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Influence of the solvent type on the morphology and mechanical properties of electrospun PLLA yarns

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Abstract
An electrospinning technique based on the use of two oppositely charged nozzles was applied to fabricate continuous twisted yarns of poly(L-lactide) (PLLA) nano/micro fibers. In this study, the effect of solvent on the electrospinning of PLLA fibrous yarns was investigated. For this purpose, yarns were electrospun using chloroform, dichloromethane or 2,2,2-trifluoroethanol as solvents at a PLLA concentration of 7 wt%. The analysis of the morphology, diameter, crystallinity and mechanical properties of electrospun yarns revealed that the vapor pressure of the solvent plays an important role. Whereas the fiber diameter decreased, the crystallinity of the fibers increased using a solvent with lower vapor pressure. In addition, mechanical properties (e.g., tensile strength and modulus) revealed that the yarns composed of fibers with smaller diameters showed higher tensile strength and modulus. In summary, fine-tuning solvent properties resulted in a modulation of fiber diameter, crystallinity, and thereby yarn mechanical properties, and are important factors to consider in the fabrication and application of electrospun yarns.

(Some figures may appear in colour only in the online journal)

1. Introduction

Electrospinning is an efficient technique to fabricate ultra-thin fibers by means of electrically charging a suspended droplet of a viscous polymer melt or solution. Electrospun mats composed of nanofibers generally feature several excellent characteristics such as a very large surface area and high porosity, which make them potential candidates for a wide range of applications [1]. Fibers with nano-sized diameters, however, are difficult to handle and cannot be used directly due to lack of strength. Therefore, in recent years the production of yarns by electrospinning has been explored.

The lateral interaction and friction between fibers in yarns may provide these structures improved physical and mechanical properties. It can be expected that nanofibrous yarns will find advanced applications in the medical field in the form of sutures, ligament replacement, high performance and functional fabrics, artificial blood vessels and tissue scaffolding materials [2, 3].

Up to now, several methods have been proposed to obtain aligned electrospun nanofibrous structures and yarns. In order to obtain strong yarns with high interconnections between the nanofibers, the yarns are twisted during the electrospinning process [4]. Up to now only a few investigations, applying two oppositely charged nozzles, have been reported for the continuous fabrication of twisted nanofibrous yarns [5–10]. Refinement of this technique involved the use a rotary collector, a grounded circular twister plate and a grounded surface collector with a twister unit [11].

Many parameters influence the electrospinning process and thereby the final fiber properties. These parameters include: (1) intrinsic solution properties like viscosity, conductivity, polymer concentration and surface tension, (2) processing conditions like applied voltage, distance from needle to collector, volume feed rate and needle diameter, and (3) ambient conditions like temperature, humidity, and atmospheric pressure [12]. All these parameters will influence the morphology and mechanical properties of the electrospun fibers and thus their possible end-use application [13]. Importantly, the mechanical properties of nanofibrous nonwoven mats or yarns rather than individual fibers depend strongly on fiber orientation within the material, bonding and cohesive forces between fibers [14].

In the past decade various natural and synthetic polymers have been successfully electrospun into fibers with sub-micrometer diameters to several nanometers [14–16]. Although some research was done on the electrospinning of nanofibrous yarns, only limited studies on PLA nanofibrous yarns and their properties have been performed. Jad *et al* [17] used a two oppositely charged spinneret method to measure the capillary flow of a colored liquid in PAN nanofibrous yarns. Hajiani *et al* investigated the mechanical properties and wicking phenomenon of PA66 nanofibrous yarns for medical applications [4]. Poly(L-lactide) (PLLA), a biodegradable thermoplastic material, has especially attracted attention for biomedical applications due to its biocompatibility and suitable chemical, biological and mechanical characteristics. Electrospun PLLA fibers have been investigated for potential application as a bioabsorbable material in tissue engineering, drug delivery and surgery [18, 19].

