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Coaxial Electrospinning of Miscible PLLA-Core and PDLLA-Shell Solutions and Indirect Visualisation of the Core-Shell Fibres Obtained

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Abstract
Core-shell fibres of semi-crystalline poly(L-lactic acid) (PLLA) (core) and amorphous poly(D,L-lactic acid) (PDLLA) (shell) were produced through the coaxial electrospinning of two miscible solutions. Due to the poor contrast between the PDLLA and PLLA, the core-shell structure of the resulting fibres could not be elucidated using TEM. An indirect visualisation method was devised consisting of a combination of SEM, selective dissolution, polarimetry and DSC. The method is evaluated here and applied in the investigation of the effect of spin solution concentration and flow rate on the morphology of the resulting fibers.

Key words: *coaxial electrospinning, core-shell, poly(lactic acid).*

Introduction

Coaxial electrospinning is a variation on the traditional needle-based electrospinning process wherein two different solutions are delivered into a compound Taylor cone through a coaxial capillary and are electrospun to form nanofibres with a core-shell structure. The ability to form nanofibrous structures of two materials that may be chemically dissimilar, or where the core material cannot be electrospun on its own, opens the door to many novel applications, including the isolation and/or encapsulation of sensitive components for tissue engineering and drug release applications, improving the biocompatibility of encapsulated materials, and reinforcing the mechanical properties of certain nanofibre materials [1].

In one of the first papers on coaxial electrospinning [2], Sun et al. described the spinning of core-shell fibres with two identical polymers (2 or 3 wt% poly(ethylene oxide), PEO) with different amounts of bromophenol added to the core and shell solutions in order to gain optical contrast. Aside from this, most subsequent papers on coaxial electrospinning have made use of a chemically dissimilar core and shell materials and transmission electron microscopy (TEM) was primarily used as the method of analysis, with the chemical dissimilarity of the materials generally leading to sufficient contrast between the fibre core and shell [2-10].

Although it might not be obvious at first glance, core-shell fibres with a chemically similar core and shell materials can also be desirable for certain applications. A single polymer composite (SPC), as the name suggests, is a type of composite material wherein the matrix and reinforcing fibres are made from chemically similar materials [11 - 13]. In structural composite applications, chemical similarity between the fibre and matrix leads to enhanced fibre-matrix adhesion and thereby to improved mechanical properties. In biomedical applications, fibre reinforced SPC's made from biodegradable polymers, such as poly(lactic acid) are fully bioabsorbable and can potentially be used to form novel tissue engineering scaffolds and/or drug release materials [13].

The coaxial electrospinning of chemically similar materials can be expected to present its own challenges. Problems may arise from the miscibility of the core and shell solutions, while additional challenges may be encountered in the characterisation of the fibres obtained. Differing opinions on the issue of core and shell solution miscibility can be found in literature. On the one hand, Li and Xia [5] demonstrated through various experiments that mixing occurred when spinning with miscible solutions and that core-shell fibres could only be obtained when spinning with an immiscible core and shell solutions. On the other hand, several other studies have shown that core-shell fibres could be obtained when using a miscible or identical core and shell solvents [2, 4, 7, 8, 10]. A recent study in our own group also showed that solution miscibility was actually a requirement for successful coaxial electrospinning of core-shell fibres containing a thermochromic dye composite [14].

The possible challenges associated with the characterisation of single polymer core-shell fibres stem from the chemical

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similarity between the core and shell materials, which leads to poor or no contrast under TEM. This renders the primary method of examination of core-shell nanofibres unusable, while leaving no clear alternative. The addition of contrast enhancing additives can be attempted, but this frequently has significant unwanted effects on the spin solution properties like electrical conductivity, solution viscosity and/or surface tension. This, in turn, can have a marked impact on the morphology of the resulting fibres, thereby rendering the results unsuitable for investigation, in isolation, of the influence of specific process parameters like solution concentration and flow rate.

In the work presented here, core-shell fibres of semi-crystalline poly(L-lactic acid) (core) and amorphous poly(D,L-lactic acid) (shell) were produced through the coaxial electrospinning of two miscible solutions. The core-shell structure of the resulting fibres could not be elucidated using TEM due to the lack of contrast between the two chemically similar materials. In an attempt to overcome this obstacle, an indirect 'visualisation' method similar to that of Wang *et al* [15] was devised, consisting of a combination of SEM, selective dissolution, polarimetry and DSC. The evaluation of this method is reported here. In addition, the efficacy of the method is evaluated for further investigation of the effect of process parameters, such as spin solution concentrations and flow rates, on the morphology of the resulting fibres.

