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PBAT/PLA Nanofibers Prepared via Coaxial Electrospinning: The Effect of Core Feed Rate on the Nanofibers Characteristics

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Abstract

This study investigates the influence of coaxial electrospinning parameters on the morphological and physicochemical properties of nanofibers composed of poly(butylene-co-adipate-co-terephthalate) (PBAT) and polylactic acid (PLA). The nanofibers were systematically characterized using scanning electron microscopy (SEM), Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), and mechanical testing. The findings reveal that the PBAT/PLA nanofibers exhibit a core-shell structure with a co-continuous phase. The electrospinning process was optimized with 10 wt% PLA, 10 wt% PBAT, an applied voltage of 16 kV, and a tip-to-collector distance of 17 cm. The shell feed rate was 0.6 mL/h, while the core feed rate was 0.15 mL/h. It was observed that PBAT demonstrates limited miscibility with PLA under the specific process conditions examined. Furthermore, the core solution feed rate was found to have a substantial impact on the nanofiber properties. Mechanical testing indicated that the core-shell PBAT/PLA nanofibers achieved an ultimate tensile strength of approximately 0.58 MPa, representing an 81% improvement over neat PLA fibers. These outcomes underline the applicability of PBAT/PLA nanofibers in areas where enhanced mechanical performance and structural control are critical.

Keywords: polylactic acid; polybutylene adipate-co-terephthalate; coaxial electrospinning; nanofiber; core feed rate.

1. Introduction

Polylactic acid (PLA), derived from renewable resources, has garnered significant attention due to its biocompatibility, biodegradability, and relatively high tensile strength. However, its glass transition temperature (Tg) of approximately 55-60 $^{\circ}$ C results in a rigid and brittle material under ambient conditions, thus limiting its utility in applications requiring flexibility and ductility [1]. Despite these inherent limitations, PLA continues to attract attention within the research and manufacturing sectors, with recent efforts directed towards optimizing processing methods and broadening its applications in biocomposites and biomedical fields [2-5].

To enhance the functional versatility of PLA, targeted modifications are necessary. Approaches such as ring-opening copolymerization and polymer blending have been employed to improve its mechanical performance, particularly in terms of toughness.

Beside that, poly(butylene-co-adipate-co-terephthalate) (PBAT), polycaprolactone, and poly(butylene succinate) are also widely recognized as biodegradable polymers with distinct physical and mechanical properties, making them suitable candidates for various applications.

PBAT, a copolymer composed of butylene terephthalate and butylene adipate, exhibits a glass transition temperature (Tg) of approximately -30 °C, resulting in significant ductility under ambient conditions. PBAT is commonly utilized as a blending agent to enhance the mechanical properties of other polymers. Due to its low elastic modulus and high elongation at break, PBAT serves as an effective toughening modifier for PLA, improving performance in applications that require increased flexibility and impact resistance [6,7].

Nanofibers, characterized by their high aspect ratio, large specific surface area, and potential for creating highly interconnected networks, have attracted significant attention across a range of applications. These include the stabilization of sensitive biological agents, protection against the degradation of unstable compounds, gas detection in sensor technologies, as well as drug delivery, tissue engineering, and wound healing in the biomedical field [8,9].

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Electrospinning has emerged as a prominent technique over the past two decades, recognized for its ability to produce ultrafine biopolymer fibers with diameters ranging from the micrometer to nanometer scale. The electrospinning method is lauded for its versatility, simplicity, and cost-effectiveness, with the added advantage of continuous fiber production. To date, more than 200 different materials, encompassing both natural and synthetic polymers, have been successfully electrospun. These include naturally derived polymers such as chitosan, collagen, gelatin, and casein, as well as synthetic polymers like PLA and PBAT. Coaxial electrospinning, a variation of the conventional electrospinning process, is an excellent technique for producing core-shell and hollow fibers, combining the advantages of different polymers while maintaining their individual properties. [10-12].

This study aims to fabricate and characterize nanofibers with a core-shell structure using coaxial electrospinning method. PLA is selected as the shell material because of its non-toxicity, biodegradability, and biocompatibility, making it an ideal candidate for applications requiring biocompatible materials. PBAT is chosen for its superior mechanical properties and biodegradability, served as the core material, providing structural reinforcement to the nanofibers.

