OLIGOMER SPIN-SOLVENT GEL-FIBER SPINNING

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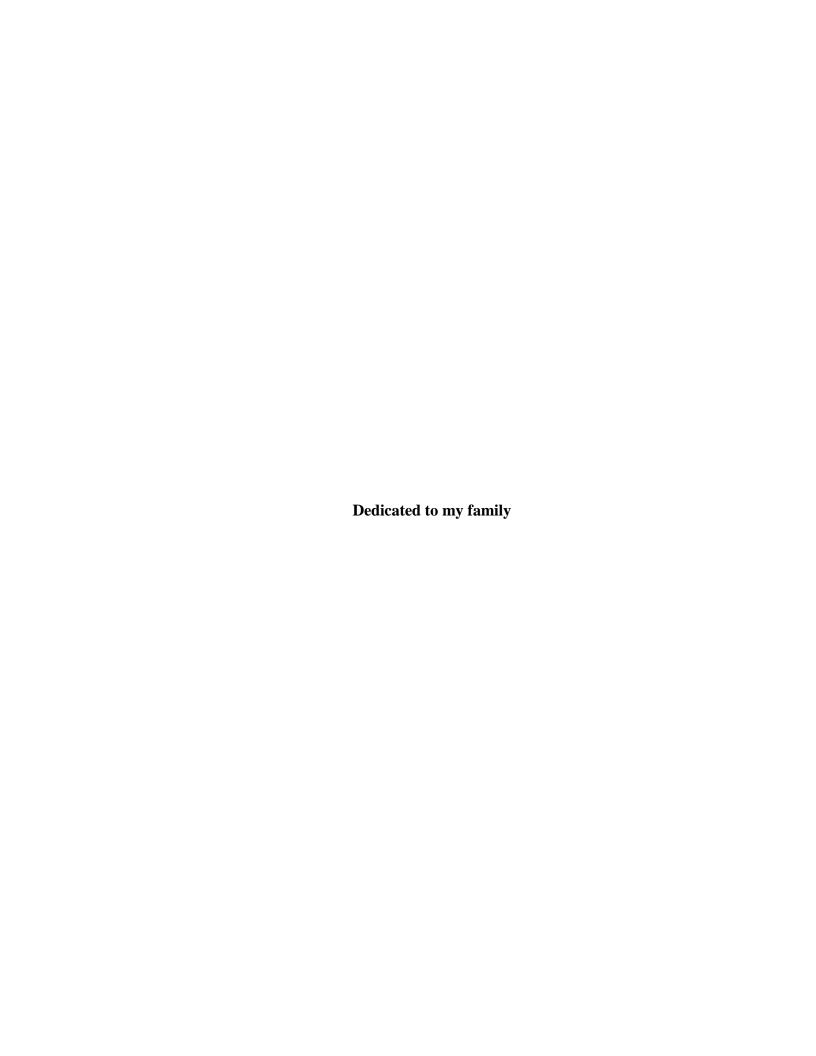# OLIGOMER SPIN-SOLVENT GEL-FIBER SPINNING

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Dedicated to my family

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SUMMARY

Successful processing of polymer molecules into well oriented fiber structures with minimal defects is difficult because molecular relaxations perpetually oppose efforts to extend and orient polymer molecules. Many polymers with unique chemical and physical properties cannot be exploited to their full potential because their tensile strength and modulus in the random, entangled configuration is insufficient for typical engineering applications. Polymer fibers from gel-spinning processes have achieved tensile moduli approaching the theoretical values, and tenacities significantly higher than their melt or solution spun counterparts; however, a fundamental approach to gel-spin high-strength fibers from polymers with different chemistries is not known.

This research demonstrates a process design for producing high-strength polymer fibers from many semi-crystalline polymers. The concept emphasizes the use of oligomers (or multimers) from the same or compatible chemical repeat unit of the polymer as a spin-solvent for gel-spinning. An oligomer solvent typically is less toxic and flammable than conventional, small-molecule, organic solvents and its boiling point can be adjusted, leading to greatly improved processing flexibility. Furthermore, the perilous search for conventional solvents for typical solvent resistant polymers such as PTFE, POM, and PPS is eliminated. The proposed process design is tested by gel-spinning two polymers that are difficult to spin into fiber using conventional techniques. The resulting fibers are significantly stronger and stiffer than their melt or solution spun counterparts. By employing the oligomer spin-solvent gel-spinning process, high strength fibers from polymers with unique physical and chemical properties can be produced to fulfill

demanding applications where known fibers would fail.

CHAPTER 1

INTRODUCTION

1.1   BACKGROUND

Fibers have been critical to advancement of mankind for thousands of years. As early as 7,000 BC, wool and cotton staple fibers were spun by hand into continuous filaments. These natural fibers were used in clothing and structural components of buildings and tools [1]. In contrast to natural fibers which have tensile properties largely controlled by the type of plant or animal which produces the staple fiber, the tensile properties of man-made polymer fibers can be manipulated through judicious processing.

Processing techniques for spinning high-strength, high-modulus synthetic polymer fibers vary depending on the physical and chemical properties of the polymer's molecular structure. The present discussion focuses on processing of high-strength fibers from flexible chain polymers. Flexible chain polymers encompass a broad range of polymers including many well-known polymers such as polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE), polyamide (PA) as well as other commercially available polymers such as polyethylene oxide (PEO), polyoxymethylene (POM), polyvinyl alcohol (PVOH), and poly(lactic acid) (PLA). Flexible chain polymer molecules are typically spun into fiber from the melt or solution state [2]. A relatively newer process, gel-spinning, is one of the most effective processes for producing high-strength and stiffness synthetic fibers from flexible polymer molecules. With respect to ultra-high molecular weight polyethylene (UHMWPE) and PVOH, gel-spinning processes produce fibers significantly stronger than their melt or solution spun

counterparts [3-6]. The following sections discuss the ability of melt, solution, and gel-spinning processes to produce high-strength fibers.

1.1.1 MELT SPINNING

Many flexible chain polymers can be melt-spun into fibers including PET, PP, PE, and PA. In the melt state, the polymer molecules are highly entangled due to the maximization of entropy which prefers a random, disordered configuration of the large molecules. Consequently, when the polymer fiber is crystallized from the melt, a significant portion of the molecular entanglements persist. These entanglements act as defects to reduce crystallinity and oppose orientation in subsequent hot-drawing stages.

Polymer molecules during melt spinning can also be oriented from the melt-state by so-called jet-stretch or draw-down techniques. In this process, the polymer melt as it exits the orifice is stretched and cooled to produce a more oriented polymer fiber. Since molecular relaxations are relatively fast in the melt-state, the jet-stretch and cooling must be applied on a correspondingly short time-scale before relaxation of the molecules reverse any applied orientation. Relatively high orientation can be achieved by jet-stretching, but several polymer fibers produced with large jet-stretch show unexpectedly low tensile strength [7]. The likely explanation for the low tensile strength, despite high orientation, has been attributed to defects in the molecular structure. Since the jet-stretch must be applied on a short time-scale, a large amount of defects are trapped within the oriented fiber structure [8]. These defects not only reduce the tensile strength of the jet-stretched fiber, they also prevent significant hot-drawing of the jet-stretched fibers in later processing stages.

1.1.2 SOLUTION SPINNING

Some flexible polymers cannot be melt spun since their melt or softening temperature is near or above their degradation temperature. To process these polymers into fibers, solution spinning processes are typically used. Rather than melting, the polymer is dissolved in a suitable spin-solvent followed by extrusion through an orifice. Depending on the type of solution spinning, the spin-solvent can be evaporated (dry-spinning) or coagulated in another solvent (wet-spinning) directly after extrusion.

Since the fiber extrudate is in solution, the spin-solvent must be extracted directly after extrusion to preserve the fiber geometry. Otherwise, the polymer solution will continue to flow on the typical processing timescale. The amount of disentanglement preserved from crystallization from the solution state is limited, however, due to the relatively fast relaxations in the solution state. Since the spin-solvent is removed from the fiber by a diffusion based process, the time period for relaxation can be large relative to the time-scale of the typical extraction process.

1.1.3 GEL-SPINNING

In the 1970's, a new type of spinning process was introduced to spin fibers from UHMWPE [9-17]. The viscosity of UHMWPE is too large for conventional melt-spinning, and UHMWPE is difficult to dissolve at temperatures commensurate with conventional solution spinning due to its high molecular weight (> ~1 million g/mol) and the chemical resistance of the relatively simple ethylene chemical repeat unit [18, 19]. The first iterations of the new spinning process involved a surface growth technique from a semi-dilute solution of UHMWPE [9-17, 20]. In this process, a

UHMWPE/decahydronaphthalene slurry is heated to high temperature to form a homogeneous solution. The solution at high temperature is rotated inside a Couette viscometer or similar device and a seed fiber is pulled from the surface of the rotor [20]. As the seed fiber is pulled, it rapidly cools while the solvent evaporates to yield an UHMWPE fiber with tensile strength of 2.6 GPa [20]. Typical solvents for the shear induced crystallization process for UHMWPE include xylene and decahydronaphthalene because their boiling temperatures are sufficiently high to minimize boiling during processing, yet these solvents are also volatile at temperatures below the UHMWPE crystallization temperature which permits a dry, solvent-free fiber to be formed.

A more robust adaptation of surface growth method, commonly called gel-spinning, was proposed in 1979 by Smith, Lemstra, and Pennings [21, 22]. The gel-spinning process employs similar UHMWPE solutions; however, the solutions are extruded at high-temperature through an orifice and quenched in a fluid to reduce the fiber temperature below the gelation temperature of the solution. The resulting fiber is called a gel filament because it exhibits solid-like behavior at room temperature, despite containing a majority of the spin-solvent [22, 23]. The solid-like behavior is generated through crystalline junctions that form upon quenching [23]. The gel-spinning process is similar to solution spinning in many aspects; however, the key difference is that evaporation or coagulation of the spin-solvent is not necessary to form a solid filament.

Despite their identical chemical repeat structure, the typical tensile strength and modulus of gel-spun UHMWPE fibers are several times greater than those of melt-spun high-density polyethylene (HDPE) [5, 6]. The disentangled morphology that was present in

solution should be better preserved through gelation, relative to solution spinning. The more disentangled precursor fiber structure allows gel-spun fibers to achieve draw ratios exceeding 100X, and tensile strengths above 5 GPa were reported for UHMWPE [24-26].

Since the introduction of the gel-spinning process for UHMWPE, only a few other polymers including poly(acrylonitrile) (PAN), PVOH, PP, and PA have been gel-spun with varying degrees of success. For the present discussion, successful gel-spinning is defined as production of fiber significantly stronger than its melt or solution spun counterparts.

Gel-spun PVOH fibers have been reported with tensile strength and Young's modulus greater than 2.5 GPa and 90 GPa, respectively [3, 27]. By contrast, solution spun PVOH fibers have tensile strengths around 1 GPa [4]. The gel-spun PVOH fibers have been commercialized by companies such as Kuraray.

PAN fibers by gel-spinning have reached tensile strengths around 1.8 GPa compared to solution spinning processes which typically report tensile strengths around 1 GPa or less [28-30]. The high-strength PAN fibers are typically used as precursor fibers for the production of carbon fibers.

The gel-spinning processes developed for PP and PA fibers have been relatively less successful. Gel-spun PP fibers achieved a tensile strength of ~1.3 GPa [31]; however, PP filaments by melt-spinning reported tensile strengths up to ~1.1 GPa [32]. Likewise, gel-spinning of PA6 has been reported to achieve tensile strengths up to ~0.6 GPa [33, 34], but melt-spun high-tenacity polyamide fibers yielded tensile strengths above 1 GPa [35].

It should be noted, however, that the gel-spun polyamide fibers can achieve relatively high Young's moduli.

Despite the relatively successful gel-spinning processes for UHMWPE, PVOH, and PAN, few other polymers have been successfully gel-spun. In the case of PP, the difficulty may be attributed to the bulky methyl branches, and for polyamide, the difficulty has been attributed to intramolecular hydrogen bonding [33, 34]. Despite these difficulties, there are numerous other flexible polymers available which do not have bulky side groups or significant hydrogen-bonding interactions. Polymers such as poly(tetrafluoroethylene) (PTFE) and poly(phenylene sulfide) (PPS), POM, and PEO are some examples that have unique physical and chemical properties which are likely to be invaluable in the form of a high-strength fiber, yet these as well as other polymers may not be achieving their highest potential in the fiber form because they have not been gel-spun.

1.2   OBJECTIVE OF THESIS

This dissertation will

- formulate a fundamental process design theory for gel-spinning high-strength polymer fibers,

- test the oligomer spin-solvent concept using two different polymers that are difficult to spin into high-strength fibers using conventional processing methods,

- demonstrate new processes to increase the efficiency of the conventional gel-spinning process.

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CHAPTER 2

FUNDAMENTAL PROCESS DESIGN

2.1   GEL-SPINNING REQUIREMENTS

Despite being one of the most effective processing methods for generating fibers with ultra-high tensile strength and modulus, gel-spinning processes have not been developed for the majority of semi-crystalline polymers with flexible chains. Polymers such as PEO, PET, POM, PTFE and PPS have been spun into fibers with varying degrees of success, but it can be assumed that their full potential has not yet been realized because they have not been gel-spun [1-5]. A gel-spinning process for these polymers should generate fibers with fewer defects and thus significantly higher tensile strength and modulus, but no successful attempts have been reported in the literature. A significant restriction on the ability to gel-spin polymers is determining a suitable spin-solvent, and in all of these cases, no such solvents have been successfully investigated for gel-spinning.

A successful gel-spinning process requires a minimum of two key characteristics: solution formation and gelation. Assuming these characteristics have been sufficiently established, the subsequent drawing process should proceed in similar nature to drawing of melt or solution spun fibers, irrespective that the precursor fibers are gel-spun: the primary difference being that the gel-spun fibers are likely to achieve higher draw ratios and thus higher tensile strength and modulus due to the more disentangled molecular starting morphology [6].

The formation of a semi-dilute polymer solution is essential to successful gel-spinning.

Since ultra-drawing to high tensile strength and modulus benefits from a more disentangled polymer network, it is beneficial to dissolve the polymer in a solvent. Dissolution may be a rudimentary task for many polymers, but gel-spinning typically involves polymers with high molecular weights and chemical resistance. For example, UHMWPE has relatively good solvent resistance and molecular weights above 1,000,000 g/mol. Furthermore, the number of available spin solvents are greatly limited due to the relatively high temperatures that are required for dissolution and extrusion of the high molecular weight polymer solutions. Many conventional solvents have boiling temperatures that are too low to be useful for gel-spinning. While gel-spinning may be possible with low boiling point solvents, the flexibility to adjust the concentration and extrusion conditions would be severely limited. A high boiling point solvent allows for higher extrusion temperatures so that the elastic effects associated with the deformation of high molecular weight polymer solutions can be mitigated even for high concentrations or faster extrusion speeds.

The second condition required for successful gel-spinning is the gelation upon cooling the solution. Unlike conventional solution spinning where the polymer solution undergoes coagulation directly after extrusion, gel-spinning must undergo gelation after extrusion. Gelation is normally achieved through crystallization. The crystalline network junctions that induce gelation are necessary to preserve the more disentangled state that was present in the semi-dilute solution. From this observation, semi-crystalline polymers should be a prerequisite for conventional gel-spinning processes. Furthermore, a solvent that is too good may prevent crystalline junctions from being formed at conventional gel-spinning temperatures. In the ideal case, the solution should undergo gelation well above

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room temperature, so that artificial cooling of the quenching medium to below room temperature is not required.

From the above discussion, the ideal gel-spinning spin-solvent can be defined by the following attributes:

1. Ability to dissolve polymer with high molecular weight and chemical resistance.

2. Relatively high boiling point, and/or ability to dissolve the polymer below the polymer's melt temperature, but above room temperature.

3. Low toxicity and flammability.

4. Permitting the polymer to form crystalline network junctions upon cooling to room temperature.

An important implication of the above attributes is that an ideal spin-solvent may be solid at room temperature, so it is not necessary to restrict oneself to "conventional" liquid solvents. To satisfy the above requirements, a new process design for gel-spinning high strength fibers is developed and tested based on an oligomer solvent instead of conventional small molecule solvents.

