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STUDY JET-BLOWING CONDITIONS ON PTFE NANO-FIBERS (nPTFE)

AND SURFACE MODIFICATION OF nPTFE USING GAS PLASMA

A Thesis in

Chemistry

by

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ABSTRACT

Polytetrafluoroethylene (PTFE) is very hydrophobic and difficult to be processed into micro / nano-sized fibers. A new jet-blowing technique developed in our lab could fabricate PTFE nanosized fibers (nPTFE) under high pressure and high temperature condition without using a solvent.

There were two aims in this work. First was to study the conditions of jet-blowing process such as gas pressure, gas type and temperature on the effect of nPTFE fiber morphology. These fibers were examined by the mean of scanning electron microscopy. Processing temperature affected the fiber size the most. With higher temperature, the resulting fiber was longer and smoother. Gas pressure caused least effect to fiber size.

Secondly, surface modifications of PTFE materials using radio frequency glow discharge (rfGD) gas plasma with different conditions were studied. Samples of nPTFE were exposed to atmospheric plasma containing N₂/Ar, O₂/Ar, or Ar gas(es). PTFE was exposed to low pressure rf plasma containing NH₃ gas. The modified surfaces were characterized by x-ray photoelectron spectroscopy, attenuated total reflection infrared spectroscopy and water contact angle measurements shortly after plasma treatment. The most fluorine depletion of nPTFE surface was caused by Ar plasma and least by O₂/Ar plasma. Oxygenated and amine functional groups were introduced to treated surfaces.
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Chapter 1
Introduction

1.1 Micro / Nano-structured Fibers

1.1.1 Features and Applications

Fibers with diameters in the range of nanometers and a few microns are intensively studied in academic and industry recently, especially synthetic polymer nanofibers. [1] These polymer nanofibers not only have the properties of the polymer, but also have properties of nanofibers, such as large surface area to mass ratio, high pore volume and tight pore size. These nanofiber materials are ideally suit for a wide range of filtration applications, filtering submicron particles from air or water. Examples are aerosol filters, facemasks, and protective clothing. They are also used in some medical applications, which include drug delivery, wound dressing in medical industry, artificial blood vessels and artificial heart-valves. [1,2]

1.1.2 Conventional Fibrillation Methods

Traditional methods available to process polymers into fibers include electrospinning and melt-blowing. Electrospinning, also known as electrostatic spraying, was discovered over 100 years ago. The schematic of the Electrospinning setup is shown in Figure 1.1. By applying 5-30 kV electrical...
charge to a polymer solution or melt, and establishing a static electric field between the liquid and a grounded collecting plate, a fiber is drawn from the tip of the nozzle. After the solvent evaporates, it results in fibers with diameters in the range of nanometers and a few microns. [3] To date, over 50 synthetic and natural polymers have been electrospun to make fibers, such as a common polymer polyethylene (PE) and a synthetic biodegradable polymer poly(lactic-co-glycolic acid) (PLGA). [1-4]

Melt-blowing is less well-known than electrospinning, but it has its own advantages over electrospinning. It was developed in the 1950’s by the US naval research laboratory. [5,6] With no electrical charge required, it is a one-step process in which high velocity hot air blows a polymer melt from an extruder die to attenuate the fiber. The polymer is stretched by air impinging it from the two opposite sides of the outer slots and fibers are extruded from the central hole. The cross-sectioned view of the Exxon melt-blowing die is shown in Figure 1.2. Diameters of these fibers are in the range of 2 – 4 µm. The polymers which can be melt-blown usually have relatively low melt viscosity. [6-8]

1.2 Polytetrafluoroethylene

1.2.1 Discover and Properties

Polytetrafluoroethylene (PTFE), with its trademark Teflon, is a fluoropolymer synthesized in 1938 by Roy Plunkett of Kinetic Chemicals when he
was attempting to make a new CFC refrigerant. It was patented by DuPont in 1941 [9] and registered with the Teflon trademark in 1944. [10]

PTFE appears as a white solid at room temperature. It has very high melting point of 327ºC. [10] The chemical structure of PTFE is shown in Figure 1.3. It has long C-C backbones completely surrounded by fluorine atoms. Its properties enable it in various applications. It is well known for coating non-stick frying pans and other cookware due to its low friction and thermal stability. Because of its chemical inertness, it is used in containers and pipe work for reactive or corrosive chemicals. It is also used in biotechnology areas, mostly cardiovascular grafts, due to its limited toxicity and biocompatibility. [10,11]

1.2.2 PTFE Fibrillation Methods

1.2.2.1 Fibrillation Difficulty

Two common fibrillation techniques are discussed in Section 1.1.2. Both techniques require the polymer resins to be soluble in a solvent to form a polymer melt and then to be either electrostatically sprayed or melt-blown to nano- or micro-fibers. Since it is not soluble in most solvents, but only soluble in expensive fluorocarbon solvents, it is not practical to using electrospinning. Melt-blowing is only suitable for polymers with relatively low viscosity. PTFE has extremely high viscosity, so it is considered “no-melt processible”. [12] Neither of the two techniques is able to produce PTFE fibers.
1.2.2.2 Paste Extrusion

It is possible to fabricate PTFE fibers via paste extrusion instead of the conventional polymer melt processes. The schematic of the paste extrusion process is shown in Figure 1.4. [13] This technique involves mixing PTFE fine powder resins with a lubricating liquid (lube) to form a paste (Figure 1.4 a), compacting the paste at a typical pressure of 2 MPa (Figure 1.4 b), and then extruding the paste through an extruder around 30°C (Figure 1.4 c). The PTFE fibrils form after the lube evaporates in an oven, and are oriented in the same direction as paste extrusion. [13-15]

