

Orientation of Carbon Fiber Precursors from 1-Butyl-3-Methylimidazolium Chloride Cellulose Solutions

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ABSTRACT: Cellulose/1-butyl-3-methylimidazolium chloride ([Bmim]Cl) solutions were wet spun at varied concentrations, temperatures and draw down ratios using a semi-hyperbolically converging die to produce fibers that were highly oriented and highly crystalline. The orientation number (N_{OR}) and the Herman's orientation factor (f_H) were compared with the fiber crystallinity. The analysis of the results indicates that the spinning parameters had a significant effect on the fiber properties, especially the orientation factor as well as the orientation number. Therefore, to spin cellulose fibers that would be suitable for carbon fiber precursors, the spinning parameters are a high concentration solution at approximately 90°C and at a medium draw ratio. This would yield fibers with a high orientation number. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: cellulose; ionic liquids; 1-butyl-3-methylimidazolium chloride; orientation factor; orientation number; wet-spinning; carbon fiber

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INTRODUCTION

The primary goal of this research was to spin highly oriented and highly crystalline cellulose fibers from a 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) solution. These fibers, in addition to their environmentally advantageous processing, have potential as precursors for carbon fibers. One prime consideration for carbon fiber precursors was the degree and size of defects. Therefore, using the elongational flow spinning technique to induce molecular orientation in the spinneret enabled the production of highly oriented, highly crystalline fibers.

A wide range of ionic liquids (ILs) have been used so far to dissolve cellulose. The best results of cellulose solution formation were obtained using [Bmim]Cl due to its anion in the IL bonding state being a strong hydrogen bond acceptor.¹ When cellulose is dissolved in a nonderivatizing solvent like [Bmim]Cl, the intramolecular hydrogen-bonding of the cellulose hydroxyl groups is disrupted and broken, for example, by the chloride ion in [Bmim]Cl. The high chloride activity and concentration of [Bmim]Cl allow for dissolving of larger amounts of cellulose at a faster rate when compared with traditional solvents.¹

When water, ethanol, or acetone are added to the cellulose/[Bmim]Cl solution, the solubility of cellulose is decreased which is reputed to be from competitive hydrogen-bonding of these components with the IL rather than to the cellulose.¹ With the addition of water to a cellulose/[Bmim]Cl solution, the cellulose is effectively removed from the IL. The best process for removing the water from the IL for its reuse is still being determined. A similar process where cellulose is dissolved in *N*-Methylmorpholine *N*-oxide (NMMO) also has the properties for spinning and uses water to remove the NMMO from the spun cellulose fiber. This process then uses evaporation or boiling to recover over 99% of the NMMO.²

As mentioned above, liquid-liquid phase separation using water is a clean, energy-efficient way to recover a solute, in this case cellulose. Other potential clean solute recovery methods include supercritical carbon dioxide extraction, crown ether extraction and pervaporation, and a membrane technique.³

Fiber Orientation Number

The semi-hyperbolic die used in this research induces elongational flow in polymer melts and nondilute solutions including

