The effect of parameters on the properties of Poly (L-lactic acid) ultrafine multi-porous fibrous film by electrospinning

Chentao Jin[a], Gang Ruo[b], Caiwei He[c],Hui Zhang[d], Qianqian Zhao[e], Yingjie Chen[f], Qiaozhen Yu[j]*

College of Materials and Textile Engineering, Zhejiang Materials & Light Chemical and Textile Engineering Experiment Center, Jiaxing University, Jiaxing Zhejiang 314001, P. R. China

[a] email: 1837004626@qq.com, [b] email: 1014189961@qq.com, [c] email: 1171950517@qq.com, [d] email: 1642879742@qq.com, [e] email: 1710723223@qq.com, [f] email: 675948742@qq.com, [j] email: w2003yqz@126.com

*corresponding author

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Abstract: The poly (L–lactic acid) (PLLA) micro/nano fibrous multi-porous films are fabricated by electrospinning. The effect of flow rate, spinning time and the type of solvent on the mechanical properties, pore volumes, distributions of pore size and specific areas of PLLA micro/nano fibrous multi-porous films were studied. The results show that the average diameter and volume of pores in the film, the specific area and mechanical property of electrospun film were strongly affected by the flow rate of solution, spinning time and the type of solvent used to prepare the solution. There is an approximately negative correlation among the average diameter of pores, average volume of pores and strength of the electrospun PLLA fibrous films.

1. Introduction

The applications of polylactic acid (PLA) have drastically increased over the past decade in areas from packaging and tableware industries to biomedical and tissue engineering applications. This is due to increasing availability of PLA and its good mechanical properties (in particular the L-form), recyclability, biodegradability, and biocompatibility [1–2]. Many researchers have engaged in fabricating multi–porous PLLA fiber film with various methods.

The electrospinning has been demonstrated to be a promising technique for developing scaffolds for different purposes, including tissue engineering. This technique has also been used for localized drug delivery and promoting wound healing [3]. One of the main advantages of electrospinning is the ability to develop a nonwoven fibrous structure (mat or film) with high interconnected porosity and specific surface area for applications such as tissue engineering and film filtration. Many of the applications of electrospun fibers could be greatly enhanced by increasing the surface area and porosity of the fibers [4]. The variables involved in the surface area and porosity of the film can be related to the concentration and viscosity of the solution as well as the type(s) of solvent; processing parameters (voltage, nozzle-collector distance and flow rate) and the ambient parameters (temperature and humidity). The increased porosity and rough texture subsequently affect the degradation rate, water absorption, optical and mechanical properties of the final film [5]. Despite the afore mentioned potential, the application of electrospun nanofibers has been limited due to the difficulties in mass production and the lack of knowledge of mechanical properties at that scale [6]. This is why there is a special interest in knowing the structural, electrical, mechanical, and thermal properties of electrospun PLA fibers [7].

In this study, PLLA micro/nano fibrous films with multi-porous structure were prepared by electrospinning. The effects of the flow rate, collecting time and the type(s) of solvent on the porosities and mechanical properties of the electrospun PLLA micro/nano fibrous films were studied.

2. Experimental Section

2.1. Materials

PLLA (MW: 100,000 ~ 70,000, Mw/Mn: 1.40) chips were purchased from Jiaxing Haobang Science and Technology Development Co., Jiaxing, China. Methylene dichloride, A. R, was supplied from Guoyao Chemical Company, Shanghai, China. Hexafluoroisopropanol (HFIP), A. R, was purchased from Huaweiruike Chemical Limited. Company, Beijing, China. All the other reagents were analytical grade, and were used without further purification.

2.2. Preparation

2.2.1 Preparation of PLLA fibrous film

12 wt % PLLA in methylene dichloride or HFIP was prepared by dissolving PLLA chips in methylene dichloride or HFIP under magnetic stirring for at least 5 hrs, the solution was held in a syringe for electrospinning. A voltage of 12 kV was applied to the solution and a rotating mandrel was used to collect the PLLA micro/nano fibrous films for different times at a rotation rate of 800 rpm. The feeding rate of the solution was varied from 0.4mL/h to 1.0 mL/h. The distance from the tip of the nozzle to the collector was 15 cm.

