

Polytetrafluoroethylene nano/microfibers by jet blowing

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Received 5 July 2006; received in revised form 26 September 2006; accepted 27 September 2006

Available online 27 October 2006

Abstract

Polytetrafluoroethylene (PTFE) fluoropolymer exhibits extreme chemical and thermal stability, low friction coefficients and many other exceptional properties. Unfortunately, very high molecular weight PTFE has an extremely high melt viscosity ($\sim 10^{10}$ – 10^{12} poise) and negligible solubility in common solvents. Under tensile stress, molten PTFE elongates and breaks rather than forming fibers and processing it is generally laborious and expensive. We have developed a simple, environmentally friendly, single step, solvent-free technique to process very high molecular weight PTFE inside of a high pressure jet of gases such as nitrogen or argon into mats of micro and nanofibers that are up to several millimeter long. Plasticization of PTFE by the hot, high pressure gases within the jet and extensional stretching in the jet nozzle appear to facilitate fiber formation even at temperatures below the melting point. Polarized Raman spectra demonstrate that the PTFE polymer chains exhibit substantial alignment along the fiber axis. The fibers are produced at a rapid rate and adhere to many different materials, allowing for facile fabrication of surface modifying coatings and dense fibrous mats to control properties such as surface hydrophobicity, drag, and biocompatibility. Jet blowing is also suitable for more conventionally processible polymers and formation of polycaprolactone (PCL) fibers is demonstrated.

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Keywords: Nanofibers; Polytetrafluoroethylene; Polycaprolactone

1. Introduction

Polytetrafluoroethylene (PTFE) is a fluoropolymer that exhibits extreme chemical and thermal stability, low friction coefficients, considerable biocompatibility, and many other exceptional properties [1]. The special properties of PTFE arise because of its strong chemical bonding and very high molecular weight, the shielding of its carbon backbone by fluorine atoms, and the intermolecular interactions between its very long, helical, $(CF_2)_n$ chains. These special chemical and structural features also give ultra-high molecular weight PTFE an extremely high melt viscosity ($\sim 10^{10}$ – 10^{12} poise) and a negligible solubility in all common solvents. Ever since it was observed that because of this high melt viscosity, molten

PTFE elongates and breaks under tensile stress [2], there has been great interest in improved methods for forming it into fibers [1]. Modern processing techniques for PTFE generally resemble those used in powder metallurgy and involve multiple steps such as lubricated paste extrusion followed by stretching and/or sintering [1,3]. We have developed an environmentally friendly, single step, solvent-free technique to process pure ultra-high molecular weight PTFE at temperatures even below its melting point into micro and nanofibers up to 3 or 4 mm long inside of a high pressure jet of gases such as nitrogen or argon. Jet-blown PTFE fibers are produced in large quantities at a rapid rate and adhere to many different materials, allowing for facile fabrication of surface modifying coatings and dense fiber mats. The fibers can be deposited at precise locations on a surface, allowing for the control of the hydrophobicity, drag, and other properties of such surfaces. Moreover, jet-blown fibers can exhibit complex nanostructure resulting from the tendency of PTFE to fibrillate. Fibers can be fabricated that are composed of fibrils that

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have diameters of 20–30 nm and exhibit substantial molecular orientation or exhibit other complex nanoarchitectures, potentially providing substantial control over the wide range of properties that depend on nanoarchitecture, including surface biological properties and bioresponse. This ability may allow for extension of the range of application of PTFE, which has been hindered by the challenges associated with processing it into useful forms. Jet blowing may also provide a novel means to fabricate micro and nanofibers of a range of other polymers that are currently difficult to process by established means such as electrospinning or melt blowing [4–6].

We find that jet blowing can also be used to make fibers of polymers that are easier to process than PTFE, such as polycaprolactone (PCL). PCL is easy to synthesize and is often used as a biodegradable scaffold. Processing of PCL into fibrous form by electrospinning has been investigated [7–9]. Jet blowing of PCL was performed near the melting temperature using nitrogen gas and large surface areas were coated with PCL microfibers.

2. Experimental section

A 0.5 g sample of commercial ultra-high molecular weight PTFE 601A or 7A (DuPont) or polycaprolactone (Aldrich) was loaded into a 1/4" ID stainless steel tube capable of containing 270 MPa. A stainless steel nozzle (see Fig. 1a) that had a 1/16" opening terminated by a capillary opening of

50–150 μ in diameter and 0.5–2 mm long was connected to this stainless steel tube via a commercial high pressure coupling and the assembly was heated to the desired jet-blowing temperature in the range of 260 °C–360 °C for PTFE and 80 °C for PCL. A valve was opened to allow high pressure argon or nitrogen into the preheated 1/4" stainless steel tube to initiate the jet-blowing process. The entire sample was discharged in fibrous form onto a substrate in less than 1 s.