In this study, an electrospinning set-up was used to make continuous twisted yarns of PLLA and the influence of solvent type on the morphology and mechanical properties of the electrospun yarns was investigated. The yarns were characterized by scanning electron microscopy (SEM), and thermal analysis (differential scanning calorimetry (DSC)) was used to study their thermal properties and crystallinity. The mechanical properties of the resulting PLLA yarns were investigated by tensile experiments.

2. Experimental

2.1. Materials

PLLA (inherent viscosity 2.51 dl g^{-1}) was a gift from Purac Biomaterials, Netherlands. Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and 2,2,2-trifluoroethanol (TFE) were used as solvents and were obtained from Merck and used without further purification.

2.2. Solutions preparation and characterization

To obtain electrospinnable solutions, PLLA was dissolved in the different solvents at a concentration of 7 wt%. PLLA/$CHCl_3$ and PLLA/TFE solutions were stirred gently at 40 °C for at least 24 h to provide a homogeneous solution. The PLLA/CH_2Cl_2 solution was stirred at room temperature for 24 h to prepare a homogeneous solution.

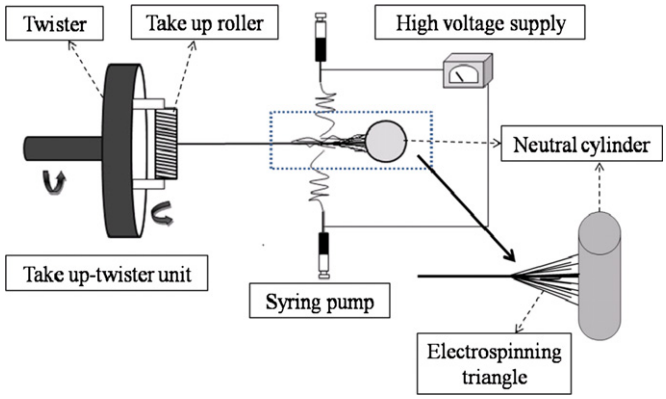

Figure 1. Schematic illustration of the electrospinning setup to produce nanofiber yarns (top view of the set-up).

The surface tension and conductivity of all prepared solutions, prior to electrospinning, were measured by a Kruss K 100SF Tensiometer and an Orion160 conductivity meter, respectively. The data have been summarized in table 1.

2.3. Electrospinning

The electrospinning set up for producing continuous twisted nanofiber yarns is presented in figure 1. This set up consists of a high voltage-power supply, two syringe nozzles with flat-tipped needles (22-gauge, ID = 0.4 mm, OD = 0.7 mm), a neutral surface (6 cm diameter × 30 cm length), and a take-up twister unit. Two digitally controlled syringe pumps (TOP-5300, Japan) were used to provide a constant feed rate of the polymer solution during electrospinning. Each needle was charged with a voltage of the same value but opposite polarization using a dc high-voltage power supply, which is capable of generating dc voltages up to 25 kV. A rotating plate was used for twisting the yarn. The twister unit consists of a rotating plate with adjustable rotational speed (1–440 rpm) and a take-up roller controlled by a stepper motor. The linear take-up speed was adjusted according to the solution feed rate. The vertical distances of the needle tips to the axis of the take-up twister unit and grounded cylinder were both 19 cm.

To produce yarns, electrospinning was started from the two nozzles having opposite charges. The grounded cylinder was vertically placed in the middle of the electric field. This resulted in a surface charge on the cylinder, which is positive on one half and negative on the other half. The electrospun fibers generated from both charged nozzles moved slightly towards the part of the cylinder having an opposite charge. After the start of the electrospinning process, a piece of yarn was placed at the convergence point to collect the nanofibers. Next, the other end of the yarn was pulled toward the take-up roller and a suspended triangle of nanofibers was formed between the convergence point and the cylinder, called the 'electrospinning triangle (E-triangle)' [4]. Finally, nanofibers were twisted by rotating the yarn around its axis by the take-up twister unit. All electrospinning experiments were performed at environmental conditions. By this method the electrospun nanofibers were to a certain extend aligned within the yarn produced. Based on this set-up, the yarn production process is

Table 1. Properties of solvents and corresponding PLLA solutions.

