High-modulus rotary jet spun co-polyimide nanofibers and their composites

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Introduction
A relatively novel nanofiber production technique, rotary jet spinning (RJS), has gained in popularity in recent years because of its promise of higher production rates and economies of scale compared to other leading nanofiber production methods [1,2]. The term RJS is also known as centrifugal spinning, rotor spinning or Forcespinning and in certain configurations allows for the production of micro- or nanofibers from either a polymer solution or melt. During the RJS process (Figure 1), pressure is build up in a spinning vessel containing orifices, which is generated by both centrifugal force and hydrostatic pressure. The ejected polymer is subsequently subjected to an elongational flow to produce an ultra-thin fiber [3], which is collected at a set distance using one of multiple collection methods.

RJS is unique among nanofiber production methods as it offers the combined benefits of low power consumption, sub-micron fiber diameters and high production rates compared to traditional polymer
nomenclature, nonwoven fibrous webs, and are simple and resemble candyfloss spinning, normally producing nonwoven fibrous webs.

Until now, RJS studies have mainly focused on the spinnability of various polymer systems and the fiber diameters obtained. Few studies have focused on the mechanical properties of RJS fibers, but it can be expected that similar to electrospun fibers, properties such as Young’s modulus and tensile strength of these fibers are at best similar to those of equivalent bulk polymers [7]. Achieving high-modulus polymeric fibers relies on introducing high levels of orientation and chain extension within the molecular network of a fiber and is traditionally realized by one of three principles. First, high-modulus fibers can be achieved directly from high elongational flow induced chain orientation when using lyotropic rigid rod molecules such as in the case of poly(phenylene terephthalamide) (PPTA) for the creation of aramid fibers [8]. Secondly, through post-drawing of as-spun fibers based on flexible chain molecules like polyethylene as in the case of Dyneema® or Spectra® fibers, to initiate molecular orientation and chain extension within the molecular network of a fiber and is traditionally realized by one of three principles. First, high-modulus fibers can be achieved directly from high elongational flow induced chain orientation when using lyotropic rigid rod molecules such as in the case of polyethylene or polypropylene, polyamide or polyesters are required to undergo post-drawing processes in the solid state (i.e. below the melting temperature) of the as-spun fiber to increase mechanical properties [9,13–15]. This is relatively easily achievable in the case of micron-sized fibers or films but becomes rather challenging at the nanoscale. Electrospun and RJS fibers typically have diameters below 500 nm and are produced in a way that does not easily facilitate post-drawing as a means to induce molecular orientation. It is for this reason that in this study we therefore reside to the third method mentioned, which involves the RJS of a polyamic acid (PAA) solution into a precursor fiber, which is subsequently converted into a highly oriented and chain extended PI fiber via a chemical imidization step. This two-step method of first spinning PAA into fibers and then subjecting them to a chemical or thermal imidization step to convert them into PI fibers is often chosen over a one-step spinning method since the majority of PIs suffer from poor solubility and a very high glass transition temperature, making them rather intractable. On the other hand, this two-step method possesses advantages of an extensive selection of different types of monomers and the use of common solvents such as N,N-dimethylformamide (DMF), dimethylacetamide, and N-methyl-2-ketoypyrrrolidone.

Selecting a PI that exhibits favorable properties for nanofiber production was the subject of a recent study by Chen et al. [16], where they investigated the options of various combinations of monomers as well as co-polymerization of monomer blocks. In their study, they found that electrospun co-polyimide nanofibers exhibited both high-modulus and high-strength while homo-polyimide fibers only showed a high modulus. 3,3’,4,4’-biphenyl-tetracarboxyl bicyanhydride (BPDA), p-phenylenediamine (PDA) and 4,4’-oxydianiline (ODA) (BPO) were the three monomers used in their study, and by altering the ratio of the flexible ODA and rigid PDA moieties, they were able to create an intermediate polymer called PAA. In this polymer strong hydrogen bonding between PAA and solvent ensured solubility – a quality required for solution based fiber spinning methods like electrospinning or RJS. In their case, the fibers were electrospun into aligned fiber bundles by collection on a rotating disc before undergoing sample characterization. Imidization was subsequently carried out for ring closure, creating a high-modulus co-polyimide fiber.

