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Single Polymer Composite Yarns and Films Prepared from Heat Bondable Poly(lactic acid) Core-shell Fibres with Submicron Fibre Diameters

Abstract
Mats of core-shell fibres of semi-crystalline poly(L-lactic acid) (core) and amorphous poly(D,L-lactic acid) (shell) produced through coaxial electrospinning were used to prepare fibre reinforced single polymer composite yarns and films. The internal molecular arrangement (fine structure) within the fibres and the potential to enhance the crystallinity of the core and heat-bond neighbouring fibres within the thermal operating window, between where the shell components fused and the melting point of the core components, were investigated. Thermal treatments were shown to increase the crystallinity and mechanical strength of the composite yarns.

Key words: *coaxial electrospinning, single polymer composites, core-shell fibres, PLLA, PDLLA.*

Introduction

Poly(lactic acid)/PLA is a commercially available biodegradable polymer with favourable mechanical properties [1, 2]. Heat-bondable PLA core-shell fibre technology can be found in patent literature whereby the overlapping fibre-shells can be fused at a temperature significantly lower than the melting temperature of fibre-cores [3]. This technology, however, has not been extended to include fibres with miniature diameters.

Coaxial electrospinning [4, 5] is a popular electrostatic fibre-spinning method that allows the combination of two or more materials into core-shell fibres with nano- to micro-diameters. Fibres with smaller diameters offer a significant advantage over larger counterparts as a result of the superior properties attainable from materials that have a higher surface-area to volume [6, 7]. Electrospun fibres (as-spun) are typically low in crystallinity [8 - 11] and only on annealing [10] and other post treatments do they possess the practical strength required for application.

Single polymer composites (SPCs) [8, 12, 13], composed of a single polymer, offer a biodegradable alternative to traditional heterogeneous fibre-reinforced composites. SPCs offer the advantage of physical and chemical compatibility between fibre and matrix components, enhancing matrix-fibre interfacial bonding [8, 12].

The motivation behind this work is the development of a versatile method of uniformly dispersing arrays of nanofibres within a matrix material to create biodegradable materials that resemble single polymer fibre-reinforced composites (SPFRCs). In the true sense of the definition the composites formed in this work are not true SPCs, because although the polymers used are both poly(lactic acid), and are chemically the same, they differ in stereo regularity (due to the monomer stereoisomerism). Poly(L-lactic acid) or PLLA is a polymer made of only L-lactic acid monomers which are ordered regularly along the polymer chain to allow chain folding into crystalline domains. Poly(D,L-lactic acid) or PDLLA is a polymer made of L-lactic acid and D-lactic acid monomers randomly alternating along the polymer chain which do not allow the formation of crystalline domains. The use of these poly(lactic acid) polymers allow many practical benefits of SPCs e.g. same mechanism of biodegradation and enhanced compatibility between components. A strong case could be brought forward to extend the definition of SPCs to include composites produced from these materials. The composite materials described in this work are practically SPCs and have been referred to as such in this work. These composites may include fused fibre webs, yarns and films. These materials have potential in medical applications e.g. self-reinforced suture yarns whereby wound healing drugs could be included in the matrix material and could be released on degradation while the cores reinforce the yarn until tissue cells regenerate and replace the suture. SPFRC films have potential in packing applications.

In this study Poly(L-lactic acid)-core/poly(D,L-lactic acid)-shell fibres prepared by coaxial electrospinning were twisted into yarns or folded into plied mats and isothermally crystallised, while under tension and pressure respectively. The internal molecular arrangement (fine structure) within the fibres and the potential to enhance the crystallinity of the core and heat-bond neighbouring fibres within the thermal operating window were investigated.

Experimental

Materials

Poly(L-lactic acid)/PLLA (PL24, Mw 291 kDa) and Poly(D,L-lactic acid)/PDLLA (PDL20, Mw 265 kDa) were purchased from Purac Biomaterials (Netherlands). PLA solutions were prepared with 70/30 (v/v) dichloromethane (DCM)/N,N-dimethylformamide (DMF).