Solvent	Density (g cm^{-3})	Vapor pressure (mmHg)	Boiling point (°C)	Surface tension[a] (mN m^{-1})	Conductivity[a] (μs cm^{-1})
Dichloromethane	1.33	350	40	7	0.2
Chloroform	1.48	156	61	7	0.1
TFE[b]	1.38	143	74	22	0.4

[a] Solution concentration of 7 wt%.
[b] TFE; 2,2,2-trifluoroethanol.

Table 2. Electrospinning conditions and set-up parameters.

Applied voltage (kV)	Feeding rate (mL h^{-1})	Twist rate (rpm)	Roller take-up speed (m h^{-1})	Distance between needles (cm)	Needle center/neutral cylinder distance (cm)	Needle center/take-up unit distance (cm)
9	0.3	200	2.4	30	2	38

continuous. The electrospinning set up parameters such as take-up speed, rotation rate of twister, main distances set, solution feed rate and applied voltage were considered in the production process. The optimal conditions for fabricating continuous nanofiber yarns were determined and the results are presented in table 2. All experiments performed were done using these parameters.

2.4. Characterization

2.4.1. Morphology. The morphology of the electrospun yarns and electrospun fibers in the E-triangle and yarn body were examined by SEM (EM 3200, KYKY). The samples were sputtered with a thin layer of gold prior to SEM analysis and an accelerating voltage of 25 kV was applied. The average diameter of electrospun fibers and yarns were determined by means of Image J 1.44p software.

The surface morphology of electrospun nano/micro fibers was evaluated by using a Bioscope Catalyst atomic force microscopy (AFM) (Bruker AXS). All samples were scanned at room temperature at ambient conditions and at a scan rate of 1 Hz.

2.4.2. Thermal analysis. DSC was used to determine the thermal properties of the electrospun yarns. Thermograms were obtained using a Mettler SW 9.01 calorimeter. Samples from the electrospun yarns of about 10 mg were weighed into sealed aluminum pans. The samples were heated from 25 to 250 °C at a heating rate of 10 °C min^{-1}, under a constant flow of dry nitrogen. Then, the samples were cooled to 25 °C at a rate of 10 °C min^{-1}. From the DSC curves the glass-transition temperatures (T_g) and melting temperature (T_m) were determined. The percent of crystallinity (χ_c) was calculated from equation (1) [20]:

$$\chi_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^o} \times 100 \quad (1)$$

where ΔH_m is the melting enthalpy, ΔH_c the enthalpy of crystallization and $\Delta H_m{}^o$ the melting enthalpy of 100% crystalline PLLA (93 J g^{-1}) [12, 21].

Table 3. Mean diameter (μm) of yarns and electrospun fibers in the E-triangle and yarn body.

	Yarn		Fibers in E-triangle		Fibers in yarn body	
Solvent	Average	S.D.	Average	S.D.	Average	S.D.
Dichloromethane	236	54	4.25	0.85	2.95	0.87
Chloroform	422	110	5.70	1.07	5.51	0.91
TFE	152	10	2.48	0.35	1.65	0.15

2.4.3. Mechanical properties. From a random area of the twisted electrospun yarns pieces with a length of 40 mm were cut, which were weighed by an electronic balance (OHAUS, USA, with the precision of 0.0001 g) to determine the linear mass density of the yarns. Mechanical properties of the twisted electrospun PLLA yarns were measured by tensile testing (Elima EMT-3050). The selected gauge length and crosshead speed were 20 mm and 1 mm min^{-1}, respectively.

3. Results and discussion

3.1. Morphological characterization

The SEM images of electrospun fibers in the E-triangle and their corresponding diameter distributions are shown in figure 2. The SEM images of the produced yarns electrospun from different solvents are illustrated in figure 3 together with AFM images of single fibers in the yarn body. The average diameters of yarns and fibers in the E-triangle are presented in table 3. The reported results are average values of 100 measurements.

