

1	Contents	
2	1 Introduction	2
3	2 Experiment	3
4	2.1 Sample Preparation	3
5	2.2 Morphology and microstructure characterizations	4
6	2.2.1 Polarized Optical Microscope (POM)	4
7	2.2.2 Small Angle X-ray Scattering(SAXS)	4
8	2.2.3 Wide Angle X-ray Scattering(WAXS)	4
9	2.3 Dynamic Property Characterization	5
10	2.4 Thermal Property Characterization	5
11	2.4.1 Thermogravimetric Analysis (TGA)	5
12	2.4.2 Differential Scanning Calorimetry (DSC)	5
13	3 Result and Analysis	5
14	3.1 Crystallization behavior	7
15	4 Conclusion	7
16	5 Acknowledgement	7

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 ϵ -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 possibility to improve
32 the overall constituents' performance.

33 Nowadays, the blending material of poly ϵ -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 some
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 improvement 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 an 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 super molecular 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. On 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. Lots of morphology, microstructure, dynamic and thermal properties are
59 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 4 mm/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 stuck to 300 °C-resistant film. The mats were deposited in a heat oven which kept an 80
73 °C environment lasting 1 hour for PCL's melting. After 1 hour, the mats were transferred 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 10 mm \times 5 mm, 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 crystals, the amorphous and crystallization zone can be clearly dis-
82 tinguished. A Linkam heating stage was used to handle the electrospinning films with the same heat
83 treatment process as the experiment in [subsection 2.1](#). The melting and the cold crystallization process of
84 different elongation samples were 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 BL16B1, Shanghai Synchrotron
87 Radiation Facility. A Pilatus 2M detector(1475 \times 1679 pixels with a pixel size of 172 μ 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(CRL) was deployed to get a 5 μ 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 WAXS experiment was carried on beamline BL16B1, Shanghai Synchrotron Radiation Facility, Pilatus 2M
95 detector (1475 \times 1679 pixels with a pixel size of 172 μ m). The X-ray wavelength was 0.124 nm, and the
96 sample to detector distance was set at 178.5 mm.

97 2.3 Dynamic Property Characterization

98 The dynamic properties of the neat PCL and its blends with various annealing histories were determined by
99 a mechanical tester at a crosshead speed of $50 \text{ mm} \cdot \text{min}^{-1}$) at 25°C using the dog-bone shaped specimens.
100 Strength and modulus values reported here represent an average of the results for tests run on 6 specimens.

101 2.4 Thermal Property Characterization

102 2.4.1 Thermogravimetric Analysis (TGA)

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

108 2.4.2 Differential Scanning Calorimetry (DSC)

109 DSC's experiments were performed in a Mettler Toledo DSC 3+ under nitrogen atmosphere (flow rate of
110 $50 \text{ mL} \cdot \text{min}^{-1}$). Sample weights of 2 mg were sealed in aluminum pans and heated from 0°C to 200°C at
111 $10^\circ\text{C} \cdot \text{min}^{-1}$. The degree of crystallinity(χ_c) was calculated through [Equation 1](#)

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

112 3 Result and Analysis

113 As shown in a is the melting and isothermal crystallization of 0 % elongation sample, b is the same process
114 of 125 % elongation sample. Compare the evolution of two samples, it can be remarkably noticed that
115 the stretching force make PLA fibers inside samples present a certain degree of orientation. During the
116 isothermal crystallization process at 30°C , the PCL grain firstly appears on the surface of PLA fiber.

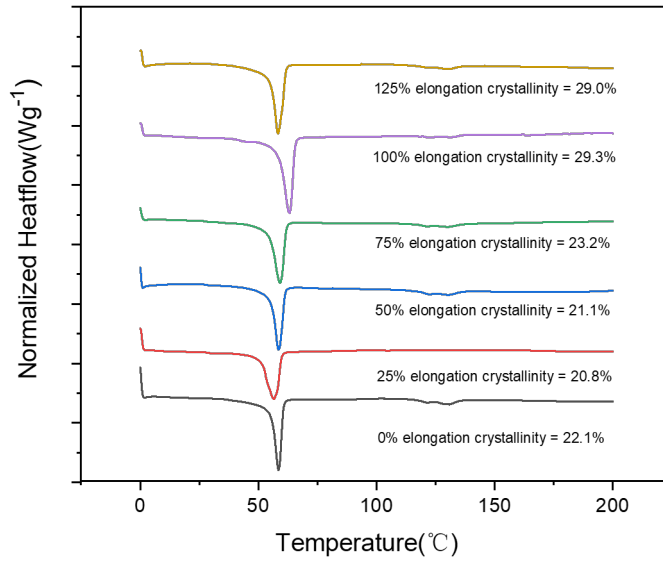


Table 1. Crystallinity of components in PCL/PLA blends

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

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

117 After a short time, the grain is fill the entire matrix.

118 3.1 Crystallization behavior

119 4 Conclusion

120 5 Acknowledgement

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