2.3. Characterization

Tensile testing was performed by using an Instron tester (Model LLY-O6B). Ten samples measured 25 × 2.0 mm^2 were tested in each group. The gauge length and cross-head speed was 10 mm and 10 mm/min, respectively. Tensile and modulus values are reported as averages ± 95% confidence interval using a t-statistic. The porosity and Brunauer-Emmett-Teller (BET) surface area of the samples were obtained from N_2 sorption/desorption isotherms at 77 K by NOVA 4000e (Quantachrome Instruments Corporation, USA). The specific surface area was obtained by Brunauer-Emmett-Teller (BET) method. The pore size distribution (PSD) was calculated by the nonlocal density functional theory (NLDFT) method. The average pore volume was estimated from the adsorbed amount at a relative pressure p/p° of 0.99.

3. Results and Discussion

3.1. The results of BET tests of electrospun PLLA fibrous films

3.1.1 The effect of spinning time on the results of BET tests of PLLA fibrous films

The results of BET tests of electrospun PLLA fibrous films fabricated with different times were listed in Table 1. As shown in Table 1, fixing the flow rate at 0.3 mm/min, and HFIP as the solvent, the average diameter and volume of pores in the film, as well as the specific area of the film all decreased with the spinning time extended from 5h to 9h. It may be mainly due to the more closed accumulation of fibers.

Table 1 Results of BET tests of the films obtained with different spinning times

Spinning time (h)	Specific area (m^2/g)		Average volume of pores (cc/g)	Average diameter of pores (nm)	
	Adsorption	Desorption		Adsorption	Desorption
5	2.380E-01	1.773E+01	9.111E-02	4.323E+00	3.582E+00
7	1.283E-01	1.569E+01	8.874E-02	4.198E+00	3.364E+00
9	1.011E-01	1.277E+01	5.142E-02	2.756E+00	2.250E+00

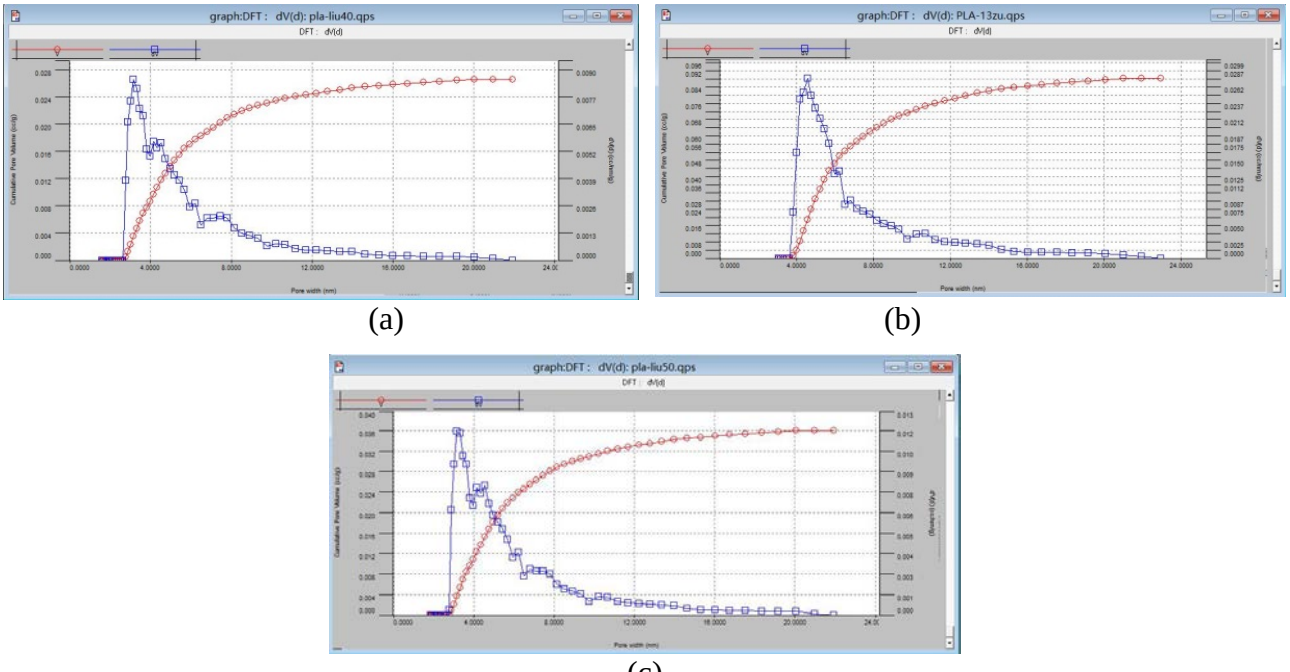
3.1.2 The effect of flow rate on the results of BET tests of the film