Figure 1. Schematic of the rotary jet spinning (RJS) process, demonstrating the forces generated by the rotation velocity, which results in polymer flow from the orifice at high speeds.
Yao et al. [17,18] expanded on this study, producing BPO co-polyimide nanofibers which exhibited very high strength, stiffness and toughness. In their paper, an elastic modulus of 59 GPa was reported for a single fiber, which is close to that of commercial high-performance synthetic fibers like Kevlar® 29 (~70 GPa [19]). This was achieved through both direct testing of aligned bundles of up to 30 nanofibers in a micro-tensile tester and indirectly in composite laminates, using micromechanical theory to back-calculate the properties of the individual fiber.

This research focuses on the ability to produce high-modulus RJS polymer nanofibers, as no existing RJS publications have been able to achieve tensile strength or modulus values significantly higher than that of the bulk modulus of the material [1]. In fact, only very few RJS publications report mechanical properties of their fibers, with those that do reporting values as low as 22% of the bulk modulus. For example, in the case of polytetrafluoroethylene fibers the modulus was as low as 348 MPa versus 1.6 GPa for bulk polymer [20] using a yarn twisting tensile test method, while for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) using tensile tests of nonwoven nanofiber mats a modulus as low as 126 MPa was reported [21]. Both of these fibrous materials can hardly claim to be ‘high modulus’ and show the limitation of current mechanical properties of RJS nanofibers.

The alignment of nanofibers from direct RJS collection methods is challenging at present due to the nature of the deposition system. Fast spinning RJS nozzles create significant amounts of turbulence and therefore influence the flight path of the depositing nanofibers which results in a random fiber orientation. Electrospinning can however employ rotating disc collectors to ‘catch’ the fiber as it progresses towards the collector, aligning the fibers on contact [2]. Combining the two technologies of RJS and electrospinning has recently had some success in introducing fiber alignment into RJS fiber webs [22,23]. On the other hand, although these methods may induce some fiber alignment, they do not address the issue of polymer chain alignment in the individual fibers.

In the current study, the potential of RJS in producing high-modulus PI fibers is explored for the first time. Properties of these fibers are evaluated in epoxy based composites and compared to those produced via electrospinning in an earlier study [17].

**Experimental**

**Materials**

BPDA, PDA, and ODA were purchased from Sigma Aldrich (UK). DMF (99.8%, anhydrous) solvent was purchased from Sigma Aldrich (UK). The two-component low viscosity epoxy resin system RX771C based on bisphenol A diglycidyl ether and aromatic amine hardener HX932C was supplied by Robnor Resins Ltd. (UK) and mixed at a weight ratio of 100:24.

**Synthesis of co-polyimide polyamic acid**

The 5.884 g (0.02 mol) BPDA, 1.081 g (0.01 mol) PDA and 2.002 g (0.01 mol) ODA (mole ratio of 2:1:1) were mixed together in 40.504 g of DMF using a three-neck flask, which was continuously ventilated with nitrogen. Intense mechanical stirring was applied in the polycondensation process at a low temperature (±0°C) for approximately 2h. A 20.7 wt% solution of PAA in DMF was used for fiber production.

**Rotary jet spinning**

A Fiberio 1000-D Cyclone Forcespipinning™ system (Figure 2) was used to conduct the fiber spinning. All samples were spun at room temperature (RT). To produce the fibers, the PAA solution was...
inserted into the spinneret, which holds approximately 2 ml of solution. 30 Gauge (internal diameter of 0.16 mm), 12 mm long blunt tip needles were used to produce the RJS fibers. To collect the fibers, a fan ducted collector box was covered with a spun-bond polypropylene mat which allowed sufficient airflow without reducing the suction caused by the fan. This was placed 16 cm away from the tip of the needle. A rotational velocity of 5500 rpm was used for all spinning trials, as this was deemed to produce the neatest fiber deposition from previous trials. Spinning was conducted for 18 min for each 90° turn of the fan box, ensuring equal coverage of the mat over 4 turns. After spinning, the mats were subsequently dried at 75 °C for 2 h to remove excess solvent, before storing in a freezer for characterization and imidization.

**Imidization**

Obtaining BPO co-polyimide fibers from the as-spun PAA fibers required heating using the following procedure in a nitrogen atmosphere. (1) Heating to 240 °C at 10 °C min⁻¹, annealing for 2 h, (2) heating to 380 °C at 1.5 °C min⁻¹, annealing for 1 h, and (3) cooling down to RT.