2.2   OLIGOMER SPIN-SOLVENT THEORY

Many polymer fibers are particularly desired for their chemical resistance; however, this natural property of the polymer poses a critical challenge in the development of a gel-spinning process since the polymer must be disentangled in a solution in order to form the disentangled gel network. While most polymers have several known solvents, polymers such as POM, PPS and PTFE represent a significant challenge. POM was

shown to be insoluble in 406 common solvents at room temperature [7], PPS has no known solvents below 200 °C [8], and PTFE is one of the most inert polymers known [9].

On the opposite side, some polymers are desired for their ability to easily dissolve in many chemicals, but this also poses a challenge for gel-spinning [10]. A gel-network with crystalline junctions should be formed upon cooling the polymer solution, so the spin-solvent should not be so good that it prevents crystallization at typical gel-spinning temperatures. For example, a polymer such as PEO is soluble in many solvents at room temperature [11], but this high degree of solubility is not necessarily desirable for gel-spinning because these solvents would require cooling the gel-fiber to a temperature below room temperature during processing in order to form a gel-network.

Instead of searching for a conventional solvent, it is proposed to disentangle the polymer in its oligomer. Initially, this concept may seem counterintuitive because the miscibility of a binary polymer system tends to decrease with increasing molar mass of the components, and the present argument proposes a solvent of relatively high molar mass (oligomer) to form a miscible blend with a polymer.

For a non-polar polymer, the innate miscibility of the polymer with its oligomer can be examined in terms of the free energy of mixing. In accordance with Flory-Huggins theory [12], and assuming no volume change during mixing, the free energy of mixing, ΔG_m , is defined as,

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad \text{(Eq. 2-1)}$$

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where ΔH_m and ΔS_m are the enthalpy and entropy of mixing at temperature T, respectively. Since miscibility occurs when ΔG_m is negative, the entropic contribution must exceed the enthalpic contribution in order for an oligomer to be miscible with its polymer:

$$\Delta H_m < T\Delta S_m . \tag{Eq. 2-2}$$

Assuming pair interactions in the mean-field theory, the enthalpic term, ΔH_m , can be expressed by,

$$\Delta H_m = RT\chi\phi_A\phi_B \tag{Eq. 2-3}$$

where R is the ideal gas constant, χ is the Flory-Huggins interaction parameter, and ϕ_A, ϕ_B are the volume fractions of the two components. Since the polymer and its oligomer share identical molecular repeat units, the Flory-Huggins interaction parameter, χ , for this binary system should be zero if we assume that the oligomer is sufficiently long to minimize the effect of chain end-groups. Milner [13] showed that the actual interaction parameter for polyethylene oligomers decreases with increasing molecular repeat units. As a consequence, the enthalpic contribution during mixing of a polymer with its oligomer is rather small. A negligible enthalpic contribution implies that the miscibility in this type of system is mainly governed by the entropy.

The change in entropy is given by

$$\Delta S_m = -R\left[\frac{\phi_A}{n_A}ln\phi_A + \frac{\phi_B}{n_B}ln\phi_B\right] \tag{Eq. 2-4}$$

where n_A and n_B are the degree of polymerization (DP) of each component. Since gel-spun polymers typically have a large molar mass (large DP), n_B for the polymer is significantly larger than the oligomer, and the relationship can be simplified to

$$\Delta S_m = -R \left[\frac{\phi_A}{n_A} ln\phi_A \right] \qquad \text{(Eq. 2-5)}$$

Considering that n_A is typically on the order of ~10 for the proposed oligomer, the entropy of mixing becomes an order of magnitude smaller in the case of the oligomer relative to a small molecule solvent. Since the enthalpy and entropy of mixing are both small for the mixing of an oligomer and polymer, the parameter determining the extent of miscibility is temperature. At high temperatures, the oligomer and polymer will be miscible. When T is reduced, a two-phase system will become more favorable. This temperature dependent miscibility is critical for gel-spinning, since the polymer must be able to form a disentangled solution at relatively high temperature and form crystalline junctions after quenching during fiber spinning to preserve the disentangled state that was present in the heated solution.

By adopting the oligomer as the spin-solvent, two critical barriers to gel-spinning are overcome on a fundamental level. First, a spin-solvent for most semi-crystalline polymers can be immediately identified since the oligomer should be producible for most polymers, although the oligomer may not be commercially available. In the case that the exact oligomer is not readily available, or the oligomer is not suitable for gel-spinning, an oligomer, monomer, or other preferably high boiling chemical with compatible chemical repeat structure to polymer can be used for gel-spinning. A suitable spin-solvent may even be a solid at room temperature, so long as it fulfills the four requirements described in the previous section. Second, the oligomer spin-solvent should naturally exhibit the desired temperature dependent phase behavior that is essential to the gel-spinning process since the miscibility for an oligomer/polymer solution is correlated to the system temperature as implied by the Flory-Huggins theory for an oligomer/polymer mixture.

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CHAPTER 3

DEVELOPMENT OF A GEL-SPINNING PROCESS FOR HIGH-STRENGTH POLY(ETHYLENE OXIDE) FIBERS

3.1   SUMMARY

This chapter describes a new gel-spinning process for making high-strength poly(ethylene oxide) (PEO) fibers. The PEO gel-spinning process was enabled through an oligomer/polymer blend in place of conventional organic solvents, and the gelation and solvent-like properties were investigated. A 92/8 wt% poly(ethylene glycol)/PEO gel exhibited a melting temperature around 45 °C and was highly stretchable at room temperature. Some salient features of a gel-spun PEO fiber with a draw ratio of 60 are tensile strength at break = 0.66 ±0.04 GPa, Young's modulus = 4.3 ±0.1 GPa, and a toughness corresponding to 117 MJ/m3. These numbers are nearly an order of magnitude higher than those previously reported for melt-spun PEO. Wide-angle x-ray diffraction of the high-strength fibers showed good molecular orientation along the fiber direction.

3.2   INTRODUCTION

Gel-fiber spinning has been applied to several polymers including UHMWPE and PVOH, typically generating fibers significantly stronger and stiffer than their melt or solution spun counterparts [1-3]. Relatively fast molecular relaxation in the melt or solution state hinders orientation of macromolecules by adopting the entropically favorable random coil conformation. Orientation of macromolecules in the solid or gel state should proceed more effectively because molecular relaxation effects opposing orientation are

significantly reduced due to the extremely large viscosity of the gel-network [1].

In the present study, a new gel-spinning process for producing high-strength poly(ethylene oxide) (PEO) continuous fibers was developed, and some salient properties of these new gel-spun PEO fibers are presented. 'Continuous fiber' is emphasized to distinguish the PEO fibers of the present study from the nano-fibers generated by electro-spinning that have been extensively studied [4-6], but are generally collected as fibrous webs rather than continuous fibers which can be further processed into yarns, ropes, and woven fabrics; for this reason, combined with a deficiency of reported tensile properties for electro-spun PEO monofilaments, electro-spun PEO fibers will not be discussed further in this study.

A review of the existing scientific literature revealed a lack of knowledge with respect to continuous PEO fiber. Melt spinning of PEO fiber is particularly difficult: low molecular weight PEO typically lacks sufficient melt strength to attenuate fiber, while higher molecular weight PEO is generally too viscous for conventional melt spinning processes [7]. An attempt to melt-spin PEO fiber produced relatively poor results with a fiber tenacity below 8.3 cN/tex (~0.1 GPa), regardless of the PEO molecular weight employed [8]. Outside of the scientific literature, a route to continuous PEO fiber from solution was described in patent US4619988 involving a shear induced crystallization method, and reporting a tensile strength and Young's modulus of at least 0.1 GPa and 0.5 GPa, respectively [9]. This method resembles the 'surface-growth' process proposed by Zwijnenburg and Pennings for UHMWPE [10], and consequently suffers from a similar detriment: the processing speed is generally too slow to be commercially interesting [1].

Furthermore, a minimum tenacity of 3 g/denier (~28 cN/tex or 0.4 GPa) has been suggested for commercial weaving or knitting operations [11]; however, the previously described PEO fiber spinning processes yielded significantly lower tenacities, severely limiting the applications available to continuous PEO fibers.

The gel-spun PEO fibers produced in this study are probably the strongest and stiffest, PEO fibers created to date, achieving a maximum tensile strength and Young's modulus of 0.66 ±0.04 GPa and 4.3 ±0.1 GPa (~55 cN/tex and 357 cN/tex), respectively, and a toughness corresponding to117 MJ/m^3. The tensile strength of these gel-spun PEO fibers reflected nearly an order of magnitude increase over the previous attempt to melt spin continuous PEO fiber, while simultaneously employing well-established gel-spinning techniques that can accommodate high-speed fiber spinning. Since PEO belongs to the unique class of water-soluble polymers, the high-strength fibers of this study may be useful as temporary support fibers. For example, they can be mixed with low strength or ultra-fine denier natural fibers wherein the high-strength PEO fiber component can be washed from the final fabric. Before this investigation, water-soluble PVOH fibers were likely the only water-soluble, synthetic fibers with sufficient strength to fulfill such applications [11].

This study addressed two major challenges to continuous PEO fiber production: inefficient processing methods and relatively poor tensile properties. The investigation focused on the processing of high strength PEO fiber and the discussion can be considered in two parts: gel spinning of PEO fiber and molecular orientation through drawing. In the first section, the solution/gel properties are discussed and the selection of

an appropriate gel-spinning solvent is critically examined. The concept of an oligomer/polymer blend is introduced and its benefits over 'traditional' spin-solvents are discussed. The section on fiber drawing describes the structure development relative to draw ratio, along with thermal and mechanical properties of these new high strength PEO fibers. The discussion concludes with the implications of this new gel-spinning process beyond high strength PEO fibers.

3.3   EXPERIMENTAL

The experimental procedure is detailed in the following subsections.

3.3.1   MATERIALS

PEO resin was kindly supplied by Dow Chemical Company and used as received. The Dow POLYOX WSR-308 resin had a reported viscosity average molar mass of 8000 kg/mol. Polyethylene glycol (PEG) with an average molecular weight Mw=200 g/mol was obtained from J.T. Baker and used as received. Spin dope was prepared by combining 8 wt% PEO powder with PEG at 20 °C and stirring the mixture in a beaker while heating to 80 °C. The mixture was then poured into a preheated batch mixer (C.W. Brabender Prep-Center fitted with twin roller blades) and mixed for 30 min at 150 °C to obtain a homogenized solution.

3.3.1 GEL SPINNING

The process sequence for gel spinning of PEO fibers is schematically shown in Fig. 3-1. It contains three major steps: (a) gel-fiber extrusion, (b) PEG extraction, and (c) hot drawing.

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Figure 3-1 Process sequence involved in gel spinning of PEO fibers.

The first step was performed through an Alex James and Associates piston extruder with a 2.54 cm bore diameter and 150 mL capacity. The homogenized PEO/PEG solution was quickly transferred into the bore (preheated 140 °C) of the extruder and allowed to equilibrate for 1 h. The solution was then extruded through a 1 mm die orifice with an aspect ratio of ~15:1 maintained at a temperature of 140 °C. The fiber extrusion speed was set to approximately 1 m/min. The PEO fiber solution was freely extruded into a 1 cm air-gap and quenched into hexane at 20 °C. The quenched gel-filaments were transferred from the hexane bath to storage under ambient conditions (40-60% relative humidity at 18-22 °C) until needed for experiments.

PEG extraction was performed by winding the gel-fiber onto a 1 inch diameter polytetrafluoroethylene (PTFE) rod. Both ends of the gel-fiber were fixed to maintain constant fiber length. The rod as prepared was submerged into an agitated bath of acetone at ~ 20 °C for 1.5 h. The PTFE rod containing the extracted gel-fiber was removed from the acetone bath and dried under forced air convection while maintaining fixed fiber ends.

Hot drawing was performed through heated SAE 30 non-detergent motor oil. The total path length through the hot bath was 0.6 m. Hot-drawing was performed between 67-69 °C with a feeding speed of 0.5 m/min and a collection speed controlled incrementally from a minimum of 1 m/min to a maximum of 3 m/min in order to obtain the desired draw ratio. Draw ratio as used in this report is defined as the ratio of the collection roller speed to the feed roller speed. The gravity induced stretch in the air-gap region was expected to be small (compared to the large drawing ratio during drawing) since a small air gap of 1 cm was used. Fibers were drawn at the desired ratio to obtain samples at least 15 m long for testing.

3.3.2   CHARACTERIZATION

Diameter measurements were obtained by weighing a known length of fiber and calculating the cross-sectional area assuming a density of 1.20 g/cm^3. Before weighing, the hot-drawn fibers were briefly rinsed with hexane to remove residual SAE30 oil from the hot-drawing stage and dried.

Tensile properties for single filaments were measured using an Instron 5566 universal testing machine. Fiber samples were wound onto wooden rods approximately 2 mm in

diameter and super-glued over the wound fiber ends. The prepared single filament samples were clamped using Instron 2711 Series Lever Action Grips rated for 5 N. Crosshead speed was 100 mm/min with a gauge length of ~10 cm. All tensile tests were performed under air-conditioned room conditions. Six samples from each of three fiber spinning experiments were tested and averaged. Experimental error was estimated using the standard error of the mean, defined as the standard deviation divided by the square root of the sample number. Wide angle x-ray diffraction data were collected on a Rigaku Micro Max 002 (Cu Kα radiation, λ=0.154 nm) operating at 45 kV and 0.65 mA using a R-axis IV++ detector. Exposure time was 30 min for 'dry' samples and 15 minutes for samples containing spin-solvent with matching exposure times for the background. The crystalline orientation factor was computed using the method developed by Wilchinsky [12]. The 110 and 120 equatorial diffractions were used to determine the orientation factor based on the monoclinic PEO unit cell with dimensions a=8.05 Å, b=13.04 Å, c=19.48 Å, and β=125°4' [13].

DSC data were collected on a TA Q200 DSC unit (TA Instruments). Samples were crimped in aluminum pans. Nitrogen atmosphere and a scan speed of 10 °C/min were used for all samples. TGA experiments were performed using a TA TGA5000 (TA Instruments). Samples were heated to 200 °C in nitrogen atmosphere and held at this temperature until the weight change approached a steady state value. Parallel-plate rheometry was performed on a TA AR2000EX unit (TA Instruments) in a temperature sweep mode with 1% strain at a frequency of 100 rad/s. SEM images were collected on a Hitachi S800. Fiber samples were mounted onto carbon tape and gold sputtered.

3.4   RESULTS AND DISCUSSION

This sections begins with the process development, followed by the complete discussions of the properties of gel-spun PEO fibers.

3.4.1   STRATEGIES FOR GEL SPINNING PEO FIBERS

Selection of an appropriate spin-solvent is critical for the gel-spinning process. In conventional dry or wet solution spinning processes, the spin-solvent is either evaporated or coagulated directly after extrusion to form a solid fiber mostly free of spin solvent. However, in the gel-spinning process, the semi-dilute polymer solution should partially crystallize directly after extrusion to form a solid network (gel), but still retain a majority of the spin solvent. This crystallization is important because it preserves the relatively disentangled morphology that was present in the semi-dilute solution, even after complete removal of the spin solvent so long as the fiber is not heated above the melting temperature [14]. Above the melting temperature, the molecules instantly rearrange back into the entropically favorable entangled state in the timescale of a typical fiber spinning processes [14]. Orientation of polymers in the gel (solid-like) state should proceed more efficiently than solution drawing because molecular relaxation effects opposing orientation are significantly reduced due to the presence of the crystallized gel-network [1]. The relatively disentangled solid state morphology allows the gel-fiber to be ultra-drawn to achieve high orientation along the drawing direction and consequently high tensile strength and Young's modulus. By comparison, melt spun fibers typically contain more entanglements in the solid state; therefore, the solid state drawability is significantly reduced leading to lower molecular orientation and lower tensile strength and Young's

modulus relative to gel-spun fibers of the same polymer.

For gel-spun UHMWPE, common spin-solvents include decahydronaphthalene and paraffin oil and these spin-solvents induce a well-defined gel-transition between 101 °C and 108 °C for UHMWPE as measured by parallel-plate rheometry [15]. Paraffin oil and decahydronaphthalene exhibit boiling points above 190 °C, well in excess of the ~140 °C UHMWPE melting temperature, which allows extrusion to proceed over a broad temperature range. Variation of the extrusion temperature is desired because it permits the viscoelastic properties to be manipulated to achieve desirable fiber properties over a wide range of solution concentrations, shear rates, and other spinning conditions. For example, Pennings and co-workers [16] demonstrated that UHMWPE/paraffin oil gel-fibers could be processed at high take-up speeds, without the typical reduction in tensile strength, by increasing the extrusion temperature from 170 °C to 250 °C. UHMWPE gel-spinning solvents such as xylene or even decahydronaphthalene cannot afford such processing flexibility because their boiling temperatures are below 200 °C.