1.2.2.3 New Jet-blowing Technique

A new technique called “Jet-blowing” is reported in this work. It is a single-step environmentally-friendly solvent-free technique which produces PTFE nanofibers. [16,17] After heating PTFE fine powders inside a jet-blowing nozzle at a temperature above 200 °C, a line of highly pressurized inert gas (N₂ or Ar) is then introduced to the system and a mixture of gas and solid is formed inside the nozzle before jet-blowing takes place. The apparatus of Jet-blowing will be discussed in Chapter 2.1.1.
1.3 Surface Modification

1.3.1 Importance of Polymer Surface

Since 1960s, synthetic polymers have been used to fabricate medical devices and millions are used in human bodies every year. [1,2] The bulk structure of the material governs its general properties, such as chemical inertness and biocompatibility. However, the surface structure and chemistry of biomaterials directly influences the biological interactions which take place between the surface of biomaterials and the biological systems. Often, synthetic polymers have the desired bulk properties but lack surface properties, particularly wettability and blood compatibility. For example, PTFE is extensively used in medical vascular devices because of its chemical stability. However, the hydrophobicity of PTFE surface limits its potential uses. Modifying the surface of the biomaterials not only retains the properties of the bulk materials, but also enhances specific surface properties to better adapt for biological interactions. [18-20]

1.3.2 Radio Frequency Glow-discharge Plasma

Common ways to modify surfaces of a material are solution treatment, ion implantation, plasma treatment and surface grafting, all of which are involved in chemical reactions, resulting a new polar surface that is firmly combined with the bulk materials. The low temperature plasma treatment is particularly active in the
area of surface modification of synthetic polymers since it causes no dramatic damage to the substrate and no changes to the bulk materials. [20-22] It is reported that many polymer surfaces can be plasma treated to modify the surface properties, such as increase the hydrophilicity. [22-26] Depending on which gas is employed, the corresponding functional groups are deposited to the surface of treated materials. For instance, when the oxygen gas is used, oxygenated functional groups, such as carboxylic group, are likely to be deposited onto the treated surface.

The principle to generate plasma is that

"When a gas under low enough pressure is subjected to a high frequency electromagnetic field, such as the radio frequency, the accelerated ions in the gas collide with the gas molecules ionizing them and forming plasma." [22]

Due to the interactions of the ionized gas particles to the material surface in the plasma environment, the surfaces of certain materials can be physically and chemically modified. A chemical reaction usually takes place between the ionized gas particles and the solid surface within the plasma environment. The types of reactions and the results of plasma treatment depend on many variables, such as the RF power, the type of processing gases, the flow rate and pressure of the gases, the type of sample being treated and the amount of time the surface of the sample is placed within the plasma. [19,21,22]

Radio frequency glow-discharge plasma (rfGD plasma) is the method used to treat the surface in this work. The rfGD plasma can be generated under either low pressure or atmospheric pressure. Under low pressure, it is performed
inside a closed reaction chamber with metal coil (such as cooper coils). An image of low pressure plasma cleaner is shown in Figure 2.2 and the setup is shown in Figure 2.3. In this case, the sample is placed on a sample holder, such as glass micro slides, and placed inside the reaction chamber. A low flow rate (2.4 – 5.0 L/min) of processing gas with low pressure at room temperature is delivered through the tubing and entering the reaction chamber to create plasma by RF electromagnetic filed. Under atmospheric pressure rfGD plasma, samples are mounted on the stainless steel sample stage and placed underneath the plasma region. The atmospheric pressure plasma set up is shown in Figure 2.4. The carrier gas (Ar or He) along with the reactive gas (O$_2$, N$_2$, or CH$_4$) is delivered through the tubing to generate the plasma via a plasma generator. It is able to generate much more powerful plasma than low pressure rfGD plasma.

1.3.3 Gas Plasma on PTFE

Due to the hydrophobic nature of PTFE bulk material, scientists are working on modifying PTFE surfaces to make it more hydrophilic and friendly to biological systems using solution treatment [27,28] and/or gas plasma treatment [23-26, 29-35]. As mentioned previously in Section 1.3.2, using gas plasma to modify PTFE surface would cause less damage on its bulk properties than other methods. The feed gases which have been studied include O$_2$ [24,26,29-34], Ar [24,26,29], N$_2$ [24,32-34] and NH$_3$ [23,24,26,35]. Depending on gas type and treatment time, the results reported in these papers varied quite significantly.
Figure 1.1: Schematic of the electrospinning setup.
Figure 1.2: a) Schematic of melt-blowing setup, b) Cross-sectioned view of Exxon melt-blowing die. [7]
Figure 1.3: a) Chemical structure of PTFE; b) ball and stick model
Figure 1.4: Schematic diagram of fibrillation mechanism of paste extrusion. [13]
2.1 Jet-blowing