Experimental

Materials

Poly(L-lactic acid) $M_w = 2.91 \times 10^5$ g/mol) and poly(D,L-lactic acid) $M_w = 2.65 \times 10^5$ g/mol) were obtained from Purac Biomaterials (Netherlands). The polymers were dissolved in a 70/30 (v/v) mixture of dichloromethane (DCM) and dimethylformamide (DMF). DCM and DMF were obtained from Sigma-Aldrich, South Africa and used as received. The polymers were first dissolved in DCM at room temperature. DMF was added to decrease the volatility of the solutions and prevent possible precipitation of the polymer out of the solution, which could cause blockage of the capillary orifices. Analytical grade ethyl acetate and chloroform were obtained from Saarchem/Merck, South Africa and used as received.

Electrospinning

Coaxial electrospinning was performed using a custom-made concentric capillary-in-capillary spinneret. The blunt tip of the stainless steel core capillary (inner diameter: 0.5 mm, outer diameter: 0.8 mm) was retracted approximately 0.5 m into the polypropylene shell capillary orifice (inner diameter: 1.2 mm). The coaxial electrospinning setup used to prepare PLLA-PDLLA core-shell fibres is presented in ***Figure 1***.

The concentration of the PLLA core solution was varied between 4, 6 and 8 wt% and its flow rate between 0.1, 0.2 and 0.3 ml/h. The concentration of the PDLLA shell solution was varied between 10 and 12 wt%, and its flow rate between 1.2 and 1.4 ml/h.

The temperature and humidity in the spinning chamber were maintained in the ranges of 20 - 25 °C and 40 - 50% RH. Fibres were spun at an applied voltage of 15.5 kV DC over a spinning distance of 15 cm.

The fibres obtained were converted into aligned fibre bundle yarns using the method of Smit and Sanderson [16]. Fibres were electrospun onto a rotating wire drum collector (diameter: 10 cm, width: 18 cm, wire spacing: 1 cm) at a linear speed of 1.23 m/s. Samples were formed by electrospinning onto the collector for exactly 20 min, with three repeats per experiment. The resulting mats of aligned fibres were taken off the collector, rolled up in the cross direction and twisted (1.5 twist/cm) to form short yarn samples (± 30 cm long). The yarn samples were then placed in a vacuum oven at 25 °C for 2 h and later stored in a dessicator until further analysis was carried out.

Indirect visualisation method

Overview

As stated in the introduction, the lack of contrast under TEM between the PLLA cores and PDLLA shells necessitated the development of a method to indirectly visualise the core-shell structure of the fibres. The method described here (illustrated in ***Figure 2***) exploits the fact that amorphous PDLLA is soluble in ethyl acetate, while semi-crystalline PLLA is not. This difference in solubility allowed the selective dissolution of the fibre shells while leaving the fibre cores intact. SEM could then be used to measure the diameters of complete core-shell fibres before the selective dissolution step, as well as those of the remaining fibre cores after the selective dissolution step. Furthermore the PLLA used to form the fibre cores is a semi-crystalline solid, optically active in solution, while the PDLLA used