To gel-spin PEO, a solvent was selected that induced similar behavior, including a well-defined gel point, while also maintaining a boiling point well in excess of the PEO melting temperature. PEO is soluble in many common solvents, for example water, ethanol, acetonitrile, benzene, and isopropanol; however, these solvents have relatively low boiling points either below or near PEO's melting temperature. Additionally, many of these solvents form PEO solutions at or below 20 °C which limits their ability to form crystalline (gel) networks at conventional processing temperatures; however, as previously described, crystallization upon quenching the extruded solution is necessary to

retain the relatively disentangled morphology from solution in the solid gel-fiber state. Some of these common solvents may precipitate crystals below 20 °C, but subsequent gel-fiber drawing and solvent extraction must also proceed at relatively low temperature, complicating the fiber spinning process. For these reasons, many conventional PEO solvents are not well suited for gel-spinning continuous, high strength PEO fibers. To overcome the unfavorable characteristics of common PEO solvents, a polymer/oligomer blend was adopted that exhibited solvent-like behavior at elevated temperature which is necessary to form a relatively disentangled PEO 'solution', while also showing a distinct gel-transition during quenching to room temperature to preserve the favorable morphology which allowed high drawing in the solid state.

The UHMWPE gel-spinning process already benefits from a polymer/oligomer blend with solution-like behavior. Upon inspection of the UHMWPE/paraffin oil gel-spinning process – it became apparent that the 'solvent' paraffin oil and the 'solute' polyethylene have identical chemical repeat units, $(-CH_2-CH_2-)_n$, but vary in the number of repeat units, n, where n is approximately 20 for heavy paraffin oil (oligomer) and approximately 100,000 for UHMWPE (polymer). DSC analysis of UHMWPE oligomer/polymer blends showed solution-like behavior with the UHMWPE melting temperature depressed from ~137 °C in the extracted precursor fiber to ~127 °C in the presence of paraffin oil [17]. Furthermore, DSC measurements of the paraffin oil/UHMWPE blend showed only a single melt peak and a single crystallization peak, both at reduced temperatures, indicating complete miscibility of polyethylene with paraffin oil [17]. From these polyethylene/paraffin oil observations, it could be hypothesized that the combination of ultra-high molecular weight PEO such as PolyOx WSR-308 from Dow Chemical and

low molecular weight polyethylene glycol (PEG) should exhibit solution-like behavior too since they have the same repeating structure, $(-CH_2-CH_2-O-)_n$,but vary in number of repeat units, n, where n is approximately 4 for PEG (Mw=200 g/mol) and approximately 181,000 for PEO (Mw=8,000,000 g/mol). DSC of an 8% wt. PEO/PEG blend showed single melting and crystallization peaks at reduced temperature relative to the neat PEO (Fig. 3-2A), suggesting complete miscibility and similarity to the UHMWPE/paraffin oil blends. The melting temperature of neat PEO is reduced from approximately 72 °C to 48 °C after mixing 8% wt. PEO in PEG.

As has already been characterized with UHMWPE [15], the viscous (solution) to solid (gel) transition can be inferred from a sharp viscosity increase approaching infinity as measured by parallel-plate rheometry during a temperature sweep from above the neat PEO melting temperature down through the gel transition temperature.

Figure 3-2 DSC-heating endotherms of (A) neat PEO powder and 8% PEO/PEG blend and (B) gel-spun PEO fiber at various stages of processing. (10 °C/min heating rate, nitrogen atmosphere)

Figure 3-3 Continued DSC-heating endotherms of (A) neat PEO powder and 8% PEO/PEG blend and (B) gel-spun PEO fiber at various stages of processing. (10 °C/min heating rate, nitrogen atmosphere)

Figure 3-4 Parallel plate rheometry of 8% PEO/PEG solution: cooling from 100 °C at a rate of 2 °C /min and 1% strain at a frequency of 100 rad/s.

Complex viscosity of the 8% PEO/PEG blend gradually increased upon cooling below 100 °C until approximately 43 °C, where the viscosity increased rapidly indicating a transition from solution to solid behavior (Fig. 3-3).

The formation of this solid structure coincides within a few degrees with the crystallization temperature measured by DSC for the same 8% PEO/PEG blend; therefore, the solid structure formed during quenching of the PEO/PEG fiber was probably analogous to the UHMWPE/decahydronaphthalene gel-network structure described by Smith and Lemstra [1] as a network of polymer molecules swollen in solvent and mechanically supported by crystalline regions which behave like physical cross-links. Due to the solution-like behavior observed for the PEO/PEG blend, the terms 'oligomer/polymer blend' and 'solution' will be used interchangeably; likewise, 'PEG' and 'spin-solvent' will also be used interchangeably through the remainder of the discussion.

3.4.2   GEL-FIBER EXTRUSION

The relatively high boiling temperature for PEG (>200 °C) allowed the fiber extrusion temperature to be manipulated over a broad range in order to obtain a uniform fiber extrudate, as opposed to the 'conventional' solvents which have significantly lower boiling points. An extrusion temperature of 140 °C produced a uniform fiber extrudate and was maintained throughout this study. This relatively high extrusion temperature would be unconventional with the 'common' PEO solvents previously described, since their boiling points are all well below 140 °C. Since PEG is relatively non-volatile in the

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processing temperature range used in this study, and the quench bath is not a solvent for PEG, the quenched gel-fiber retained most of the spin-solvent. This solvent-rich gel-fiber was slightly opaque and similar in appearance to those gel-fibers produced from polyethylene [1]. The PEO/PEG gel-fibers were notably strong despite containing a majority of spin-solvent, and could be easily wound onto spools without breaking or significantly deforming. These solvent-rich gel-fibers could also be extended above 3000% strain at room temperature before failure. The PEO/PEG gel-fiber drawability at room temperature is about an order of magnitude greater than the UHMWPE gel-fibers produced by smith et al. [1], 3000% vs 350%, despite having higher molecular weight polymer and higher concentration of polymer. The additional drawability, in spite of the increased likelihood of chain entanglements due to higher molecular weight and higher concentration could arise from the difference in chemical structure. While both PEO and UHMWPE are linear, unbranched macromolecules, it is anticipated that in addition to van der Waals forces, the ether linkage in the PEO repeat unit would allow greater rotation about the carbon-oxygen bond imparting more flexibility in the molecule. The lone-pair of electrons on the ether oxygen in PEO may also contribute to favorable intermolecular forces between PEO molecules.

Figure 3-4A shows a WAXD pattern of the PEO/PEG gel-fiber containing a majority of the spin-solvent. The diffuse halo at low two-theta angles resulted from the PEG spin-solvent, and the isotropic rings indicated that no significant orientation was retained from the fiber extrusion process. A gel-fiber structure with low orientation should be expected since molecular relaxation occurs rapidly at the extrusion temperature (well above the PEO melting temperature) and the extrusion speed was relatively low; therefore, shear

induced orientation through the die orifice would be less likely retained in the quenched gel-fiber. Furthermore, the free-falling extrudate was exposed to a minimal amount of stretching prior to reaching the quenching bath. These factors all contributed to the development of a gel-fiber with relatively low c-axis orientation parallel to the fiber.

Figure 3-5 WAXD patterns of gel-spun PEO fiber at various draw ratios (fiber direction is vertical): A – undrawn gel fiber containing solvent; B –10X drawn gel fiber before xtraction; C –10X drawn gel fiber after extraction; D – 60X total draw ratio fiber.

Figure 3-6 Characteristic wide-angle x-ray diffractograms of gel-spun PEO fiber (without solvent) at various draw ratios; miller indices corresponding to typical monoclinic PEO crystal planes are noted.

The WAXD pattern obtained was typical of the PEO monoclinic unit cell, showing intense diffractions at 2θ of 19.1° and 23.3° corresponding to the 120 and 032 planes of the monoclinic PEO unit cell, respectively (Fig. 3-5). SEM image of the undrawn fiber showed a relatively uniform fiber (Fig. 3-6A). The solvent-rich gel-fiber exhibited a melting point around 53 °C which corresponded to a slight increase above the bulk spin dope which was measured as roughly 48 °C (Fig. 3-2A&B).

The procedure described to this point demonstrates how to spin PEO resin of relatively high molecular weight into a gel-fiber; the remainder of the discussion involves solid state orientation of the newly created gel-filaments. For gel-spun polyethylene, many studies have been devoted to the drawing process [18-21]. Drawing in two stages

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appeared particularly effective, especially to obtain higher draw ratios, compared to other drawing methods such as single stage drawing at fixed temperature or through a temperature gradient, the former generally limited to lower total draw ratios while the latter required more complex drawing equipment with minimal benefit relative to two stage drawing [18,19,22-24].

3.4.3   FIRST-STAGE DRAWING

For these reasons, the PEO fibers of the present study were subjected to a two stage drawing process. Selecting appropriate conditions for each drawing stage is critical, and for gel-spun polyethylene, significant changes in tensile properties have been reported depending on the drawing conditions such as temperature and deformation rate [25]. For gel spun UHMWPE, favorable drawing temperatures appeared to be in the range of the 80-148 °C [18-25]. At lower temperatures, there was insufficient molecular mobility to achieve high draw ratios, while at higher temperatures, the fiber can melt.

A similar principle was applied to the PEO fibers of the present study: first-stage drawing occurred at an appropriate temperature which allowed sufficient molecular mobility to attain high draw ratios, but not so high as to initiate melting of the PEO gel-fibers. The previous gel-fiber spinning section demonstrated that the solvent-rich PEO gel-fiber can sustain relatively high elongation before failure at room temperature; therefore, room temperature (24 °C), was deemed adequate for the first drawing stage of the solvent-rich gel-fiber. A first-stage draw ratio of 10X proved to be robust.

Figure 3-7 SEM images of gel-spun PEO fibers without spin solvent. A − undrawn precursor; B − 10X drawn first stage fiber; C − 60X total draw ratio fiber; D − 60X total draw ratio fiber, higher magnification.

By comparison, immediate hot-drawing on extracted precursor fibers (with solvent removed) resulted in decreased tensile properties. Therefore, throughout this study, the first stage drawing was conducted on solvent-rich gel-fibers at a constant draw ratio of

10X. The influence of first-stage drawing conditions will be reserved for forthcoming studies. WAXD of the 10X drawn gel-fiber shown in Fig. 3-4B was similar to the undrawn fiber in Fig. 3-4A. The peak melting temperature of the 10X drawn solvent-rich gel-fiber measured by DSC slightly increased from 53 ℃ to 54 ℃ (Fig. 3-2B).

Since the PEG spin solvent depressed the melting point of the PEO gel-fiber, it was desirable to extract PEG prior to the second drawing stage to allow hot drawing near the solvent-free PEO fiber melting temperature of ~67 ℃ as opposed to the lower gel-fiber melting temperature of 54 ℃ (Fig. 3-2B). The PEG spin-solvent was extracted from the PEO/PEG gel-fibers with acetone.

Low molecular weight PEG is soluble in acetone at room temperature while higher molecular weight PEO is not. Equally important, acetone readily evaporates at room temperature and pressure allowing the extracted fiber to dry without additional extraction/drying procedures. TGA performed on pure PEG, and the PEO/PEG gel-fiber before and after extraction are shown in Fig. 3-7.

The pure PEG spin-solvent evaporates almost completely after 20 min at 200 ℃ in nitrogen atmosphere (Fig. 3-7). A similar TGA experiment on the undrawn, solvent-rich gel-fiber showed a weight reduction of 80% which was assumed to result from evaporation of the PEG component; therefore, the composition of the solvent-rich gel-fiber was estimated to be 80% PEG and 20% PEO (Fig. 3-7).

Figure 3-8 TGA curves of gel-spun PEO fibers rapidly heated to 200 ℃ and held isothermal for 20 min in nitrogen atmosphere; TGA of pure spin-solvent included for reference.

A PEG content of roughly 80% differed from the initial solution concentration of 92% for PEG. The reduced PEG content in the gel-fiber likely resulted from phase separation that occurred during the time between extrusion and actual testing of the gel-fiber [17]. As expected, the PEG content measured by TGA became minimal after extraction in acetone - approximately 3% (Fig. 3-7), suggesting that the extraction process employed was sufficient to obtain a PEO fiber, mostly free of the PEG spin-solvent. The extracted, dried gel-fiber is hereafter referred to as a 'precursor fiber' in the remaining discussion. SEM of the precursor fiber (Fig. 3-6B) showed that a relatively smooth fiber surface morphology was maintained after extraction of PEG and evaporation of acetone. The WAXD pattern of the precursor fiber (Fig. 3-4C) showed a partially oriented crystalline structure. The relative intensities of the 120 and 110 diffractions as a function of

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azimuthal diffraction angle for fibers with draw ratios of 0X, 10X, and 60X are plotted in Fig. 3-8A & 3-8B. The 120 reflection as a function of azimuthal diffraction angle showed greatest intensity around the meridian (0°) with little diffraction occurring near the equator (fiber axis) for the undrawn fiber (Fig. 3-8A). The same holds true for the 110 diffraction (Fig 3-8B), but given the relatively lower intensity of 110 diffractions, further analysis is restricted to the 120 diffraction.

Although c-axis orientation perpendicular to the fiber axis seems counterintuitive, Pennings and co-workers [26] described similar behavior for gel-spun UHMWPE/paraffin oil fibers after constrained extraction in hexane. The perpendicular crystalline orientation was only observed for gel-fibers extruded at relatively slow speeds and/or high temperatures [26]. This perpendicular orientation was attributed to lamellar crystalline regions oriented with the c-axis perpendicular to the fiber axis. Since the gel-fibers of the present study were processed under similar conditions as the fibers studied by Pennings, namely a relatively slow extrusion speed (1 m/min) at relatively high temperature for PEO (140 °C) followed by constrained extraction, it is hypothesized that lamellar crystals are present in the PEO precursor fiber and exhibit similar preferential c-axis orientation perpendicular to the fiber axis. Interestingly, this perpendicular orientation was also shown by the same authors to produce final drawn fibers with higher tensile strength than fibers drawn from precursors with c-axis orientation parallel to the fiber axis [26].

Figure 3-9 Relative intensity of the 120 [A] and 110 [B] as a function of the azimuthal diffraction angle for PEO fibers after constraint extraction (without solvent).

It was argued that c-axis orientation parallel to the fiber axis induced during fiber spinning at high speed and/or low temperature extrusion contained significantly more molecular defects which had the effect of limiting the maximum drawability of the fiber and thus reduced the maximum achievable tensile strength. Drawing to a ratio of 10X reduced the relative intensity around the meridian, but began to increase in intensity

around the equator indicating the presence of c-axis orientation parallel to fiber direction (Fig 3-8). The perpendicular c-axis orientation is essentially removed at the maximum 60X draw ratio while a single intense peak around the equator developed which is indicative of an oriented fiber. The peak melting temperature increased from roughly 54 ℃ in the 10X drawn gel-fiber before extraction to 67 ℃ in the 10X drawn fiber after extraction (Fig. 3-2B).

3.4.4   SECOND-STAGE DRAWING

The precursor fiber was subjected to a second drawing stage at approximately 68 ℃. This temperature is near the peak melting temperature of the first-stage fibers, and was chosen based upon the notion for gel-spun UHMWPE fibers that suggested maximum draw ratio increased with increasing drawing temperature up to the fiber melting temperature [18]. Hot-drawing of the precursor fiber at temperatures higher than 68 ℃ resulted in frequent breakage, probably a result of the fiber melting.

The 10X drawn precursor fibers from the first drawing stage were hot drawn in the second stage at ratios of 3X, 5X, and 6X, so that total draw ratios of 30X, 50X, and 60X were obtained. Figure 3-9 plots representative tensile stress-strain curves. Tensile strength and Young's modulus of 0.66 ±0.04 GPa and 4.30 ±0.1 GPa, respectively, were obtained at the maximum draw ratio.