This research systematically explores the influence of key electrospinning parameters including concentration, feed rate, applied voltage, and the distance between the needle tip and collector on the resulting core-shell fiber morphology, with the aim of optimizing these parameters to enhance the performance of PBAT/PLA nanofibers. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) are employed to elucidate the morphological characteristics of the nanofibers, enabling a detailed assessment of fiber diameter and distribution. Furthermore, the study investigates the tensile strength of the PBAT/PLA fiber membranes, aiming to correlate the electrospinning conditions with the mechanical properties of the resultant nanofibers.

The goal of this research is to optimize the processing conditions for creating PLA/PBAT nanofibers with a core-shell structure. The results of this study will indicate that understanding how the parameters of coaxial electrospinning affect the characteristics of PLA/PBAT nanofibers is essential.

2. Materials and methods

2.1. Materials

Polylactic acid, product code: Luminy L105 (M_W of 50,000, density of 1.24 g/cm³) was purchased from Total Corbion (Netherlands) and poly (butylene co-adipate co-terephthalate), product code: TH 801T (M_W of 50,000, density of 1.21 g/cm³) was purchased from Xinjiang Lanshan Tunhe (China). Chloroform ($\geq 99\%$) and N, N-dimethylformamide (>99.5%) were supplied by Xilong Scientific Co., Ltd., China. All the chemicals were used without any purification.

2.2. Preparation of PBAT/PLA nanofiber scaffolds

To prepare the shell nanofiber solution, a 10.0 wt.% PLA solution was formulated by dissolving PLA particles in a solvent mixture comprising chloroform and N, N-dimethylformamide (DMF) in an 80/20 weight ratio. This solution was subjected to continuous magnetic stirring for 24 hours at room temperature to ensure complete dissolution of the PLA. For the core solution, PBAT was dissolved in a chloroform/DMF solvent mixture with a weight ratio of 75/25. The concentration of PBAT was varied at 8.0 wt.%, 10.0 wt.%, and 12.0 wt.% to assess the impact of these concentration levels on the resulting fiber characteristics. The PBAT solution was subjected to continuous magnetic stirring for 24 hours at room temperature to ensure complete dissolution of the PBAT.

The nanofibers were fabricated via coaxial electrospinning, utilizing the prepared solutions of PBAT and PLA. Following preparation, the solutions were cooled to room temperature and transferred into separate 5 mL syringes, each connected to a coaxial spinneret. The inner syringe contained the core solution, administered through a 30G needle (inner diameter: 0.16 mm, outer diameter: 0.31 mm), while the outer syringe delivered the shell solution through a 21G needle (inner diameter: 0.51 mm, outer diameter: 0.82 mm). The flow rates were precisely controlled by independent syringe pumps, and the coaxial setup was connected to a high-voltage power supply to initiate the electrospinning process. The resulting nanofiber scaffolds were analyzed to determine the influence of the electrospinning parameters on their structural and material properties.

As process parameters, the distance between the needle and collector was set from 15 to 18 cm; the applied voltage was adjusted from 14 to 20 kV; the shell (PLA solution) feed rate was set to 0.6 mL/h, while the core (PBAT solution) feed rate varied from 0.1 to 0.25 mL/h. All the electrospinning processes were done at around room temperature (about 25 °C) and moderate humidity (50%). A schematic view of the coaxial electrospinning process is shown in Figure 1.



Fig. 1 Schematic view of coaxial electrospinning process

2.3. Characterization of prepared scaffolds

The nanofiber morphology was evaluated using scanning electron microscopy (SEM). The SEM images were analyzed with ImageJ software as an imaging tool, to measure the average fiber diameter and assess its distribution across the samples. For statistical accuracy, 100 fibers were randomly selected for analysis.

The core-shell structure of PBAT/PLA nanofibers was analyzed using a transmission electron microscope - TEM (JEM 2100, Jeol, Japan) operating at an electron acceleration voltage of 200 kV. For this analysis, samples of the nanofibers were prepared by electrospinning PBAT/PLA solutions directly onto copper grids coated with a carbon film. This process took approximately 5 seconds. The prepared grids were then examined with the TEM, where electron beams were transmitted through the samples to capture detailed images of the core-shell structures. Since the electron beams must pass through the full diameter of the nanofibers, the analysis was limited to fibers with diameters smaller than 300 nm to accurately visualize the core-shell structure.