2.1.1 Jet-blowing Apparatus

The general experimental set up is shown in Figure 2.1. PTFE fine powder resins were loaded inside a high pressure tube which was placed inside a thermocouple. The thermocouple was connected to a temperature controller, which was connected to a computer. When the sample inside the tube was heated to a desired temperature, the high pressure pump from Newport Scientific (Model 46-14021-2) connecting to a gas tank started pumping gas while the pressure gauge connecting to the pump indicated the pressure. The valve controlled the open access of the gas to the nozzle through high pressure tubing. When it reached at a certain pressure, the valve was opened to release the pressurized gas to the system. A mixture of gas and solid was formed inside the tube and was pushed through the nozzle by the pressurized gas to jet blow a PTFE fiber mat on a substrate, such as a glass micro slide. [16,17]

2.1.2 Jet-blowing Materials

PTFE fine powder (Teflon® PTFE 601A) obtained from DuPont was used in all jet-blowing experiments in this study. It is a white powder composed of
agglomerated PTFE particles. Being DuPont’s highest molecular weight fine powder resin, its melting point is 340 °C (644 °F). It can maintain its useful properties at temperature between -240 °C (-400 °F) and 260 °C (500 °F). It was used as received.

Gases used to generate the high pressure system were purchased from Penn State General Store, and were used as received.

2.1.3 Jet-blowing Condition

Jet-blowing can take place in various conditions depending on the material. In this work, due to the high melting point of PTFE, the temperatures that we studied were ranging from 200 °C up to 300 °C, under the melting point of PTFE. The temperature of the heaters usually is set 5 or 10°C above the final jet-blowing temperature to accelerate heating. Gases employed were N\textsubscript{2} and CO\textsubscript{2} gases. The gas pressures from 5,000 to 14,000 psi were used to jet blow.

2.2 Surface Modification

2.2.1 Plasma Materials

Two types of samples were used in plasma experiments: PTFE film and jet-blown PTFE nanofibers (nPTFE).
The PTFE film (0.012” thick) used in this work was purchased from McMaster Carr (Cat# 1761 T22). The film was cut to 1 cm X 1 cm squares (shown in Figure 3.8 a), sonicated with acetone, distilled water and ethanol (1:1:1) for 5 minutes and air-dried before plasma treatment.

All nPTFE fiber mats were jet-blown at the same condition: the PTFE 601A resins were first heated to 200 ºC and then jet-blown with N₂ at 10,000 psi. The mats with relatively flat surface were cut into 5 mm X 10 mm in size.

2.2.2 Low Pressure Glow-Discharge Plasma

The low pressure plasma treatment on PTFE materials was performed using Harrick PDC-32G Plasma Cleaner shown in Figure 2.3. The plasma cleaner setup is shown in Figure 2.3. The sample was placed on a piece of glass microslide and placed in the reaction chamber. Low flow rate of ammonia gas was delivered to the reaction chamber with RF electromagnetic field and creating plasma. The input power was 100 W and output power 18 W was used. The plasma cleaner was connected to a vacuum pump, which had a pumping speed of 1.4 m³ / hr. Since ammonia gas is caustic and hazardous, the plasma experiments were carried out under a fume hood. The treatment time was longer than the atmospheric pressure plasma, usually 30 – 60 minutes.
2.2.3 Atmospheric Pressure Glow Discharge Plasma

The atmospheric pressure plasma treatment on polymer surface was performed using the atmospheric RF plasma generator (model# MyPL-100 from Atmospheric Process Plasma Co, Ltd., South Korea) and a 13.56 MHz RF power supply with an L-C matching unit from SEREN Industrial Power System. The schematic of the plasma setup is shown in Figure 2. The atmospheric plasma was generated under glow discharge condition. The usable plasma area was 1 cm by 10 cm. Plasma containing three gas mixtures were studied: O\textsubscript{2}/Ar, N\textsubscript{2}/Ar, and Ar gas(es). The gas flow rate of O\textsubscript{2} or N\textsubscript{2} was controlled in the range of 10 – 180 sccm (standard cubic centimeter per minute). Ar flow rate was always at 4.0 L/min. The RF power was controlled in the range of 100 – 200 W. Samples were placed on a stainless steel sample stage right underneath the plasma region. In this work, the amount of time a sample underneath the plasma region was defined as the plasma treatment time. It varied from 10 sec to 120 sec.

2.3 Instrumentation

Several complementary instruments and techniques were used to analyze jet-blowing nPTFE as well as plasma treated nPTFE. They are scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), water contact angle (WCA) measurement, and Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR).
2.3.1 Scanning Electron Microscopy

SEM uses a focused electron beam to scan small areas of solid samples. [36] Two different types of SEM techniques were used in the study to obtain scanning electron micrographs: Environmental SEM (ESEM) using a FEI Quanta 200 instrument and Field-Emission SEM (FESEM) using a JEOL 6700F instrument.

ESEM was performed in low vacuum mode, which the pressure inside the sample chamber was 0.68 Torr. The accelerating voltage of the electron gun was 15 – 20 kV. The magnification of each sample was in the range of 150X to 8,000X. The lateral resolution was 3.5 nm. Samples were attached to a stainless steel sample stub with double-adhesive carbon tapes.

FESEM was performed in ultra-high vacuum mode, which the pressure inside the chamber was always $9.63 \times 10^{-5}$ Pa. The gun voltage was 1.0 kV. The magnification was in the range of 5,000X to 40,000X. The lateral resolution was 1 nm. Samples were first mounted to a sample stub with double-adhesive carbon tape and then sparked with ruthenium metal to compensate the electric charging during spectra taking.