Micro-Raman spectra (Dilor XY, 514 nm excitation) were collected in a back-scattering geometry with a 100×0.95 numerical aperture objective, except for spectra collected on multiple fibers or powders, which were collected with a 10×0.2 numerical aperture objective to average over many orientations. Polarized micro-Raman spectra were collected on PTFE 601A fibers jet blown at 310 °C using a rotating half-wave plate located behind the microscope objective, as described by Duesberg et al. [10]. Because the half-wave plate is located behind the microscope objective, both the laser polarization and the polarization of the Raman scattered light are rotated by it. In this configuration the laser polarization can be rotated with respect to the fiber axis in a manner equivalent to a simple physical rotation of the fiber [10]. (It is difficult to physically rotate very small fibers and maintain the laser spot in the same position on the fiber.) Any rotation of the polarization as the laser passes through the half-wave plate is compensated by the rotation of the Raman light scattered back through the wave plate. It is thus not necessary to change

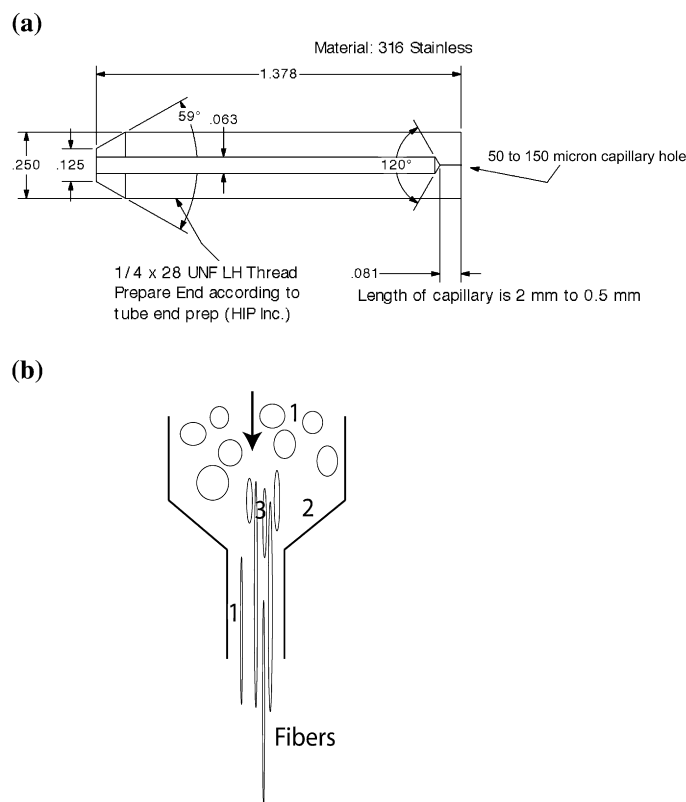


Fig. 1. (a) Engineering drawing of the nozzle used for jet blowing. (b) Schematic representation of the jet-blowing process. High pressure gas at an elevated temperature forces particles of PTFE starting material through an approximately 25:1 axisymmetric contraction. Numbers indicate regions of principally shear flow (1), a vortical region (2), and an extensional flow region just upstream of the contraction (3), where fiber formation likely occurs.

the polarization axis of the analyzer of the Raman instrument, which was kept perpendicular to the entrance slits (vertical) at all times, and no correction was needed for the variation in instrument efficiency with polarization. The 100× microscope objective focuses the laser to a spot size of approximately 1 μm, which allowed for sampling of individual micron to sub-micron size fibers that were well isolated from any neighboring fibers. No beam displacement was observed when the laser polarization was rotated by the half-wave plate; therefore precisely the same spot on an individual fiber could be analyzed with the laser polarization parallel and perpendicular to the fiber axis. Differences in Raman mode intensities as a function of half-wave plate rotation were only observed for fiber samples that had molecular alignment; no differences in Raman mode intensity with rotation of the laser polarization were observed for particles of the PTFE starting materials.