The thermal properties of the produced nanofibers, including both neat and core-shell variants, were examined using differential scanning calorimetry (DSC). The DSC analysis was performed in a nitrogen environment, with samples placed in alumina pans and heated from 25 °C to 200 °C at a rate of 10 °C per minute using the Discovery DSC 25 instrument. The glass transition temperatures (Tg) and melting temperatures (Tm) of PBAT/PLA neat resins and PBAT/PLA nanofibers were recorded, providing insights into the effects of the coaxial electrospinning process on their thermal properties.

TGA experiments of the PBAT/PLA nanofiber, pristine PBAT and pristine PLA, were performed under N2 atmosphere and heated from 50 °C to 600 °C with a heating rate of 10 °C min⁻¹ using a PerkinElmer TGA 4000 equipment.

Attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR) was employed as an approach to examine neat polymer and coaxial nanofiber mats using the Nicolet iS20 machine. The aim of the analysis was to find out about the different structures and properties of different fibers. The resulting spectra were recorded in transmission mode in the wave number range of 500-4000 cm⁻¹.

Viscosity of the PLA solution and PBAT solutions were determined using a Brookfield DV-E digital viscometer with LV-1 spindle at 100 rpm, at 25 °C according to ASTM -D2196. The reported viscosity for each solution was the average of five assessments.

The electrical conductivities of PLA solution and PBAT solutions were measured at 25 °C using a conductivity meter (MeterLab CDM210, Radiometer Analytical - France).

The tensile test was used to examine the mechanical properties of the neat PLA and core-shell PBAT/PLA nanofibers. Samples were made into dog bone shape according to ASTM D882-10.

The hydrophilicity of nanofiber mats was tested using the contact angle system, based on the sessile drop technique. Three replicates were tested in different areas for each sample. The average of them was the WCA result, which was determined from photographs using ImageJ software.

3. Results and Discussion

3.1. Effect of the needle tip-to-collector distance

Electrospinning technology enables production of continuous polymer nanofibers from polymer solutions or melts in high electric fields. When the electric force on induced charges on the polymer liquid overcomes surface tension, a thin polymer jet is ejected. The charged jet is elongated and accelerated by the electric field, under goes a variety of instabilities, dries, and is deposited on a substrate as a random nanofiber mat. This study investigated the effect of the needle tip-to-collector distance (TCD) on the morphology of electrospun PBAT/PLA nanofibers. The viscosity and electrical conductivity of the core and shell solutions have been investigated in advance to clearly explain their influence on later processing conditions. The viscosity and electrical conductivity of 10 wt.% PLA solution and PBAT solutions (8 wt.%, 10 wt.% and 12 wt.%) are presented in Table 1.

Solution	Viscosity, cP	Conductivity, µS/cm
PLA 10 wt.%	123.6	5.23
PBAT 8 wt.%	117,4	3.04
PBAT 10 wt.%	118.1	2.88
PBAT 12 wt.%	121.0	2.56

Table 1: Viscosity and electrical conductivity of PLA and PBAT solutions

The results presented in Table 1 show that the viscosity of both core-shell solutions is not much different. PLA solution and PBAT solutions in general show intrinsically very low electrical conductivities. This is due to the nature of polymers is insulating materials. Obviously, the electrical conductivity of the solution plays an important role for the formation of shape and diameter nanofibers.

The electrospinning processes were performed with PLA and PBAT solution concentrations of 10 wt. % and PLA and PBAT flow rates of 0.6 mL/h and 0.15 mL/h, respectively. An applied voltage set at 16 kV. Different TCDs (15 cm, 16 cm, 17 cm, and 18 cm) were selected. Figure 2 shows SEM images of PBAT/PLA electrospun nanofibers with varying TCDs. As shown in Figure 2, TCD did not significantly influence the morphological characteristics of the core-shell nanofibers under the conditions studied.



Fig. 2 SEM images and distribution of diameters of PBAT/PLA fibers at different TCDs: a) 15 cm; b)16 cm; c) 17 cm; d) 18 cm

The morphology and diameter of PBAT/PLA nanofibers remained consistent with TCDs ranging from 15 cm to 17 cm, resulting in continuous nanofibers. However, at a TCD of 18 cm (Figure 2.d), nanofiber breakage occurred. This is attributed to the solvent evaporation time and fiber travel distance; an excessive TCD (greater than 17 cm in this case) can lead to overstretched fibers that harden near the collector drum, resulting in breakage under electric force and stress.