Tensile strength and Young's modulus increased with increasing total draw ratio while the strain at maximum load decreased with increasing draw ratio.This general behavior was also observed for gel-spun UHMWPE fiber [1].

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Figure 3-10 Characteristic stress-strain curves of gel-spun PEO fibers at total draw ratios of 30X, 50X, and 60X.

The relatively large strain at maximum load may suggest that the fibers can be further drawn; however, with the conditions employed in this study, the maximum stable draw ratio was limited to 60X. WAXD of the PEO fiber drawn to 60X total draw ratio showed a highly-oriented, crystalline structure developed with hot drawing (Fig. 3-4D) when compared to the precursor fiber (Fig. 3-4C).

Meridian and equator scans of the undrawn, 10X, and 60X fiber are shown in Fig. 3-10. In the meridian scan, the undrawn fiber and the 10X drawn fiber showed the greatest intensity with major peaks near 19° and 23° from the 120 and 032 diffractions, respectively (Fig. 3-10A). The highly drawn 60X fiber showed a flat profile in the meridian scan indicating no significant orientation perpendicular to the fiber axis. As expected, the equator scan indicated significant crystalline alignment along the fiber direction for the 60X drawn fiber with the two strongest intensities occurring near 15°and

19° from the 110 and 120 diffractions, respectively (Fig 3-10B). The 110 and 120 diffractions were also used in the calculation of the crystalline orientation factor for the 60X fiber. The crystalline orientation factor of 0.84 computed for this highly drawn fiber supports good crystalline c-axis alignment along the fiber direction.

The ratio of the 120 peak intensity relative to the 032 peak intensity shifted lower as a result of the hot drawing (Fig. 3-5). Similar behavior was observed for hot-pressed PEO films at different temperature, wherein the authors attributed the intensity shift to the development of orientation in the films [27]. The highly drawn fiber showed a peak melting temperature near 70 ˚C with a broad shoulder extending to higher temperatures (Fig. 3-2B).

The highly drawn PEO fiber exhibited a relatively uniform surface morphology from the SEM images of Figs. 3-6C and 2-6D. The 4.33 GPa Young's modulus obtained for these highly oriented PEO fibers approached nearly one half of the 10 GPa theoretical modulus estimated by x-ray for the helical PEO crystal [28]. The tensile properties of these high-strength PEO fibers, including the toughness of 117 MJ/m^3, exceed that of many melt spun polymeric fibers. Since PEO belongs to the unique class of polymers that are water soluble, these high strength PEO fibers rank amongst the strongest and toughest room-temperature, water-soluble fibers in existence. By comparison, 20 ℃ water-soluble PVOH fibers commercially available from Kurrary under the trade name Kuralon K-II WN2, have a reported tenacity of approximately 60 cN/tex (0.78 GPa) with a failure strain of 20%.

Figure 3-11 Meridian [A] and equator [B] scans of the extracted fiber before drawing, at 10X draw ratio, and 60X times draw ratio.

3.4.5   RECOMMENDATIONS AND OUTLOOK

In this study, a gel-spinning process to produce strong and stiff PEO continuous fibers was demonstrated. The PEO gel-spinning process utilized well-established gel-spinning techniques which allowed relatively efficient fiber spinning, and consequently, the PEO gel-spinning process shared many similarities to the UHMWPE gel-spinning processes.

The oligomer/polymer blend concept was introduced, and its benefits over conventional organic solvents were explained. While the oligomer/polymer blend of the present study shared identical molecular repeat units, the oligomer/polymer blend concept may also be effective for spinning fibers from oligomer/polymer blends with only similar repeat units, especially when a suitable oligomer that matches the polymer repeat unit exactly is not widely available. For example, gel spinning of ultra-high molecular weight polypropylene fibers has been performed using paraffin oil as a 'solvent' [3].

While the present study focused on gel-spun fibers, it should be apparent that this process can be applied to the production of high strength PEO films. High strength PEO films may be useful for pharmaceutical coatings or for water soluble chemical capsules that are commercially available in the form of encapsulated dishwasher detergent tablets and encapsulated pesticides.

3.5   CONCLUSIONS

In this study, a gel-spinning process for the production of high-strength, continuous PEO fiber was developed and investigated. Specifically, PEO was mixed with PEG, an oligomer with the same repeating unit, to form a spin dope which was subsequently extruded, solvent extracted, and hot drawn. The process was demonstrated using a spin dope containing 8 wt% PEO and 92 wt% PEG. DSC and parallel-plate rheometry were used to determine suitable extrusion and drawing conditions for generating high-strength PEO fibers. The results showed that the blend was miscible having a single melting temperature around 45 ℃, below which the material behaved like a gel with large extensibility. The extruded gel-fiber was able to be stretched at room temperature for

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more than 10 times without breakage or development of non-uniform surface appearance. A two-stage drawing sequence was developed and found to be suitable for producing high-strength PEO fibers. After solvent extraction, the precursor fiber resulting from the first-stage drawing had a melting temperature around 67 °C, which was chosen as an approximate temperature for final hot drawing in oil bath. The highly drawn, gel-spun PEO fibers exhibited remarkably higher tensile strength and Young's modulus compared to melt-spun and surface-grown PEO fibers. Tensile strength and Young's modulus increased with increasing draw ratio. The high-strength, gel-spun PEO fibers showed a highly oriented crystalline structure as measure by x-ray diffraction. All these results indicated that the oligomer/polymer spinning approach is effective in producing high-performance PEO fibers and may be adapted to other polymer systems.

3.6 REFERENCES

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CHAPTER 4

HIGH-STRENGTH POLYOXYMETHYLENE
FIBERS BY GEL-SPINNING

4.1   SUMMARY

A new gel-spinning process for producing high-strength poly(oxymethylene) (POM) fibers is introduced. The POM gel-spinning process is developed using the oligomer spin-solvent approach first applied to gel-spun PEO fiber. Since POM homopolymer undergoes rapid degradation in solution at high temperature in an oligomer spin-solvent, caprolactam is used as both spin-solvent and stabilizer. The gelation and solvent-like properties are investigated. A 80/20 wt% caprolactam/POM gel is highly stable and exhibits a melting temperature around 145 ℃. Some salient features of a gel-spun POM fiber with a draw ratio of 40 are a tensile strength at break of 1.8 ±0.04 GPa (~15 g/denier) and a Young's modulus of 36 ±0.06 GPa (~290 g/denier). The tensile properties are amongst the highest reported for POM fiber, yet the diameter of the gel-spun POM fiber (~ 20 μm) is significantly smaller than the monofilaments (> 1 mm) typically reported. Tensile and creep performance of the gel-spun POM fibers are introduced. The results suggests that a gel-spun ultra-high molecular weight POM may lead to improved tensile properties.

4.2   INTRODUCITON

Polyoxymethylene (POM) structures of high strength and high modulus have been extensively investigated; however, spinning POM fibers with high strength and high modulus has not received sufficient attention. In its injection molded form, POM exhibits

a unique combination of chemical resistance, tensile strength, stiffness, creep resistance, and retention of tensile properties at elevated temperature that are unmatched by any other thermoplastic polymers. A high strength POM fiber is expected to fill a performance gap in the current commercial high performance fiber market. POM fiber should have better resistance to chemicals than polyamide and polyester fiber [1], improved creep resistance and strength retention at high temperature than UHMWPE fiber, and significantly better resistance to attack by water than poly(vinyl alcohol) (PVOH) fiber while at the same time being equally unaffected by long-term exposure to alkalis permitting POM fiber to be a possible alternative to PVOH fiber in reinforced concrete composites [2]. To date, however, the benefits of a high-strength POM fiber have not been fully exploited, probably because conventional spinning of POM fiber has proven difficult.

Conventional melt spinning of POM has limited success, primarily because the high crystallization rate of POM can cause in-fibril voids and thus the fiber is easily cut during melt spinning [3]. Melt spinning of POM homopolymer is not well studied. An attempt to melt spin POM copolymer achieved a tensile strength and modulus of approximately 1 GPa and 9 GPa, respectively [4]. A separate patent on melt spinning of POM copolymer with specifically formulated ratios of the copolymer so as to control the crystallization rate so that the occurrence of in-fibril voids was inhibited yielded fibers with tenacities up to 13 g/d [5]. The gel-spun POM fibers of the present study are 80% and 15% stronger than the previously described melt-spinning methods, respectively. The Young's modulus of the new gel-spun POM fibers is approximately 4 times higher than the melt-spun POM copolymer fibers [4].

Solution spinning of POM fiber is also difficult. The high crystallinity of POM, which imparts it with excellent chemical resistance, works to detriment of dissolution for solution spinning. POM has been shown to be insoluble in over 200 chemicals at room temperature [1]. A process for electrospinning POM fibers was demonstrated using the rather exotic solvent, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), which can dissolve POM at relatively low temperature [6]. The major drawback to electro-spun POM fiber is that fibers are typically collected as fibrous webs instead of continuous filaments that can be spun into yarns and woven into fabric. Additionally, the strength of the electro-spun fiber bundles was shown to be only 300 MPa [6]. A patent on spinning POM fiber with a "viscosity reducing material" up to 50% by weight reported tenacities up to 14 g/denier with moduli up to 180 g/denier [7]. The gel-spun POM fibers of the present study have slightly higher tensile strength and the modulus is approximately 50% higher those reported on the previously described patent which provided examples for copolymers of POM [7].

The following study demonstrates a new gel-spinning process for producing POM continuous fibers with tensile strength and modulus above 1.8 GPa and 36 GPa, respectively. The POM gel-spinning spin-solvent selection follows the oligomer spin-solvent concept previously demonstrated on gel-spun polyethylene oxide (PEO) fibers [8]. The gel-spun POM fibers of the present study are among the strongest, stiffest, POM continuous fibers ever created. While the present study focuses on POM homopolymer, high strength fibers from POM copolymers can be gel-spun using the proposed POM gel-spinning process.

Before continuing to the discussion on gel-spun high strength POM continuous fibers, some of the other high strength, high modulus structures of POM will be briefly mentioned here to highlight how the new gel-spun POM fibers fill a critical void that has not been satisfactorily addressed in the scientific literature. POM structures with tensile strength above 1.7 GPa and modulus above 35 GPa were achieved by drawing a billet of POM [9]. Other studies involving pressurized drawing of POM tubes yielded POM structures with tensile strength above 2 GPa and modulus above 50 GPa [10]. The die-drawing and pressurized drawing processes generically describe the final product as "fiber"; however, the fiber diameters are on the order of millimeters. Yarns, ropes, or fabric made of these large "fibers" would be impractical for many commercial applications because the bending stiffness would be enormous relative to the typical high-performance fibers currently on the market which typically have diameters less than 100 μm. The gel-spun POM fibers of the present study have diameters on the order of ~20 micron making these high-strength POM fibers comparable in denier to high performance commercial fibers such as Dyneema®, Spectra®, Kuralon®, Innegra®, and Kevlar®. As such, the gel-spun POM fibers of the present study can be more confidently compared to these high performance fibers without significant size-effects distorting the results. The POM gel-spinning process presented here represents new process for spinning POM fibers with relatively high strength, high stiffness, and small diameter consistent with commercial high performance fiber production.

The focus of this investigation is to demonstrate the POM gel-spinning process. The discussion begins by selecting an appropriate gel-spinning spin-solvent which is arguably

the most challenging aspect of developing a new gel-spinning process. Structure development throughout the spinning process is characterized. Comparisons will be drawn between the new POM gel-spinning process, and the well-established UHMWPE gel-spinning processes to highlight their similar characteristics. Some salient features of these new fibers will be presented and the mechanical properties of gel-spun POM relative to a commercial gel-spun UHMWPE fiber will be introduced. UHMWPE fiber is chosen over other high performance fibers for comparison because it has similar molecular physics: both POM and UHMWPE are semi-crystalline, linear thermoplastic polymers without significant hydrogen bonding interactions. The primary inter-chain interactions for both polymers occur through Van der Waals interactions. The study concludes by leveraging the fundamental benefits of the gel-spinning process to formulate a hypothesis for further improving the tensile properties of gel-spun POM fibers.

4.3 EXPERIMENTAL

The experimental details are described in the following sections.

4.3.1 MATERIALS

DuPont Delrin® POM (acetal) homopolymer resin was kindly supplied by DuPont Performance Polymers. The Delrin® POM was a higher molecular weight experimental grade resin with a reported density of 1.42 g/cm^3 and average molecular weight, Mn = ~80,000 Da. For reference, the commercially available Delrin® 100P NC010 resin has a reported Mn = ~66,000 Da. Polyethylene glycol (PEG) with average molecular weight of 400 Da was obtained from J.T. Baker. Propylene glycol (PG) was 99.9% pure USP food

grade. Caprolactam was obtained from Brüggemann Chemical. Spectra S2000 fibers were supplied by Honeywell. All chemicals were used as received. Municipal water was used for the extraction process.

Spin dopes were prepared by melt mixing POM pellets in C.W. Brabender Prep-Center fitted with twin roller blades at 200 °C until a uniform melt was obtained (approximately 5-10 minutes). The desired spin-solvent was slowly added until a uniform solution developed. The concentration of POM in solution was 20% by weight. Once a uniform solution was obtained, the mixing temperature was reduced to 180 °C mixed for an additional 3 min to obtain a homogenized solution.

4.3.2 GEL SPINNING

Fiber spinning was performed through an Alex James and Associates piston extruder with a 2.54 cm bore diameter and 150 mL capacity. The homogenized POM/caprolactam solution was quickly transferred into the bore (preheated to 170 °C) of the extruder and allowed to equilibrate for 30 min. The solution was extruded through a 1 mm die orifice with an aspect ratio of ~15:1 maintained at a temperature of 170 °C. The solution was extruded at a speed of approximately 2 m/min. The fiber solution was quenched into a 20 °C water bath 5 cm from the die exit. The quenched gel-fiber was collected onto spools at 20 m/min so as to apply 10 times jet-stretch to the fiber solution as it exited the die. The spools of gel-fiber were stored in a 40% caprolactam/water solution to prevent drying and successive phase separation of caprolactam before extraction and hot-drawing experiments were performed.

4.3.3 SPIN-SOLVENT REMOVAL

Caprolactam in the gel-filament was removed by extraction in water. The gel-fibers fibers were prepared by winding onto a 1 inch diameter polytetrafluoroethylene (PTFE) rod. Both ends of the gel-fiber were fixed to maintain constant fiber length. To simulate a counter-flow type extraction process, the rod as prepared was submerged into an agitated bath of water at ~ 50 °C for 0.5 h. The volume of water was ~5000 larger than the volume of the gel-fiber in order to maintain a maximum concentration gradient throughout the extraction process. The PTFE rod containing the extracted gel-fiber was removed from the water bath and dried under forced air convection while maintaining fixed fiber ends.

4.3.4 HOT-DRAWING

Hot-drawing was performed in three stages, and the fiber was rinsed after each stage. The first two stages were performed through a heated oil bath. The total path length through the hot bath was 0.6 m. The bath temperature was maintained within ±1 °C of the set point. The first stage of hot-drawing was performed at 140 °C with a feeding speed of 1 m/min and a collection speed of 12 m/min to obtain a draw ratio of 12X. The second stage of hot-drawing was performed at 150 °C with a feeding speed of 0.5 m/min and a collection speed of 1 m/min to obtain a draw ratio of 2X (total draw ratio 24X). A third drawing stage was performed on three successive godet rollers with the middle roller heated to 160 °C. The rollers had speeds of 10-10-17 m/min from first to last, respectively, to obtain a draw ratio of 1.7X (total draw ratio ~40). Draw ratio as used in this report is defined as the ratio of the collection roller speed to the feed roller speed. Fibers were drawn at the maximum ratio to obtain samples at least 50 m long for testing.

4.3.5 CHARACTERIZATION

Diameter measurements were obtained by weighing a known length of fiber and calculating the cross-sectional area assuming a density of 1.42 g/cm^3. Spectra S2000 fibers were measured in a similar fashion assuming a density of 0.97 g/ cm^3.