The images indicate that the use of solvents with different properties caused significant changes on the fiber diameter distribution, shape and surface morphology. As can be seen from figure 3 and table 3, TFE-based electrospun yarns have smaller diameters and are more uniform than those produced from the other solvents. It is observed that using $CHCl_3$ and CH_2Cl_2 as solvents, broad fiber diameter distributions (2.78–7.75 μm and 2.10–7.19 μm respectively) are obtained with mean diameters of 5.70 ± 1.07 and 4.25 ± 0.85 μm, respectively (figure 2). The diameters of fibers electrospun

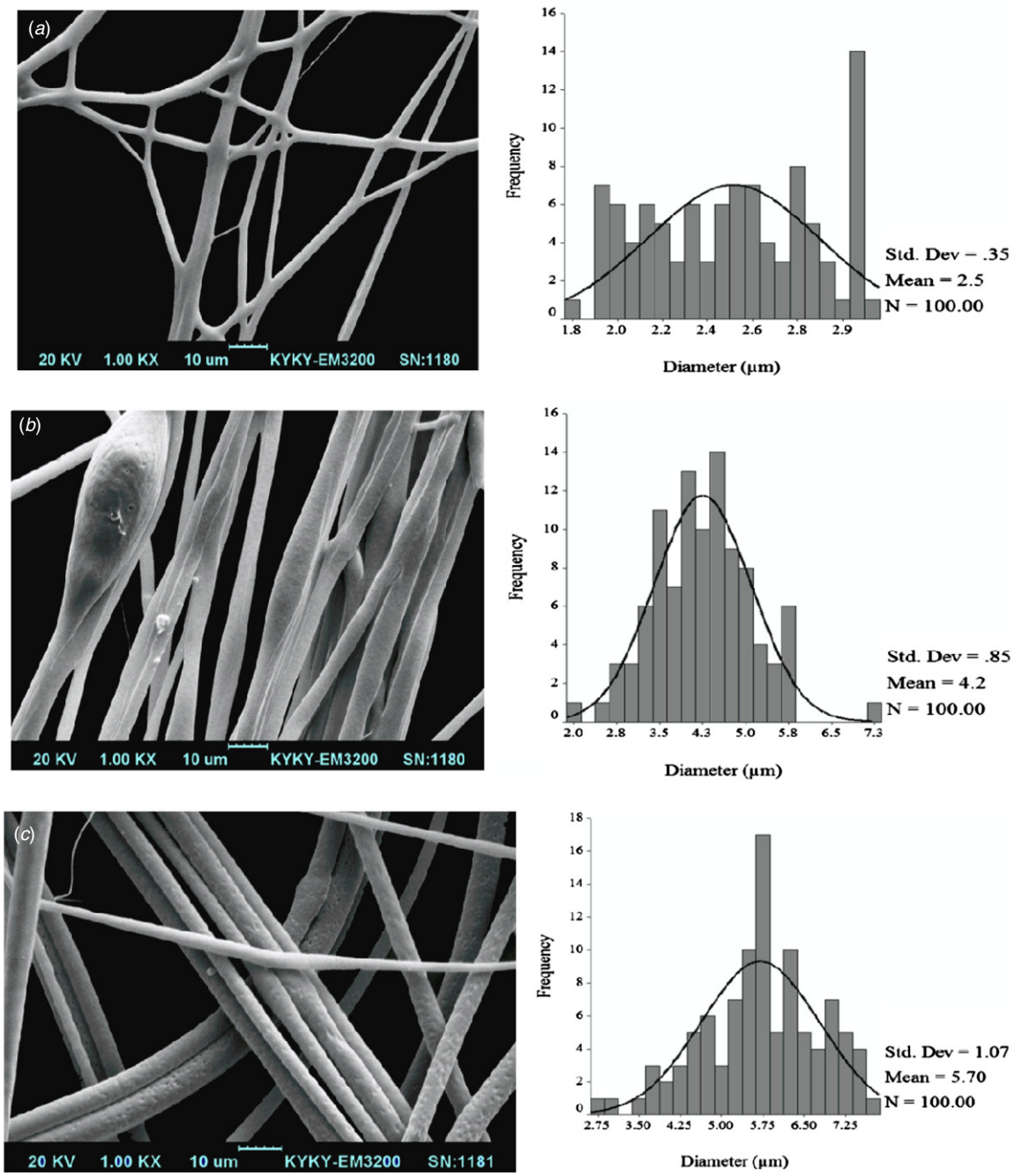

Figure 2. SEM images and diameter distribution of PLLA fibers generated in the E-triangle region upon electrospinning polymer solutions (5 wt%, 25 °C) in (*a*) TFE, (*b*) CH_2Cl_2, and (*c*) $CHCl_3$.

from $CHCl_3$ and CH_2Cl_2 are too large to form uniform yarns. In these cases, the effect of electrostatic forces in the yarn production process decreased, resulting in non-uniform yarns (figures 3(*b*) and (*c*)). Moreover, in the case of yarns produced from PLLA/CH_2Cl_2 solutions beaded fibers were observed (figure 2(*b*)). The fibers produced from PLLA/TFE solutions do not show beads, have a smooth surface morphology and narrow diameter distribution (1.8 to 3 μm), with a mean diameter of 2.48 $\pm$ 0.35 μm.

The vapor pressure and boiling point of the solvents are indicative for their volatility influence the morphology of the PLLA electrospun fibers. If the polymer jet is collected prior to complete solvent evaporation, ribbon like flat nanofiber morphologies or conglutinated nanofibers are obtained [22]. As can be seen in figure 2(*a*), the electrospun PLLA fibers using TFE as a solvent, tended to stick to each other, due to incomplete solvent evaporation. Electrospinning PLLA solutions using solvents with a high vapor pressure and lower boiling points, like CH_2Cl_2 and $CHCl_3$, afforded fibers with porous surfaces (figure 3). These pores are likely a result of solvent evaporation and consecutive phase separation during fiber formation. Phase separation and the possibly of fast crystallization causes the formation of solvent-rich and polymer-rich regions, which lead to the porous appearance of