The results in Figure 2 also indicate that when the TCD is set at 17 cm, the resulting nanofibers exhibit both the smallest and most consistent diameters. The fiber diameters range from 250 nm to 450 nm, with a mean diameter of 346.48 nm and a variation of 59.47. To find the optimal conditions for producing uniform and smaller nanofibers, a TCD of 17 cm was chosen for further studies.

3.2. Effect of the applied voltage

The applied voltage is another crucial parameter in the electrospinning process. Figure 3 shows the morphology and diameter of PBAT/PLA nanofibers at voltages ranging from 14 to 20 kV (with the TCD set at 17 cm). At 14 kV (Figure 3.a), large and uneven nanofibers were produced. It can be seen from Figure 3.b that the nanofiber diameter was uniform at 16 kV applied. At applied voltages above 18 kV (Figure 3.c and 3.d), bead formation and flying fibers were observed. This can be explained by the fact that higher voltage applied to the metal needle increases coulombic attraction and energy in the polymer solution, leading to faster movement.

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Fig. 3 SEM images of PBAT/PLA nanofibers at different applied voltages: a) 14 kV; b) 16 kV; c) 18 kV; d) 20 kV

Both low or high voltages may cause bead formation. Low voltage results in longer fiber flight time and smaller fibers. The number of fibers with small diameters tends to increase when the voltage is below 16 kV. The high voltage causes rapid fiber flight time, leading to segments with excessive charges and mutual Coulombic repulsion, creating beads and uneven fiber sizes as well as larger fiber diameters.

Table 2 illustrates the impact of applied voltage on fiber diameter and standard deviation. The data suggests that increasing the voltage beyond 16 kV leads to both a noticeable rise in fiber diameter and a broader standard deviation.

Applied voltages, kV	Mean diameter, nm	Standard deviation
14	481.81	75.53
16	348.48	59.47
18	462.73	75.14
20	473.52	73.45

This observation can be attributed to the fact that at higher voltages, the shell solution is ejected more rapidly, leading to a greater volume of resin being extruded, which produces fibers with greater diameters. Additionally, in relation to the polydispersity index, the higher voltage may facilitate the stretching of polymer chains with lower molecular weights, while chains with higher molecular weights are more resistant to extension. This disparity in the stretching behavior of polymer chains contributes to the observed increase in fiber diameter variation under these specific manufacturing conditions. In addition, it can be seen that because the shell and core solutions have low electrical conductivity, increasing the voltage is only effective within a certain range, enough to pull the fiber towards the drum collector. Exceeding the threshold (higher than 16 kV), the effect of increasing the voltage is not very meaningful.

3.3. Effect of core solution concentration on morphology and size of fibers

The study also examined the effect of core solution concentration (PBAT) on fiber morphology and nanofiber size. The shell solution concentration (PLA) was fixed at 10.0 wt.%, while the core solution concentration varied from 8.0 wt.% to 12.0 wt.%. Figure 4 shows SEM images of PBAT/PLA nanofibers.



Fig. 4 SEM images of PBAT/PLA nanofibers and optical microscope images of needle tip at different core solution concentrations: a) 8.0 wt. %; b) 10.0 wt. %; c) 12.0 wt. %

The core solution concentration minimally affected fiber morphology except at higher concentrations. When the core solution concentration is low, such as at 8 wt.%, the fiber diameter is large, with most fibers exceeding 420 nm in diameter (Figure 4a), and the fibers exhibit a flattened shape. This may be due to the low concentration leading to a higher solvent content in the core, resulting in more solvent needing to evaporate during fiber formation. The retained solvent in the PLA shell may prevent complete drying, which could alter the fiber's shape. Similarly, at a high core concentration of 12 wt.%, the fiber diameter is generally above 440 nm (Figure 4c), and the fibers appear twisted and stretched, lacking a uniform round shape. This could be due to the high viscosity in the core and low solvent content, causing the fibers to dry out as they are drawn to the collector's surface, leading to fiber stretching.