From Table 2, with the increase of flow rate, it can be seen that average volume and diameter of pores increased, while specific area fluctuated. Figure 1 shows the distribution of pore size of the

films obtained from different flow rates. It can be found that flow rate had little effect on the adsorption curve, but had visible effect on the desorption curve. When the flow rate was 0.4 mL/h or 1.0 mL/h, the adsorption peak was at about 3.4 nm, and it was at about 4.5 nm as the flow rate was 0.7 mL/h, indicating the distribution of pore size of the films was shifted to larger pores with the increase of the flow rate. As shown in Table 2, with the flow rate increased from 0.2 mL/h to 0.7 mL/h, the average diameter and volume of pores in the film increased, but as the flow rate increased from 0.7 mL/h to 1.0 mL/h, the pore size of most of pores in the film decreased. While specific area decreased with the increase of flow rate. It may be attributed to the increased diameter of fibers.

Table 2 Results of BET tests of the films with different flow rates

Flow rate (mL/h)	Specific area (m^2/g)		Average volume of pores (cc/g)	Average diameter of pores (nm)	
	Adsorption	Desorption		Adsorption	Desorption
0.2	4.900E-02	3.321E+01	1.800E-02	3.217E+00	1.698E+00
0.4	4.047E-02	2.955E+01	3.839E-02	3.073E+00	3.035E+00
0.5	4.000E-02	2.324E+01	3.900E-02	3.130E+00	3.081E+00
0.7	3.283E-02	1.569E+01	8.874E-02	3.198E+00	3.364E+00
1.0	2.635E-02	4.272E+00	2.856E-02	3.344E+00	3.396E+00



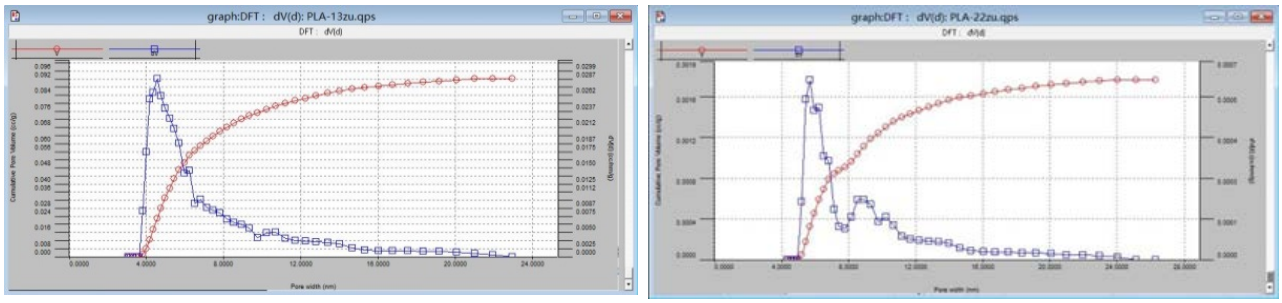
(a) (b) (c)