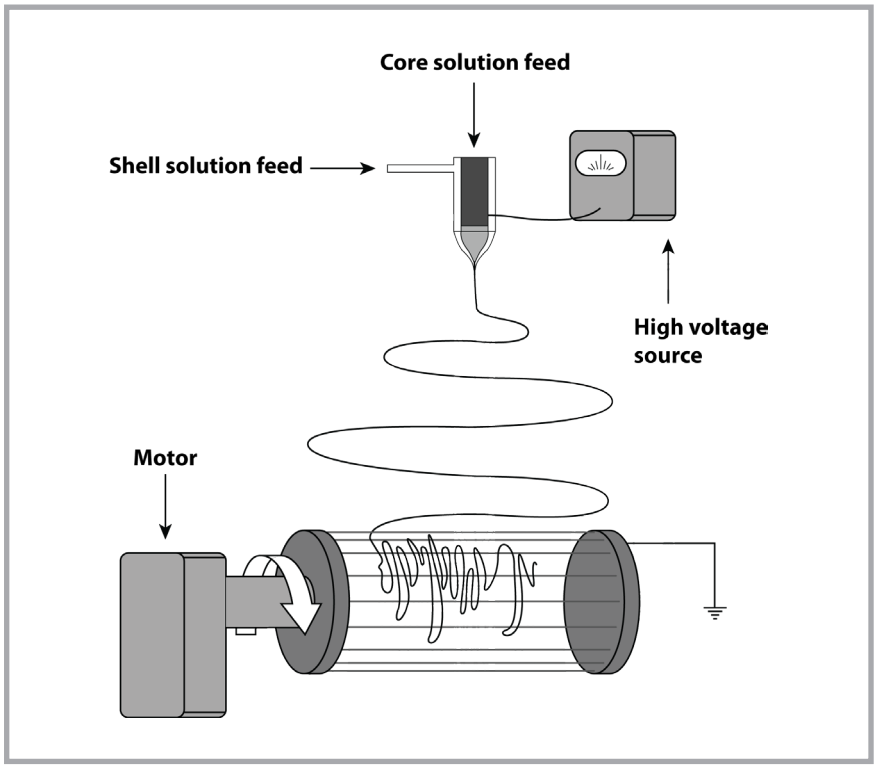

Figure 1. *Coaxial electrospinning setup used to prepare PLLA-PDLLA core-shell fibres.*

