



# Fabrication and properties of poly(tetrafluoroethylene) nanofibres via sea-island spinning



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## ABSTRACT

Polytetrafluoroethylene (PTFE) has some unique properties such as high hydrophobicity and high resistance to elevated temperatures, chemicals and solvents which make it of interest for fibres and textiles. However, PTFE normally decomposes before melting, meaning that it cannot be readily melt-spun into fibres. In addition, PTFE is insoluble in all common organic solvents, prohibiting its use in common solution spinning methods such as dry, wet or electrospinning. Here we aim to develop an easy and environmentally friendly alternative for the production of PTFE nanofibres, using a modified island-in-the-sea solution spinning process. For this, first a dispersion of a PTFE homopolymer, PVA and water are compounded to create a blend of PTFE particles in a PVA solution. After the solid-state drawing of this blend and removal of the PVA, we are able to collect PTFE nanofibres with finest diameters of around 50 nm and lengths up to 15  $\mu\text{m}$ . The effects of blend composition, morphology and drawing on PTFE fibre formation and properties are studied and discussed.

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## 1. Introduction

Poly(tetrafluoroethylene) PTFE is a high-density polymer, comprising of carbon and fluorine, that exhibits some unique characteristics such as chemical inertness, hydrophobicity, UV stability, wear resistance, low friction, and excellent fire properties and many other outstanding properties of interest for use in fibres and technical textiles [1]. However, despite these interesting properties, its intractable nature prevents the straightforward fabrication of PTFE fibres. PTFE has a very high molecular weight ( $M_w > 10^7$  g/mol), which results in extremely high melt viscosities ( $10^{10}$ – $10^{12}$  Pa s) prohibiting its use in common thermoplastic polymer fibre processing techniques such as melt-spinning and extrusion [1,2]. In addition, PTFE is insoluble in all common organic solvents, preventing its use in solution processing methods such as wet- or dry-spinning and electrospinning [1,3].

Over the years, a variety of methodologies have been proposed for the production of PTFE fibres, including the split-peel process,

“matrix spinning” followed by sintering and removal of the matrix material, and paste extrusion followed by sintering [4–6]. Early work at DuPont involved the dispersion of PTFE into a viscose rayon spinning dope followed by extrusion into an acid bath, where the dispersion coagulates and the PTFE forms filaments, which after heat treatment and sintering, fused into coherent filaments [4]. The process is commonly referred to as “matrix spinning”, as the PTFE is spun in a (cellulose) matrix. After spinning and fusion of PTFE particles the cellulose is oxidised or burnt off, with the cellulose residue giving this material its characteristic brown appearance. In another process known as the split-peel process, a very thin layer is skived off of a billet of PTFE [1]. Nowadays, most non-matrix spun PTFE fibres are manufactured by some form of paste extrusion. Here PTFE suspensions are used to create a paste, which is extruded into a strand of aggregated PTFE particles, followed by drawing and/or sintering to create a fibre with increased mechanical properties [7]. In short, many of the current methods available for producing PTFE fibres are rather cumbersome and therefore not cost-effective. However, despite their high-cost PTFE fibres still have found their way into a number of applications like filtration, membrane support fabrics, anti-friction applications, spacesuits, UV-durable fabrics, sewing threads and dental floss.

An interesting breakthrough in PTFE processing was recently

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suggested by Tervoort et al. [8], who developed a method based on blending high and low molar mass PTFE grades into bimodal grades which were found to be melt-processable, while at the same time exhibiting good mechanical behaviour. In a subsequent study, the same authors also demonstrated that PTFE's of narrow molecular weight distribution comprising a very small (0.04 mol.% - 0.4 mol.%) amount of perfluoro(propyl vinyl ether) (PPVE) results in melt-processable PTFE [9]. These materials are referred to as modified PTFE homopolymers as the minute comonomer content does not compromise the unique properties of PTFE-like in the case of commercial PTFE copolymers, which typically contain 1.5 mol.% PPVE or 5 mol.% of hexafluoropropylene. It was shown that these modified homopolymers with melting temperatures of around 320 °C could be melt-spun into fibres without the need of special additives (pastes) [10]. Fibres could be produced with a thickness of approximately 20 µm and a maximum Young's modulus and tensile strength of 1.9 GPa and 258 MPa.

Despite the potential of these modified grades for creating micron sized PTFE fibres through melt-spinning, these grades still are not soluble in common organic solvents hampering their use in solution-based processes such as electrospinning. Electrospinning is currently regarded as the method of choice for nanofibre fabrication, with potential applications in filtration, textiles, composites and biomedicine. Various polymers have been successfully electrospun into ultrafine fibres in recent years, mostly from solutions. Recently, an alternative method for the creation of ultrafine PTFE fibres was proposed [11]. This so-called "jet-blowing" method is performed in a tube at temperatures around the melting temperature of PTFE by blowing a high-pressure nitrogen and argon gas into a melt. Although, in principle a relatively simple process, the processing conditions are often not stable due to the extremely high viscosity of PTFE melts and as a result, there is a high portion of undrawn PTFE particles present in the resulting fibre mats. Besides, jet-blowing facilities are rather uncommon, particularly when compared to standard extrusion lines, meaning that they are not easily introduced into an industrial environment.