DSC analyses were performed on a TA Instruments calorimeter at a heating rate of 10 °C/min. Wide-angle X-ray scattering (WAXS) patterns were collected with a step-scan diffractometer (Phillips, Cu K α radiation) on randomly oriented samples of the PTFE 601A fibers jet blown at 310 °C and of the PTFE 601A starting material. Low magnification SEM analyses were performed with an environmental SEM (FEI-Quanta 200) on uncoated fibers in the presence of several torr of water vapor to prevent charging. High resolution images were collected with a field emission SEM (JEOL-6700F) after coating the samples with gold. Nitrogen solubility measurements were performed using a volumetric sorption technique described by Duda et al. [11]. XPS measurements were performed using a Kratos spectrometer. The contact angle of water droplet on the PTFE fibers was measured using a contact angle meter at room temperature with an accuracy of $\pm 3^\circ$. The reported values are the average of three measurements made at different positions of a fiber mat.

3. Results and discussion

Jet blowing is performed in a single step by spraying a two-phase mixture of gas and solid polymer at elevated temperature and pressure through a single capillary orifice. We have used orifices ranging in diameter from 50 to 150 μm and in lengths from 0.5 to 2 mm (Fig. 1a). Behind the orifice the flowing high pressure gas and polymer are mixed in a tube that is larger in diameter, such that there is an approximately 25:1 axisymmetric contraction. The flow driven through this abrupt contraction at the entrance of the capillary by the large pressure drop has strong extensional and shear components, which result in deformation, extension, and reorientation of the polymer chains to form fibers (Fig. 1b). It is not possible to form fibers of PTFE by conventional melt blowing or electrospinning, in which a polymer extruded through an orifice is stretched outside of it by a pair of nearly parallel impinging jets of gas or an electric field, respectively [4,5]. Thus PTFE is typically considered to be neither melt nor solvent processible [1]. In contrast, during the jet-blowing process a two-phase mixture of gas and polymer is driven by pressure through a single nozzle, resulting in fiber formation inside

the nozzle accompanied by much higher shear rates and extensional stretching than are otherwise possible. Jet blowing is different from a simple extrusion process because the multiple fibers formed in parallel within the nozzle are much smaller than the nozzle diameter.

The flow field within the nozzle can be qualitatively characterized as shown in Fig. 1b: (1) regions of shear-dominated flow far upstream and downstream of the contraction, (2) a vortical corner region at the capillary entrance, and (3) the extensional flow region just upstream of the contraction. In the fully developed regions far upstream and downstream of the contraction (1), the flow field can be locally characterized by simple shear flow which contains both extensional and rotational components. The presence of vorticity in simple shear flow allows the polymer chains to rotate as they deform, thereby reducing the extent of chain stretching. In region (2), the vortical flow field will rotate the polymer chains without significant deformation. In the entry region (3) near the centerline just upstream of the 50–150 μm diameter capillary, on the other hand, the flow field can be locally characterized as pure straining flow. The polymer chains will experience their maximum deformation/elongation in this extension-dominated region, which likely plays a critical role in fiber formation.

Using both nitrogen and argon, we have jet-blown the DuPont Teflon 601A PTFE, a “fine powder” resin, [1] into dense mats of fibers up to 3–4 mm long. The fibrous mats readily adhere to substrates such as silicon or glass. Scanning electron microscope (SEM) analyses of these substrates show that the fraction of fibrous material deposited is very high (Fig. 2a,b). The fiber diameters range from submicron to a few microns, depending on the processing conditions. The pressure required to deposit fibers ranges from approximately 100 MPa at 260 °C to 13 MPa at 360 °C. Thus jet blowing of fibers is possible at temperatures much below the melting point of virgin PTFE 601A, which is 340 °C at 0.1 MPa. Fibers processed below the melting point exhibit micro-Raman spectra (Fig. 3a) and a melting point determined by differential scanning calorimetry (DSC) after processing was identical to that of the starting material (340 °C), indicating that they have not been decomposed or chemically altered. X-ray photoelectron spectra (XPS) showed that the surface composition is principally carbon and fluorine in the expected stoichiometric ratio, with 0.2% or less oxygen; virtually no surface oxidation is present.

The crystallinity and degree of chain alignment are important characteristics of polymer fibers. Lehnert et al. have reported a thorough investigation and comparison of techniques for the characterization of the crystallinity of PTFE and found excellent correlations between the trends observed by means of WAXS, DSC, density measurements, and infrared and Raman spectroscopies [12,13]. Little or no amorphous background was observed in the WAXS patterns (inset Fig. 3a) for either the jet-blown fibers or the starting material, indicating that both are highly crystalline [13,14]. Lehnert et al. concluded that the best Raman spectroscopic signature of the degree of crystallinity is the ratio of the integrated intensity of the shoulder present on the 1381 cm⁻¹ mode (see