Coaxial electrospinning

PLLA-core/PDLLA-shell fibres were electrospun into fibre mats using a home made capillary-in-capillary spinneret (dimensions: shell id 1.2 mm, core id/od 0.5/0.8 mm) and coaxial electrospinning set-up. The core capillary was retracted 0.5 mm from the shell capillary orifice. The coaxial electrospinning parameters [4] used are shown in *Table 1*. Fibre mats were deposited on a grounded rotating wire drum collector after 20 mins of spinning.

Table 1. *Coaxial electrospinning parameters.*

Designation	Polymer solutions (solvent ratio)	Solution concentration, wt%	Flow rate, ml/h	Applied voltage, kV	Distance, cm	Collector speed, m/s	Temp. & relative humidity
Core	PLLA (70/30 DCM/DMF)	8	0.3	15.5	15	1.23	20 - 24 °C & 40 - 50% RH
Shell	PDLLA (70/30 DCM/DMF)	10	1.2				

Yarns and films: preparation and annealing

Electrospun fibre mats (20 replicates) were twisted into yarns with 1.5 twists/cm in a mechanical yarn twisting device (ASANO Machine MFG 60, Osaka, Japan) and held taut by clamping. Ten clamped yarns were annealed in a convection oven set at 110 °C for 5 h. The yarns were removed from the oven and allowed to condition in a standardised air-conditioned laboratory (standard temperature: 20 ± 2 °C and relative humidity 65 ± 2%) prior to analysis and mechanical testing. These yarns were referred to as annealed core-shell yarns and the ten that were not treated were referred to as as-spun core-shell yarns. Plied core-shell fibre mats were processed into transparent films by pressing between two metal plates at 110 °C under 10 kN pressure for 30 mins.

Characterisation of fibres, yarns and films

A Leo® 1430VP Scanning Electron Microscope (Central Analytical Facility, Stellenbosch University) and custom image analysis software (SEM Image Studio) were used to analyse fibre diameters and sample morphology.

The crystallinity of the yarns and film were investigated by wide-angle X-ray diffraction (WAXD) with a BRUKER AXS D8 Advance diffractometer. Diffractograms were obtained by scanning between 5 – 35° in Δ2θ increments and 0.01 deg/step. A custom made yarn holder (not shown here) was fabricated to eliminate any background effects from conventional supports i.e. glass slides that give an amorphous halo that overlaps with significant peaks in the diffractograms. Yarns were parallel to the X-ray source.
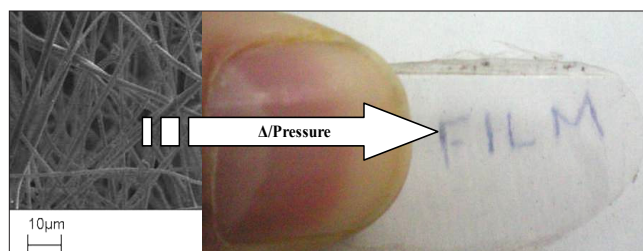
XRD data were correlated with differential scanning calorimetry (DSC) measurements. DSC analysis was conducted using a TA Instruments Q100 differential scanning calorimeter, conducted under nitrogen atmosphere. Samples were heated from 10 to 200 °C at a rate of 10 °C/min, held at 200 °C for 1 min, and cooled at the same rate to 10 °C. The percentage crystallinity was determined using TA Universal Analysis software: by calculating the area under the melt endotherm of the thermogram and using 203.4 J/g as the heat of fusion for a theoretical 100% crystalline PLLA material [14]. The mass ratio of the crystallisable core (PLLA) and amorphous shell (PDLLA) material were taken into account so that the percentage crystallinity was determined using only the mass of PLLA. The mass of the PLLA component was determined as described previously [15].

The mechanical behaviour of the yarns was examined using an INSTRON 4444 with an INSTRON Max 50N Load Cell. Yarn samples were conditioned for 24 hours in a standardised climate controlled laboratory (20 ± 2 °C/65 ± 2% RH) prior to mechanical testing. A 50 mm test length was used. Determination of the single-end breaking force and elongation at break of the yarns was conducted at a constant-rate-of-extension - 50 mm/min and load displacement measurements were made.

The selective dissolution method [15] was used to confirm that all yarns formed had the core-shell fibre structure. The shell components were selectively dissolved with ethyl acetate. The separated cores and shell components were dried and analysed by DSC and re-dissolved in chloroform for optical rotation measurements using a polarimeter (Bellingham & Stanley Ltd ADP 220). Optical rotation measurements were conducted with a 100 mm sample tube and measurements (average of three) were recorded at room temperature (RT) at a nominal wavelength of 589 nm. The specific optical rotation values were normalised.

