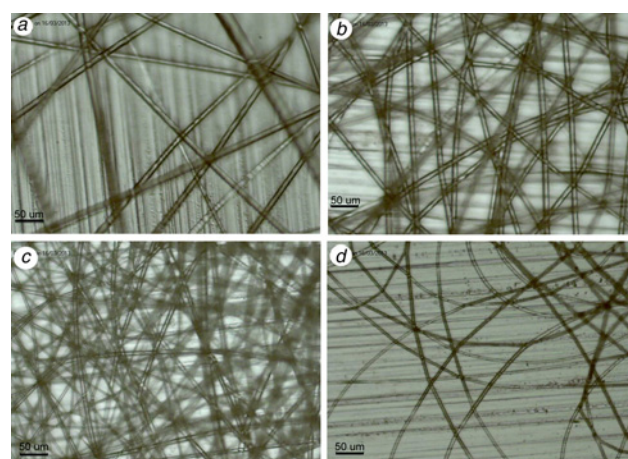
blend fibres with a diameter in the range of 3–6  $\mu\text{m}$ , which is obtained at a voltage of 70 kV. It may be possible to manufacture sub-micron scale PLA/PEG fibres by varying the processing parameters. The fabricated PLA/PEG non-woven mats may have potential applications in tissue engineering directly.

**4. Conclusion:** In this reported work, PLA/PEG blends prepared using various PEG content and microfibres have been successfully fabricated via the melt-electrospinning process. The PEG concentration varied from 0 to 30 wt%. By increasing the concentration of PEG in the molten blend, the zero-shear rate viscosity decreased from 3000 to 190 Pa.s at the spinning



**Figure 5** Optical microscopy images of fibres obtained at spinning temperature of 220°C

a PLA  
b PLA/PEG  
Scale bar is 50  $\mu\text{m}$



**Figure 6** Optical microscopy images

a PLA/10 PEG  
b PLA/20 PEG  
c PLA/30 PEG fibres at voltage of 50 kV  
d PLA/30 PEG fibres at voltage of 70 kV, spinning temperature of 200°C  
Scale bar is 50  $\mu\text{m}$

temperature of 200°C. The cold crystallisation peaks shifted towards lower temperatures and the crystallinity content increased from 0 to 19.5%. The observed melt and thermal properties of PLA verified the improved polymer chain mobility and extensibility in the presence of PEG as a plasticiser. Easily melt-spun PLA/PEG microfibres with the minimum diameter of  $5.9 \pm 1.7 \mu\text{m}$  for the 30 wt% PEG loading at the spinning temperature of 200°C were obtained. It is possible to fabricate sub-micron scale PLA/PEG non-woven mats by optimising the material and processing parameters.

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