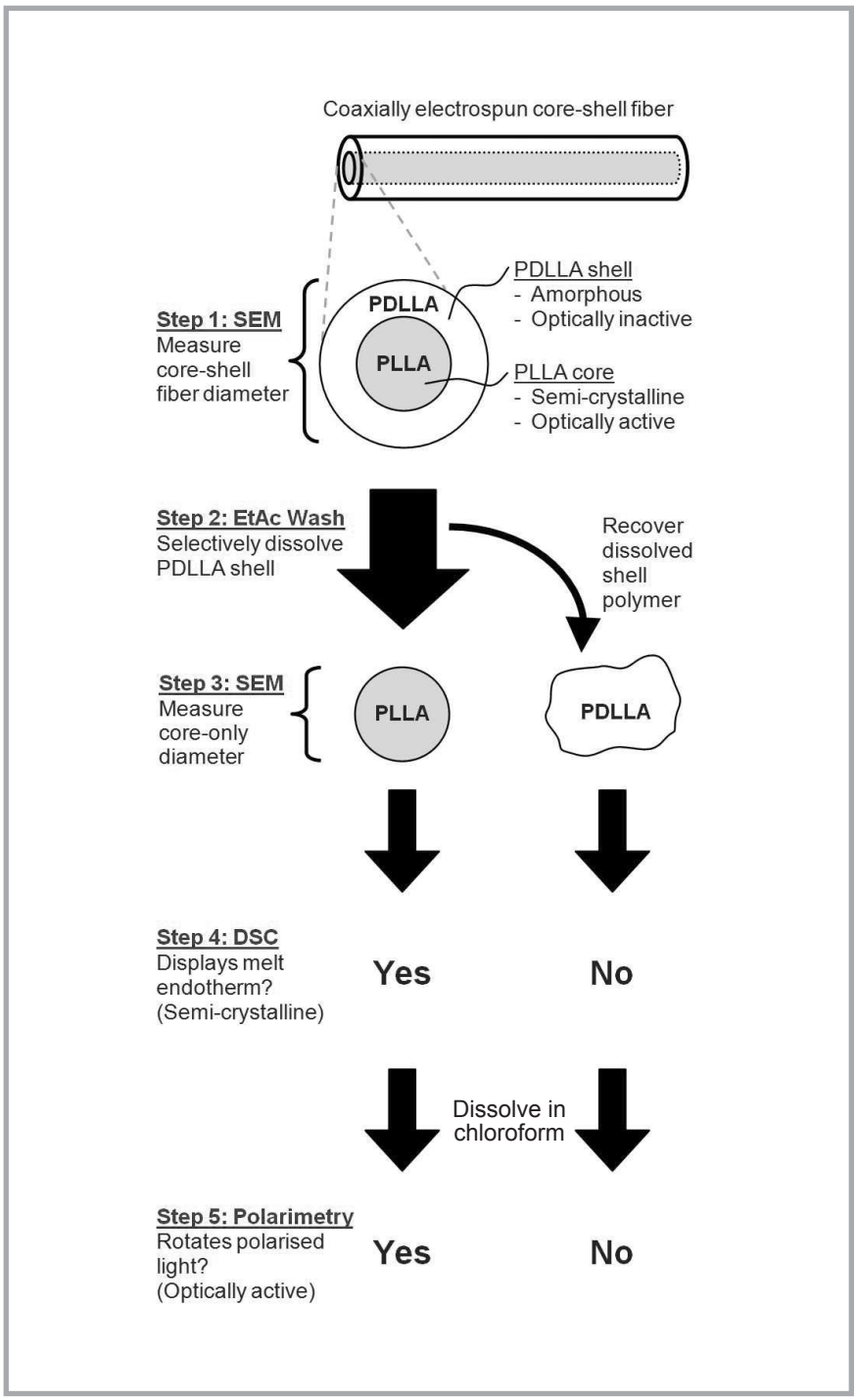

Figure 2. *Flow diagram of an indirect method of visualisation of the core-shell structure of fibres with chemically similar PLLA cores and PDLLA shells.*

to form the shells is an amorphous solid, also optically inactive in solution. The core-shell structure of the fibres could therefore be re-confirmed by demonstrating that the selectively dissolved shell material was the PDLLA, and by showing that the dissolved polymer (after re-precipitation) showed no melt endotherm in DSC nor optical activity in the polarimeter. Similarly it could be shown that the fibre core polymer remaining after the selective dissolution step was the PLLA, which was confirmed by a melt endotherm observed in DSC, and that the polymer (dissolved in chloroform) displayed optical activity in the polarimeter.

Shell removal

Twisted yarns of aligned core-shell fibres were secured, at either end, in a C-shaped clamping device (yarn holder) that simultaneously allowed for good circulation of ethyl acetate around the yarn, whilst maintaining the yarn under mild tension. The yarn holders were immersed into glass poly-tops filled with ethyl acetate. The poly-tops were then subjected to two steps to dissolve the PDLLA shell: Step 1 - a slow rocking action at room temperature for 2 h, and Step 2 - replacing the initial ethyl acetate with clean ethyl acetate, followed by sonication for 30 min in an ultra-sonic bath (50 Hz). Steps 1 and 2 were repeated three times. The yarns before and after washing as well as the ethyl acetate wash solutions were placed in a vacuum oven (25 °C, 0.10 MPa) overnight to evaporate the ethyl acetate. The dried polymer samples were stored in a dessicator prior to analysis.

Analysis

SEM

The gold sputter coated as-spun core-shell fibre yarns were imaged using a Leo® 1430VP SEM. Average fibre diameters were determined from analysis of the SEM images with custom image analysis software (SEM Image Studio). Three images per sample were captured at various locations on the yarns and approximately 100 fibre diameter measurements were taken per image.

DSC

Thermal transitions were measured using DSC (TA Instruments Q100) in a nitrogen atmosphere. 5 - 10 mg samples were sealed in aluminium pans for the measurements. The samples were heated from 10 °C to 200 °C at a rate of 10 °C/min, held at 200 °C for 1 min, and cooled at the same rate to 10 °C. This cycle was repeated twice. The percentage crystallinity was determined using TA Universal Analysis software by calculating the area under the melt endotherm of the thermogram, using 93.7 J/g as the heat of fusion for theoretically 100% crystalline PLLA material.

Optical rotation

Optical rotation measurements, using a polarimeter (Bellingham & Stanley Ltd ADP 220), were performed on the separated fibre components (the remaining fibres on the yarn holders and the polymer extract recovered from ethyl acetate) after dissolving the polymers in chloroform. The average of three optical rotation measurements was taken for each separated component from each yarn sample. A 100 mm sample tube was used, and measurements were recorded at room temperature at a nominal wavelength of 589 nm. The specific optical rotation was