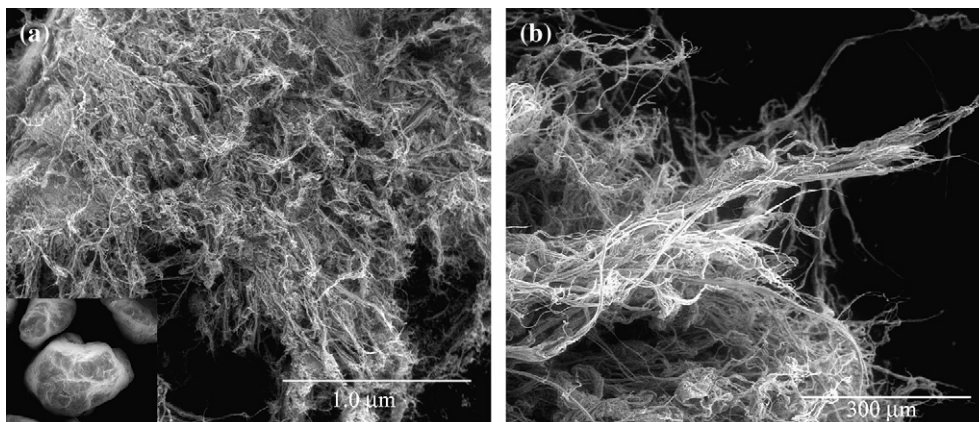


Fig. 2. SEM micrographs of a fiber mat (a) formed by jet-blowing of PTFE 601A fine powder starting material with a granule size of ~ 0.5 mm (see inset) in nitrogen at a temperature (310 °C) below the melting point (340 °C). (b) Individual fibers can be seen projecting out of the edge of the mat.

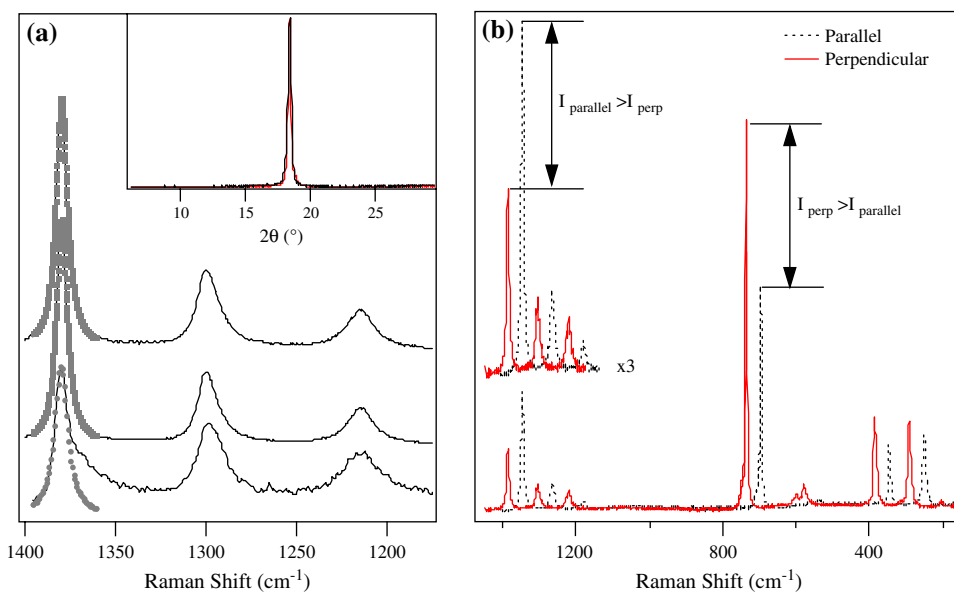


Fig. 3. (a) Micro-Raman spectra in the region of the 1381 cm^{-1} CF_2 stretch mode of PTFE. This mode has been reported to be sensitive to the crystallinity of PTFE [10,11]. Shown are the spectra at 0.1 MPa and 20 °C of virgin PTFE 601A (top), a PTFE 601A fiber jet blown at 310 °C (middle), and PTFE that has been melted once by heating above 340 °C (bottom) and then solidified. Grey dots are a Lorentzian fit to the 1381 cm^{-1} mode. Only the PTFE that has been melted (bottom) exhibits the low frequency tailing of 1381 cm^{-1} mode associated with reduced crystallinity and melts at 326 °C, according to DSC. No difference is observed in the intensities and positions of the modes of virgin PTFE 601A and jet-blown PTFE 601A, which were also identical throughout the rest of the Raman spectrum. The inset shows two overlaid X-ray diffraction patterns for virgin PTFE 601A and a jet-blown PTFE 601A fiber, which were nearly identical and thus cannot be distinguished in the figure. (b) Polarized Raman spectra of individual PTFE 601A fibers jet blown at 310 °C parallel (solid) and perpendicular (dashed, offset by -40 cm^{-1} for clarity) to the fiber axis. For both polarizations spectra were collected on single, isolated fibers in exactly the same location along the length of the fiber.