This method was also used to selectively remove the matrix material of the SPC films to prove that the cores acted as a reinforcing component in the films.

Films were cryo-fractured under cryo conditions (liquid nitrogen -196 °C) and the point of fracture was analysed by SEM.
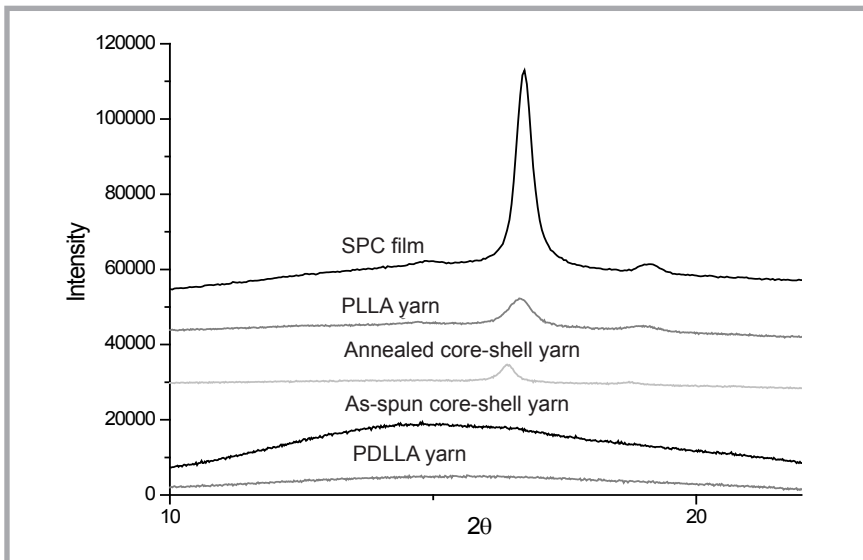
■ Results and discussion

Morphology

The coaxial electrospun yarns, before and after annealing, are shown in *Figure 1*.
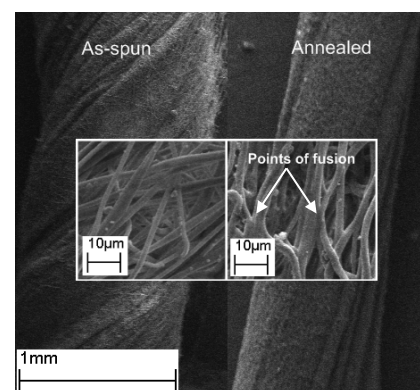
Figure 1. *Coaxial electrospun fibre yarns before (left) and after (right) annealing.*

The average fibre diameter of the yarn before fusion was shown to be 1518 nm. The annealed core-shell yarn showed that fusion occurred for overlapping fibres at the yarn surface. Cross-sections (not shown here) of the yarns showed that the fibres were completely fused in the yarn interior.

Heat-pressing a coaxial electrospun fibre mat (ave. fibre diameter 1518 nm) produced a flat transparent film, as shown in *Figure 2*.

Figure 2. *Coaxial electrospun PDLLA-PLLA mat before heat pressing (left) and the SPC film (right) in front of a piece of paper with the word 'FILM' written on it to show the transparency of the film.*