2.3.2 X-ray Photoelectron Spectroscopy

XPS is a powerful tool for analyzing the relative amount of elements at the surface of a bulk material. Irradiating a solid surface with monoenergetic soft X-rays (Mg or Al Kα), emitted electrons with specific energies are collected and
analyzed. A plot of the number of detected electrons per second versus the binding energy is generated to tell the specific elements since every element has a unique binding energy. XPS is surface sensitive, normally able to measure up to 10 nm beneath the surface, due to its “short escape depth of emitted photoelectrons”. [21,36]

The XPS instrument utilized in this study was a Kratos Analytical Axis Ultra X-ray Photoelectron Spectrometer. This instrument utilized a monochromatic Al anode operated at 280 W of gun power with 14 keV anode voltage and 20 mA anode current as a soft X-ray source. The analysis size was 700 µm X 300 µm in hybrid mode. The aperture setting was 48.5 mm and Iris setting was 0.55. Sampling depth was in the range of 0 – 10 nm and the lateral resolution was ~ 15 µm. The base pressure of this instrument was < 1.0 X 10^{-7} Torr while the pressure during operation was 5.0 X 10^{-9} Torr. The take-off angle was 0º from the surface normal for most of the samples analyzed, resulting in a sampling depth of approximately 100Å. All binding energies were referenced to C 1s CF₂ peaks at 292.5 eV. [37] Samples were mounted to a stainless steel fixed bar sample holder with aluminum foil and copper adhesive tapes. Charge compensation was provided by a 3.4 eV flood gun. Survey scan was acquired for each sample and high resolution scan was acquired only when needed. In general, four elements (F, C, N, and O) were analyzed using CasaXPS (version 2.3) software to obtain their relative population.
2.3.2.1 **Survey Scan Acquisition Conditions**

Pass energy: 80 eV  
Step Size: 1.0 eV  
Dwell time: 150 – 250 msec  
Take-off angle: 0° from sample surface normal  
Binding energy range: 1350 – 0 eV

2.3.2.2 **High Resolution Scan Acquisition Conditions**

Pass energy: 20 eV  
Step size: 0.1 eV  
Dwell time: > 500 msec  
Take-off angle: 0° from sample surface normal  
Elements scanned: F 1s, O 1s, N 1s, and C 1s

2.3.3 **Contact Angle Measurement**

Contact angle is defined as the angle between the solid surface and the tangent of the liquid/vapor interface of a sessile drop. [21] The liquid used in the study was nanopure water filtered through a nanofilter machine (Millipore system, 18 MΩ/cm) mounted in the lab. Water contact angle measurements were obtained using a Rame-Hart contact angle goniometer. A needle attached to a Gilmont microliter syringe filled with nanopure water was used to generate water
droplets (10 µL in size). After detachment from the needle tip, a droplet was placed on a sample surface and images of the drop silhouette were taken by a camera. The water contact angles were measured using ImageJ software and each reported values were the average of three measurements.

2.3.4 FTIR – ATR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is primarily a qualitative tool used to identify functional groups. Attenuated total reflectance (ATR) spectroscopy, sometimes known as internal reflection spectroscopy (IRS), is a surface analyzing technique developed independently by Harrick and Fahrenfort in 1960. It can be used to study the surface of a sample provided good and uniform contact with the ATR element. [36,38] Since the samples used in this study were not light-transmissionable in conventional transmission IR spectroscopy, a Bruker IFS 66/S FT-IR spectrometer with 20X ATR accessory was utilized in this study. The ATR element consists of Ge crystal with 80 µm diameter contact surface. The sampling area was ~ 50 X 50 micron, with 6 cm⁻¹ resolution and 400 scans.
Figure 2.1: Schematic diagram of Jet-blowing setup
Figure 2.2: Harrick PDC-32G plasma cleaner
Figure 2.3: Schematic of low pressure plasma setup using plasma cleaner
Figure 2.4: Schematic of atmospheric pressure plasma setup
Chapter 3
Results & Discussion

3.1 Jet-blowing Results

3.1.1 Comparison of Jet-blowing with Paste Extrusion and Melt-blowing

These techniques all use high pressure gas to fabricate polymer fibers. Referring to Figure 1.2, in melt-blowing process, hot air impinging from two opposite sides of die’s outer slot and polymer melt is extruded from the die’s central hole to form fibers. The melt-blowing technique is only able to fabricate polymers with low melt viscosity. It is not suitable for high melt viscosity polymers, such as PTFE. However, the jet-blowing and paste extrusion techniques are both capable of producing PTFE nanofibers. Paste extrusion still requires PTFE resin to form a lube before processing, while jet-blowing method does not have such requirement.

Shown in Figure 3.1, nozzle configurations of paste extrusion and jet-blowing have similarities and differences. Both nozzles have a capillary zone, which is the exit to extrude polymers to form fibers. In paste extrusion, a piston is used on top of the die to generate high pressure system to compress polymer resins inside the die. In jet-blowing process, no piston is used. Instead, a line of
highly pressurized gas is introduced into the system to form a two-phase mixture of gas and polymer inside the nozzle.

### 3.1.2 Jet-blowing Fiber

Figure 3.2 shows ESEM images of the starting PTFE 601A fine powder resins. Figure 3.3 shows ESEM images of the resolidified PTFE resins after heating to 200 °C and 340 °C, respectively. As seen in these images, after the resins were heated to high temperature, even at its melting point of 340 °C, the microstructure of the resins was still the same as the starting material. Compared to these images, ESEM images of jet-blown nPTFE in Figure 3.4 clearly show different morphology of PTFE than the starting material. Even at small magnification in Figure 3.4 a and c, fibers can be seen to project out of the surface. The fibers are more visible under a larger magnification shown in Figure 3.4 b and d. These fibers were produced by heating the starting PTFE material to 200 °C and jet-blowing with 10,000 psi and 14,000 psi N₂ gas, respectively. It indicates jet-blowing technique can fabricate PTFE fibers without using a solvent.