Tensile properties for single filaments were measured using an Instron 5566 universal testing machine. Fiber samples were wound onto wooden rods approximately 2 mm in diameter and super-glued over the wound fiber ends. The prepared single filament samples were clamped using Instron 2711 Series Lever Action Grips rated for 5 N. Crosshead speed was 50 %/min with a gauge length of ~10 cm. Tensile tests were performed under ambient conditions (40-60% relative humidity at 23 °C) except where noted otherwise. Six samples from each of three fiber spinning experiments were tested and averaged. High temperature tensile testing was performed inside an Instron 3119-600 series heated chamber. The fiber samples were added to the preheated chamber and quickly extended to a strain of 0.1 % and allowed to equilibrate for 60 s at the desired temperature before beginning the tensile test. Experimental error was estimated using the standard error of the mean, defined as the standard deviation divided by the square root of the sample number.

Differential scanning calorimetry (DSC) data were collected on a TA Q200 DSC unit (TA Instruments). Samples were crimped in hermetic aluminum pans. Nitrogen atmosphere and a scan speed of 10 °C/min were used for all samples. Thermogravimetric analysis (TGA) experiments were performed using a TA TGA5000 (TA Instruments). Samples were heated in nitrogen atmosphere. Scanning electron microscopy (SEM)

images were collected on a LEO 1550. SEM samples were mounted onto carbon tape and gold sputtered.

4.4   RESULTS AND DISCUSSION

Selection of an appropriate spin-solvent is critical for a successful gel-spinning process. The key requirements for an ideal gel-spinning spin-solvent are good compatibility with the polymer at high temperature and gelation upon cooling to ambient temperature. These requirements are uniquely different from solution spinning where the spin-solvent need only dissolve the polymer because it will be immediately coagulated in another solvent or evaporated upon exiting the die during fiber spinning. In the gel-spinning process, the spin-solvent should allow partial crystallization of the polymer upon cooling so as to form a gel-network. This requirement is critical, because it allows the relatively disentangled polymer morphology from the semi-dilute solution state to remain relatively disentangled in the solid gel-state. By preserving the relatively disentangled polymer network, solid-state ultra-drawing can be effected to achieve fibers with good orientation and high tensile strength and modulus. Drawing in the solid-state should be more efficient than drawing in the viscous solution state because molecular relaxations should progress significantly slower in the solid-state. The draw ratios for solution-spun fibers are typically much lower than gel-spun fibers because molecular relaxations can continue to occur during the coagulation or evaporation stage until all of the solvent has been extracted from the fiber. Because a good gel-spinning solvent allows partial crystallization of the polymer upon cooling, the relatively disentangled state can be preserved, even though the spin-solvent is still present inside the gel-network. The

relatively disentangled gel-network formed upon cooling is highly stable, and persists even after complete extraction of the spin-solvent [11]. It has been shown that the gel-spun polymer precursor fiber retains a relatively disentangled morphology up to the polymer's melting temperature, above which the molecules rapidly rearrange back into the entropically favorable entangled state in the timescale of a typical spinning process [11]. This temperature stability is desired because now the polymer can be hot-drawn at temperatures up to its melting point without significantly compromising the relatively disentangled state. Drawing at elevated temperatures is preferred because it has been shown that extending the polymer network at lower temperatures can cause excessive defects to be generated leading to poor tensile properties [12].

From the previous discussion, it should be clear that selection of a gel-spinning spin-solvent can be difficult. This is especially true for POM which is inherently solvent resistant [1]. To overcome this challenge for POM, the oligomer spin-solvent approach demonstrated using PEO [8] is adopted.

The oligomer spin-solvent concept implies that many non-hydrogen bonded polymers should be "dissolvable" in their respective oligomers at elevated temperature and should exhibit gelation upon cooling. The fundamental description supporting this argument has been described in detail elsewhere (in chapter 1 of this thesis) and is outside the scope of this chapter. In the case of PEO, the PEG oligomer is readily available: both PEO and PEG share identical chemical repeat units. A mixture of PEO and PEG formed a miscible solution at high temperature and formed a gel-network upon cooling back to ambient temperature. The gel-spun PEO fibers were the strongest PEO fibers ever created [8].

For the present case, POM has the oligomer, paraformaldehyde, commercially available; however, this system was not investigated due to the carcinogenic nature of the formaldehyde by-products which can be readily generated upon heating paraformaldehyde. In cases where the exact oligomer is not suitable or available for gel-spinning, the oligomer spin-solvent approach suggests that a chemically similar oligomer can be substituted [8]. An obvious substitute in the case of POM is PEG. PEG is relatively non-toxic, yet chemically similar to POM, differing only by one methylene unit: [-CH2-CH2-O-] compared to [-CH2-O-].

A spin-dope of 20% wt POM dissolved in PEG formed a translucent solution above POM's melting temperature offering strong support for the oligomer spin-solvent concept; however, relatively fast degradation of the spin-dope occurred as noted by outgassing (likely formaldehyde) and viscosity reduction during continued mixing at elevated temperature. POM is known to degrade through several mechanisms [13]. Acidolytic degradation of POM can occur due to acid catalyst contaminants, acids generated through the oxidation of formaldehyde, and acetic acid formed from an acetate end group on a chain which has depolymerized from other degradation mechanisms [13, 14]. In the case of PEG, it's possible that catalysts from the synthesis of PEG are accelerating the degradation. Irrespective of the mechanism, the PEG/POM solution degrades too rapidly to be considered as a spin-solvent for a robust gel-fiber spinning process.

Since POM is known to degrade by acidolytic and oxidative mechanisms at elevated temperature [13-15], a stabilizer would be beneficial for the gel-spinning process.

Oxidative degradation can be mitigated by addition of routine antioxidants [16]. The acidolytic degradation requires specific chemicals to react with formaldehyde to disrupt the reaction, commonly referred to as zippering. The zippering reaction is accelerated at higher temperatures; therefore, minimizing this type of degradation is critical [17]. Rather than simply add a stabilizer to the POM/PEG solution - which may require a large percentage of stabilizer possibly affecting the quality of the solution or the fiber; a more elegant approach is proposed.

Instead of a separate stabilizer, the spin-solvent itself should be capable of reacting with formaldehyde to slow the decomposed POM at elevated temperature in solution. The range of suitable spin-solvents is now further reduced to those capable of reacting with formaldehyde; however, a promising candidate is proposed: caprolactam.

Low molecular weight polyamides are known to react with formaldehyde, and have been shown to significantly improve the thermal stability POM [15, 17]. The thermal stability of POM was shown to increase with increasing polyamide content [17]. Since formaldehyde primarily reacts with the amide group of the polyamide, caprolactam is expected to provide similar stabilizing effect. More specifically, caprolactam has been shown to react with formaldehyde yielding a methylolation adduct, N-methylo-caprolactam and two condensation products, N,N'-methylene-bis(caprolactam) and N,N'-oxy-bis(methylene)-bis(caprolactam) [18]. Having a spin-solvent acting as a stabilizer should be highly effective due to the relatively high concentrations of spin-solvent used in gel-spinning.

Figure 4-1 DSC melting endotherms of caprolactam, the bulk POM/caprolactam gel material after mixing, and the gel-fiber after quenching but before extraction.

From a purely statistical point of view, a formaldehyde molecule that separates from the POM chain has a 4 to 1 chance of reacting with caprolactam instead of another POM molecule assuming the spin-dope concentration used in this study. A final benefit of a caprolactam spin-solvent is that it is relatively non-toxic and water soluble, making extraction in later processing stages relatively simple.

To support these assumptions, as well as verify that caprolactam is a suitable gel-spinning spin-solvent for POM, a 20% wt solution of POM/caprolactam was prepared using identical conditions as previously described for POM/PEG. The POM/caprolactam mixture forms a translucent solution at the mixing temperature. The POM/caprolactam solution is stable, with no noticeable outgassing or viscosity reduction over the processing time scale.

60

Figure 4-2 DSC melting endotherms of the neat Delrin® POM homopolymer pellet, and of the POM fiber in various stages of the spinning process. Data for the POM pellet is from the second heating cycle after removal of the thermal history.

The POM/caprolactam spin-dope is also stable inside the bore of the piston extruder at elevated temperature for several hours without any obvious signs of decomposition. The POM/PEG solutions became too degraded during the mixing stage and could not be safely transferred to the extruder.

The DSC data in Fig. 4-1 show a reduced melting point of the POM/caprolactam solution after mixing. The melt temperature of the gel is approximately 145 °C, about 30 °C less than the neat POM pellet's melting temperature (Fig. 4-2). This reduced melting temperature for the solution is expected, and is similar to UHMWPE and PEO gel-spinning solutions [8, 19]. The reduced melt temperature of the spin-dope is indicative of the relatively good compatibility between POM and caprolactam. If there were no

favorable interactions between POM and caprolactam, the melt temperature of POM would be expected to remain around 175 ℃.

The large reduction in melt temperature in this instance cannot be attributed to degradation of the POM polymer because the melt temperature of POM precursor fiber returns to 174 ℃ immediately after extraction of the caprolactam in water. A small melting peak around 60 ℃ for the bulk gel in Fig. 4-1 is too low to be attributed to phase separated caprolactam. This melting may result from the reaction products of caprolactam with formaldehyde, some of which have melting temperatures below 65 ℃ [20]. Regardless of their presence in the bulk gel, the melting peaks around 60 ℃ are not present in the gel-fiber or extracted fibers (Fig. 4-1) suggesting that molecules undergo further chemical changes, or were removed in the quenching bath. The quenched gel-fiber has a peak melting temperature approximately 15 ℃ higher than the bulk material. The 10X jet-stretch applied during spinning likely induces molecular orientation in the gel-fiber contributing to the increase. Another factor is the partial extraction of some caprolactam in the water quench bath which would also lead to a higher melt temperature. UHMWPE gel-fibers also show an increase in melt temperature when the spin-solvent content is reduced [21].

Further evidence of the stabilizing effect of caprolactam is shown in Fig. 4-4. The normalized torque over a time span of 30 min at 200 ℃ are presented; the first 3 min have variations due to addition of the material into the torque rheometer. The normalized torque is presented here to highlight the differing trends. The POM/caprolactam solution maintains a nearly constant torque for the duration of the test, while the neat POM resin

shows a decaying trend. If significant degradation was occurring in the POM/caprolactam solution, a large decrease in the solution viscosity would be expected; however, these data suggest that the solution is surprisingly stable, showing almost no variation throughout the testing. Fig. 4-4 shows that the thermal stability of the POM resin is not significantly altered by the gel-spinning process. The precursor fiber after extraction of caprolactam shows a similar degradation profile to the unprocessed POM resin upon heating to 400 °C using TGA. The gel-fiber exhibits a weight loss onset at lower temperatures; however, this is expected due to evaporation of the caprolactam.

Figure 4-3 Normalized torque vs. time curve at 200 °C and 80 rpm. Material was added to rheometer during first three minutes.

Figure 4-4 TGA weight loss curves of POM pellet and fiber before and after solvent extraction as a function of temperature. Fibers heated at rate of 20 °C/min in nitrogen atmosphere. Pure caprolactam is included for reference.

Considering the second derivative of the curves, the maximum rate of weight loss in the gel-fiber occurs near the same temperature as the maximum rate of weight loss from the pure caprolactam reference sample. Considering the efficacy of the spin-solvent extraction, these data in Fig. 4-4 also indicate that the caprolactam is completely extracted from the extracted precursor fiber because the extracted fiber does not show a weight change until significantly higher temperatures.

The tensile properties of the gel-spun POM at room temperature are presented in Fig. 4-5A. At the maximum draw ratio of 40X, the POM fiber achieve a tensile strength and

Young's modulus greater than 1.8 ±0.04 GPa and 36 ±0.6 GPa, respectively.

Figure 4-5 Representative tensile stress-strain curves of gel-spun POM fibers at maximum draw ratio and Spectra S2000 UHMWPE gel-spun fiber tested at temperatures: A) 23 °C and B) 120 °C.

These tensile properties are amongst the highest reported for POM fibers. Some reported POM structures have achieved somewhat higher tensile strength and modulus; however, the processing methods and fibers deniers are not consistent with commercial high-performance fiber processes [22,23]. For example, Clark et. al. achieved tensile strength and modulus of 1.7 GPa and 35 GPa, respectively, by drawing a "billet" of POM at elevated temperature [9]. They noted that the temperature and drawing rate were both critical to process. No fiber diameter is given; however, it can be assumed to be relatively large since the precursor is a "billet" and the draw ratio is only 22X. Separately, a pressurized drawing method on extruded hollow tubes of POM several millimeters in diameter achieved tensile strength and modulus of 2.0 GPa and 58 GPa, respectively [10]. The pressurized drawing at high temperature was shown to reduce the voids in the fibers which promoted higher tensile strengths [3]. This process, however, also produces fibers with diameters too large to be suitable for many commercial applications where high performance fibers currently are used. The gel-spun POM fibers of the current process yield diameters around 20 μm and similar in size to commercially gel-spun UHMWPE fibers such as Dyneema® or Spectra®. The gel-spun POM fibers are almost two orders of magnitude smaller in diameter than those previously reported, yet have similarly high strength. SEM images of the POM gel-spun fibers show a dense, uniform appearance (Fig. 4-6). Striations at the higher draw ratios (Fig. 4-6 B & C) imply a fibril morphology was developed during the spinning process.

The presence of voids in POM fibers has been shown to significantly affect the fiber's physical and chemical properties [2,3]. Voids with cross-sectional areas above 1 μm^2

were shown to significantly reduce the tensile strength while voids less than ~0.3 μm^2 had little effect on the tensile properties [3]. Fig. 4-6D shows a high magnification SEM image of a gel-spun POM fiber with a draw ratio of 40X. On the length scale of this image, no voids with cross-sectional area greater than 1 μm^2 can be seen, indicating that the gel-spinning process does not promote the formation of detrimental voids in POM. Furthermore, the size and quantity of voids in POM fibers were shown to increase with draw ratio at high draw ratios.

Figure 4-6 Typical SEM images of POM gel-spun fibers at various stages of hot-drawing; draw ratio indicated is total draw ratio: A) First Stage 12X; B) Second Stage 24X; C) Third Stage 40X; D) Third Stage at higher magnification.

For the gel-spun POM fibers in imaged in Fig. 4-6, no signs of large voids can be detected at any of the draw ratios imaged. Internal voids are possible, but unlikely since the surface appears completely dense and similar to the surface of pressurized drawn POM fibers [2,3].

Injection molded POM exhibits relatively good retention of tensile properties at elevated temperature and high resistance to creep. To assess these properties in the fiber form, the tensile properties of the gel-spun POM fibers were tested at 120 °C (Fig. 4-5 B) and the POM fiber creep was also tested over 24 h with loads of 10% and 20% of the averagebreaking load (Fig. 4-7). A commercially available, high-performance gel-spun UHMWPE Spectra 2000, was also tested under identical conditions for comparison. Since the Spectra S2000 fiber and the gel-spun POM fibers have similar diameters, ~ 20 μm, size effects can be minimized. UHMWPE fiber is selected for comparison since it is structurally similar to POM: both polymers are linear and unbranched without significant hydrogen-bonding interactions.

UHMWPE is known to undergo crystalline slippage, especially at elevated temperature. Studies have shown that tensile strength decreases rapidly with increasing temperature. Also, the melting temperature for UHMWPE fiber is around 145 °C, about 30 °C lower than POM. Fig. 4-5 inset shows that the tensile strength of UHMWPE fiber decrease approximately 70% to about 1 GPa. Gel-spun POM fiber shows significantly better retention of tensile strength dropping only 30% to about 1.2 GPa. At 120 °C, gel-spun POM is stronger than UHMWPE fiber, even though the tensile strength of POM fiber at room temperature is only half that of UHMWPE.

Figure 4-7 Creep curves for Spectra S2000 fiber and POM gel-spun fiber at 10% & 20% of the breaking load (BL). Testing performed at 23 °C and 45-55% relative humidity.

Another interesting feature is the shape of the tensile curve at high temperature. UHMWPE exhibits a yield stress at relatively low strain (2%) and undergoes significant plastic deformation until failure at ~15% strain. This failure mode is significantly different from the typical brittle failure at 23 °C for UHMWPE fibers (Fig. 4-5). The mode of tensile failure for the gel-spun POM fiber is relatively unaltered at high temperature. The gel-spun POM fiber exhibits a failure at roughly the same strain, irrespective of the testing temperature. A comprehensive analysis of the tensile properties of gel-spun POM fiber is reserved for future studies.