Fig. 3a) to that of the 1381 cm^{-1} mode itself [13,14]. There is no shoulder in the spectra of either the 601A starting material or the jet-blown PTFE fibers (Fig. 3a), consistent with highly crystalline material. DSC analyses of them gave enthalpies of melting of 73.0 and 72.0 J/g, respectively. These values are near the upper end of the range observed for various PTFE samples [13], again indicating that the degree of crystallinity is high.

The small size of the fibers makes it difficult to probe their orientation by means of X-ray diffraction. Polarized Raman spectroscopy, however, is an excellent tool for probing the orientation of the polymer chains in fibers [15]. Micro-Raman

spectra of PTFE 601A fibers jet blown at 310 °C exhibited substantial intensity differences when the laser polarization was rotated from parallel to a fiber axis to perpendicular to it (Fig. 3b). The intensities of the 1381 and 732 cm^{-1} modes, in particular, changed considerably relative to the intensity of the 1301 cm^{-1} mode, which did not change. These intensity changes can only be present when there is orientation of the polymer chains with respect to the fiber axis. The same pattern of Raman mode intensity changes upon rotation of the laser polarization (which are determined by the orientation of the polymer chains and the mode symmetries) has been reported for paste extruded PTFE fibers [3] and was also observed in

a highly uniaxially oriented, high strength fiber supplied by W.L. Gore Associates. Thus the alignment of the long PTFE molecules in the jet-blown fibers must be, like that of the >0.5 mm diameter paste extruded fibers and the high strength fiber from Gore, parallel to the fiber axis. No changes in mode intensities were observed upon polarization rotation when a low magnification objective was used to collect spectra averaged over many fibers within a jet-blown PTFE mat or from the starting material. We conclude that the high pressure jet-blowing process is not merely “disintegrating” the starting material into smaller structures, but rather forming aligned fibers of 3–4 mm long. Moreover, ratio of the intensities observed for the 1381 cm^{-1} mode in the parallel and perpendicular polarization directions is 1.89, larger than the maximum ratio observed (as a function of extrusion pressure) for the paste extruded fibers of 1.73 [3]. Thus the degree of alignment in the jet-blown fibers is larger than that reported for the paste extruded fibers.

Like many other forms of PTFE, 601A starting material that has been melted at least once exhibits reduced crystallinity, as evidenced by a low frequency tailing of the 1381 cm^{-1} Raman mode (Fig. 3a), a lowered melting point of approximately $326\text{ }^{\circ}\text{C}$ upon a second melting, and an enthalpy of melting of 27.1 J/g [12,13,16,17]. These features are not observed for fibers jet blown at temperatures below the melting point of virgin PTFE (Fig. 3); there is no tailing of the 1381 cm^{-1} Raman mode, the melting point remains $340\text{ }^{\circ}\text{C}$, and the enthalpy of melting is much larger, 72.0 J/g . Such features are characteristic of crystalline PTFE that has never been melted. We conclude that the physical structure of the fibers has not been changed in the manner associated with melting during jet blowing. Even though the fibers are processed at a temperature below the melting point of pure PTFE, dissolution of high pressure gas or fluids into PTFE might conceivably lower the melting point, as happens when supercritical carbon dioxide dissolves in PTFE [18]; such a depression of the melting point does not appear to happen in the present experiments. The ability to process PTFE in one step into fibers at temperatures below the melting point and without lubrication may afford advantages such as additional control over the PTFE micro/nanostructure, crystallinity, and the avoidance of decomposition, which has been identified as a source of halogenated organic acids that are environmentally deleterious in even very small concentrations [19].

The question remains how fiber formation from solid PTFE actually occurs within the jet-blowing nozzle given that its high shear modulus should prohibit it. A complete answer to this question will require considerable further investigation. However, we note that at $67\text{ }^{\circ}\text{C}$ and 51 MPa the solubility of nitrogen in PTFE is approximately $3.5\text{ wt}\%$ and increases with temperature [20,21]. Our measurements of the solubility show that at $260\text{ }^{\circ}\text{C}$ and a considerably lower pressure of 10 MPa , the solubility is $1\text{ wt}\%$, about the same as at $67\text{ }^{\circ}\text{C}$ at the same pressure. Thus at least a few wt% solubility of nitrogen can be expected at the pressures and temperatures typically used for jet blowing. We suggest that this dissolved nitrogen plasticizes and softens the PTFE and facilitates fiber