At 12 wt. % PBAT concentrations, the fibers became less uniform, changing from cylindrical to flat. Figure 4.c shows the less stable flow, multi-directional fiber jet, and solidification at the nozzle tip. This instability is likely due to the needle tip becoming clogged with dried polymer solution, hindering proper fiber formation. Higher concentrations tend to cause needle clogging, which affects the fiber shape. Table 3 shows the distribution of diameters of PBAT/PLA nanofibers with varying core solution concentrations.

Core solution concentration, %	Mean diameter, nm	Standard deviation
8	444.71	30.65
10	348.48	59.47
12	467.26	31.26

Table 3. Distribution	of diameters of PF	BAT/PLA nanofiber	with varving	core solution	concentrations
Lable 5. Distribution	of utameters of f	DAT/I LA nanonocia	s with varying	core solution	concentrations

From Table 3, the findings revealed that the lowest standard deviation values, 30.65 and 31.36, were observed at the 8 wt.% and 12 wt.% concentrations, respectively, indicating greater uniformity in fiber size at these levels compared to the 10 wt.% concentration. At 8 wt.%, it is hypothesized that PBAT was more completely dissolved, facilitating the extrusion process and leading to more uniformly sized fibers.

Conversely, at 12 wt.%, although clogging phenomena were observed (with the resin hardening at the needle tip – Figure 4), the resin streams that overcame the blockage exhibited consistent molecular weights, contributing to uniform fiber formation.

These results suggest that while a 10 wt.% concentration might be optimal, concentrations both above and below this threshold can still yield fibers of consistent size under certain conditions.

3.4. Effect of core feed rate on morphology and properties of PBAT/PLA nanofibers

Unlike uniaxial electrospinning, the presence of two different materials at the needle tip in coaxial electrospinning affects Taylor cone formation. During fiber production, free charges in both solutions accumulate only on the outer surface of the shell solution, meaning the core solution does not experience electrical potential difference. The shell solution, stretched by electrostatic force, induces drag on the inner solution. This property allows even non-spinnable materials to be used as core material in nanofiber production. Feed rate is a crucial and controllable parameter in this process, determining the balance between solution input and solvent evaporation under the electric field.

Figure 5 shows SEM images of PBAT/PLA fibers and Table 4 shows the distribution of PBAT/PLA nanofiber diameters at different core feed rates. As core feed rate increases (exceeding 0.15 mL/h in this case), the fiber diameter enlarges, and bead formation occurs due to an excessive solution being pumped into the electric field, leading to incomplete solvent evaporation (Figure 5.c, d). The plasticity of the formed fiber also contributes to bead formation.



Fig. 5 SEM images of PBAT/PLA fibers at different core feed rates: a) 0.1 mL/h; b) 0.15 mL/h; c) 0.2 mL/h; d) 0.25 mL/h

Core feed rate, mL/h	Mean diameter, nm	Standard deviation
0.10	531.85	67.02
0.15	348.48	59.47
0.20	546.05	53.34
0.25	512.73	72.48

ole 4: Di	stribution of	f diameters	of PBAT/PL	A nanofibers	with	different	core feed rates
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The data in Table 4 demonstrate a significant correlation between the core feed rete and the nanofiber diameter, as well as its associated standard deviation. Specifically, when the core feed rate deviates from 0.15 mL/h, either increasing or decreasing, the average fiber diameter exceeds 512 nm, while the standard deviation falls within the range of 67 to 72 nm.

This phenomenon can be attributed to the effect of applied voltage on the electrospinning process. The electric field primarily influences the outer surface of the polylactic acid (PLA) shell, leaving the core solution relatively unaffected. As a result, the extrusion of the core solution is largely governed by the mechanical thrust of the pump. Consequently, any mismatch between the core injection speed and the shell's drawing velocity under the influence of the electric field can lead to inconsistencies in fiber formation, resulting in an increase in both fiber diameter and its standard deviation.

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Fig. 6 TEM image (a) and SEM image (b) of the PBAT/PLA nanofibers with the core feed rate of 0.15 mL/h

TEM and SEM analyses confirmed the core-shell structure and morphology of PBAT/PLA fiber mats with the core feed rate of 0.15 mL/h are shown in Figure 6. The TEM image clearly shows the core-shell structure, with minor interpenetration between PBAT and PLA (Figure 6.a). The high-magnification SEM image reveals a roughness fiber surface, suggesting the presence of PBAT on the PLA shell surface. The results also indicate that PBAT/PLA fibers exhibit a homogeneous and co-continuous phase structure (Figure 6.b).

