# Modulus increase and crystallization evolution during gel spinning and post drawing of UHMWPE fibers

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### ABSTRACT

a novel We present gel-spinning apparatus to determine the effect of the asspun crystalline structure on the drawability and final tensile properties of ultra-high molecular weight polyethylene (UHMWPE) From SAXS measurements, we fibers . show that the extensional flow field applied during spinning significantly affects the crystalline morphology, starting from randomly oriented lamellae to lamellae oriented in the flow direction to the start of shish-kebab. The well-defined as-spun fibers are drawn using the VADER 1000 in fiber mode, which allows for direct monitoring of strain, strain-rate, and stress in-situ during the The VADER 1000 also allows for direct quantification of modulus and strength of fibers at low, intermediate, and high draw-ratios.

## INTRODUCTION

UHMWPE is a material of interest as it has an inert chemical structure, low density, a low dielectric constant, a hydrophobic surface<sup>1</sup>, theoretical mechanical and properties comparable to steel.<sup>2,3</sup> UHMWPE fibers are considered in applications such as ballistic resistant composites, rope, and durable apparel. Despite extensive study over the years, very little is understood regarding the structure evolution of fibers during processing.<sup>4,5</sup> Furthermore, there is still discrepancy regarding the preferred fiber structure that leads to the maximum modulus and strength during the gelspinning and subsequent fiber drawing processes, see Ohta *et al.*<sup>9</sup>

Gel-spinning is a technique first popularized by Pennings et al.<sup>6</sup> The fibers produced by this process are generally referred to as the as-spun-fiber (ASF). The low number of entanglements of the polymer solution produces a sample that can be drawn to many times its original length. The ASF draw ratio is typically defined through the ratio of the extrusion velocity to the velocity of the take up spindle and very little is known about the rate of deformation compared to the sample relaxation time.

ASF After spinning, the requires additional drawing to achieve the desired high modulus and strength. The ASF can be drawn to higher draw ratios without failure by drawing under elevated temperatures. Experiments utilizing NMR and SAXS have shown that significant crystalline orientation occurs during the drawing process.<sup>7,8,9</sup> Amorphous domains are gradually incorporated into the extended crystal by drawing, and the corresponding increase in modulus and strength is attributed the increase in percent crystallinity.

In this work, we investigate the influence of strain rate during spinning as compared to the polymer solution relaxation time, i.e. the Weissenberg number:

$$Wi = \dot{\epsilon} \tau_d \tag{1}$$

where  $\dot{\epsilon}$  is the average strain-rate applied during spinning and  $\tau_d$  is the characteristic disengagement time measured from linear viscoelasticity. We determine the effect of extensional flow on rate of crystallization, crystalline morphology, and overall strain on the material. This starting material is then drawn using the VADER 1000 to determine the evolution of crystalline structure as a function of draw ratio and drawing velocity.

### EXPERIMENTAL

The novel gel-spinning apparatus is shown in Fig. 1. It provides precise control of temperature, extrusion rate, take up velocity, and other parameters. A laser micrometer is used to measure the diameter of the fiber as a function of distance from the extrusion nozzle. A motor driven spindle at the base applies the extensional force to the filament. After spinning, samples are dried overnight in a vacuum oven to remove UHMWPE was used as excess solvent. received 3M Mw (Sigma Aldrich). 98 percent pure mixture of cis and trans Decahydronaphthalene (Decalin) (Sigma Aldrich) was used as received to dilute the UHMWPE.

For accurate and controlled drawing of the samples, the VADER 1000, an extensional rheometer Rheo Filament ApS, was modified for use as a drawing apparatus. The oven allows for controlled temperature to 0.1°C and a laser micrometer monitors the local deformation of the fiber under constant stress, strain-rate, or velocity type drawing. Using the diameter reported by the micrometer we determine a diameter draw ratio. An oven can be closed around the sample to control temperature during the drawing process. The drawn samples are cooled to room temperature before measuring the tensile properties of the fiber using the VADER 1000. Elastic modulus was measured both by unloading and loading of the drawn specimens. Furthermore, confirmation of modulus values were determined by loading different segments of the drawn specimens. Fig. 2 shows an example of the fibers before and after drawing using the VADER 1000 fiber clamps.



Figure 1. Image of the gel-spinning apparatus.



Figure 2. Fiber clamped and drawn using VADER 1000.

## RESULTS

#### Rheology

Fig. 3 shows the storage and loss moduli for an 8wt% solution of UHMWPE at 120° C. The low frequency crossover for the solution,  $\omega_d = \frac{1}{\tau_d} = 0.15 \text{ s}^{-1}$  or as seen in Eq. 2, solved for  $\tau_d$ .



Figure 3. G' and G" at 120°C for an 8wt% solution of UHMWPE.

$$\tau_{\rm d} = \frac{1}{\omega_{\rm d}} = 6.67 \, {\rm s.}$$
 (2)

while typically the Wi number is put in the context of the Rouse time, however due to the polydisperse nature of UHMWPE, we use the low frequency crossover as the characteristic time. This time scale is not the true disengagement time as there is a distribution of disengagement times for these solutions. Note, that all timescales longer than this one would result in higher Wi numbers.

#### Gel-Spinning

Typical spinning apparatuses are not equipped to measure the deformation of the ASF during processing, instead the ratio of the extrusion velocity to the take up velocity is used. Since our apparatus has independent measure of the deformation history, we can generate an image of the ASF at any position and time from the nozzle tip. Furthermore, with an optical camera we can determine a characteristic crystallization time by denoting the transmission of light through the sample during spinning. An example profile of the gel leaving the nozzle tip up to the point of crystallization is shown in Fig. 4.