### 3.1.3 Influence of Process Variables on Fiber Size

Different process parameters, such as type, pressure and flow rate of an inert gas and processing temperature, determine the formation and size of
resulting nanofibers. The process parameters need to be carefully controlled to achieve the desired size and shape of the fiber. Different process parameters such as gas pressure, gas type and processing temperature, and their effects on fiber sizes will be discussed in this chapter.

3.1.3.1 Gas Pressure

Jet-blowing can take place in a gas pressures range of 1000 psi to 15000 psi depending on the processing temperature. Experiments found out that at higher processing temperature, lower pressure is required to jet blow PTFE. However, pressure is not a major factor affecting fiber size or morphology on nPTFE in this work. Compare Figure 3.4 b with Figure 3.4 d, two samples of nPTFE fibers jet-blown at same temperature (200 °C) with different pressure of N₂ gas. ESEM images of these two samples showed similar fiber size and morphology even they were jet-blown at different pressures.

3.1.3.2 Type of Gas

The types of gases employed in jet-blowing process are also a critical factor in the resulting fiber morphology. Gases used should be inert to PTFE at any condition, such as nitrogen, argon, helium and carbon dioxide. PTFE has different solubility in these gases at high temperature and pressure, which results slightly different amount of PTFE powder being dissolved and getting processed.
A recent study has reported using supercritical carbon dioxide as a solubilizing and suspending media for processing fluoropolymers. [39] PTFE can be swollen by supercritical carbon dioxide, and then it can be molded or extruded through a die or extrusion orifice. [40] In this work, nitrogen and carbon dioxide were the two gases used to process PTFE. Figure 3.5 shows FESEM images of two samples of nPTFE processed at temperature of 240 ºC using a) CO$_2$ and b) N$_2$, respectively. Both were taken at 20,000X magnification, showing nanosize nodules connected by nanofibrils. Longer fibrils are observed in the CO$_2$ processed sample than the N$_2$ sample, which is probably due to higher solubility of PTFE in the supercritical CO$_2$ gas during jet-blowing when the two-phase mixture is formed.

3.1.3.3 Temperature

Temperature setting is one of the most important parameters of jet-blowing condition. Jet-blowing temperature depends on the material being jet-blowed. [16] Jet-blowing of PTFE can take place in the range of 200 to 300ºC. Experiments found out that higher temperature used to process PTFE would result longer and smoother fibers. ESEM and FESEM images of an nPTFE sample are shown in Figure 3.6. The sample was jet-blown at 300 ºC with 10,000 psi N$_2$. Compared to samples jet-blown with same pressure and gas but at different temperatures, such as samples shown in Figure 3.4 a and b and Figure 3.5 b, the morphologies of these nPTFE samples are quite different.
Compare ESEM images in Figure 3.6 with Figure 3.4 a and b, high temperature (300 °C) produced much more fibrous and smoother samples than low temperature (200 °C). Also, Compare FESEM images in Figure 3.6 with Figure 3.5 b, samples jet-blown at high temperature (300°C) appeared much longer fibrils connecting between nodules, indicating more fibrous structure.

With processing temperature at or below 300 °C, PTFE sample was able to be jet-blown to form some amount of fibers. However, experiments with temperature higher than 300 °C were performed with no success to jet blow PTFE. Causes are still not clear.
Figure 3.1: Nozzle configurations of a) Paste extrusion; b) Jet-blowing
Figure 3.2: ESEM images of PTFE 601A resin
Figure 3.3: ESEM images of PTFE resins after heating to a) 200 °C at 80X magnification, b) 340 °C at 70X
Figure 3.4: ESEM images of nPTFE jet-blown after heating to 200 °C with a) 10,000 psi N$_2$ at 150X magnification, b) 10,000 psi N$_2$ at 1000X, c) 14,000 psi at 130X, d) 14,000 psi at 1000X
Figure 3.5: FESEM images of two nPTFE samples jet-blown at 240 °C with 10,000 psi gas: a) CO$_2$; b) N$_2$
Figure 3.6: a) and b) ESEM images of nPTFE sample jet-blown at 300 °C with 10,000 psi N₂, c) and d) FESEM images of same sample
3.2 Plasma Treatment Results

3.2.1 Low Pressure vs. Atmospheric Pressure Plasma

Described in 2.2.2 and 2.2.3, low pressure plasma is performed in a low pressure mode using low power plasma cleaner connected to a vacuum pump, while the atmospheric pressure plasma is performed at atmospheric pressure using an atmospheric rfGD plasma generator without a vacuum pump. The atmospheric plasma could generate much higher power than low pressure plasma. Therefore it takes much shorter time to plasma-treat a sample, usually 10 seconds to a minute. In this study, only ammonia gas was used as the feeding gas in low pressure plasma, while N\(_2\), O\(_2\) and Ar gases were used in atmospheric plasma treatment. Atmospheric plasma was much more intensively studied than low pressure plasma in this work.