UHMWPE fiber is highly susceptible to creep under constant loads which restricts the applications for which UHMWPE is suitable [24]. Despite both POM and UHMWPE

being linear polymers, with primary interactions occurring through Van der Waals forces, their creep behavior is significantly different. Fig. 4-7 shows the creep behavior of gel-spun POM fiber relative to Spectra S2000 fibers. At 10% and 20% breaking load (BL), the gel-spun POM fiber exhibits significantly less creep over the duration of the test. While relatively good creep performance in polyamides can be attributed to hydrogen-bonding interactions, the difference in creep behavior from UHMWPE must be explained differently; especially considering that the molecular weight of UHMWPE is nearly an order of magnitude larger than the POM used in this study, and creep is expected to be reduced with higher molecular weights. The higher activation energy for POM with its higher melting temperature may contribute to the improved creep performance over UHMWPE. The creep data are presented here to highlight some salient features of this new, gel-spun, high-strength POM fiber; a comprehensive study on the creep behavior of gel-spun POM fiber is beyond the scope of this investigation.

4.5 CONCLUSIONS

In this study, a gel-spinning process for high-strength POM fibers was developed. The process followed the oligomer spin-solvent concept for producing high-strength polymer fibers by gel-spinning. Caprolactam was found to be both a suitable gel-spinning spin-solvent and stabilizer against thermal degradation of the POM during the spinning process. Complete extraction of caprolactam from the gel-fibers using hot-water was verified by TGA. After hot-drawing the extracted precursor fiber in three stages to a maximum ratio of 40X, the POM fiber tensile strength and Young's modulus reached 1.8 GPa and 36 GPa, respectively, and the fiber diameter was ~20 μm. The POM fiber tensile

strength at 120 °C and the creep at 23 °C were shown to be significantly better than a commercial UHMWPE fiber (Spectra S2000). A gel-spun ultra-high molecular weight POM fiber is expected to have improved tensile and creep properties.

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CHAPTER 5

FAST SOLVENT REMOVAL BY MECHANICAL TWISTING FOR GEL-SPINNING OF ULTRA-STRONG FIBERS

5.1   SUMMARY

A new method for solvent removal in gel-fiber spinning is investigated. Instead of solvent evaporation or coagulation as conventionally used, the new method involves mechanically twisting the gel fiber along the fiber axis. By removing the majority of solvent in the gel fiber by mechanical twisting, the emission of solvent vapor and the production of waste solvent mixture or coagulation byproducts are minimized. The new solvent removal method is demonstrated through gel spinning of high-strength ultra-high molecular weight polyethylene fibers using both volatile and nonvolatile spin solvents. Approximately 90% of the spin solvent is removed by a single-step twisting process and the resulting fiber retains the high mechanical properties conventionally obtained. With respect to the gel spinning industry, the new solvent removal method holds a promise of simplifying the solvent removal and recovery steps and improving the production rate, leading to more efficient and effective gel spinning processes.

5.2   INTRODUCITON

The gel spinning process for ultrahigh-molecular-weight polyethylene (UHMWPE) fiber, beginning in the late 1970s through the work of Smith et al. [1, 2], has grown into several commercial processes for the production of ultra-strong fibers. Solvent concentration in excess of 80% is typical for commercial gel-spun UHMWPE fiber production making the

process inherently inefficient in that for every kilogram of high strength fiber produced, another 4 kg of solvent byproduct are created [3–5]. Aside from economics, the hazardous nature of common gel-spinning solvent byproducts requires that they be recovered and recycled. Spin-solvent removal and recovery methods depend primarily on whether a volatile solvent such as decahydronaphthalene (decalin) or an essentially nonvolatile solvent such as paraffin oil is used (volatility determined here at the typical spinning temperature). For both volatile and nonvolatile solvents, methods for solvent removal are needed to form a dry, essentially solvent free filament on which the majority of the hot drawing takes place.

Volatile solvents used in gel spinning are commonly removed from the gel filaments by evaporation at elevated temperature [6]. In the case of decalin, a preferred volatile spin-solvent for UHMWPE, solvent vapor from the evaporation process is typically recylced [6, 7]. Recycling decalin vapor adds complexity to the spinning process not withstanding the potential dangers it introduces. Because decalin is flammable, the spinning process should take place in an inert atmosphere (usually nitrogen or carbon dioxide) typically at a pressure above atmospheric pressure to minimize air infiltration. Sufficient flow of inert gas is required to keep the solvent vapor concentration below the lower explosive limit (32 g/m3 at 100 °C in air) [6]. The inert gas stream containing a relatively low concentration of solvent is passed through a solvent recovery system where the majority of the spin solvent vapor is condensed, separated, and returned to the solution forming stage. The small amount of solvent vapor remaining in the inert gas stream can be returned to the gel-fiber drying oven or passed through an adsorbent bed containing activated carbon to extract additional solvent vapor; however, both of these options

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reduce the efficiency of the process. If the gas stream containing a small amount of uncondensed solvent is directly returned to the drying oven, lower removal rates can be expected, while recovery of spin solvent from beds of activated carbon requires steam stripping, condensation, decanting, and drying before the spin solvent can be reclaimed [6]. Aside from the complexity of the volatile spin solvent removal/recovery process, inefficient energy use results from first heating the inert gas stream during evaporation from the gel-fiber and subsequently cooling the gas stream during condensation to recover the solvent vapor, especially because large volumes of solvent vapor are generated and exceptionally larger volumes of inert gas are needed to keep the spin solvent vapor concentration below the flammability limit.

Nonvolatile UHMWPE spin solvents such as paraffin oil present additional removal and recovery challenges. Since the spin solvent in this case cannot be readily evaporated, the gel filaments are typically extracted in a second solvent with a boiling point below the gelation temperature with UHMWPE. One commercial processes specifically stipulates minimal stretching of the spinline, but the relatively slower extraction rate from larger unstretched gel-fibers results in this processes being discrete, rather than continuous. In this discrete process, the unstretched gel-fiber containing the nonvolatile spin-solvent is first collected onto a large perforated roll [8]. The fiber containing roll is then flushed with the extraction solvent to replace and extract the nonvolatile spin-solvent before being dried and subjected to hot-drawing [8]. Depending on the selection of primary extraction solvent, a secondary extraction solvent may be used to remove the first extraction solvent. Honeywell for instance, discusses paraffin oil extraction with the first extraction agent being diethylene glycol butyl ether, and the second extraction agent

being water, followed by evaporation of the water to form an essentially solvent free fiber that can be subsequently hot drawn [6]. Continuous processes with nonvolatile spin solvents are possible dependent on the speed of the fiber exiting the extraction stage relative to desired input speed for the hot-drawing stage [9]. The evaporation and recovery of the extraction solvent(s) to form a xerogel proceeds similarly to volatile spin-solvent process described earlier, with the added complexity of distillation that is now required to separate the two liquid solvents. While the nonvolatile spin-solvent extraction process adds additional processing steps, it has the benefit of being relatively nonflammable and nontoxic by judicious selection of the extraction solvents. Trichlorotrifluoroethane, with its low boiling point and non-flammability is a known extraction solvent; however, it is a chlorofluorocarbon (CFC) and its ability to destroy ozone poses significant environmental hazards [6, 9].

The mechanical solvent removal method investigated in this study applies to both volatile and nonvolatile spin solvents; however, the focus of this study was on decahydronaphthalene. The mechanical solvent removal method relies on the application of mechanical force to the gel-filaments in the form of torsion, achieved by applying a controllable amount of twist to the gel-filaments. It will be shown that this mechanical solvent removal process does not significantly affect the ultimate fiber tensile strength, Young's modulus, surface morphology, or geometry when compared to conventional spin-solvent evaporation. Owing to the simplicity of the mechanical solvent removal method, complex fiber production lines involving pressurized inert gas flow, flammable vapors, condensing and distillation towers to separate solvent vapors and liquids, and activated carbon adsorption beds, among other specialized industrial equipment may be

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minimized or even eliminated for the production of gel-spun ultra-strong polyethylene fibers with solvent recovery.

5.3   MECHANISM FOR GEL TWISTING

Gel-spinning, as the name implies, involves an intermediate gel formation step. In this discussion, the gel-fiber intermediate is formed when a solution of UHMWPE in spin solvent such as decahydronaphthalene is cooled below the solution gelation temperature during the quenching stage. This gel consists of a macroscopic network of polymer molecules with crystallites acting as physical junction points [1, 2]. The crystalline junctions in the gel promote solid-like behavior at the typical fiber production concentrations. In a recent Ph.D. Thesis, Winters [10] showed that in the gel, polyethylene chains strongly interact with the solvent, yet at relatively high solvent concentrations, a large portion of the solvent remains as a separate domain from the polyethylene network. This gel can keep its integrity under normal materials handling conditions; however, phase separation occurs when a compressive stress field is applied. For example, when a UHMWPE/decahydronaphthalene gel is compressed or squeezed, decahydronaphthalene is expelled from the gel network, and the gel network becomes denser. This is understandable with the consideration of the large contrast in rheological properties between the solvent and the polymer network. In this study, this idea was further explored and used as a basis for developing a new solvent removal method suitable for gel spinning.

Figure 5-1 Twisting of a gel-fiber.

To preserve the circular gel-fiber geometry during mechanical squeezing, torsion can be applied to the gel-fiber by rotating the fiber about its longitudinal axis, as illustrated in Fig. 5-1. The shear stress on the face of each circular cross-section is not uniform, but rather increases from zero at the center of the fiber to a maximum at the fiber surface.

The shear deformation caused by twisting the fiber about its longitudinal axis is considered the driving mechanism for the present solvent removal method. This solvent removal mechanism can be compared to water suspended in a saturated sponge, where the water is squeezed out by compression (or twisting) of the sponge matrix. The density of the sponge material remains constant, but the total occupied volume of the sponge is reduced by an amount equal to the volume of water displaced. In the case of the gel-fiber, the polymer network is considered the sponge material, and the spin-solvent is equivalent to water. While the polymer network in this case is visco-elastic, unlike the elastic sponge, the mechanics of the liquid phase separation is similar.

The primary difference is that the sponge will fully recover its original shape when the force is removed, but the twisted gel-fiber will retain a majority of the twist as permanent deformation.

5.4   EXPERIMENTAL

The processing details are including in the following sections.

5.4.1   MATERIALS

The UHMWPE used in this study is a Ticona GUR resin, in powder form, with weight-average molecular mass about 4 million Da. To prepare the spin dope, 2 wt% UHMWPE powder was added into decahydronaphthalene (AflaAesar, cis1trans, 98%) in a beaker at room temperature and slowly stirred to form a slurry. This slurry was then poured into a preheated batch mixer (C.W. Brabender Prep-Center fitted with twin roller blades) and mixed for 30 min at 150 ℃ to obtain a homogenized solution.

5.4.2   GEL SPINNING

Spinning was performed through an Alex James and Associates piston extruder. The homogenized UHMWPE/ decahydronaphthalene solution was quickly transferred into the bore (preheated 150 ℃) of the extruder and allowed to equilibrate for 40 min. The solution was then extruded through a 1 mm die orifice with an aspect ratio of approximately 15:1 at a temperature of 150 ℃. The solution was freely extruded and quenched into a 5 ℃ hexane bath placed approximately 2 cm from the die exit. The quenched gel-filaments were quickly transferred to a room temperature bath of decahydronaphthalene for temporary storage while solvent removal experiments were

being performed. Decahydronaphthalene in the gel-filament was removed by two methods: evaporation and mechanical solvent removal.

Evaporation was performed in air by drying a gel-filament at fixed length between two rods at room temperature. Mechanical solvent removal by twisting was performed by fixing one end of the gel-filament and attaching the free end to a motor with adjustable rpm from 0 to 4000 rpm. To minimize the effects of solvent evaporation during twisting, the twisting time in each experiment was held constant, while the rpm was adjusted to achieve the desired amount of twist. The control sample was attached to the device for an equivalent amount of time without applying twist. Immediately after twisting, a soft absorbent tissue was gently passed along the bottom of the fiber to remove any residual solvent droplets. The control sample without twist was similarly wiped.

Hot drawing was performed in two stages through heated glycerol. The total path length through the hot bath was kept constant through both stages at 0.8 m. The first stage drawing was performed at 120 ℃ with a feeding speed of approximately1 m/min and a collection speed of 30 m/min (draw ratio 30). The second stage drawing was performed at 135 ℃ with a feeding speed of 0.5 m/min and a collection speed controlled incrementally from a minimum of 1 m/min to a maximum limited by the drawability of the fiber. Maximum draw ratio was determined by stepwise increasing the second stage collection speed at appropriate time intervals until fiber breakage. Fibers were drawn at each incremental ratio to obtain samples at least 10 m long for testing.

5.4.3   CHARACTERIZATION

Diameters of hot-drawn fibers were obtained by weighing a known length of fiber and calculating the cross-sectional area assuming a density of 1000 kg/m3.

Tensile properties for single filaments were measured using an Instron 5566 universal testing machine. Fiber samples were wound onto wooden rods approximately 2 mm in diameter and super-glued over the wound fiber ends. The prepared single filament samples were clamped using Instron 2711 Series Lever Action Grips rated for 5 N. Crosshead speed was 50 mm/min with a gauge length of approximately 10 cm. All tests were performed at room temperature. Six samples from each prepared fiber were tested and averaged. Experimental error was estimated using the standard error of the mean, defined as the standard deviation divided by the square root of the sample number. The percentage of error was calculated by dividing the error by the mean.

Wide angle X-ray diffraction (XRD) data were collected on a Rigaku Micro Max 002 (Cu Ka radiation, k50.154 nm) operating at 45 kV and 0.65 mA using a R-axis IV11 detector. Exposure time was 30 min for all samples including the background. Peak analysis was performed using Jade, an XRD analysis software from Materials Data. Fiber surface and appearance were observed by an optical microscope (Olympus BX51 optical microscope installed with an Olympus UC30 digital camera) and a scanning electron microscope (SEM) (Hitachi S800). Fiber samples for SEM imaging were mounted onto a carbon tape and gold sputtered.

5.5 RESULTS AND DISCUSSION

The solvent removal is discussed first, followed by the mechanical properties of the fibers.

5.5.1 SOLVENT REMOVAL

To quantify the amount of solvent removed from the as-spun gel-filaments, a number of gel-fibers with a length of 0.5 m and a diameter of approximately 1 mm were prepared from a 2 wt% spinning solution. The amount of twist applied to the gel-fibers is defined in terms of turns per mm (*TPmm*) given by

$$TPmm = \frac{t \cdot rpm}{L},$$ (Eq. 5-1)

where L is the fixed length between fiber ends in mm, t is the twisting time in minutes, and *rpm* is the rotations per minute. For these twisting experiments, the twisting time was fixed at 1 min. A TPmm from 0 to 8 was applied to the gel-fibers by varying the rpm, and the resultant mass loss from the gel-fiber was measured.

The mass loss is assumed to be entirely from removal of the spin solvent, and the experimental data are plotted in Fig. 5-2. A TPmm of 0 represents the amount of solvent removed from a sample without twist, and the solvent removal in this case can be attributed to factors such as evaporation during the timescale of the experiment and loss from surface contact by handling the fiber between measurements.

Figure 5-2 Percentage of solvent removed by twisting.

The percent solvent extracted in Fig. 5-2 was calculated according to

$$\% \, Solvent \, Removal = \frac{M_{before} - M_{after}}{M_{before} \cdot c} \times 100 \, . \qquad \text{(Eq. 5-2)}$$

The values M_{before} and M_{after} are the gel-fiber mass (g) before and after twisting, respectively, and c is the initial concentration of solvent in the fiber. From the experimental results, it can be seen that the majority of solvent (90%) can be removed by twisting at a TPmm of 4. Further increases in TPmm does not significantly increase solvent removal.

At 0 TPmm (i.e., no mechanical twisting), the solvent loss is approximately 14%. This 14% loss can be primarily attributed to evaporation, although other factors such as residual solvent removed from the gel-fiber surface on contact with laboratory surfaces likely contributes to the solvent loss.

The experimental values above 2 TPmm approach an asymptotic maximum around 90% solvent removal. The 10% difference from complete extraction may be related to the intrinsic affinity between the solvent and the gel network so that the gel-fiber surface remains "wetted" by the spin-solvent - even at large TPmm.