Figure 3. *X-ray diffractograms comparing the crystalline diffraction intensities of PDLLA, as-spun core-shell, annealed core-shell, and PLLA yarns with the SPC film.*
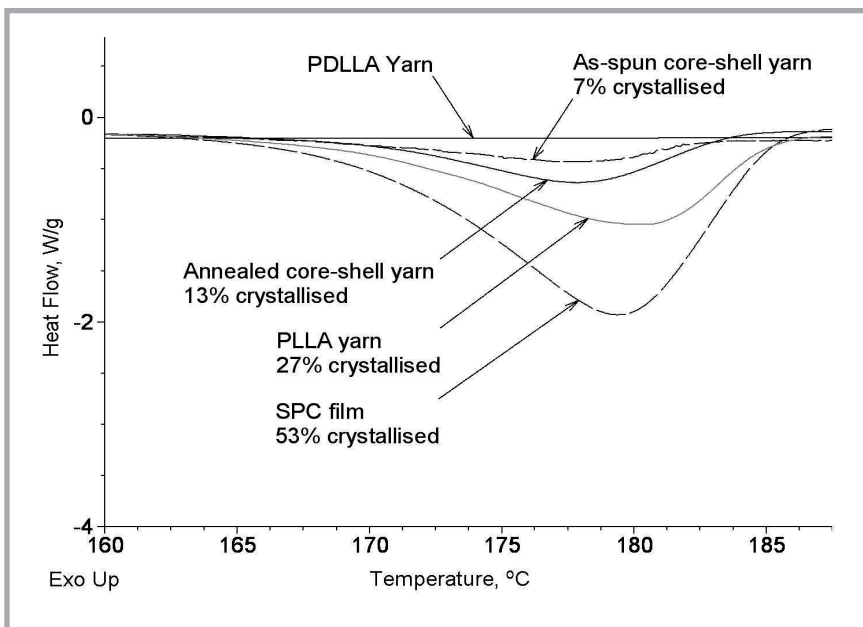
Figure 4. *DSC thermogram comparing the crystalline melting endotherms of PDLLA, as-spun core-shell, annealed core-shell, and PLLA yarns with the SPC film.*

Crystallinity

X-ray diffractograms comparing the crystalline diffraction intensities of PDLLA, as-spun core-shell, annealed core-shell, and PLLA yarns with the SPC film are shown in ***Figure 3***. These data show the influence of annealing and heat pressing on the coaxial electrospun fibres. Anisotropic scattering is shown in the form of a halo, indicative of non-crystalline materials, for the PDLLA and as-spun coaxial electrospun yarn. This halo shows that no extensive crystallisation occurred for these as-spun yarns. A small diffraction peak is present for the PLLA yarn and annealed core-shell yarn in the crystalline phase at a 2θ value of approximately 17°. This indicates that some minimal initial crystallinity does exist for as-spun PLLA and that annealing the core-shell yarn crystallised its PLLA core component to some extent. The SPC film showed the most significant crystallisation with a large diffraction peak (17°).

DSC thermograms comparing the crystalline melting endotherms of PDLLA, as-spun core-shell, annealed core-shell, and PLLA yarns with the SPC film are shown in ***Figure 4***. On heating, through the crystalline melting region of semi-crystalline PLA (160 - 200 °C), the elec- trospun PDLLA yarn showed no melt endotherm, whereas the PLLA yarn was shown to be 27% crystallised. Annealing the coaxial electrospun yarns increased the crystallinity from 7% for the as-spun core-shell yarns to 13%. Heat-pressing plied fibre mats into a film resulted in significantly larger percentage crystallinity (53%). This value is significantly larger than the PLLA yarn (27%) although the mass component of the PLLA in the film is only 44% of that of the pure PLLA yarn. This could be explained by the faster heating rate (10 °C/min) that was used during DSC analysis compared to the conditions (110 °C under 10 kN pressure for 30 mins) used to create the film. These crystallinity values are not purely based on the initial crystallinity values of the samples but were enhanced to some degree as a function of the cold crystallisation and re-crystallisation processes of PLLA on heating in the DSC analysis. However, the fact that thermal treatments resulted in larger crystallinity values for the annealed core-shell yarn and SPC film compared to the as-spun core-shell yarn is indicative of higher initial crystallinity with these samples. This is confirmed by correlation with the XRD data.

Mechanical testing

Stress/strain curves from mechanical tests of the as-spun and annealed yarns are shown in ***Figure 5***. The annealed core-shell yarns showed that the crystallinity induced into the core of the fibres and the fusion of the shell components resulted in an increase in the modulus and breaking strength and decrease in elongation compared with as-spun fibres. Necking (not shown here) was seen for both as-spun and annealed core-shell yarn samples, indicating the ability of the fibres to tolerate a certain amount of force (load) before breaking, which could be attributed to the deformation of the non-crystalline regions and amorphous PDLLA shell material.