3.2.2 Atmospheric Pressure Plasma Results

For atmospheric pressure plasma, N\(_2\), O\(_2\) and Ar gases were used. In this work, effects of gas type, gas flow rate, RF power and plasma treatment time were studied intensively.
3.2.2.1 XPS

XPS was the major analytical tool in this work, since it could provide us most useful information about our samples.

Survey scan spectra of untreated PTFE film and nPTFE materials are shown in Figure 3.7. The binding energy (BE), full width at half-maximum (FWHM), atomic percentage (atomic%) of C 1s and F 1s peaks for both untreated materials are listed in Table 3.1. The C 1s peak of both untreated samples was symmetrical and narrow with BE of 292.5 eV and FWHM of 1.74 eV (1.63 eV for nPTFE). The F 1s peak was also found to be symmetrical and sharp (FWHM = 1.99 eV) at BE of 689.6 eV. The F/C ratio was measured to be 2.04, which corresponded to the chemical structure of PTFE with repeat unit of CF₂.

According to this table, chemical components of PTFE and nPTFE surface are identical. This indicates jet-blowing did not alter the chemical nature of PTFE, at least not on its surface.

Since atmospheric plasma is much more powerful than low pressure plasma, the plasma treatment time we studied using atmospheric plasma was limited to 2 min. Shown in Figure 3.8 b, the PTFE film was treated under O₂ plasma with 200 W RF power for 10 min and it was severely burned.

The plasma conditions for gas plasma with three different gas combinations mentioned in 2.2.3 were carefully studied. The best results, which gave the highest O% or N% in each case, are listed in Table 3.2, in which lists plasma condition and atomic % of O and N. Survey scan spectra for three best
samples are shown in Figure 3.9. The expanded spectra along with the atomic % of O and N are shown in Figure 3.10. The peak around 530 eV indicates O 1s peak, and peak around 400 eV indicates N 1s peak. Spectrum for O₂/Ar plasma treated nPTFE shown in Figure 3.9 c looks more similar to the untreated nPTFE shown in Figure 3.7, in which not much of O 1s and N 1s peaks are seen. The spectrum for N₂/Ar treated sample was found to be similar to that of Ar treated sample. Both O and N 1s peaks were observed in the spectra, shown in Figure 3.10 a and b. The highest N% of 4.2% was generated using N₂/Ar plasma, while the highest O% of 4.4% was generated using Ar gas plasma. Table 3.3 lists XPS peak information, such as BE, FWHM. According to this table, the F/C ratio of sample c, which was the O₂ treated sample, did not change significantly, indicating not much chemical composition change on the surface with only a very small incorporation of oxygen moieties. However, the F/C ratio of other two samples dropped noticeable, especially sample a (Ar treated sample) with the biggest decrease to 1.41. Also, the higher O% resulted in a smaller F/C ratio.

High-resolution spectra for N₂/Ar treated nPTFE and Ar treated nPTFE are discussed in the sequence of C 1s, O 1s and N 1s are illustrated in Figure 3.11. After carefully curve fitting using CasaXPS software (version 2.3), atomic % and BE of deconvoluted peaks are listed in Table 3.4. Chemical assignments for deconvoluted peaks were based on BE found in the literature. [37] After curve fitting of C 1s peaks, compare to untreated samples, the plasma treated samples have four (N₂/Ar-treated) or five (Ar-treated) peaks in addition to the CF₂ peak at 292.5 eV. This is mainly due to the defluorination and deposition of different
ammine and oxygenated functional groups to the treated surface. Chemical assignments for deconvoluted C 1s peaks were listed in Table 3.4. They are mainly C=O, C–O, C–N and C–C bonds, and also correspond to the deconvoluted O 1s and N 1s peaks shown in Figure 3.11.

### 3.2.2.2 FTIR-ATR

Figure 3.12 shows IR spectra of untreated nPTFE and three gas plasma treated nPTFE samples. All spectra show two big CF$_2$ stretching bands on 1202 and 1148 cm$^{-1}$ wavelength. In the IR fingerprint region, CF$_2$ wagging bands (637 and 625 cm$^{-1}$) and CF$_2$ rocking band (553 cm$^{-1}$) are also observed. It indicates the majority chemical composition on the surface is CF$_2$. Expanding the region with wavelength between 2000 and 1600 cm$^{-1}$, two peaks at 1883 and 1792 cm$^{-1}$ wavelength are observed on both spectra of Ar treated and N$_2$/Ar treated nPTFE samples. The spectrum of O$_2$/Ar treated sample looks very similar to that of untreated nPTFE, but only a little of peak is observed at 1792 cm$^{-1}$. Based on IR vibrational frequencies in the literature [41], they correspond to anhydride and acyl halide shown in Figure 3.13, which both contain carbonyl function groups, indicating oxygen incorporated onto the treated surface.
Figure 3.7: XPS survey scan spectra for both untreated PTFE and nPTFE
<table>
<thead>
<tr>
<th>Sample</th>
<th>Name</th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Atomic%</th>
<th>ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>F 1s</td>
<td>689.6</td>
<td>1.99</td>
<td>67.1</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>C 1s</td>
<td>292.5</td>
<td>1.74</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>nPTFE</td>
<td>F 1s</td>
<td>689.5</td>
<td>1.92</td>
<td>65.9</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>C 1s</td>
<td>292.5</td>
<td>1.63</td>
<td>34.1</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.8: a) image of PTFE film; b) image of burned PTFE film after plasma treatment, red arrows indicate burn areas.
Table 3.2: Optimal XPS results for plasma treated nPTFE samples in different gas plasma