Under the current conditions, the twisting process removes solvent from gel-fibers more efficiently than the conventional solvent evaporation process. Compared to solvent evaporation represented by 0 TPmm in Fig. 5-3, the twisting process extracts at least 600% more solvent (for 2 TPmm) in the same amount of time. As an added advantage, twisting removes solvent from the fiber in the liquid state; that is, liquid phase solvent is expelled from the gel-fiber. This implies that the spin solvent removed during twisting could be directly recycled in a commercial process, whereas solvent removed by evaporation would require condensing and separation before it could be recycled back into the process. With respect to safety, the generation of large volumes of flammable solvent vapor associated with evaporation inherently increases the risk of fire and explosion. Since evaporation is not required by the mechanical solvent removal process, nonvolatile spin solvents such as paraffin oil can also be mechanically removed from gel-fibers with the present method. A full investigation of mechanical spin solvent removal from paraffin oil gel-fibers will be presented in forthcoming chapter.

5.5.2   *FIBER TOPOLOGY AND APPEARANCE*

The surface appearance of precursor fibers (undrawn xerogels) prepared by mechanical twisting were examined. Samples were prepared by first applying the desired amount of

twisting (0-4 TPmm) and then air drying the samples at fixed length for 24 h so that residual solvent content was virtually zero for all samples.

Optical images of precursor fibers dried by twist-drying at different TPmm are shown in Fig. 5-3. TPmm of 0 corresponds to the purely evaporated xerogel fiber. From Fig. 5-3, the helical appearance indicative of the twist applied by the mechanical spin solvent removal process becomes visible at a TPmm of 1. Based on these images, the actual TPmm can be estimated from the distance between the repeating helical pattern. For a fiber with 2 TPmm applied, the distance to repeat the helical pattern is approximately 380 mm, which corresponds to an actual TPmm of 2.6. At a TPmm of 4, the pitch becomes 215 mm, which corresponds to an actual TPmm of 4.65. These measured values of TPmm are close to the applied experimental amounts. These results indicate that the twist applied during twist-drying was well preserved throughout drying, and the TPmm applied to the gel-fibers can be considered permanent after drying; that is, the dried xerogels prepared by the mechanical solvent removal process did not show an obvious tendency to unwind when unconstrained.

Even though the undrawn precursor fibers dried by using twist have a different physical appearance than the purely evaporated gel-fiber, the final drawn fibers do not show a helical appearance. At a relatively low hot-draw ratio of 30, the fibers prepared by mechanical solvent removal become indistinguishable from those dried only by evaporation, as shown in Fig. 5-4.

Figure 5-3 Optical images of precursor fibers dried by twist-drying at different TPmm.

This observation is understandable since the precursor fiber has been extended to 30 times its original length, so the initial TPmm has been reduced by a factor of 30. For an initial TPmm of 2, the net TPmm after 30 times drawing becomes approximately 0.07. At such a low TPmm, the helical features would only repeat every 1.5 cm; therefore, on the current length scale, the effects from mechanical twisting would not be clearly visible.

As the draw ratio increases, the effective TPmm further decreases. For example, at a draw ratio of 100, the effective TPmm for a mechanically dried gel-fiber with an initial TPmm of 2 becomes 0.02. Therefore, these twist-dried fibers after second-stage hot-drawing have nearly identical surface appearance on a length scale of approximately 5 cm, compared to those conventionally dried (i.e., at 0 TPmm).

TPmm=0; Draw Ratio = 30	TPmm=2; Draw Ratio = 30
TPmm=0; Draw Ratio = 100	TPmm=2; Draw Ratio = 100

Figure 5-4 SEM images of hot drawn fibers.

Even though the twist-drying process imparts a helical pattern on the undrawn precursor fiber, the diameter of the final hot-drawn fiber remains independent of the extent of mechanical spin solvent removal. The result is expected because the gelfiber is twisted over a constant length. Assuming constant density and uniform twist, the linear density of the polyethylene matrix in the gel-fiber cannot be changed by twisting according to the conservation of mass.

Figure 5-5 shows the fiber diameters obtained over a range of TPmm at a total draw ratio of approximately 100. Regardless of the solvent removal conditions, the hot-drawn fiber diameters are relatively unchanged, even when compared to pure evaporation (0 TPmm).

5.5.1   MECHANICAL PROPERTIES OF DRAWN FIBERS

The tensile strength and modulus of the drawn fibers as a function of TPmm are shown in Fig. 5-6. The fibers were drawn in two stages to a draw ratio of approximately 100. TPmm of 0 corresponds to the fibers hot-drawn from the sample prepared purely by evaporation. It can be seen in Fig. 5-6A that both tensile strength and Young's modulus are essentially unaffected by the twist-drying process. For TPmm 0 through 2 the tensile strength is statistically similar around 4.5 GPa and the Young's modulus is statistically the same around 175 GPa.

Commercial Spectra® 2000 fibers from Honeywell were used as control in tensile test. Representative tensile testing curves of Spectra 2000 fibers and drawn, twist-dried are shown in Fig. 5-7. For Spectra 2000 fibers, the average tensile strength and Young's modulus derived from the tensile testing curves are 3.5 and 140 GPa, respectively.

These values are relatively in line with those reported by Honeywell and provide additional validation of the fiber testing results. Nevertheless, it is not intended to argue that the fibers prepared by twist-drying are stronger and stiffer than Spectra 2000. The actual properties of the fiber indeed depend on a number of parameters including the type of resin used and the drawing conditions. The comparison to commercially available UHMWPE fiber prepared by traditional solvent extraction techniques, however, shows that the mechanical spin solvent removal process of this study can effectively dry gel-fibers while retaining the useful fiber mechanical properties.

Figure 5-5 Diameter of final drawn fiber at a draw ratio of ~ 100 with varied TPmm applied during twist-drying.

Figure 5-6 Tensile strength (A) and Young's modulus (B) of drawn fibers at a draw ratio of ~ 100 vs. TPmm applied in twist-drying.

Figure 5-7 Tensile stress-strain curves for Spectra 2000 fibers (A) and fibers prepared by twist-drying and hot drawing (B).

5.5.2   X-RAY DATA

The crystallinity of the mechanically extracted fiber (2 TPmm) and purely evaporated fiber (0 TPmm) were measured by WAXD. The peaks were empirically fitted using Jade software with the corresponding 2D patterns shown in Fig. 5-8.

Twist-Drying TPmm=2; First Stage (draw ratio=30)

Figure 5-8 WAXD data for the dried xero-gel fibers and drawn fibers prepared under different conditions. (Figure 5-8 continued on next page)

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Evaporation TPmm=0; First Stage (draw ratio=30)

Twist-Drying TPmm=2; Second Stage (draw ratio=90)

Evaporation TPmm=0; Second Stage (draw ratio=90)

Fig. 5-8 continued on next page.

Twist-Drying TPmm=2 Xerogel

Evaporation TPmm=0 Xerogel

Figure 5-8 WAXD data for the dried xero-gel fibers and drawn fibers prepared under different conditions.

The fiber crystallinity was calculated from the WAXD data for the dried xero-gel, first stage hot-drawn fiber (draw ratio 30), and second stage hot-drawn fiber (draw ratio 90). At a draw ratio of 30, the fibers from the first stage hot-drawing showed a crystallinity of 69 and 70% for TPmm 2 and TPmm 0, respectively. After the second stage hot-drawing, the crystallinity for TPmm 2 and TPmm 0 increased to 77 and 78%, respectively. However, no significant influences from TPmm on the percent crystallinity were observed.

5.6   CONCLUSIONS

In this study, a mechanical spin-solvent removal method was investigated. Specifically, decahydronaphthalene/UHMWPE gel-fibers were twisted about their fiber-axis to initiate liquid phase solvent removal. Approximately 90% of the spin-solvent can be mechanically removed from the gel-fibers. The final fiber tensile strength and Young's modulus were unaffected by the mechanical solvent removal process relative to evaporation alone. The final fiber surface appearance and diameter remained unchanged by mechanical solvent removal compared to conventional evaporation. The fiber crystallinity measured from X-ray data after the first and second stages of hot-drawing showed no significant difference between this mechanical removal process and evaporation. These results indicated that the mechanical solvent extraction process is compatible with the production of high-strength UHMWPE gel-spun fibers, and may be adapted to other gel-spinning processes.

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CHAPTER 6

DIRECT DRAWING OF GEL FIBERS ENABLED BY
TWIST-GEL SPINNING PROCESS

6.1   INTRODUCITON

Gel-spun ultra-high molecular weight polyethylene (UHMWPE) fiber exhibits remarkable tensile properties [1, 2]; however, the relatively complex processing involved in its production leads to costs almost 10 times more than conventional melt-spun fiber [3, 4]. Commercial UHMWPE gel-spinning processes are inherently inefficient, requiring spin-solvent concentrations in excess of 80% [5]. Efficient extraction of large volumes of spin-solvent is a major limiting factor using conventional techniques since the rate of spin-solvent extraction is generally limited by diffusion related variables such as concentration gradient, fiber diameter, and temperature. The present chapter introduces a new twist-gel spinning process where a majority of non-volatile spin-solvent is removed from the gel-fiber by applying mechanical twisting. The twisted gel-fiber can be directly hot-drawn, allowing conventional solvent extraction to proceed significantly faster after drawing.

In the previous chapter, it has been demonstrated that volatile spin-solvent contained in the gel-fiber can be effectively removed by mechanical twisting which liberates the spin-solvent evaporation from many diffusion related restrictions [6]. Decahydronaphthalene was used as spin-solvent in the previous study to demonstrate the feasibility of the mechanical solvent removal process. Decahydronaphthalene is a common volatile spin-solvent in commercial UHMWPE gel-spinning processes, and it is typically evaporated

from the gel-fiber at elevated temperature; however, it is flammable and toxic to humans [7, 8].

A more environmentally friendly process uses the non-volatile spin-solvent, paraffin oil [9]. Non-volatile gel-spinning introduces new processing challenges since the spin-solvent can not be directly evaporated from the gel-filament. Paraffin oil is a multimer containing multiple ethylene repeating units. It is relatively non-volatile at typical processing temperatures in gel spinning, mandating the use of an extraction solvent for spin-solvent removal. The introduction of extraction solvent to the spinning process increases solvent byproducts by two or more orders of magnitude; however, with judicious selection of the extraction solvent, the non-volatile UHMWPE gel-spinning process can remain non-toxic and non-flammable relative to the dry spinning process using decahydronaphthalene [9].

In commercial non-volatile gel-spinning processes, the extraction of the spin-solvent occurs after quenching but before extensive drawing of the filament [9]. Drawing of the gel-filament at relatively low temperatures was shown to prematurely induce preferential c-axis orientation associated with the generation of defects, leading to reduced drawability and poor tensile strength [10]. Drawing the gel-filament at relatively high temperatures before extracting the spin-solvent is difficult or even impossible because the gel-fiber is relatively weak containing at least 80% spin-solvent and will return to a solution state at a temperature well below the typical UHMWPE melting temperature due to the significant presence of spin-solvent. Because of these limitations, extraction of the spin-solvent preferentially occurs on the undrawn gel-fiber. For typical spin-dope

concentrations, the initial gel-fiber must have a diameter on the order of 1 mm so that the final fiber after solvent extraction and ultra-drawing does not enter the sub-denier regime because processing would then become even more complex. This large diameter represents another major limiting factor for solvent extraction.

The present study introduces a non-volatile twist-gel spinning process that is relatively non-toxic and non-flammable with minimal generation of solvent by-product while simultaneously increasing the process efficiency. The process is enabled by removing a majority of spin-solvent from the gel-filament by mechanical twisting which permits extensive drawing of the gel-filament before the relatively slow diffusion based spin-solvent extraction is applied. Using mechanical twisting, it will be shown that more than 75% of the non-volatile spin-solvent, paraffin oil, can be efficiently removed from the relatively large, undrawn gel-filament. Mechanically removing a majority of the spin-solvent imparts the gel-fiber with sufficient strength and temperature stability to be directly hot-drawn to 20X in a first drawing stage. Consequently, the initial gel-fiber diameter is reduced by a factor of about ~10 from the combined draw ratio and fiber volume reduction due to mechanical solvent removal. Processing of the reduced diameter gel-fiber proceeds using conventional extraction, but two significant benefits arise from the twist gel-spinning process. Since the pre-extraction fiber diameter is 10X smaller, the resulting diffusion based extraction on the twisted gel-fiber should occur 100X faster compared to the large diameter filament associated with conventional gel-spinning. Furthermore, since 75% of the spin-solvent is removed mechanically, the conventional extraction during twist gel-spinning consumes 75% less extraction solvent. It will be further shown that this twist-gel spinning process does not significantly affect the

ultimate fiber tensile strength, Young's modulus, surface morphology, or geometry when compared to conventional gel-spinning processes. As a result of the significantly improved efficiency, the twist-gel spinning process should reduce the production cost of gel-spun high-strength fibers promoting the broad expansion of high performance fibers into applications that were previously cost prohibitive.

6.2 EXPERIMENTAL

The processing details are described in the following sections.

6.2.1 MATERIALS

Ticona GUR UHMWPE resin was kindly supplied by Celanese with a viscosity average molar mass of approximately 4 million Da. Hydrobrite 550 PO white paraffin oil with average molecular weight of 541 Da was kindly supplied by Sonneborn Inc. The Hydrobrite 550 paraffin oil has viscosity of about 100 cSt at 40 ℃ and a vapor pressure less than 0.01 mmHG at 20 ℃. Spin dope was prepared by combining 6 wt% UHMWPE powder with paraffin oil at 20 ℃ to form a slurry. The slurry was poured into a preheated batch mixer (C.W. Brabender Prep-Center fitted with twin roller blades) and mixed for 30 min at 150 ℃ to obtain a homogenized solution.

6.2.2 GEL SPINNING

Fiber spinning was performed through an Alex James and Associates piston extruder with a 2.54 cm bore diameter and 150 mL capacity. The homogenized UHMWPE/paraffin oil solution was quickly transferred into the bore (preheated 250 °C) of the extruder and allowed to equilibrate for 1 h. The solution was extruded through a 1 mm die orifice with

an aspect ratio of ~15:1 maintained at a temperature of 250 °C. The solution was extruded at a speed of approximately 1 m/min. The fiber solution was quenched into a 20 °C glycerol bath 2 cm from the die exit. The quenched gel-fiber was collected onto spools at 2 m/min so as to apply 2 times jet-stretch to the fiber solution as it exited the die. The spools of gel-fiber were rinsed with water and stored on spools under ambient conditions (40-60% relative humidity at 20-22 °C) until needed for experiments.

6.2.3   SPIN-SOLVENT REMOVAL

Paraffin oil in the gel-filament was removed by two methods: conventional extraction in a chemical solvent and mechanical solvent removal. Conventional extraction was performed using n-hexane. Control fibers were prepared by winding the gel-fiber onto a 1 inch diameter polytetrafluoroethylene (PTFE) rod. Both ends of the gel-fiber were fixed to maintain constant fiber length. To simulate a counter-flow type extraction process, the rod as prepared was submerged into an agitated bath of n-hexane at ~ 20 °C for 0.5 h. The volume of hexane was ~5000 larger than the volume of the gel-fiber in order to maintain a maximum concentration gradient throughout the extraction process. The PTFE rod containing the extracted gel-fiber was removed from the n-hexane bath and dried under forced air convection while maintaining fixed fiber ends. Mechanical solvent removal was performed by fixing one end of the gel-filament and attaching the free end to a motor with adjustable rotations per minute (rpm). A control sample was attached to the device for an equivalent amount of time without applying twist. After twisting, a tissue was gently passed along the bottom of the fiber to remove any residual solvent droplets. The control sample without twist was treated similarly. The amount of mechanical solvent removal applied to the gel-fibers is defined in terms of turns per mm (*TPmm*) given by,

$$TPmm = \frac{t \cdot rpm}{L}, \hspace{3cm} \text{(Eq. 6-1)}$$

where L is the fixed length between fiber ends in mm, t is the twisting time in minutes, and rpm is the rotations per minute. A TPmm from 0 to 8 was applied to the gel-fibers by varying the removal time, and the resultant mass loss from the gel-fiber was measured. The mass loss is assumed to be entirely from removal of the spin solvent.