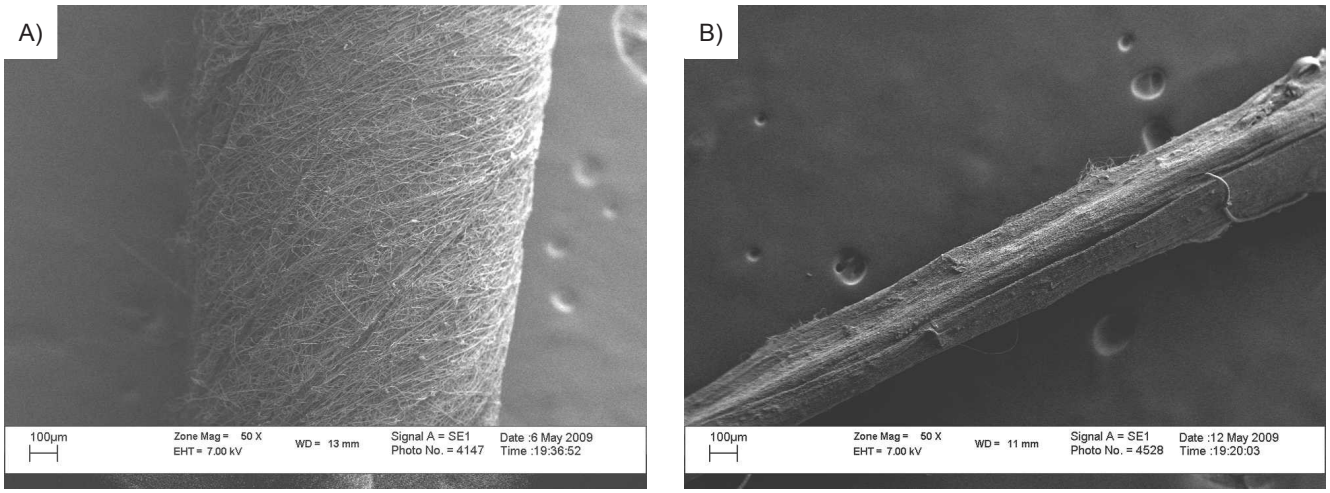

Figure 3. *SEM image of yarn of electrospun PLLA-core/PDLLA-shell fibres before (A) and after (B) washing with ethyl acetate. Scale bar = 100 µm.*

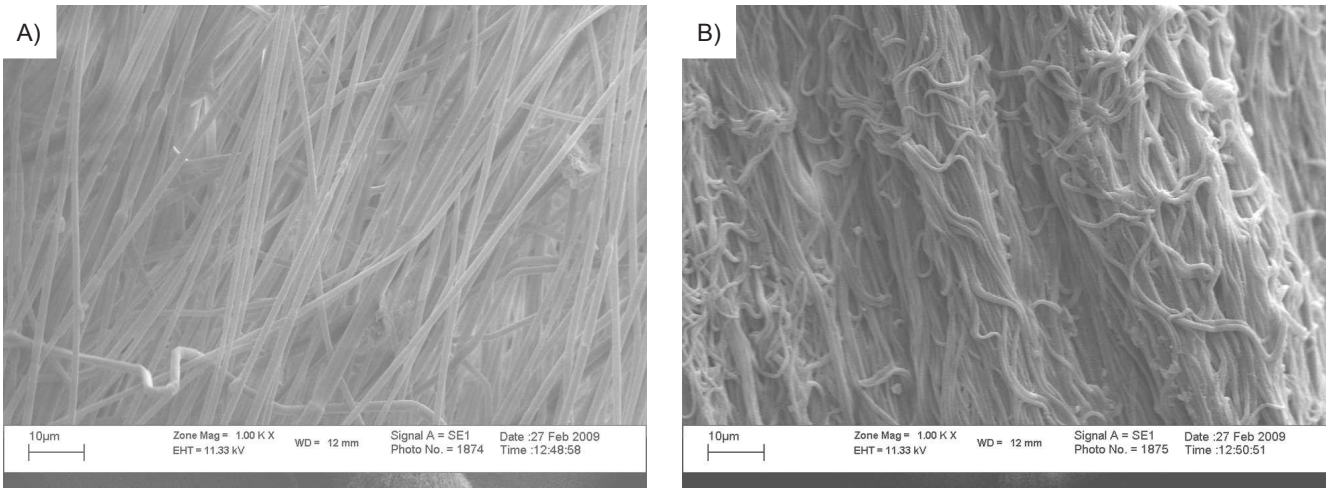

Figure 4. *SEM image of electrospun PLLA-core/PDLLA-shell fibres before (A) and after (B) washing with ethyl acetate. Scale bar = 10 µm.*

normalised by dividing the degree of rotation measured by the product of the sample tube length and the concentration of the polymer in chloroform.

Parameter study

The efficacy of the indirect visualisation method was evaluated through investigation of the effect of solution concentration and flow rate on the morphology of the resulting core-shell fibres. The parameter sets investigated are shown in ***Table 1***. In Experiment A1 - 6, core and shell polymer solution concentrations were varied, while flow rates were kept constant. In Experiment B7 - 12, polymer solution concentrations were kept constant, while flow rates were varied.