**Composite fabrication**

Fifteen plies of nonwoven PI nanofiber mats (6 cm × 8 cm) were impregnated with epoxy resin and stacked to produce a composite laminate. A 4 kg weight was used to compress the composite lay-up whilst curing for 12 h in a vacuum oven at 120 °C. This resulted in a void-free nanocomposite laminate with a fiber loading of 7.3 wt%, which is equivalent to 6.1 vol% based on an epoxy resin density of 1.17 g cm⁻³ and a polyimide fiber density of 1.41 g cm⁻³.

**Characterization**

Rheological characterization of the PAA was conducted with a TA Instruments Discovery HR-3 Rheometer (UK), using a 40 mm Peltier plate attachment. The morphology of the nanofibers was investigated using a scanning electron microscope (SEM, Jeol JSM-6300F, Japan). All samples were Au-coated before imaging.

Thermogravimetric analysis (TGA) was conducted on a TA Instruments Q500 (UK) under a N₂ atmosphere from RT to 600 °C at 10 °C min⁻¹. Differential scanning calorimetry (DSC) tests were also conducted using a TA Instruments DSC25 (UK), ramping at a rate of 10 °C min⁻¹ from RT to

![Figure 3](image-url). Low temperature polycondensation reaction from BPDA, PDA and ODA (BPO) monomers to polyamid acid (PAA) with N,N-dimethylformamide (DMF) as solvent, and subsequent imidization processing to produce BPO co-polyimide.
Fourier transform infrared (FTIR) characterization was conducted to confirm the chemical structure of the fibers before and after imidization using a Bruker Tensor 27 instrument (USA).

Tensile tests were conducted on co-polyimide nanofiber-reinforced epoxy composites using a Deben micro-tensile tester (UK) equipped with a 100 N load cell. Test specimens with average dimensions of 30 mm × 5 mm × 0.3 mm were cut from the composite laminate and were tested using a gauge length of 10 mm.

Results and discussion

**Synthesis of 3,3′,4,4′-biphenyltetracarboxylic dianhydride/p-phenylenediamine/4,4′-oxydianiline polyamic acid**

The polycondensation process (Figure 3) of the monomers BPO in organic solvent is effective and rapid. The synthesis is therefore performed at low temperatures to inhibit side reactions. Several concentrations were produced for rheological characterization, however the 20.7 wt% solution of PAA in DMF was used for fiber production and subsequent analysis.

Figure 3 shows the chemical structure of the monomers used in the polycondensation reaction to produce the PAA. After synthesis of the PAA, spinning was performed, and the fibers were imidized to produce a BPO co-polyimide fiber.

FTIR was used to analyze the success of the PAA synthesis and the subsequent imidization process. Figure 4 shows that the broad absorbance peak at 2900–3600 cm⁻¹ has disappeared after imidization. This peak is attributed to the stretching vibration of the carbonyl groups and amide groups of the PAA. The peak at 1375 cm⁻¹ is attributed to the stretching vibration of the -C-N- in the imide ring, whereas both the peaks at 1776 and 1715 cm⁻¹ are an indication of the stretching vibration of the C=O in the imide. It should also be noted that the absorption peak at 1238 cm⁻¹, which appears in both spectra can be attributed to the stretching of the -O-C=O- bond, which is a confirmation of the existence of flexible ODA units in the copolymerized molecular chains. These results indicate that the BPO polyamic acid has been completely transformed to BPO co-polyimide (Figure 5).

The rheological properties of the solutions were tested to confirm their spinnability, which through experimentation has been evaluated to require shear viscosities between 1 and 12 Pa·s when using 30 Ga needles [3]. A viscosity higher than 12 Pa·s (P1003) adversely affected the ability of the fluid to flow through the needles to form a fiber, whereas viscosities significantly below 1 Pa·s (P1002) resulted in beaded discontinuous fibers being formed due to insufficient chain entanglement and increased solvent evaporation time.

To establish the correct viscosity regime, solutions were initially prepared at 5 wt% intervals from
20 to 30 wt% to establish the viscosity characteristics which would enable fiber production – labeled PI001, PI002 and PI003, respectively. These solutions were all produced from the same batch of PAA and diluted accordingly. Upon further analysis, it was apparent that the polycondensation reaction duration affected the viscosity due to changes in molecular weight, which resulted in solutions PI004 and PI005 being produced from a new batch of PAA to achieve the desired viscosity for fiber production.