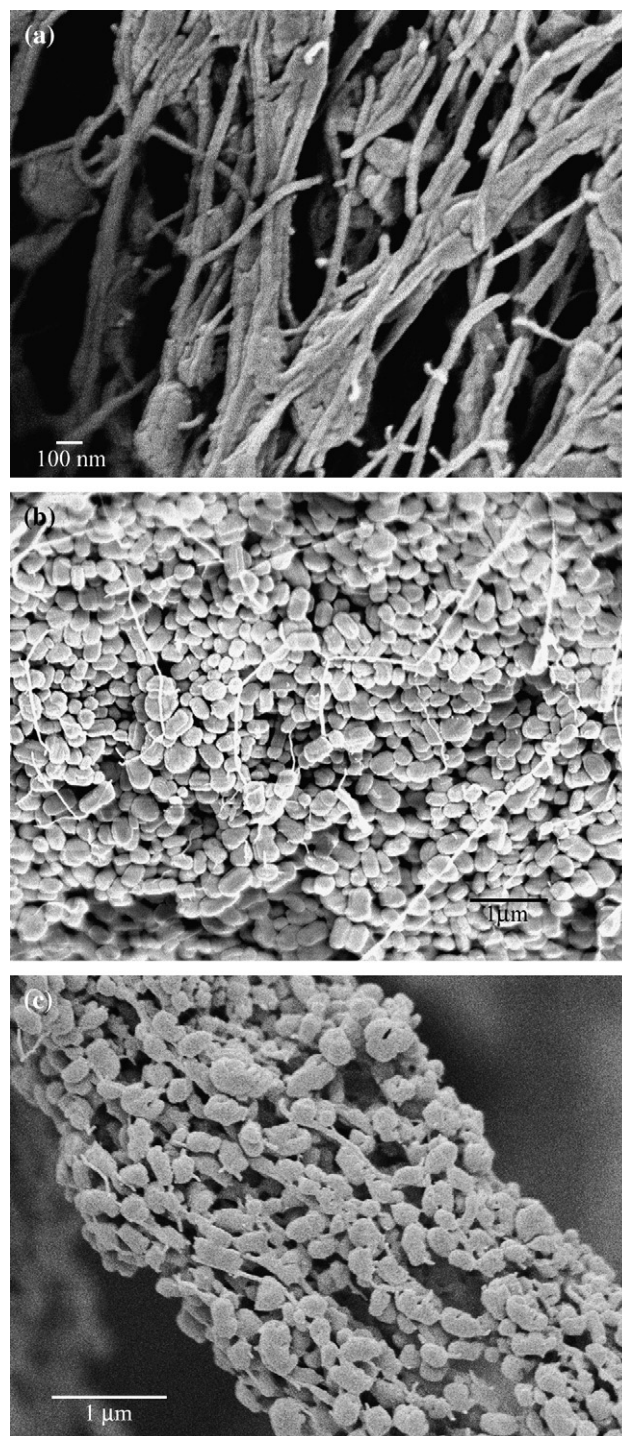


Fig. 4. High resolution field emission SEM micrographs of (a) PTFE 601A jet blown at $350\text{ }^{\circ}\text{C}$ exhibiting nanoscale fibrils, (b) virgin PTFE 601A showing nanoscale nodules and (c) a single PTFE 601A fiber jet blown at $310\text{ }^{\circ}\text{C}$ exhibiting shorter, but still aligned, nanoscale fibrils interconnecting the nanoscale nodules.

formation. It is not unreasonable to expect some plasticization of PTFE by dissolved nitrogen in view of the considerable reduction in viscosity observed when carbon dioxide dissolves in it [18]. Plasticization of PTFE by high pressure nitrogen at $80\text{ }^{\circ}\text{C}$ has been reported [22] although there is some uncertainty about the effect of temperature on these measurements

[20]. If there were no reduction in the viscosity of PTFE, particularly below the melting point, then it is unlikely that jet blowing through the capillary orifice to form fibers would occur. Once the viscosity of PTFE is reduced enough to allow for flow through the nozzle, the forces experienced by the polymer within the extensional region of the jet may further decrease the viscosity of the viscoelastic PTFE and thus also facilitate fiber formation.