3.5. Chemical, thermal characteristics, and wettability of PBAT/PLA nanofiber at different core feed rates ATR-FTIR characterization

By identifying distinct vibrational modes of various chemical bonds, Attenuated total reflectance Fourier-transformed infrared spectroscopy (ATR-FTIR) was used to examine the differences in chemical characteristics on the surfaces of PBAT/PLA nanofiber scaffolds (Figure 7).

The peaks in PLA at 1755 cm⁻¹, 1185 cm⁻¹ and 1090 cm⁻¹ were attributed to the tensile vibration of -C = O, C-O-C stretching, and tensile vibration of C-C(O)-O, respectively.

For pristine PBAT resin, the absorption peak at 2958 cm⁻¹ was assigned to the stretching vibration of -CH 2 -, and the absorption peak at 1715 cm⁻¹ was attributed to the stretching vibration of C=O. The peak at 1271 cm⁻¹ was ascribed to C-O-C stretching and the peak was associated with CH- plane bending at 727 cm⁻¹.

The spectra of PBAT/PLA fibers showed weak signals of aromatic C-H stretching (727. cm⁻¹) and aliphatic C=O stretching (1714 cm⁻¹), indicating the presence of PBAT on the surface of nanofibers. The higher the core feed rate (in this study, higher than 0.15 mL/h), the more pronounced the peaks at 727 cm⁻¹ and 1714 cm⁻¹ become. This could be due to the increased core feed rate, which facilitates the migration of PBAT resin from the core to the fiber surface during the process of moving toward the fiber collector.



Fig. 7 ATR-FTIR spectra of neat PBAT, PLA, PBAT/PLA fibers fabricated at different core feed rates Sample code: FR 0.1: core feed rate 0.1 mL/h; FR 0.15: core feed rate 0.15 mL/h; FR 0.2: core feed rate 0.2 mL/h and FR 0.25: core feed rate 0.25 mL/h

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Thermal characterization

The thermal properties of pristine PBAT, PLA, and PBAT/PLA nanofibers were analyzed using differential scanning calorimetry (DSC). The resulting curves are shown in Figure 8, and the relevant thermal properties of PLA, PBAT/PLA nanofiber at different core feed rates are summarized in Table 5.

As shown in Figure 8, pristine PLA resin exhibited a glass transition temperature (Tg) of 55.38 °C and a melting temperature (Tm) of 149.27 °C. In contrast, PBAT displayed a Tg of -30 °C and a Tm of 125.13 °C. The broad endothermic peak observed between 90-120 °C is indicative of the random copolymer structure and low crystallinity of PBAT. Differential scanning calorimetry (DSC) analysis revealed that PBAT/PLA fibers prepared with a core feed rate of 0.1 ml/h exhibited a Tg of 55.3 °C and a Tm of approximately 149.5 °C



Fig. 8 DSC curves for neat PLA, PBAT, PBAT/PLA fibers at different core feed rates

Sample ID	Tg, °C	Tm, ⁰C
PLA	55.38	149.27
PBAT	- 30	125.13
FR 010	54.30	149.53
FR 0.15	55.22	149.88
FR 0.20	57.50	152.15
FR 0.25	58.09	153.10

Table 5: Thermal properties of PLA, PBAT and PLA/PBAT fibers at different core feed rate

The core feed rate influenced both the fiber diameter and the melting temperature, with Tm increasing from 149.9 °C to 153.1 °C at the highest feed rate employed in this study. According to the Fox equation, a shift in Tg would be expected if the amorphous regions of PBAT were miscible with PLA. The change in Tg from 55.38 °C to 58.09 °C suggests limited miscibility between PBAT and PLA, indicating the occurrence of a blending phenomenon.

The use of thermogravimetric analysis (TGA) experiments can also confirm the resistance of the pristine PBAT, PLA and PBAT/PLA nanofiber to thermal degradation. The curves in Figure 9 show the thermal stability of neat PBAT, neat PLA and PBAT/PLA nanofiber prodiced at the core feed rate of 0.15 mL/h.