Figure 1 Distribution of pore size of the films obtained from different flow rates (mL/h) (a) 0.4; (b) 0.7; (c) 1.0

3.1.3 The effect of the type(s) of solvent on the results of BET tests of the film

Figure 2 shows the distribution of pore size in the films fabricated with different solvents. It can be seen that there was an adsorption peak at about 4.5 nm both in the curves of the films fabricated with methylene dichloride and HFIP as solvent. To our surprise, there is another obvious adsorption peak at about 9.0 nm in the curve of the film fabricated with methylene dichloride as solvent, while there was a little adsorption peak at about 11.5 nm in the curve of the film fabricated with HFIP as solvent, indicating the distribution of pore size of the film was affected by the type of solvent. As listed in Table 4, the film fabricated with methylene dichloride as solvent had higher average volume of pores and specific area than those of fabricated with HFIP as solvent, while average diameter of pores in the film fabricated with methylene dichloride as solvent was larger than that in

the film fabricated with HFIP as solvent. The main reason may be the different volatilization rates between the two solvents.



(a) (b)

Figure 2 Distribution of pore size of the films fabricated with different solvents (a) Methylene dichloride; (b) HFIP

Table 3. The results of BET tests of the films fabricated with different type(s) of solvent

Solvent	Specific area (m^2/g)		Average volume of pores (cc/g)	Average diameter of pores (nm)	
	Adsorption	Desorption		Adsorption	Desorption
Methylene dichloride	4.412E-03	1.740E+00	3.451E-03	3.375E+00	3.839E+00
HFIP	8.874E-02	1.283E-01	1.569E+01	4.198E+00	3.364E+00

3.2 Mechanical properties of PLLA fibrous films

The Load and elongation curves of electrospun PLLA fibrous films fabricated with different times were shown in Figure 3, From Figure 3, it can be seen that all the tensile stress-strain curves exhibited the ductile behavior in which failures occurred after yield.

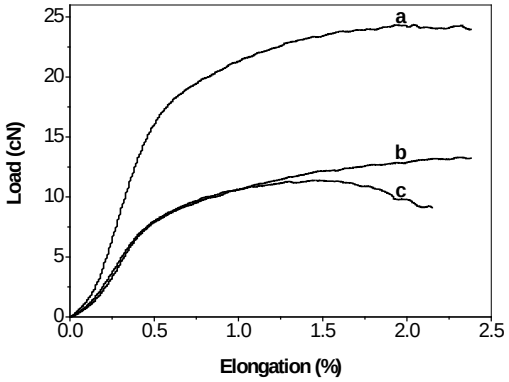


Figure 3 Load and elongation curves of electrospun PLLA fibrous films fabricated with different times (a) 9 h; (b) 7h; (c) 5h.

3.2.1 The effect of spinning time on the mechanical properties of PLLA fibrous films

The basic tensile parameters of electrospun PLLA fibrous films fabricated with different times were listed in Table 4. Fixing the flow rate at 0.3 mm/min and HFIP as the solvent, with the spinning time extended from 5h to 9h, strength increased from 45.44 ±1.02 cN/tex to 82.35 ±1.05 cN/tex; initial modulus increased from 16.59±0.95 cN/tex to 22.59±1.37 cN/tex; elongation at break decreased from 36.25±1.20 % to 41.14±1.07 %, respectively. These indicate that the tensile strength, initial modulus and elongation at break of electrospun PLLA fibrous films increased with the spinning time extended. This is mainly due to the fact that the length of the fiber and the thickness of electrospun PLLA fibrous film increased，resulting in the increase of the tangle points and the number of the fibers bearing the load.