Film reinforcement

On selectively dissolving away the PDLLA matrix material from the one hemisphere of the film, fibres remained (***Figure 6***). The fibre diameters of those fibres remaining after the PDLLA was selectively dissolved from the SPC film were shown to be significantly smaller (603 nm ave. fibre diameter) than core-shell fibres before heat-pressing (1518 nm ave. fibre diameter). This is in the same fibre diameter range for the same fibres (yarns with
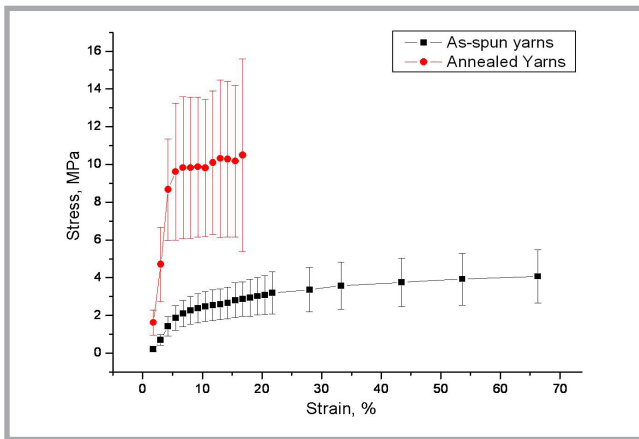
Figure 5. Stress vs. strain curves of as-spun and annealed yarns.
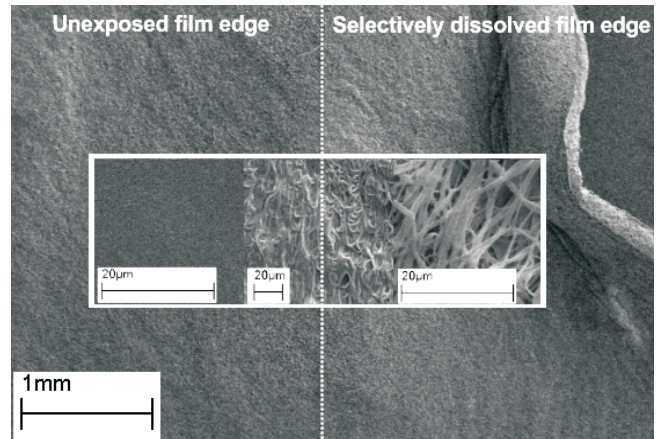
Figure 6. SEM images of a SPC film having had one hemisphere selectively dissolved in ethyl acetate.

fibres spun under the same parameters but not heat-treated) that were subjected to the selective dissolutions method (not shown here).

DSC analysis (not shown here) showed a sharp melt endotherm for the remaining fibres and no melt endotherm for the material selectively removed from the film. The remaining fibres when dissolved in chloroform rotated polarised light, whereas the selectively removed material did not. The remaining fibres and selectively dissolved material were therefore the semi-crystalline PLLA core material and amorphous PDLLA matrix material, respectively.

Cryo fracturing of the films exposed fibrous structures at the point of fracture, which confirms that the cores remained intact as fibrous structures (*Figure 7*). However, the low number of these exposed cores indicates a strong interaction between the core and shell components. The material should theoretically have a low susceptibility to delamination and should display excellent transfer of
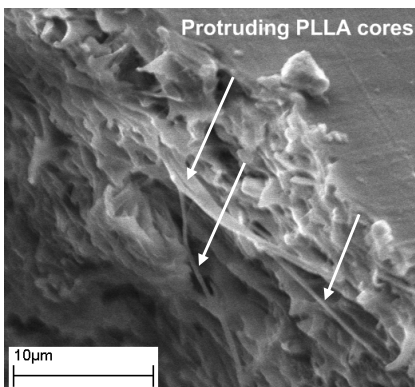

Figure 7. SEM image of SPC film at point of fracture.

stresses from the matrix (PDLLA) to the reinforcing cores (PLLA). The fine fibre diameter of the cores, the chemical similarity and the intimate interaction between core and shell materials may explain the transparency of the films seen in *Figure 2*.

■ Conclusions

It was shown that annealing/heat-pressing the core-shell fibres fuse the shells while enhancing the crystallinity of the cores. It was shown that enhancing the crystallinity is important for mechanical strength but it has also been shown elsewhere that this is important for biodegradability [9, 16]. These core-shell fibres allow for continuous fibre reinforcement of biodegradable materials that resemble SPCs. They offer a simple route to disperse nano-fibres homogeneously in a transparent matrix resin (compared with solvent casting impregnation methods) [17].

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