The objective of the current study is to develop a simple method to produce ultrafine fibres from PTFE homopolymer using an easy and environmentally friendly process with the potential for industrial scaling-up. For this, a modified island-in-the-sea spinning method was explored. Traditional island-in-the-sea spinning involves the use of two incompatible polymers that are melt-blended together to form a morphology that resembles an islands-in-sea morphology [12,13]. In the blend, the island parts are polymer that will be drawn into fibres while the sea part is the matrix that is used to facilitate the drawing process and will be removed in a final processing step after drawing, leaving discontinuous 'staple-like' fibres. In this study, we choose water soluble PVA as the matrix, as it can be easily removed in an environmentally friendly process using only water.

Technically speaking the method proposed is not a conventional sea-island method as both polymers are not processed above their respective melting temperatures since PVA decomposes already below its melting temperature and PTFE has little fluidity in the melt. In order to enable the processing of these two (melt) intractable polymers, we choose to disperse solid PTFE particles (islands) into a PVA solution (sea). Therefore, instead of melt blending and a sea-island morphology driven by phase separation, here we use a solution-suspension mixture that is processed at temperatures below the melting temperatures of both polymers. After cold drawing, the solid PTFE particles are stretched into PTFE fibres. As mentioned earlier, water is selected as a solvent because of its environmentally friendly character and the low processing temperatures involved, while it also allows for an easy removal of the PVA in the subsequent matrix extraction step that finally leaves the

ultrafine PTFE fibres.

## 2. Experimental

Poly(vinyl alcohol) (PVA), 98–99% hydrolyzed, with a typical weight average molecular weight  $M_w$  of 95,000–124,000 g/mol was purchased from Sigma-Aldrich Co Ltd. Poly(tetrafluoroethylene) (PTFE) was used in the form of a Teflon® (PTFE TE-3893 N) aqueous dispersion from Dupont de Nemours Int'l S.A. containing 60 wt% PTFE particles in water with particle diameters ranging from 50 nm to 500 nm, and an average diameter of 210 nm [14]. This PTFE resin has a crystalline melting temperature of 337 °C and cannot be processed by solvent or melt techniques but is instead typically processed as a dispersion for making coated or impregnated fibre or wire products. Received as a milky white dispersion in water with a viscosity at room temperature of approximately 25 mPa s, it also contains approximately 6% (by weight of PTFE) of a non-ionic wetting agent and stabiliser. According to DuPont's Product Information sheet, in its final form as thin film, Teflon® PTFE TE-3893 N has a typical tensile strength of 24 MPa.

A DSM X'plore 15 micro-compounder was used for the preparation of the final suspensions. First, we pre-mixed the PVA powder, as-received PTFE suspension (35 wt% water) and some additional water in a beaker to obtain mixtures of different compositions (PTFE content in the PTFE/PVA are respectively 5.7, 12, 19, 26, 35 vol %), with the PVA concentration in water maintained at around 25 wt%, as this concentration gave a good consistency for processing. Compounding was performed in two steps with the first step being a pre-mixing step without recirculation at low speed (20 rpm) and 85 °C. This pre-mix was subsequently re-compounded at 85 °C for 10 min at a speed of 50 rpm. This two-step mixing procedure was followed to avoid liquid-solid separation and to ensure homogeneous blends of PTFE in the PVA solution.

After compounding and pelletizing, blends were dried in an oven for 3 h at 80 °C and then hot-pressed into films of 1 mm thickness, using a Collin P 300 E hot-press at 130 °C. One strand of 50 mm length was pressed into one film. Films of different compositions were made with the final PTFE content ranging from zero to 35 vol%. These films are cut into strips (10 mm × 50 mm) and drawn by hand into oriented tapes on a hot-plate at 100 °C using pliers. The final step of the sea-island process is the removal of the PVA from the drawn tapes using hot water of around 80 °C and magnetic stirring. After draining the PVA/water solution through filter paper (MF-Millipore mixed cellulose membrane filter, 0.1 µm pore size) (Merck) the PTFE nanofibres are obtained. Fibres were rinsed a few times more to remove PVA remains of the surface of the PTFE fibres.

Mechanical properties of blend tapes with dimensions around 50 mm × 5 mm × 0.2 mm were tested using a universal tensile tester (Instron 5566) equipped with a 1 kN load cell at a test speed of 5 mm/min. The melting temperature ( $T_m$ ) was measured using Differential Scanning Calorimetry (DSC) (Mettler-Toledo 822e) and involved a temperature scan from room temperature to 400 °C at a rate of 5 °C/min. Because of the degradation of PVA, we only take the first heating curve of DSC. Specimens – tapes as well as films – were cold-fractured in liquid nitrogen and sputtered with gold for Scanning Electron Microscopy (SEM) (FEI Inspector-F) investigations. Microstructures were observed using a SEM equipped with Energy Dispersive Spectroscopy (EDS) to identify the PTFE fibres in the blend, which is further confirmed with FTIR test in ATR mode. Fourier transform infrared (FTIR) spectra of various samples were measured with a Bruker Tensor 27 spectrometer. Attenuated total reflectance (ATR) mode was taken for the IR measurement. The spectra were obtained by collecting 64 scans at a  $4\text{ cm}^{-1}$

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