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## Abstract

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## 27 1 Introduction

28 There is a great deal of interests in the development of viable green technologies aimed at the enhancement  
29 of biodegradable and biocompatible polymer materials, such as the blend of poly  $\epsilon$ -caprolactone (PCL)  
30 and polylactide (PLA) Blending is a low cost, easy implement process for modification of polymer mixture.  
31 Mixing several immiscible polymer with different physical and chemical properties has possiblity to improve  
32 the overall constituents' performance.

33 Nowadays, the blending material of poly  $\epsilon$ -caprolactone (PCL) and polylactide (PLA) shows a wide  
34 application in many areas. PLA has excellent biocompatibility, biodegradability and dynamic property,  
35 which shows broad prospects for tissue engineering development and other areas. But pure PLA has some  
36 drawbacks, including poor toughness, low degradation rate. Moreover, the crystallinity of PLA is low.  
37 These drawbacks severely restrain the application of PLA material. Researchers have attempted several  
38 polymer to make blends with PLA. PHB, PCL, PP and other material which has good performance has  
39 been attempted in recent years.

40 Physical property improvment has been found in some researchers' blending experiments. PCL The  
41 blend of PCL and PLA shows high degradation rate , better tensile strength, which is the properties  
42 originated from PLA, while PCL with much slower degradation rate and better toughness. The blend  
43 of PCL and PLA is a promising material which can meet the requirement of environment and physical  
44 conditions. Qiaolian Lv et al.[1] used a injection molding blend of PCL and PLA. They got a maximum  
45  $\sigma = 29.8 \pm 0.9$  MPa and  $E = 922.5 \pm 9.8$  Mpa. For electrospun process, Pisani et al.[2] got a maximum  
46  $E = 49.10 \pm 0.12$  Mpa.

47 The physical property of PCL-PLA blend depends on the supermolecular structure, which is dominated  
48 by the crystallization condition. The melting point ( $T_m$ ) and glass transient temperature ( $T_g$ ) of PCL are

49 far lower than those of PLA, and the crystallization temperature ( $T_c$ ) of PCL is even lower than the  $T_g$   
50 of PLA. Someone's research manifests that the presence of minor PCL phase favors cold crystallization of  
51 PLA in their blend system because PCL is in its molten state during PLA crystallization, reducing system  
52 viscosity as a result, or acts as additional substrates.

53 The goal of this research work to improve the physical properties of the blend. Stretching of the  
54 electrospun mat induces the inner fibers to align in one direction. The unmolten PLA fibers offer crystal-  
55 lization loci for PCL phase. One the other hand, the molten PCL phase favors cold crystallization of PLA  
56 fibers. The present works lack this kind research method. Does this process improve the performance of  
57 blends? This question interests the author. Therefore, in this work electrospinning, stretching and hot  
58 pressing experiments are carried. The some morphology, microstructure, dynamic and thermal properties  
59 are characterized.

## 60 2 Experiment

### 61 2.1 Sample Preparation

62 Firstly, electrospinning process was carried out. PLA was supplied by PCL was supplied by 20 wt%  
63 PCL solution and 20 wt% PLA solution were prepared. 2 nozzles containing PCL solution and 1 nozzle  
64 containing PLA solution were used in the electrospinning process, so the mass ratio of PLA : PCL was  
65 33:67. The electrospinning voltage was set at 8 keV. The humidity of electrospun environment was 40%,  
66 the temperature was 25 °C. The electrospun mats were made as standard size samples.

67 On the next stage, the electrospun mat was stretched by a mechanical tester. The electrospinning  
68 mats were stretched to a series of elongation ratios. The velocity of the tensile process was 4mm/minute,  
69 which is a low speed to avoid the fracture of the samples. 25%, 50%, 75%, 100% and 125% elongation ratio  
70 mats were made. After that the mats' double edges were fixed by heat-resistant tape in order to keep the  
71 elongation status since the mats had a rebound trend. Subsequently, the extended mats were put between  
72 two foils which sticked to 300 °C-resistant film. The mats were deposited in a heat oven which kept an  
73 80 °C environment lasting 1 hour for PCL's melting. After 1 hour, the mats were transfered into another

74 heat oven which kept a 30 °C environment lasting 30 minutes for isothermal crystallization.

75 Finally, the sample was tailored into a dimension of 10mm  $\times$  5mm, and the thickness was recorded  
76 by a film thickness gauge. Abundant standard sample with same length and width were prepared for the  
77 following characterizations.