**Rotary jet spinning of polyamic acid, imidization and characterization**

Morphological characterization was required to ascertain fiber orientation and average fiber diameter, which was essential for understanding the structural properties of the fibers produced. The fiber diameters were measured before and after imidization to assess the changes in morphology and physical characteristics. Figure 6 illustrates the scanning electron microscopy images and fiber size distributions of (a) PAA fibers and (b) BPO co-polyimide fibers. Picture insets show the morphology before and after imidization. The average fiber diameters were 298 nm before imidization and 296 nm after imidization, with size distribution and curves representing the standard deviation.
diameters. SEM imaging and subsequent analysis was conducted on 100 random fibers both before and after imidization, which yielded an average diameter just below 300 nm. SEM images from before and after imidization are shown in Figure 6, along with fiber diameter histograms. Around 500 co-polyimide fibers were analyzed for their orientation, showing almost no preferred orientation at all.

Larger fiber diameters were discarded due to RJS start-up effects. Previous studies have shown that during the initial few seconds of RJS, fibers are produced that can be significantly larger than those produced after the process has stabilized (typically 30 s) [24] (Figure 7).

**Thermal analysis**

TGA was performed to evaluate the change in decomposition temperature of the samples before and after imidization. It was found that the decomposition temperature increased from 119°C for PAA fibers to 550°C for the BPO co-polyimide fibers. DSC analysis showed no melting enthalpy peaks in the range of characterization. Pre-imidized fibers were tested to 100°C, while post-imidized fibers were tested to 500°C.

![Image of fiber orientation distribution](image)

Figure 7. Orientation of BPO co-polyimide fibers after imidization, showing no significant preferred orientation in the nonwoven fiber mats used for composite mechanical testing.

**Mechanical properties**

The experimental characterization of the Young’s modulus of individual polymer nanofibers is a challenge due to their small size. Primarily, these issues are due to the ability to manipulate them effectively as well as finding suitable modes of observation. Methods such as atomic force microscopy cantilever bending [25–27] or nano-tensile testing [28,29] have been attempted in the past with single and bundled nanofibers. Specific issues involved in this type of testing include the availability of accurate and sensitive force transducers with high enough resolution to measure single nanofiber properties [30].

In the current research we have opted for a more simplistic - albeit indirect - approach to mechanical characterization of polymer nanofibers by creating a nanofiber composite and using the generalized rule of mixtures (RoM) to back-calculate the Young’s modulus of the fiber [31,32].

\[
E_c = \eta_L \eta_0 E_f V_f + E_m (1 - V_f) \tag{1}
\]

where \(\eta_L\) is the length correction factor. Here \(\eta_L\) is taken as 1 since fibers are continuous. \(\eta_0\) is the fiber orientation distribution factor (0.2 or 0.375), \(E_m\) was taken as 3.2 GPa and is the elastic tensile modulus of the epoxy matrix as measured separately according to ASTM D638 Type V. \(V_f\) is the fiber volume fraction (6.1 vol%), and \(E_f\) is the fiber modulus. Using this approach, the unknown fiber modulus can be back-calculated from the composite data listed in Table 1. Figure 8 shows a schematic of the manufacturing process of the co-polyimide/epoxy composites together with SEM imaging of these nanofiber-reinforced composites. Figure 9 shows stress–strain curves of individual composite samples tested to failure. Samples that failed close to the clamps were discarded.

In the current study, this indirect fiber characterization method was only conducted for the imidized BPO co-polyimide fibers. As-spun PAA fibers were not characterize in this way as they are expected to have properties similar to epoxy with no reinforcement effect envisaged. In our previous work on electrospun co-polyimide fibers we have reported oriented fiber bundles properties before and after

| Sample | Width (mm) | Thickness (mm) | Modulus (GPa) | Strength (MPa) | \(3D\) \(\eta_0 = 0.2\) | \(2D\) \(\eta_0 = 0.375\) |
|--------|------------|----------------|---------------|---------------|-----------------|-----------------|
| 1      | 4.86       | 0.26           | 3.85          | 112           | 69.3            | 36.9            |
| 2      | 4.92       | 0.28           | 4.05          | 123           | 85.7            | 45.7            |
| 3      | 5.00       | 0.30           | 3.65          | 116           | 52.9            | 28.2            |
| 4      | 5.14       | 0.32           | 3.90          | 118           | 73.4            | 39.1            |
| 5      | 5.22       | 0.32           | 3.55          | 110           | 44.7            | 23.8            |
| Average| 4.88       | 0.28           | 3.80          | 116           | 65.2            | 34.7            |
imidization [17]. Such a direct comparison is unfortunately not possible for RJS fibers as we could not obtain oriented fiber bundles using this technique. However, as the chain extension step is chemically induced rather than flow induced, the expected property improvements should be similar to those reported for electrospun co-polyimide fibers [17,18].