Figure 4. Fiber profile, showing the diameter of the gel filament as it exits the nozzle. Profile ends at the crystallization point.

Fig. 4 can be used to calculate the strain as a function of distance from the nozzle. Since the flowrate of gel from the nozzle tip is a controlled parameter, distance from the nozzle tip can further be converted to time. A representative strain diagram is shown in Fig. 5. Note that the strain is the true Hencky strain as calculated in Eq. 2,

$$\varepsilon(t) = 2\ln\left(\frac{D_0}{D(t)}\right)$$
 (3)



Figure 5. Hencky Strain as a function of time for data in Figure 4.

where D(t) is the diameter at any time, t, and  $D_o$  is the initial diameter. From here we can also compute the average and maximum strain rate ( $\dot{\gamma}$ ) applied during processing.

The crystallization point can be determined optically via the laser micrometer display. Two images of the extrudate are shown in Fig. 6. The top image shows clearly the transmission of light through the sample, while the bottom clearly shows a gradient in transmitted light from the top of the image to the bottom of the image. The crystallization point is taken to be the position from the nozzle where no light transmits through the sample.



Figure 6. Bottom shows an image of the fiber close to the crystallization point.

Fig. 7 displays the measured time for the fiber to fully crystallize as a function of the strain rate applied during spinning. A decrease of ~10s is observed for increasing strain-rate from 0.09s<sup>-1</sup> to 0.17s<sup>-1</sup>. These strain-rates correspond to Wi=0.6 and 1.1, respectively, indicating that in both cases we expect orientation and stretching of the chain during the spinning process. This hypothesis will be tested via SAXS in the following section. More data points will be presented the at AERC meeting Copenhagen.



Figure 7. characteristic crystallization time versus the max strain rate during spinning.

### Small Angle X-Ray Scattering

After drying the residual solvent from the ASF, SAXS was used to characterize the structure prior to drawing. The 2-D SAXS pattern for both ASFs is shown in Fig. 10. The pattern in Fig. 10a shows the presence of polydisperse, un-oriented lamellae<sup>10</sup>. This can be contrasted to the pattern in Fig. 10b, for the higher strain-rate ASF, which shows a degree of anisotropy (orientation) and a comparatively narrow size distribution of lamellae. This data can be quantified even more, by looking at the q and radial averages of the patterns, which will be discussed in depth at the AERC meeting.



Figure 8. The true stress measured during post drawing the ASFs.

#### Post Drawing

Drawing was performed using the VADER 1000 at 120°C, and with a constant draw velocity of 0.5mm/s. The force is monitored in-situ during the experiment, and converted to a true stress using the diameter measured by the laser micrometer. Fig. 8 shows the true stress applied to the fibers as a function of time for a single post drawing process. In Fig. 8, the fibers are at similar draw ratios, however, it is evident that the 0.17 s<sup>-1</sup> ASF has a significantly lower stress than the  $0.09 \text{ s}^{-1} \text{ ASF}$ . This implies that the Young's modulus of the 0.17 s<sup>-1</sup> ASF is smaller than the other. We use mechanical testing after drawing to quantify the tensile properties.

### Mechanical Testing

Stress and strain measurements were performed using the VADER 1000 as discussed earlier. The moduli at two different total draw ratios (TDR) are shown in Fig 10 for the two ASF samples. The TDR is a product of the draw ratio applied during spinning, DR<sub>1</sub>, and the overall draw ratio applied during post drawing, DR<sub>2</sub>:

$$TDR = DR_1 \times DR_2 \tag{4}$$

Fig. 9 shows that the 0.17 s<sup>-1</sup> ASF requires more draw to achieve the same elastic modulus as the 0.09 s<sup>-1</sup> ASF. This data implies that the starting crystalline structure has an immediate impact on an ASF's drawability. More data points in ASF with different strain-rates and draw ratios are necessary to confirm the trends suggested in Fig. 9.

#### DISCUSSION AND CONCLUSIONS

Our SAXS measurements show that the extensional flow during spinning has a direct impact on the crystalline structure. Our analysis of the extensional strain-rates during processing compared to the relaxation time of the polymer solution, show that the Wi is greater than 0.5, which

suggests orientation and stretching of the polymer chains during spinning.



Figure 9. Moduli of the 0.09s<sup>-1</sup> to 0.17s<sup>-1</sup> fibers at different draw ratios.



Figure 10. 2D SAXS pattern of ASFs spun at (a) strain rate of  $0.09s^{-1}$  and (b)  $0.17s^{-1}$ 

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The oriented and stretched chains have a direct impact on the time to crystallization as observed in Fig. 7. The crystal patterns appear to go from slightly ordered polydisperse lamellae to uniform highly oriented lamellae in the flow direction, as observed in Fig. 10. The results of post-drawn samples imply that the modulus as a function of draw ratio is highly dependent on the starting crystalline structure. Fig. 9 suggests that the more ordered lamellae structure requires more drawing to achieve the same modulus as the less ordered starting structure.

To draw more conclusive arguments regarding the dependence of tensile properties on starting crystalline morphology, a series of experiments are planned with increasing Wi number during spinning as well as various draw ratios during post-drawing. These results will give a clearer understanding as to the necessary processing parameters and structure that leads to ultra-strong tensile properties of UHMWPE fibers.

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