As shown in Figure 9, both pristine PBAT and PLA sample display a single degradation step that occur in the range of 325 - 428 °C, with a low residual mass. The PBAT/PLA nanofiber also shows a clear first degradation step at around 325 - 382 °C, which is probably related to the degradation of pristine PLA resin. The second degradation step is related to PBAT chains and has its maximum at around 427 °C, suggesting a higher thermal stability compared with that of pristine PLA. The char residue is similar to neat PLA. The shift of the two peaks from 382 - 376 °C and from 428 - 427 °C of the PBAT/PLA nanofiber, located between the peaks of the PBAT resin, shows that there is a partial blend of the two resins in the nanofiber.



Fig. 9 (a) TGA and (b) differential thermogravimetric (dTG) curves for pristine PBAT, PLA and PBAT/PLA nanofiber

Mechanical testing

Tensile tests evaluated the mechanical properties of pristine PLA and core-shell PBAT/PLA nanofibers (Figure 10). Pristine PLA nanofibers displayed a tensile strength of 0.32 MPa. Core-shell PBAT/PLA nanofibers showed an ultimate strength of approximately 0.58 MPa, representing an 81% increase compared to neat PLA fibers.

The tensile strength increased with higher core feed rates, reaching the highest strength at a core feed rate of 0.25 mL/h. This improvement is attributed to macromolecular stretching and possible crystallization under electromagnetic force, which enhances fiber strength. To further analyse the mechanical behaviour of PBAT/PLA nanofibers, additional tests were conducted to evaluate the elongation at break and Young's modulus. The elongation at break increased significantly with the incorporation of PBAT, indicating improved ductility.



Fig. 10 The stress-strain curves of PLA and PBAT/PLA nanofibers at different core feed rates.

Water contact angle (WCA) measurements

Wettability, a critical property of surfaces, is influenced by multiple factors, including chemical composition, surface microstructure, hierarchical architecture, and the age of surface growth. To investigate the effects of core feed rate on the wettability of PBAT/PLA nanofibers, static water contact angle measurements were employed as shown in Figure 11.



Fig. 11 Water contact angle of PLA and PBAT/PLA nanofibers at different core feed rates

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As shown in Figure 11, the contact angle exhibits significant variation with changes in the core feed rate. The contact angle for pristine PLA was determined 112.8°, serving as a baseline for comparison. In contrast, the contact angles for PBAT/PLA nanofibers fabricated with different core feed rates were consistently lower, ranging from 109.7° to 103.8°. These findings demonstrate a notable reduction in the contact angle compared to pristine PLA, highlighting the impact of core feed rate on the surface wettability of PBAT/PLA nanofibers.

The contact angle of PBAT/PLA nanofibers exhibits a decreasing trend with an increase in the core feed rate. This can be explained that the increased core feed rate facilitating the migration of PBAT resin to the surface of the PLA shell. The resultant exposure of PBAT on the surface, combined with the formation of pores on the fiber structure and roughness of fiber surface contributes to an increase in the hydrophilicity of the nanofibers. These observations are corroborated by TEM image and SEM image with 15000x magnification and ATR-FTIR spectra (Figures 6 and 7), which clearly demonstrate the surface morphology and chemical shifts indicative of this behavior.

4. Conclusions

This study investigated the influence of various processing parameters on the properties of PBAT/PLA fibers. Optimal conditions were found to be a needle tip to collector distance of 17 cm, an applied voltage of 18 kV, core and shell solution concentrations of 10 wt.%, a shell feed rate of 0.6 mL/h, and a core feed rate of 0.15 mL/h. All electrospinning processes were conducted at room temperature (25 °C) and moderate humidity (50%). SEM and TEM analyses confirmed the core-shell structure, with core and shell average diameters of about 95 \pm 7 nm and 348 \pm 59 nm, respectively. DSC, TGA and FTIR tests indicated that the nanofibers exhibited properties of both PBAT and PLA resins, providing evidence for successful core-shell PBAT/PLA nanofiber fabrication.

The results show that processing parameters such as TCD, core/shell concentration, applied voltage all affect the properties of the resulting fibers. However, the values of the above parameters can fluctuate within a large range without much affecting the properties of the fibers such as diameter or standard deviation. Meanwhile, vvariations in core feed rate significantly affect diameter, standard deviation, melting temperature, and the hydrophobic characteristics of the fibers.

The study also confirmed that core-shell PBAT/PLA nanofibers enhance the quality and exhibit superiority over neat PLA and PBAT fibers.

5. Conflicts of interest

There are no conflicts to declare

6. Acknowledgment

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