In general individual jet-blown micro or nanoscale PTFE fibers exhibit considerable further nanostructure on length scales much smaller than the fiber diameter. The tendency of PTFE to fibrillate is well known and is exploited in the formation of semi-permeable expanded PTFE membranes [1]. We find that fibrillation also occurs for jet-blown PTFE, although in a manner quite different from that observed for the expanded PTFE. For example, when PTFE 601A is jet blown at a temperature of 350 °C, a temperature above the melting point, a field emission SEM micrograph of a portion of a single fiber reveals that it is composed of 20–30 nm diameter fibrils (Fig. 4a) that are largely oriented in the direction of the fiber axis (observed by low magnification SEM). This nanostructure is very different from that of the 601A starting material, which consists of nanoscale nodules that form in the emulsion polymerization used for synthesis [1] (Fig. 4b).

The degree of fibrillation in jet-blown fibers is strongly influenced by the processing temperature; fibers processed at temperatures below the melting point of 340 °C show less fibrillation, whereas those processed above the melting point

have a lower viscosity and therefore are more easily fibrillated. A PTFE fiber jet blown at 310 °C, for example, exhibits relatively short, but still substantially aligned (as evidenced by the aforementioned polarized Raman spectral data) fibrils connecting the original nanoscale nodules (Fig. 4c).

Even “granular” DuPont PTFE 7A resins that exhibit little or no nanoscale structure (Fig. 5a) can be jet blown at 310 °C into fiber mats (Fig. 5b) and fibrous structures that exhibit a large number of relatively uniform nanoscale pores when imaged under higher magnification (Fig. 5c) or at 330 °C into bundles of nanoscale fibrils (Fig. 5d). Thus the fiber morphologies can be tuned by varying the jet-blowing temperature. Processing of granular PTFE 7A at lower temperatures (310 °C) requires higher pressure for fiber formation and mainly results in fibers with uniform nanoscale pores. However, jet blowing at higher temperature (330 °C) does not require high pressures and mainly resulted in bundles of nanoscale fibrils. Obtaining an understanding of the details of the origin of these differences will again require further investigation. We speculate that more gas may dissolve into PTFE when processed at higher pressures and lower temperatures (310 °C) and allow for pore formation upon the release of the gas when exiting the nozzle.

Dense resins such as PTFE 7A are so difficult to process so that they are typically used only for fabricating structures by high pressure sintering techniques and are not used to make fibers or expanded PTFE, as they cannot be lubricated for extrusion [1]. The ability of jet blowing to fabricate fibers of

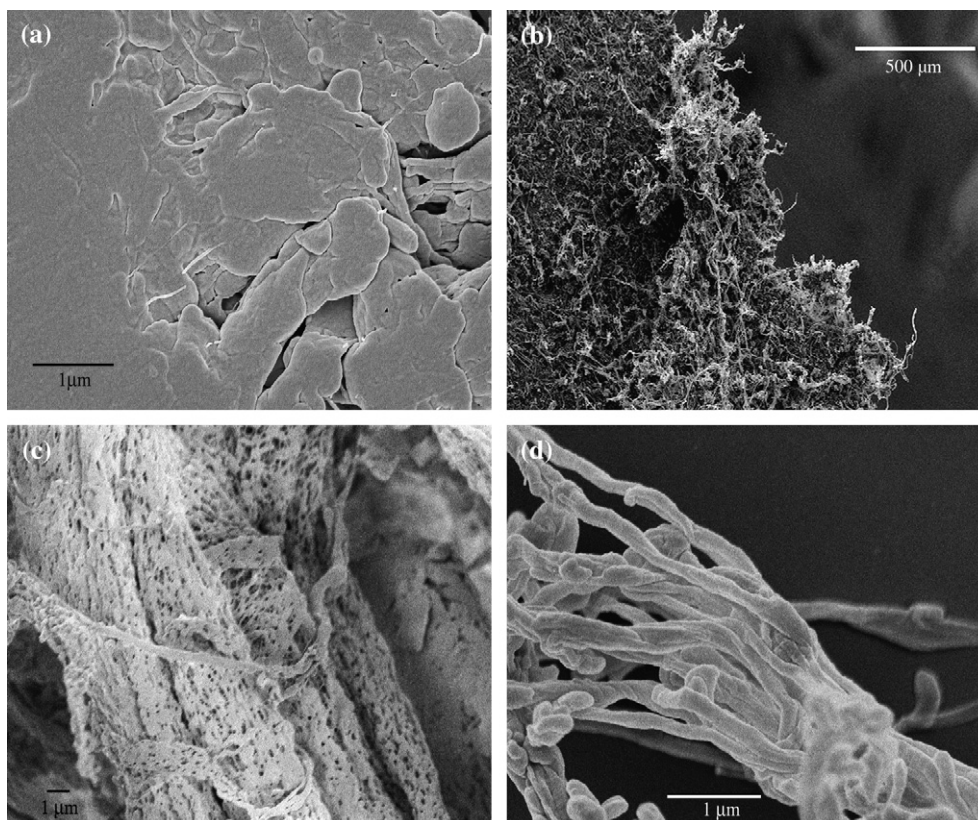


Fig. 5. SEM micrographs of (a) virgin PTFE 7A, (b) the edge of a fiber mat of PTFE 7A, (c) PTFE 7A jet blown at 310 °C exhibiting nanopores and (d) a PTFE 7A fiber jet blown at 330 °C composed of nanofibrils.