<table>
<thead>
<tr>
<th></th>
<th>O₂ or N₂ flow rate (sccm)</th>
<th>Ar flow rate (L/min)</th>
<th>RF Power (W)</th>
<th>Treatment Time (s)</th>
<th>O%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Ar only)</td>
<td>0</td>
<td>4</td>
<td>200</td>
<td>30</td>
<td>4.4</td>
<td>2.8</td>
</tr>
<tr>
<td>b (N₂ / Ar)</td>
<td>100</td>
<td>4</td>
<td>150</td>
<td>10</td>
<td>1.9</td>
<td>4.2</td>
</tr>
<tr>
<td>c (O₂ / Ar)</td>
<td>10</td>
<td>4</td>
<td>150</td>
<td>5</td>
<td>0.8</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 3.9: XPS survey spectra of nPTFE samples with optimal plasma results for each gas plasma: a) Ar only, b) N₂/Ar, c) O₂/Ar.
Figure 3.10: XPS survey spectra of nPTFE samples with atomic% of O and N: a) Ar only, b) N\textsubscript{2}/Ar, c) O\textsubscript{2}/Ar.
Table 3.3: XPS data for gas plasma treated nPTFE samples: a) Ar only, b) N$_2$/Ar, c) O$_2$/Ar

<table>
<thead>
<tr>
<th>Sample</th>
<th>a BE (eV)</th>
<th>b BE (eV)</th>
<th>c BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F 1s</td>
<td>689.5</td>
<td>689.5</td>
<td>689.5</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.68</td>
<td>2.34</td>
<td>2.22</td>
</tr>
<tr>
<td>Atomic%</td>
<td>54.3</td>
<td>59.7</td>
<td>65.7</td>
</tr>
<tr>
<td>C 1s</td>
<td>292.5</td>
<td>292.5</td>
<td>292.5</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.81</td>
<td>2.17</td>
<td>2.02</td>
</tr>
<tr>
<td>Atomic%</td>
<td>38.6</td>
<td>34.2</td>
<td>34.3</td>
</tr>
<tr>
<td>O 1s</td>
<td>533.5</td>
<td>532.5</td>
<td>532.5</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>3.73</td>
<td>3.12</td>
<td>5.50</td>
</tr>
<tr>
<td>Atomic%</td>
<td>4.4</td>
<td>1.9</td>
<td>0.8</td>
</tr>
<tr>
<td>N 1s</td>
<td>401.5</td>
<td>400.5</td>
<td>0</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>3.04</td>
<td>3.43</td>
<td>0</td>
</tr>
<tr>
<td>Atomic%</td>
<td>2.8</td>
<td>4.2</td>
<td>0</td>
</tr>
<tr>
<td>F/C ratio</td>
<td>1.41</td>
<td>1.75</td>
<td>1.92</td>
</tr>
</tbody>
</table>
Figure 3.11: XPS high resolution spectra for a) Ar treated nPTFE, and b) N$_2$/Ar treated nPTFE
Table 3.4: Integrated peak areas for deconvoluted high resolution C 1s, O 1s and N 1s spectra, a) Ar only, b) N₂/Ar

<table>
<thead>
<tr>
<th>Sample Binding Energies (eV)</th>
<th>C 1s</th>
<th>O 1s</th>
<th>N 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>C 1s</td>
<td>285.5</td>
<td>286-287.7</td>
<td>288-289.5</td>
</tr>
<tr>
<td>a (%)</td>
<td>2.1</td>
<td>6.5</td>
<td>6.9</td>
</tr>
<tr>
<td>b (%)</td>
<td>2.2</td>
<td>4.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Chemical Assignment</td>
<td>C=C</td>
<td>C-NH₂</td>
<td>C-O-C</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>C-NH₃⁺</td>
<td>C=NH</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>O-C=O</td>
<td>N-C=O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O-C=O</td>
<td></td>
</tr>
<tr>
<td>Binding Energies (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>532.5-533.5</td>
<td>534.5</td>
<td>400.5</td>
</tr>
<tr>
<td>a (%)</td>
<td>52.2</td>
<td>47.8</td>
<td>15.1</td>
</tr>
<tr>
<td>b (%)</td>
<td>70.3</td>
<td>29.7</td>
<td>30.0</td>
</tr>
<tr>
<td>Chemical Assignment</td>
<td>C=O</td>
<td>C-O</td>
<td>C-N</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>C-N</td>
<td>-NH₃⁺</td>
</tr>
</tbody>
</table>
Figure 3.12: IR spectra of a) Ar treated nPTFE, b) N$_2$/Ar treated nPTFE, c) O$_2$/Ar-treated nPTFE, and d) untreated nPTFE
Figure 3.13: Chemical structures of a) anhydride, b) acyl halide
3.2.2.3 Water Contact Angle

Images of water drop silhouette are shown in Figure 3.14. Water contact angle of untreated PTFE film is 110 ±2 ° (Figure 3.14 a) and untreated nPTFE material was 148 ±3 °(Figure 3.14 e). The jet-blown nPTFE is much more hydrophobic than the PTFE film due to the high surface area to mass ratio of the nanofiber structure. Figure 3.14 f-h shows water contact angles of plasma treated nPTFE samples in Table 3.5. They all show decrease water contact angles after plasma treatment, indicating the decrease of hydrophobicity or increase of wettability of the surface. The Ar treated nPTFE resulted in a most hydrophilic surface among these samples.