Young’s modulus and tensile strength of the co-polyimide/epoxy composites were approximately 3.80 GPa and 116 MPa and are noticeably higher than that of the neat epoxy matrix at 3.20 GPa and 80 MPa, respectively. These values are particularly impressive given the low fiber volume fraction of 6.1%. Also the strain-at-break of the nanocomposites (4–6%) was slightly higher than that of the pure epoxy matrix (3–5%), suggesting good fiber-matrix adhesion and the presence of some crack-arresting ability.

Using the RoM to back-calculate the fiber modulus relies significantly on the fiber orientation distribution factor ($\eta_0$), which varies from 0.375 for 2D (in-plane) random to 0.2 for full 3D random. In-plane random orientations might be expected in nonwoven mat based composite laminates.
However, within the RJS nonwoven fiber mats some fibers experience out-of-plane orientations, which can significantly alter the 2D orientation distribution factor, shifting it more towards that for 3D random orientations. The average Young’s modulus of a single fiber is therefore expected to lie between 35 GPa as calculated assuming $\eta_0 = 0.375$ (2D), increasing to 65 GPa assuming $\eta_0 = 0.2$ (3D). Therefore, because of some out-of-plane fiber orientations, a realistic value for the elastic modulus of RJS co-polyimide nanofibers is around 50 GPa.

Although the realistic modeling of composite strength is far more complicated than the modeling of elastic modulus, as a first approximation, we can extend the generalized rule-of-mixtures of Equation (1) to composite strength by simply replacing stiffness properties for strength properties [31,33]. Based on a measured composite strength of 116 MPa and matrix strength of 80 MPa, a fiber volume fraction of 6.1%, and a fiber orientation factor of 0.3, we can obtain an estimate for the BPO co-polyimide fiber strength of 2.3 GPa, which is well within the region of high-performance synthetic fibers.

Both these modulus and tensile strength values compare well with our previous work on electrospun BPO co-polyimide [17], where bundles of ±30 nanofibers were tensile tested, resulting in a fiber Young’s modulus of 59 GPa, and a tensile strength value of 1.6 GPa. Moreover, these fibers compare well with as-spun BPDA–ODA fibers prepared by Zhang et al. [34] and BPO co-polyimide fibers by Chang et al. [35] who reported Young’s moduli and tensile strengths of 33 and 53 GPa and 0.4 and 2.5 GPa, respectively, for micron-sized wet-spun fibers. Fibers of higher moduli (>100 GPa) have been obtained but only in case these fibers were subjected to extensive drawing [34,36]. All of this suggests that RJS is as efficient as electrospinning in achieving high mechanical properties in PI nanofibers, while having the additional benefit of higher production rates. Moreover, similar to other aromatic PI fibers these fibers are expected to possess various other interesting properties, including good chemical and irradiation resistance, high thermal stability, and excellent electrical and dielectric properties [37]. All of this making them a promising material for the aircraft and aerospace industry as well as for the production of heat protective clothing [34].

Conclusions

In this work, we have set out to evaluate the ability of RJS or centrifugal spinning to produce high-modulus and high-strength polymer nanofibers. Methods of nanofiber production like RJS and electrospinning do not lend themselves easy to traditional techniques used to induce molecular orientation and chain extension in polymer fibers. In the case of polymer nanofibers, post-processing techniques such as cold-drawing are nearly impossibility to apply due to their small size. In the current study, rather than using post-drawing, here chain extension and orientation was induced via a heat treatment. RJS was successfully used to produce polyamic acid (PAA) precursor fibers of around 300 nm in diameter, using DMF as a solvent. These precursor fibers were subjected to a chemical imidization process, which induced chain extension, leading to high-modulus BPO co-polyimide nanofibers. The mechanical properties of these fibers were measured indirectly by embedding them into an epoxy matrix and mechanically testing the composites. Tensile tests and subsequent back-calculation
of the fiber properties using the generalized RoM resulted in a BPO co-polyimide fiber modulus of around 50 GPa and tensile strength of around 2 GPa, making them the stiffest and strongest centrifugal spun fibers ever reported. These values of co-polyimide nanofiber properties correspond well with earlier reported data for electrospun fibers of the same polymer. This work has therefore shown that RJS is a viable method for the high volume production of high-performance polyimide nanofibers.

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Disclosure statement

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