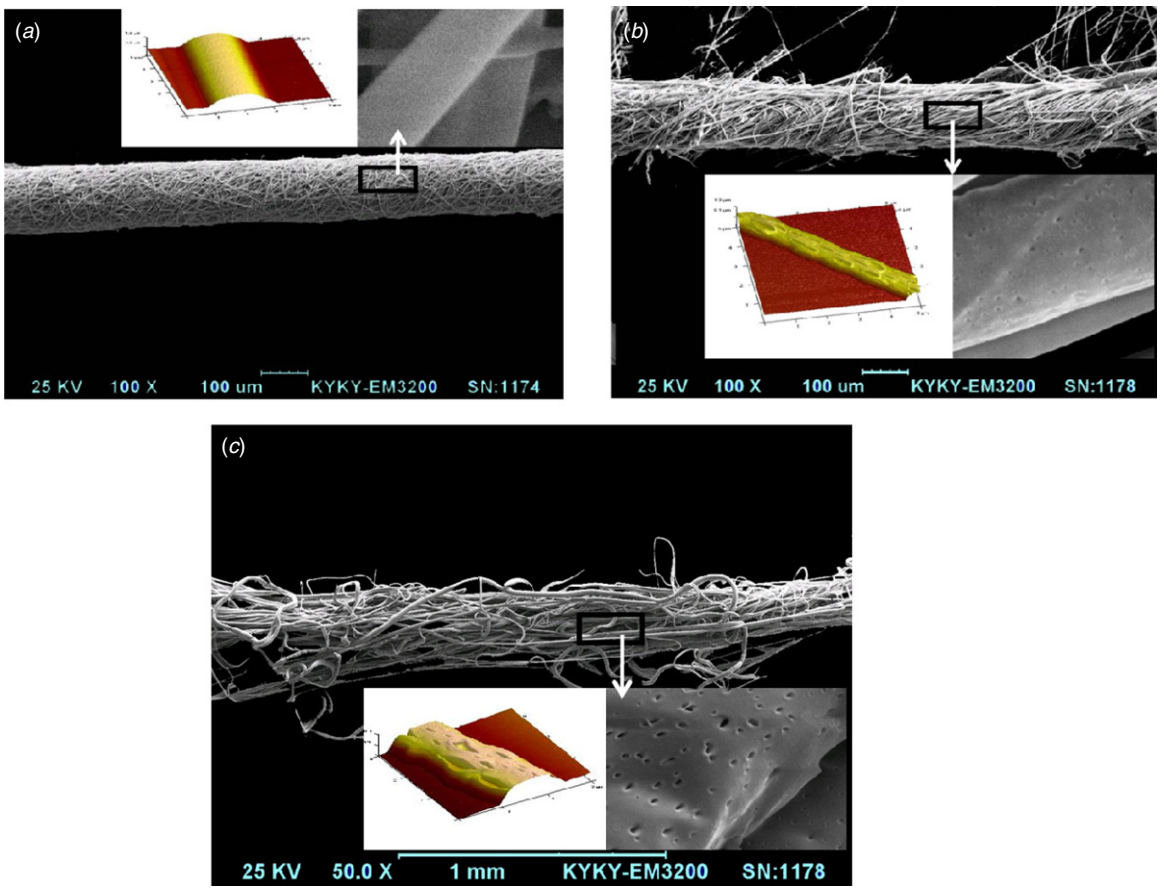

Figure 3. SEM and AFM images of electrospun yarns from PLLA solutions; (*a*) TFE, (*b*) CH_2Cl_2 and (*c*) $CHCl_3$.

Table 4. Thermal transitions of electrospun PLLA fibrous yarns manufactured using different solvents.

Solvent	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})	ΔH_c (J g^{-1})	χ_c[a] (%)
Dichloromethane	60.9	176.4	100.2	43.9	14.4	31.7
Chloroform	62.2	175.9	96.8	48.3	13.9	37.0
TFE	61.5	177.5	95.7	51.6	9.6	46.6

[a] The melting enthalpy ΔH_m of totally crystallized PLLA is 93 (J g^{-1}) [21].

the fibers, a process also observed in previous reported works [12, 23].

3.2. Thermal analysis (DSC)

The DSC curves of electrospun PLLA yarns are shown in figure 4. The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and crystallinity (χ_c) were determined from the DSC thermograms and are given in table 4.

Similar to any semi-crystalline polymer, PLLA has an amorphous phase, with randomly arranged macromolecules, and a crystalline phase with a regular structure. When the polymer solution is electrospun, the jet ejects from the needle tip and polymer chains are stretched in the direction of the electrostatic field (along the fiber direction). The solvent starts evaporating within a very short time scale [12].

It is noticeable that the melting temperature for the electrospun PLLA fibrous yarns did not change significantly, which indicates that the solvent vapor pressure has no pronounced influence. When using a solvent with high vapor pressure like CH_2Cl_2, the time for crystals to grow is not sufficient, and the electrospun fibers exhibited a lower crystallinity (31.53%). In contrast, solvents with a lower evaporation rate such as TFE allow more time for the crystals to grow and facilitate the development of a relatively high crystalline structure. As a result, the electrospun TFE yarns exhibited a higher crystallinity of 46.3% (see table 4).