3.2.3 Low Pressure Plasma Results

Ammonia gas plasma was reported able to deposit amine groups onto polymer surface. [23,24] After PTFE films were treated for 10, 30, 60 min in the reaction chamber, XPS analysis was performed on those samples. The survey scan spectra are shown in Figure 3.15. The BE, FWHM, and atomic% of each peak for all samples are listed in Table 3. As treatment time increased, the amount of nitrogen and oxygen found on the surface increased as well. However, the long plasma time did not dramatically increase the percentage of oxygen amount. It increased about 0.5% when treatment time increased to 60 min from 30 min. Nitrogen amount increased about 1% when going from 30 min to 60 min. Compare atomic% in Table 3. with Table 3.2, atmospheric N₂/Ar and Ar gas
plasma is more efficient to treat PTFE surface in a much shorter time than low pressure plasma. It has already taken about 60 min to obtain 2.6% of O on the PTFE surface. It would be even harder and longer to treat super hydrophobic nPTFE with nanosize structures. Meanwhile, long treatment time would also encounter surface etching problem. [29] The low power low pressure plasma cleaner would not be efficient to surface treat this type of polymer.

Figure 3.14 b-d shows the water contact angle measurements of the three PTFE samples treated by NH₃ plasma. As seen, even though their treatment time was quite different, the resulting water contact angles were relatively close in the range of 85 – 95°. Low pressure NH₃ plasma treatment on PTFE materials could lower its hydrophobicity in some degree.
Figure 3.14: Images of water drop silhouette on a) untreated PTFE, b) NH$_3$ treated PTFE for 10 min, c) NH$_3$ treated PTFE for 30 min, d) NH$_3$ treated PTFE for 60 min, e) untreated nPTFE, f) O$_2$/Ar treated nPTFE, g) N$_2$/Ar treated nPTFE, h) Ar treated nPTFE
Figure 3.15: XPS survey scan spectra for PTFE after low pressure plasma treatment
Table 3.5: XPS data for PTFE sample after low pressure plasma treatment

<table>
<thead>
<tr>
<th>Sample treatment time</th>
<th>10min</th>
<th>30min</th>
<th>60min</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>F 1s</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>689.7</td>
<td>689.7</td>
<td>689.7</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.96</td>
<td>1.98</td>
<td>1.93</td>
</tr>
<tr>
<td><strong>Atomic%</strong></td>
<td>62.6</td>
<td>62.1</td>
<td>60.9</td>
</tr>
<tr>
<td><strong>C 1s</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>292.5</td>
<td>292.5</td>
<td>292.5</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.64</td>
<td>1.66</td>
<td>1.26</td>
</tr>
<tr>
<td><strong>Atomic%</strong></td>
<td>35.4</td>
<td>35.7</td>
<td>35.3</td>
</tr>
<tr>
<td><strong>O 1s</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>533.4</td>
<td>533.4</td>
<td>533.2</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.36</td>
<td>2.18</td>
<td>1.93</td>
</tr>
<tr>
<td><strong>Atomic%</strong></td>
<td>1.7</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>N 1s</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>401.7</td>
<td>401.9</td>
<td>400.8</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.32</td>
<td>2.30</td>
<td>2.23</td>
</tr>
<tr>
<td><strong>Atomic%</strong></td>
<td>0.3</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>F/C ratio</td>
<td>1.77</td>
<td>1.74</td>
<td>1.73</td>
</tr>
</tbody>
</table>
4.1 Conclusion

Demonstrated in ESEM and FESEM images, jet-blowing is a novel solvent-free technique to fabricate PTFE fine powder resin into nanosize fibers under high pressure and high temperature condition. The jet-blowing process takes place below the melting point of PTFE, which ensures the unmodified properties of the bulk material. Within the processing condition studied so far, higher temperature (300 °C) and CO₂ gas would result longer and smoother jet-blown nPTFE fibers, while gas pressure has very little effect on fiber morphology.

Atmospheric Ar, N₂/Ar and O₂/Ar gas plasma and low pressure NH₃ gas plasma were studied on surface modification of PTFE and nPTFE materials. Atmospheric plasma generates much higher RF power than low pressure plasma. It works more efficiently to plasma treat nPTFE surface in a much shorter time. Ar plasma could yield 4.4% of oxygen deposit and 2.8% of nitrogen deposit on nPTFE surface in 30 seconds. N₂/Ar plasma could yield 1.9% of oxygen and 4.2% of nitrogen deposit on the surface in 10 seconds. According to F/C ratio, the most fluorine depletion of the nPTFE surface was caused by Ar and least by O₂/Ar plasma. XPS and IR results demonstrated C-C, C-O, C=O, and C-N functional groups were incorporated onto the polymer surface after plasma treatment. According to water contact angle measurements, nPTFE is much
more hydrophobic than PTFE. All gas plasma treatments generated smaller water contact angles than untreated samples. The decreased water contact angle implies more wettable and less hydrophobic surface after gas plasma treatment, indicating the incorporation of oxygen onto the surface.

4.2 Future Work

A lot of work still can be done and a lot of questions still need to be answered on this work. The mechanism of jet-blowing process inside the nozzle is still not well understood. The reason why jet-blowing does not occur at processing temperature above 300 °C with our current apparatus is not very clear. After plasma treating nPTFE, we will perform a coupling reaction to have specific peptides link to the surface of nPTFE to have the material more biocompatible to biological systems.
Bibliography