Alternative mathematical approach

As an alternative to measuring the core-shell and core-only diameters under SEM, one could use the weights of the separated core and shell polymers to mathematically estimate the ratio of the core diameter to the total fibre diameter using the formula:

$$\frac{r_{core}}{r_{total}} = \sqrt{\frac{\left(\frac{m_{core}}{\rho_{PLLA}}\right)}{\left(\frac{m_{shell}}{\rho_{PDLLA}} + \frac{m_{core}}{\rho_{PLLA}}\right)}} \qquad (1)$$

where

r_{core} - radius of the fibre core (i.e after the ethyl acetate wash)

r_{total} - radius of the core-shell fibre (i.e. before the ethyl acetate wash)

m_{core} - dry mass of the core polymer left after the ethyl acetate wash

m_{shell} - dry mass of the shell polymer recovered after the ethyl acetate wash

ρ_{PLLA} - density of PLLA in the core

ρ_{PDLLA} - density of PDLLA in the shell

This approach does, however, depend on the assumption that the core-shell fibres obtained are perfectly cylindrical and co-axial, and that the fibre core is continuous

Table 1. *Coaxial electrospinning process parameter sets evaluated for testing the efficacy of the indirect visualisation method.*

Experiment #	Conc., wt%		Flow rate, ml/h	
	Core	Shell	Core	Shell
A1	**4%**	**10%**	0.3	1.2
A2	**6%**			
A3	**8%**			
A4	**4%**	**12%**		
A5	**6%**			
A6	**8%**			
B7	8%	10%	**0.1**	**1.2**
B8			**0.2**	
B9			**0.3**	
B10			**0.1**	**1.4**
B11			**0.2**	
B12			**0.3**	

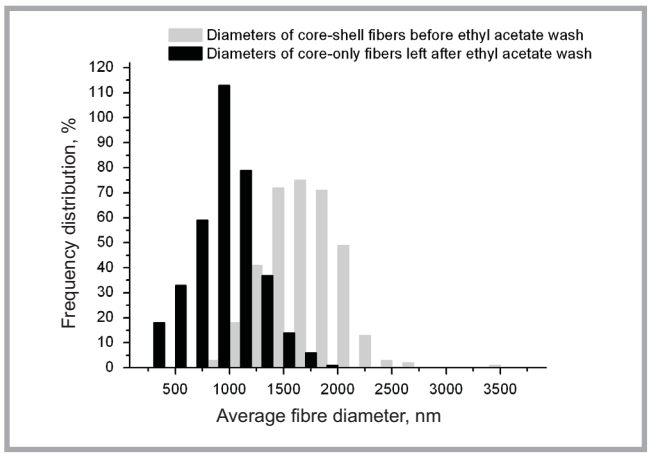

Figure 5. *Histogram illustrating the average diameter of the as-spun fibres before and the residual fibres after washing with ethyl acetate.*

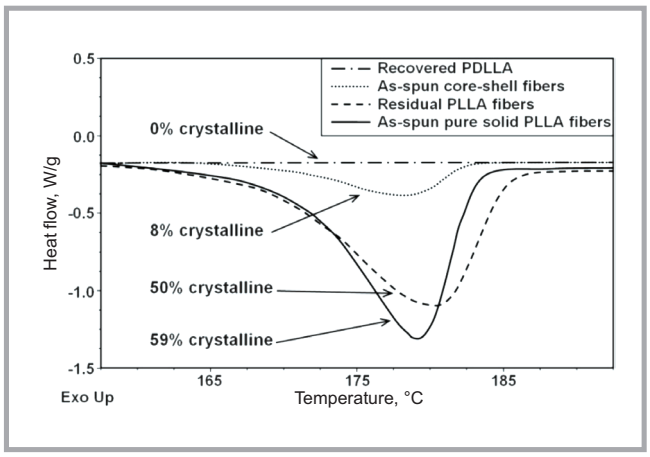

Figure 6. *DSC thermograms showing the degrees of crystallinity of the as-spun PLLA-core/PDLLA-shell fibres, the shell polymer and residual core polymer recovered, as well as pure PLLA-only fibres.*

along the entire length of the fibre. The derivation of this formula and its evaluation from experimental data are given in the Supplementary Material. The r_{core}:r_{total} ratios obtained through SEM measurements and the ratios calculated using ***Equation 1*** differed significantly and did not appear to follow clear trends. The differences between the measured and calculated ratios could possibly be ascribed to deviations in the actual fibre morphology from the idealised core-shell fibre morphology, upon which the calculated values were based. For these reasons, this approach was not followed here.