3.3. Mechanical properties of electrospun yarns

In table 5 the mechanical properties of the fabricated electrospun PLLA yarns are presented. It can be seen that the solvent type influenced the mechanical properties as elongation at break, modulus and the strength of the yarns. It is well known that electrospinning provides non-oriented deposition and, therefore, exhibit poor mechanical properties, namely, the strength and modulus [24]. This study clearly shows that the modulus and tensile strength are much higher for the electrospun yarns made from TFE compared to those spun using the other solvents (table 5). The results may be due to the difference in surface morphologies as well as in

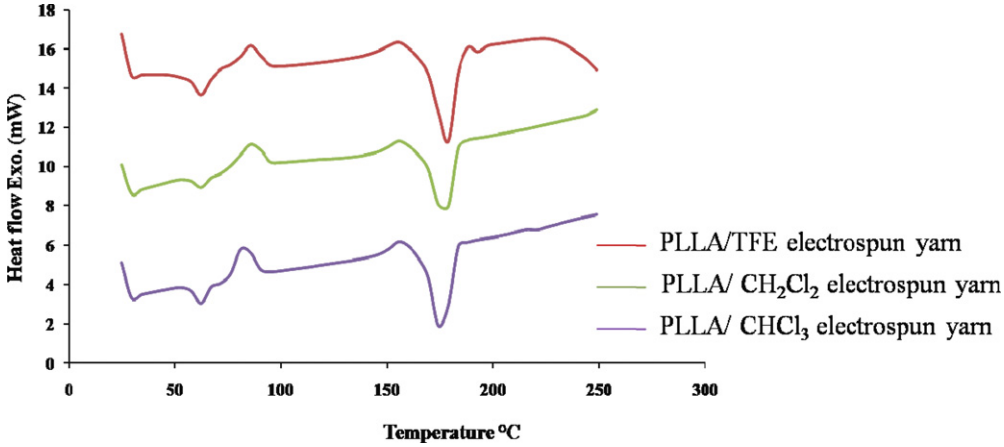

Figure 4. DSC curves of electrospun fibrous yarns obtained from different PLLA solutions.

Table 5. Mechanical properties of electrospun PLLA yarns from different polymer solvent systems.

	Linear mass density	Stress at break		Strain at break		Modulus[a]	
Sample	Tex	MPa	S. D.	%	S. D.	MPa	S. D.
Chloroform	15.00	2.34	0.53	27	14	26.8	8.6
Dichloromethane	18.75	9.30	2.64	47	11	140	69
TFE	8.75	48.29	7.56	153	31	598	57

[a] The modulus was calculated from data in between 2 and 5% strain.

crystallinity, which can both affect the mechanical properties of the yarns [14].

The results showed that the modulus and tensile strength of the yarns decreased at increasing average fiber diameters, which can be attributed to the higher molecular orientation in thinner fibers. Similar results were observed by other researchers [12, 25]. In addition, fibers with a smaller diameter have a higher surface area to volume ratio. The larger contact area between fibers in the yarn results in higher yarn strength [4, 25, 26]. Thus the mechanical properties of the electrospun fibers are relatively dependent on the solvent vapor pressure, which has a large effect on the final morphology and diameter of the electrospun fibers and yarns [27].

In addition, an increase in crystallinity and crystal orientation are other important factors to be considered when analyzing the yarns' mechanical properties. It can be expected that a higher crystallinity will lead to a higher modulus. Furthermore, the crystallinity of the electrospun fibers is influenced by the rate of evaporation of the solvent during electrospinning. Thus, the electrospun PLLA yarns that are produced from polymer solutions using solvent with a low evaporation rate like TFE have a higher degree of molecular orientation and crystallinity, and consequently a larger strain at break (table 5).

4. Conclusion

In the present study, the effects of solvent type on the morphology, diameter, crystallinity and mechanical properties of electrospun PLLA yarns were investigated. The data revealed that the vapor pressure of the solvent is a vital factor, which affects the fiber morphology, diameter and crystallinity and consequently influences also the mechanical properties of the yarns prepared from the fibers. Solvents with a low vapor pressure like TFE allowed enough time for crystals to grow during fiber formation resulting in a high crystallinity. Moreover the average diameters fibers are smaller and provide more uniform yarns. The tensile strength and modulus of yarns produced from these fibers have higher tensile strength and modulus then yarns produced from fibers electrospun from PLLA-dichloromethane or chloroform solutions.

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