6.2.4   HOT-DRAWING

Hot-drawing was performed through heated PEG. The total path length through the hot bath was 0.6 m. The bath temperature was maintained within ±1 °C of the set point. The first stage of hot-drawing was performed at 120 °C with a feeding speed of 0.9 m/min and a collection speed of 18 m/min to obtain a draw ratio of 20X. The second stage of hot-drawing was performed at 130 °C with a feeding speed of 0.5 m/min and a collection speed increased incrementally to obtain the maximum draw ratio. Draw ratio as used in this report is defined as the ratio of the collection roller speed to the feed roller speed. Fibers were drawn at the maximum ratio to obtain samples at least 15 m long for testing.

6.2.5   CHARACTERIZATION

Diameter measurements were obtained by weighing a known length of fiber and calculating the cross-sectional area assuming a density of 1.0 g/cm^3. Before weighing, the hot-drawn fibers were briefly rinsed with water to remove residual PEG from the hot-drawing stage and dried.

Tensile properties for single filaments were measured using an Instron 5566 universal testing machine. Fiber samples were wound onto wooden rods approximately 2 mm in

diameter and super-glued over the wound fiber ends. The prepared single filament samples were clamped using Instron 2711 Series Lever Action Grips rated for 5 N. Crosshead speed was 100 mm/min with a gauge length of ~10 cm. All tensile tests were performed under ambient conditions (40-60% relative humidity at 20-22 °C). Six samples from each of three fiber spinning experiments were tested and averaged. Experimental error was estimated using the standard error of the mean, defined as the standard deviation divided by the square root of the sample number.

Wide angle x-ray diffraction (WAXD) data were collected on a Rigaku Micro Max 002 (Cu Kα radiation, λ=0.154 nm) operating at 45 kV and 0.65 mA using an R-axis IV++ detector. Exposure time was 30 min for all samples. The crystalline orientation factor was computed using the method developed by Wilchinsky [11]. The 110 and 200 equatorial diffractions were used to determine the orientation factor based on the orthorhombic UHMWPE unit cell [12].

Differential scanning calorimetry (DSC) data were collected on a TA Q200 DSC unit (TA Instruments). Samples were crimped in hermetic aluminum pans. Nitrogen atmosphere and a scan speed of 10 °C /min were used for all samples. Thermogravimetric analysis (TGA) experiments were performed using a TA TGA5000 (TA Instruments). Samples were heated to 250 °C in nitrogen atmosphere and held at this temperature until the sample weight approached a steady state. Scanning electron microscopy (SEM) images were collected on a LEO 1550. SEM samples were mounted onto carbon tape and gold sputtered.

6.3   RESULTS AND DISCUSSION

The as-quenched gel-fibers are not in an equilibrium state: a small fraction of spin-solvent naturally phase separates from UHMWPE gel-fiber until an equilibrium concentration is reached [13, 14].

Figure 6-1 Spin solvent phase separation in UHMWPE/paraffin oil gel-fibers as function of time with exponential curve fit as indicated.

The phase separation that occurs in the gel-fibers in the time period following quenching has been described in terms of the free energy of mixing. The large temperature change during quenching from solution (~150 °C) to gel (~20 °C) state reduces the entropic contribution to mixing which induces phase separation between the solvent and the polyethylene until a new equilibrium is reached [14]. The extent of phase separation has been shown to depend on the spin-dope concentration as well as the quenching conditions [13, 14].

Figure 6-2 Conventional spin-solvent extraction of paraffin oil in n-hexane; x-axis is time in log scale with exponential curve fit as indicated.

Figure 6-1 shows the change in gel-fiber linear density as a function of time. The linear density of the gel-fibers approaches a constant value after approximately 24 h; therefore, it assumed that the gel-fibers have reached an equilibrium state with respect to the natural phase separation. All solvent extraction and mechanical removal experiments were performed one day after fiber gel extrusion so that the initial gel-fiber concentration remained constant during testing.

Conventional extraction of non-volatile spin-solvent requires an extraction solvent [9]. With sufficient exposure time and volume of extraction solvent, the fiber weight change as a function of extraction time approaches a steady state (Fig. 6-2). For the present study, complete extraction (>99.9% solvent removal) of the spin-solvent takes about a whole day in the extraction solvent based on the data shown in Fig. 6-2.

Using the weight reduction of the fiber after 24 h in the extraction solvent, the initial concentration of the gel-fiber is calculated to be 12% UHMWPE / 88% paraffin oil. The initial gel-fiber concentration is expected to be higher than the 6% spin-dope concentration because of the phase separation described previously.

Figure 6-3 Mechanical solvent removal from gel-fibers as a function of the amount of twist applied.

Mechanical spin-solvent removal by twisting does not require an extraction solvent [6]. Detailed descriptions of the mechanical solvent removal procedure were given in a previous report [6]. The extent of non-volatile spin-solvent mechanically removed is plotted in Fig. 6-3. A TPmm of 0 represents the control sample without twist, and the solvent removal in this case can be attributed to mass loss from surface contact by handling the fiber between measurements. The percentages of spin-solvent removed in Fig. 6-3 were calculated according to

$$\% \, Solvent \, Removal = \frac{M_{before} - M_{after}}{M_{before} \cdot c} \times 100 \qquad \text{(Eq. 6-2)}$$

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The values M_{before} and M_{after} are the gel fiber mass before and after twisting, respectively. The concentration of spin-solvent in the gel-fiber, c, is defined to be 88% in this study based on the initial gel-fiber concentration. The majority of solvent ($\sim 73\%$) can be removed by twisting to 4 TPmm. Further increase in TPmm does not significantly increase solvent removal; however, excessive deformation of the gel-fiber occurs at higher TPmm leading to instability of the process, and reduced tensile properties in the final hot-drawn fiber. The effect of increasing TPmm on the tensile properties of gel-spun UHMWPE fibers was reported in a previous publication [6]. No significant change in the tensile properties of the hot-drawn fibers was observed with increasing TPmm; however, a maximum TPmm was also observed above which the fiber becomes non-uniformly deformed and frequently breaks [6].

SEM images of the fibers after mechanical spin-solvent removal are shown in Fig. 6-4. The helix-like features are most visible on the 4 and 8 TPmm fibers, and the distance between repeating features in both fibers is consistent with the amount of twist applied during the mechanical spin-solvent removal process.

The residual paraffin oil content in the gel-fibers after the mechanical spin-solvent removal process was also measured by TGA. The neat paraffin oil almost completely evaporates with about 5% residue remaining, probably consisting of the relatively high molecular weight components in the paraffin oil (Fig. 6-5).

Figure 6-4 SEM of gel-fibers mechanically extracted using different level of twisting: A) TPmm=0; B) TPmm=2; C) TPmm=4; D) TPmm=8.

The fiber conventionally extracted in hexane shows no significant weight loss, indicating that nearly all of the paraffin oil was extracted. Fiber mechanically treated to 4 TPmm shows a weight reduction of about 40%.

For hot-drawing to proceed effectively, a sufficient amount of spin-solvent should be removed from the gel-fiber before hot-drawing. Too much spin-solvent remaining in the gel-fiber reduces the melt temperature, thereby reducing the maximum drawing temperature that the fiber can sustain.

Figure 6-5 TGA weight loss curves as a function of time. Fibers heated to 300 °C in nitrogen atmosphere for 180 min to evaporate paraffin oil. Neat paraffin oil is included for reference.

Orienting the gel-fiber at relatively low temperatures has been shown to significantly reduce the tensile strength of the drawn fiber, likely due to the creation of defects [10]. Figure 6-6 shows that the peak melting temperature of gel-fibers can be increased solely by mechanical solvent removal without the use of an extraction solvent. The peak melting temperature of the gel-fiber increases from about 123 °C in the un-twisted fiber to about 130 °C for the fiber with 4 TPmm. The increase in melting temperature likely results from the increased polyethylene concentration in gel after removing a portion of the spin-solvent. The conventionally extracted gel-fiber exhibits a peak melting temperature around 137 °C, which is higher than the mechanical process, but a longer extraction time is needed and a relatively large volume of extraction solvent is consumed.

Figure 6-6 DSC melting endotherms of mechanically extracted gel-fibers; gel-fibers before extraction and conventionally extracted are included for reference.

The mechanical solvent removal process imposes deformation to the gel-fiber; however, this deformation does not impart significant orientation to the gel-fiber. As previously noted, orientation at relatively low temperatures can impart significant defects in the fiber. No significant fiber axis crystal orientation can be detected from the 2-D patterns of the mechanically treated gel-fibers in Fig. 6-7, regardless of the amount of mechanical solvent removal applied. The conventionally extracted fiber in Fig. 6-7 shows diffractions along the meridian indicating crystalline orientation perpendicular to the fiber axis. This perpendicular orientation is typical for polyethylene gel-fibers spun and extracted with similar conditions [10].

Figure 6-7 WAXD 2-D patterns of mechanically extracted gel-fibers with TPmm 0, 0.5, 2, 4 and 8 as noted and conventional fiber extracted in hexane.

Since the mechanical spin-solvent removal process sufficiently increases the gel-fiber melting temperature and does not impart harmful orientation at low temperature, the mechanical solvent removal can be used exclusively (without the need for an extraction solvent) to gel-spin UHMWPE fiber. This new process represents an efficient, safe, and environmentally preferable method of spinning high-strength fibers. Since paraffin oil spin-solvent is the only solvent required, the process is relatively non-toxic and non-flammable. To demonstrate the effectiveness of this new process, gel-fibers were mechanically extracted to 4 TPmm corresponding to approximately 75% removal of paraffin oil spin-solvent. Direct hot-drawing to a total draw ratio of 60X yields fibers with a tensile strength of 2.25 ±0.2 GPa and a Young's modulus of 114 ±6 GPa. A

representative stress-strain curve is shown in Fig. 6-8. WAXD shows intense equatorial diffractions in the 2-D patterns and azimuthal integrations of the 110 and 200 diffractions (Fig. 6-9) are consistent with crystalline orientation in the fiber direction. The corresponding orientation factor was calculated to be 0.864 suggesting good crystalline alignment along the fiber direction.

Figure 6-8 Representative tensile stress-strain curves of UHMWPE fibers at maximum draw ratio and processed with different paraffin oil extraction conditions; Conventional: spin-solvent extracted using conventional solvent based process; Twisted: 75% spin-solvent removed mechanically (no chemical based extraction used).

Combining mechanical solvent removal with conventional solvent extraction significantly increases the extraction rate while simultaneously reducing the amount of extraction solvent required to produce ultra-high strength UHMWPE fiber. To demonstrate the mechanical solvent removal process, gel-fibers twisted to a TPmm of 4

were continuously passed through an n-hexane bath (residence time of 30 s), followed by direct hot-drawing to a maximum draw ratio of 80X. For comparison, a control sample prepared solely using conventional extraction in n-hexane for 30 min was hot drawn to a maximum draw ratio of 80X. Figure 6-8 shows that nearly identical tensile behavior results from the two separate processes. The control fiber and the twisted fiber reach tensile strengths of 3.93 ±0.1 GPa and 3.73 ±0.1 GPa, respectively. Table 5-1 summarizes the average tensile strength, Young's modulus, strain to break, and diameter of fibers from both processes; all these data are statistically similar, even though the twist gel-spun fibers were produced using ~75% less extraction solvent. The WAXD 2-D patterns and azimuthal integrations of the (110) and (200) diffractions are shown in Fig. 6-9 and do not exhibit significant differences. Correspondingly, the orientation factors for the control and twist gel-spun fibers were calculated to be 0.946 and 0.945, respectively.

The surface morphology and the geometry of the ultimate fibers can be seen from the SEM images in Fig. 6-10. Despite the relatively large amount of twist applied to the precursor fiber, both the control fiber and the twisted fiber after hot-drawing exhibit similar surface appearance and shape on the length-scale of the images. This result would be expected since the twist occurs before hot-drawing, and the original four rotations per mm of fiber (TPmm 4) will be reduced by a factor 80 since the fiber is extended 80 times during drawing. Therefore, the twisted fiber will have an apparent TPmm of 0.05 or about 5 rotations per meter after hot-drawing. This small amount of twist cannot be easily characterized by SEM or optical microscopy because the field of view of these instruments is normally less than 20 cm: not sufficient to capture a complete rotation.

Figure 6-9 Wide angle X-ray diffraction of hot-drawn fibers. TOP: 2-D patterns for conventional fiber (left) and twisted fiber (right); BOTTOM: azimuthal integrations of the [110] and [200] diffractions of the conventional and twisted fibers – offset by 1° for clarity.

Table 6-1 Tensile data of fibers hot-drawn to the maximum draw ratio. The solvent in the fibers were removed by three different methods: conventional spin-solvent extraction, mechanically-assisted spin-solvent extraction, and purely mechanical extraction.

Processing Condition	Max Draw Ratio	Tensile Strength (GPa)	Young's Modulus (GPa)	Strain at Break (%)	Fiber Diameter (µm)
Conventional Extraction	80	3.93 ±0.1	154 ±4	3.87 ±0.2	17
Mechanically Assisted	80	3.73 ±0.1	146 ±11	3.67 ±0.2	17
No Extraction Solvent	60	2.25 ±0.2	114 ±6	2.95 ±0.2	20

Figure 6-10 SEM of 80X hot-drawn fibers: A) conventionally processed fiber; B) fiber processed by twist gel-spinning.

6.4   CONCLUSIONS

In this study, a mechanical spin-solvent removal process for the production of efficient and environmentally preferable, high-strength, UHMWPE fiber was developed and investigated. More than 75% of the non-volatile spin-solvent, paraffin oil, was mechanically removed from gel-fibers without using an extraction solvent. An extraction solvent free process was demonstrated by directly drawing the mechanically extracted fiber to a draw ratio of 60X achieving a tensile strength of 2.25 ±0.2 GPa. A twist gel-spinning process was demonstrated by combining the mechanical spin-solvent removal process with the conventional chemical based spin-solvent extraction process. The twist gel-spinning process consumes 75% less extraction solvent than the conventional extraction process, and the resulting fiber achieved a tensile strength of 3.73 ±0.1 GPa which was statistically similar to the control fiber processed using conventional extraction (3.93 ±0.1 GPa). All of these results indicated that the twist gel-spinning process is compatible with the production of high-strength fibers through efficient UHMWPE fiber gel-spinning processes.

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1   CONCLUSIONS

A fundamental process design for gel-spinning semi-crystalline polymers was developed. An oligomer-spin solvent was shown to fulfill the requirements of an ideal gel-spinning spin-solvent. The concept was tested on two polymers that are difficult to spin into fiber using conventional techniques: POM and PEO.

Fibers produced by gel-spinning a PEO/PEG solution achieved tensile strength greater than 0.6 GPa and Young's modulus greater than 4.3 GPa, significantly stronger and stiffer than PEO fibers spun from conventional spinning techniques.

POM gel-spinning with PEG spin-solvent exhibited degradation due to the innate chemistry of the POM molecule. Using caprolactam as the spin-solvent produced a stable spin-dope and yielded fibers with tensile strength greater than 1.8 GPa and Young's modulus greater than 36 GPa.

The efficiency of the gel-spinning process was improved through a mechanical spin-solvent extraction process. Twisting the gel-fiber was shown to remove more than 80% of the spin-solvent from the gel-fibers without requiring an additional extraction chemical. The mechanical extraction process was shown to be effective for both volatile and non-volatile spin-solvents. The tensile properties and surface morphology of the mechanically extracted fibers after hot-drawing were shown to be nearly identical to gel-fibers extracted using the conventional chemical extraction process.

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7.2   RECOMMENDATIONS

The oligomer spin-solvent concept has been tested for semi-crystalline, linear polymers without significant hydrogen bonding interactions. To further define the scope, the concept should be tested with polymers of both branched structures and polymers with strong hydrogen bonding interactions. For example, a PA6/PA6 oligomer (or caprolactam) gel-spinning solution should be attempted.

POM of relatively low molecular weight was gel-spun in this thesis study; however, gel-spinning processes particularly benefit from higher molecular weight resins due to the lower concentration (less entangled) solutions that can be spun. Gel-spinning of a higher molecular weight POM resin at lower spin-dope concentrations is recommended to further improve the tensile strength.

Mechanical spin-solvent extraction was demonstrated using UHMWPE with both volatile and non-volatile spin-solvents. In order to show that the gel-network structure behaves similar in other polymer gels, it is suggested to test the mechanical spin-solvent extraction process on other gel-spun polymers.

Finally, since linear polymers without significant hydrogen bonding interactions have been particularly successful with the oligomer spin-solvent, polymers such as PTFE and PPS should be explored using their respective oligomers as the spin-solvent.

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