Results and discussion

The indirect visualisation method was first evaluated using core-shell fibres prepared by coaxial electrospinning 8 wt% PLLA-core and 10 wt% PDLLA-shell solutions at core and shell flow rates of 0.3 and 1.2 ml/h, respectively. Ten yarn samples were prepared using identical process parameters.

SEM

The diameters of the yarns showed a pronounced decrease after the ethyl acetate wash (***Figure 3.A*** and ***3.B***). Yarns of continuous fibres (***Figure 4.B***) remained on the yarn holders after the wash, and on evaporation of the ethyl acetate, a polymer film was recovered from the washing solvent. Fibres in the yarns remaining on the yarn holders after the ethyl acetate wash appeared crimped or curled (***Figure 4.B***), compared to the smooth uniform as-spun fibres (***Figure 4.A***), and the average fibre diameter had decreased by approximately 44%. A histogram illustrating fibre diameter distributions before and after washing the yarns in ethyl acetate is shown in ***Figure 5***.

DSC

Thermal analysis strongly supported the hypothesis that the as-spun fibres consisted of semi-crystalline PLLA cores surrounded by amorphous PDLLA shells. DSC thermograms were obtained for the as-spun fibres, the polymer recovered from the wash solvent, and for the residual fibres that remained on the yarn holders after the ethyl acetate wash (***Figure 6***).

The polymer recovered from the ethyl acetate wash solution did not show any melt endotherm (i.e. 0% crystallinity) and displayed only a glass transition at ± 40 °C (not shown). The residual fibres remaining on the yarn holders after the ethyl acetate wash exhibited a sharp melt endotherm with a melt temperature maximum of ± 179 °C and an average of 50% crystallinity. The thermogram of the as-spun (core-shell) fibres exhibited intermediate characteristics, with a melt endotherm with a melt temperature maximum of ± 177 °C and an average of 8% crystallinity, in line with what would be expected of fibres consisting of a phase-separate combination of amorphous PDLLA and semi-crystalline PLLA. For reference, the DSC of as-spun pure PLLA fibres was recorded and included in the thermogram in Figure 5. The fibres exhibited a sharp melt endotherm with a melt temperature maximum of ± 178 °C and an average of 59% crystallinity. Although PLLA does not dissolve in ethyl acetate, the semi-crystalline nature of the polymer implies that it contains amorphous regions that could be susceptible to some absorption and swelling in the presence of solvent, which could lead to a slightly lower degree of crystallinity observed for the residual fibre cores (50%) compared to untreated pure as-spun PLLA fibres (***Figure 6***).

Polarimetry

When the polymer of residual fibres remaining on the yarn holders after washing in ethyl acetate was dissolved in chloroform, all samples exhibited optical rotation with an average rotation of -208.4°. The specific optical rotation [α] for PLLA has been reported to be between -150 and -160° [16, 17]. The reason for the higher optical rotation values was not investigated in greater detail here. The polymer recovered from the ethyl acetate wash solution did not exhibit any optical rotation. These observations served as further supporting evidence that the coaxially electrospun fibres consisted of PLLA cores and PDLLA shells.

Parameter study

The indirect visualisation method described above was used to evaluate the effect of the spin solution concentration and flow rate on the diameters of the as-spun core-shell fibres, as well as those of the fibre cores (measured after selective dissolution of the shell polymer). The solution concentrations and flow rates were varied as given in ***Table 1***. The mean diameters of the core-shell and core-only fibres obtained are depicted in ***Figure 7*** as a function of the solution concentration, and in ***Figure 8*** as a function of the solution flow rate. Error bars indicate the standard deviation.