Table 4 Mechanical properties of PLLA fibrous films fabricated with different spinning times

Time (h)	Strength (cN/tex)	Elongation (%)	Initial Modulus (cN/tex)
5	45.44±1.02	36.25±1.20	16.59±0.95
7	57.07±1.32	38.01±1.03	17.75±1.03
9	82.35±1.05	41.14±1.07	22.59±1.37

3.2.2 The effect of flow rate on the mechanical properties of electrospun PLLA fibrous films

The basic tensile parameters of electrospun PLLA fibrous films fabricated with different flow rates were listed in Table 5. Fixing the spinning time at 3 h and methylene dichloride as the solvent, with the increase of flow rate from 0.3 mm/min to 1.0 mm/min, strength increased from 6.38±0.07 cN/tex to 7.75 ±0.05 cN/tex; initial modulus increased from 0.53±0.05 cN/tex to 1.70±0.32 cN/tex; elongation at break decreased from 50.40±1.22 % to 36.30±1.01 % when the flow rate increased from 0.3 mm/min to 0. 5 mm/min, but increased from 36.30±1.01 % to 40.62±1.03 % when the flow rate increased from 0.5 mm/min to 1.0 mm/min, respectively. These indicate that the tensile strength and initial modulus of electrospun PLLA fibrous films increased, but elongation at break fluctuated with the increase of the flow rate. This is mainly due to the two facts. The first was the diameter of the fiber increased with the increase of the flow rate, resulting in the increase of defects in the fibers. The second was the increase of the thickness of the film and the varied pore volume and pore size in the film.

Table 5 Mechanical properties of PLLA fibrous films fabricated with different flow rates

Flow rate (mm/min)	Strength (cN/tex)	Elongation (%)	Initial Modulus (cN/tex)
0.3	6.38±0.07	50.40±1.22	0.53±0.05
0.5	7.48±0.32	36.30±1.01	1.15±0.03
1.0	7.75±0.05	40.62±1.03	1.70±0.32

3.2.3 The effect of the type(s) of solvent on the mechanical properties of PLLA fibrous films

Table 6 listed the basic tensile parameters of electrospun PLLA fibrous films fabricated with different solvents. Fixing the spinning time at 5 h, flow rate at 0.3 mm/min, the strength and initial modulus of the film obtained from methylene dichloride as solvent were lower than those of obtained from HFIP as solvent, while elongation was a little larger than that of the film obtained from HFIP as solvent. The main reason may be the different volatilization rates between the two solvents. The methylene dichloride has higher volatilization rate than HFIP, resulting in the larger pore size in the fibers, as reported by Yu et al. [4].

Table 6 Mechanical properties of PLLA fibrous films fabricated with different type(s) of solvent

Solvent	Strength (cN/tex)	Elongation (%)	Initial Modulus (cN/tex)
Methylene dichloride	13.80±0.03	40.40±1.25	2.53±0.07
HFIP	45.44±1.02	36.25±1.20	16.59±0.95

4. Conclusions

The tensile stress-strain curves of electrospun PLLA fibrous films fabricated with different parameters all exhibit the ductile behavior in which failures occurred after yield. But the mechanical properties and the results of BET tests were strongly affected by the flow rate of solution, spinning time and the type of solvent used to preparation the solution. The average diameter and volume of pores in the film, as well as the specific area of the film all decreased, while the tensile strength, initial modulus and elongation at break of electrospun PLLA fibrous films all increased with the spinning time extended from 5h to 9h. With the increase of flow rate, average volume and diameter of pores in the film increased, while specific area fluctuated, resulting in the tensile strength and initial modulus of electrospun PLLA fibrous film increased, but elongation at break fluctuated. The film fabricated with methylene dichloride as solvent had higher average volume of pores and

specific area, lower average diameter of pores than those of the film fabricated with HFIP as solvent, resulting in lower strength and initial modulus, a little larger elongation than those of the film fabricated with methylene dichloride as solvent. There is an approximately negative correlation between the average diameter and volume of pores and strength of the electrospun PLLA fibrous films.

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