## 78 2.2 Morphology and microstructure characterizations

### 79 2.2.1 Polarized Optical Microscope (POM)

80 POM is an effective facility to observe the microstructure of polymer material. With Maltese cross phe-  
81 nomenon in birefringence polymer crystall, the amorphous and crystallization zone can be clearly distin-  
82 guished. A Linkam heating stage was used to handle the electrospinning films with the same heat treat-  
83 ment process as the experiment in [subsection 2.1](#). The melting and the cold crystallization process were  
84 observed and recorded by a Leica POM.

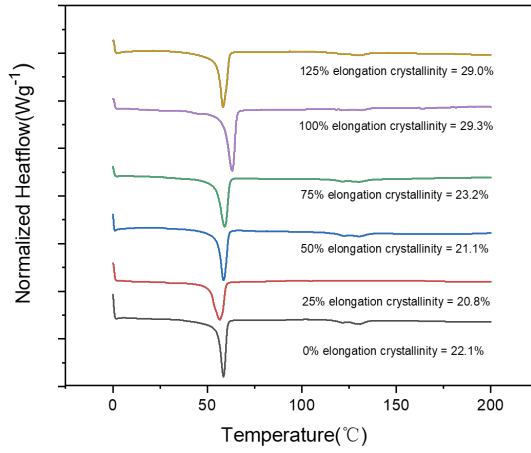
### 85 2.2.2 Small Angle X-ray Scattering(SAXS)

86 Small Angle X-ray Scattering(SAXS) experiment was carried on beamline BL19U2, Shanghai Synchrotron  
87 Radiation Facility. A Pilatus 1M detector(981  $\times$  1043 pixels with a pixel size of 172 $\mu$ m) was performed  
88 to collect the SAXS pattern. The X-ray wavelength was 0.103 nm, and the sample to detector distance  
89 was set at 2131 mm. Considering the scale of X-ray pattern on BL19U2 is much larger than the diameter  
90 of PLA fibers inside the samples. It was essential to focus the X-ray pattern. A beryllium compound  
91 reflective lens(CRLs) was deployed to get a 5 $\mu$ m diameter X-ray pattern. Besides a portable POM was  
92 placed on the light path in order to determine location on blends characterized by the SAXS method.

### 93 2.2.3 Wide Angle X-ray Scattering(WAXS)

## 94 2.3 Dynamic Property Characterization

95 The dynamic properties of the neat PCL and its blends with various annealing histories were determined  
96 by an Instron Mechanical Tester (ASTM D638) at a crosshead speed of 50 mm $\cdot$ min<sup>-1</sup>) at 25 °C using



the dog-bone shaped specimens. Strength and modulus values reported here represent an average of the results for tests run on 6 specimens.

## 2.4 Thermal Property Characterization

### 2.4.1 Thermogravimetric Analysis (TGA)

TGA measurements were carried out in a Mettler Toledo TGA 2 thermal analyzer. The experiments were performed under nitrogen atmosphere (flow rate of  $50 \text{ mL} \cdot \text{min}^{-1}$ ). Each sample was heated from  $0 \text{ }^{\circ}\text{C}$  to  $600 \text{ }^{\circ}\text{C}$  at  $10 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ . The initial degradation temperatures ( $T_0$ ) were determined at 5% mass loss, whereas temperatures at the maximum degradation rate ( $T_{max}$ ) were calculated from the first derivative of the TGA curves (DTG).

### 2.4.2 Differential Scanning Calorimetry (DSC)

DSC experiments were performed in a Mettler Toledo DSC 3+ under nitrogen atmosphere (flow rate of  $50 \text{ mL} \cdot \text{min}^{-1}$ ). Sample weights of 2 mg were sealed in aluminum pans and heated from  $0 \text{ }^{\circ}\text{C}$  to  $200 \text{ }^{\circ}\text{C}$  at  $10 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ . The degree of crystallinity ( $\chi_c$ ) was calculated through [Equation 1](#)

Table 1. Crystallinity of components in PCL/PLA blends

Sample	Crystallinity (%) of PCL phase	Crystallinity (%) of PLA phase	Melting point(°C) of PCL phase
0%	22.1	-	58.7
25%	20.8	-	56.6
50%	21.1	-	58.6
75%	23.2	-	59.1
100%	29.3	-	63.0
125%	29.0	-	58.5

$\chi_c$  calculated using  $\Delta_m^c$  of PCL of  $139.5(\text{J} \cdot \text{g}^{-1})$

$$\chi_c = 100\% \times \left[ \frac{\Delta H_m - \Delta_{cc}}{\Delta H_m^c} \right] \frac{1}{W_{PCL}} \quad (1)$$

## 110 3 Result and Analysis

### 111 3.1 Crystallization behavior

## 112 4 Conclusion

## 113 5 Acknowledgement

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