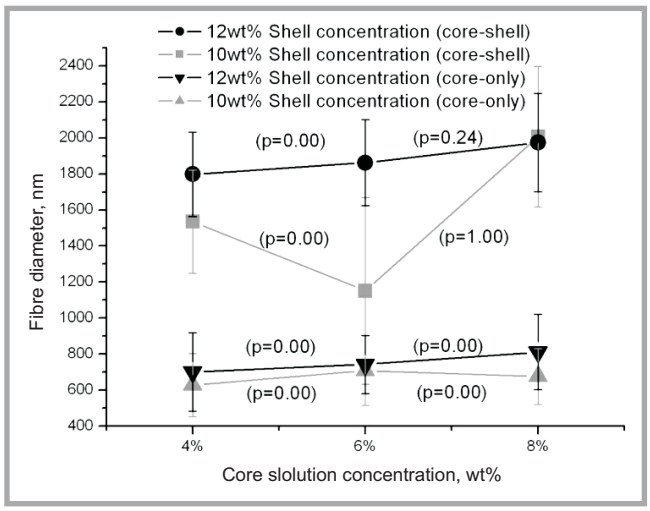

Figure 7. *Effect of core and shell spin solution concentration on fibre diameters before and after washing in ethyl acetate. Bonferroni test values for a significant difference between two parameter sets are give in brackets on each line ($p < 0.05$ – statistically significant difference, $p \geq 0.05$ – statistically insignificant difference).*

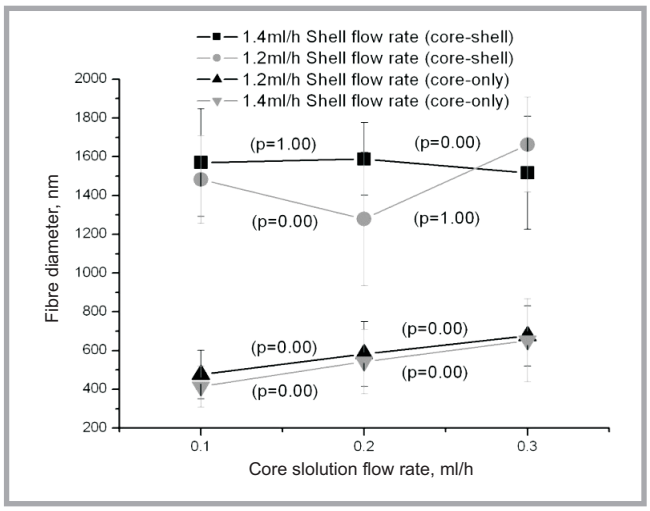

Figure 8. *Effect of the core and shell spin solution flow rate on fibre diameters before and after washing in ethyl acetate. Bonferroni test values for a significant difference between two parameter sets are give in brackets on each line ($p < 0.05$ – statistically significant difference, $p \geq 0.05$ – statistically insignificant difference).*

The relatively large standard deviations of the diameter values necessitated testing of the significance of the differences in mean diameter values obtained for different input parameters. The Bonferroni test was used in order to minimise the probability of type 1 errors (i.e. false positive) when testing the statistical significance of multiple differing mean values within each group. The Bonferroni test values (p) between specific points in each series are indicated in brackets in ***Figures 7*** and ***8*** on each line connecting two specific parameter sets. A p-value < 0.05 indicates a statistically significant difference, while a p-value ≥ 0.05 indicates a statistically insignificant difference.

Careful inspection of the two figures shows that the core-only diameters showed small, but statistically significant, increases when either the core solution concentration (when shell solution concentration was 12 wt%) or the core solution flow rate was increased (shell flow rate 1.2 and 1.4 ml/h). The change in core-shell fibre diameters did not follow such linear dependencies, as reported in the work by Wang *et al* [15]. Such increasing trends might be expected, since increasing the solution concentration or flow rate should theoretically result in more material being pumped into the core of the fibre, thereby resulting in an increased core-only diameter. Following the same line of reasoning, one might also expect the total core-shell diameter to increase with increases in the core solution concentration or flow rate, or that total the core-shell diameter would necessarily be higher at greater shell flow rates. However, it is clear from the figures that these parameters do not follow trends with such simple rules. The fact that core-shell and core-only fibre diameters do not follow predictable trends (linear or otherwise) leads us to believe that there are other process variables that also have a significant influence on the morphology of the fibres obtained; however, these were not included in this investigation. From electrospinning fundamentals these variables could include parameters such as the spin solution surface tension or interfacial tension, electrical conductivity, and spin solution rheology (e.g. shear thinning behaviour). Investigation of the influence of these parameters fell outside the scope of this study but will be explored in future work.

Conclusion

It was demonstrated here that core-shell fibres with semi-crystalline PLLA cores and amorphous PDLLA shells could be made through the coaxial electrospinning of miscible solutions. Although direct visualisation of the core-shell structure using TEM was not possible, an indirect visualisation method was devised, which could be used to investigate the influence of electrospinning process parameters on the core-shell and core-only diameters of the fibres obtained. It was found that these diameters were significantly affected by the spin solution concentration and flow rate and that other parameters, not investigated here, also played a role in the diameters of the fibres finally obtained.

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