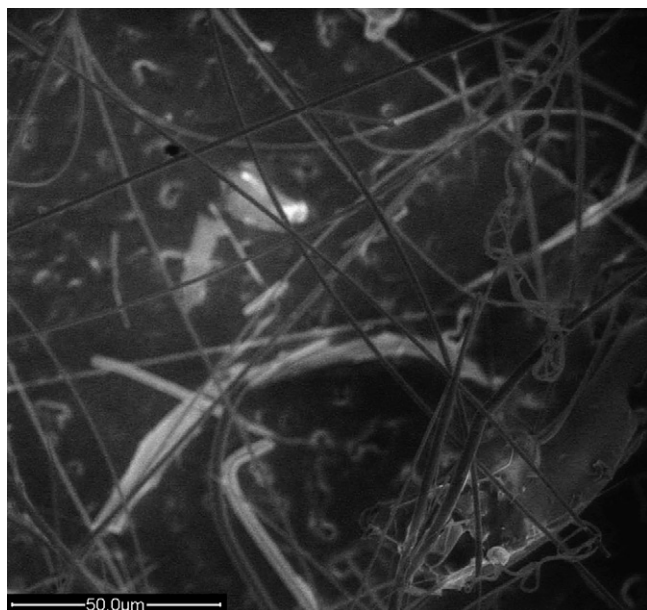


Fig. 6. E-SEM image of PCL jet blown at 80 °C.

dense, extremely viscous and very difficult to process resins such as 7A is a notable advantage of the technique. The complex three dimensional nanostructure of the jet-blown 7A fibers, such as the nanoscale pores, is also unusual for PTFE materials.

PTFE is intrinsically hydrophobic and the complex structure down to the nanoscale of the surfaces coated with jet-blown fibers might be expected to further increase the hydrophobicity. There is considerable interest in the fabrication of superhydrophobic surfaces from both scientific and applied perspectives [23]. Water droplets placed upon the surface of jet-blown PTFE 601A fibers exhibit a contact angle of 147°, much higher than the contact angle of a flat PTFE surface, which is 113° [24]. Thus jet blowing allows for single step fabrication of very hydrophobic surfaces that exhibit extreme chemical inertness.

Jet blowing is not limited to forming fibers of difficult to process polymers such as PTFE. Commercial PCL has the melting temperature of 60 °C and when jet blown at 80 °C an almost quantitative yield of microfibers was obtained, SEM images of these materials show formation of fibers with diameters of 2–3 μm (Fig. 6). In contrast to PTFE, PCL does not exhibit a tendency to fibrillate and jet-blown PCL fibers show no evidence of fibrillation. Thus fibrillation in jet-blown polymers only appears to be favored in those polymers, such as PTFE, that already have an intrinsic tendency to fibrillate.

4. Conclusions

We have observed that it is possible to fabricate millimeter long micro/nanofibers of PTFE both above and below its melting point of 340 °C with a high pressure jet of nitrogen or argon. Although the range of application of PTFE structures is already quite large [1], yet many more applications have been hindered by the large challenges involved in processing this insoluble, extremely viscous polymer. Jet blowing may

provide means to coat surfaces with thin films of fibrous PTFE or embed mats of PTFE fibers that themselves are porous or expanded into matrices of other materials, further extending the range of application. Currently there is considerable interest in designing of polymer nanoarchitectures that give desired biological compatibilities and response; in particular there is great interest in reducing the biofouling or selectively enhancing the growth of a given type of cell or tissue on a surface. PTFE is already noted for its biocompatibility; the ability to straightforwardly process it into fibrous materials that can have different, complex three dimensionally structured nanoarchitectures (depending on the starting material and processing conditions) may allow for improved control of the in vivo biological response to it. Jet blowing can also be extended to process polymers that have lower melt viscosities, such as polycaprolactone.

Acknowledgements

The authors thank Drs. H. R. Allcock, J. L. Duda, and A. Borhan for valuable discussions. The technical assistance for ultrathincryotomy by Missy Hazen is also acknowledged. This work was supported by the National Science Foundation. We thank W.L. Gore and Associates, Inc. for the uniaxially oriented PTFE threads.

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