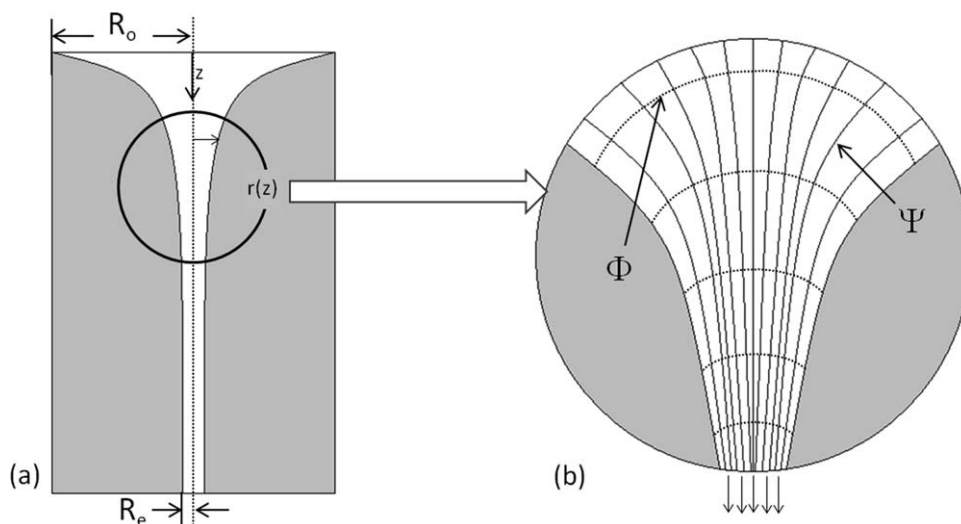


Figure 1. (a) Diagram of a semi-hyperbolic die. (b) The stream function and the potential function in a semi-hyperbolically convergent die.⁴

cellulose/[Bmim]Cl solutions. The die shape can be defined by eq. (1) and illustrated in Figure 1(a).

$$R_0^2 z = C \quad (1)$$

where R_0 is the radius at a centerline distance of z from the die entrance and C is a constant that is characteristic of the particular stream surface, for the die shape that is the die wall. The Hencky strains, ε_H , was calculated from the die entrance radius, R_0 and the die exit radius R_e using the eq. (2)

$$\varepsilon_H = \ln \frac{(2R_0)^2}{(2R_e)^2} \quad (2)$$

At a constant volumetric flow rate, the hyperbolic shape results in a constant elongational strain rate under appropriate processing conditions.⁴ The stream function, Ψ , and the potential function, Φ , can be defined by eqs. (3) and (4), where $\dot{\varepsilon}$ is the elongational strain rate.⁴

Figure 1(b) illustrates the flow streamlines as the stream function Ψ and the potential function Φ . Ψ and Φ are orthogonal and in shear free flow Φ is proportional to the isobaric pressure.

$$\Psi = -\frac{\dot{\varepsilon}}{2} r^2 z \quad (3)$$

$$\Phi = \frac{\dot{\varepsilon}}{2} \left(\frac{r^2}{2} - z^2 \right) \quad (4)$$

The use of a semi-hyperbolic die enables orientation of the cellulose chains, to begin at the entrance of the die and continue to develop as the cellulose/[Bmim]Cl solution travels through the die. Under proper processing conditions, slip is induced at the wall resulting in shear free flow that due to the die geometry results in a linearly accelerating plug flow. As a result, significant orientation is induced without vortices and the only velocity gradient is in the streamline direction.⁴ The orientation

number is a function of the average relaxation time, the elongation strain rate, and the Hencky strain and can be defined as eq. (5) below:

$$N_{OR} = \lambda \dot{\varepsilon} \varepsilon_H \quad (5)$$

where N_{OR} is the orientation number, λ is a characteristic relaxation time, ε_H is the Hencky strain, and $\dot{\varepsilon}$ is the elongational strain rate. Because of the proportional relations between these parameters, it is expected that imposed orientation should increase as any one of the terms in the product increase as the others are held constant.⁵ The proper processing conditions result when the orientation number, N_{OR} , is greater than one. The orientation number proposed represents the amount of orientation occurring in a solution or melt as well as whether or not slip occurs at the die wall.⁵ Several studies have recently determined that the elongational rheology was dependent on both the elongational strain rate and time.^{6,7} In many instances, the Hencky strain increases with process time. The product $\lambda \dot{\varepsilon} \varepsilon_H$, that is, the orientation number, is likely to be more broadly applicable than just in semi-hyperbolic die applications. A melt or solution that has a constant elongational strain rate in an isothermal shear free system indicates a hyperbolic shape due to the geometric constraints imposed by a constant elongational strain rate.

An orientation number of approximately one is an indication that the effects controlling the flow of the system balance. However, an orientation value less than about one suggests the flow is relaxation dominated and for values greater than about one, the flow is orientation dominated with a transition region between. In the semi-hyperbolic die, an orientation number greater than one suggests that slip at the wall is occurring.⁵ The level and distribution of orientation in a fiber should also be dependent on the orientation number because as the orientation number increases the effect of relaxation will decrease in significance in relation to the simultaneously imposed orientation. As the orientation number approaches one from a lower value, the

orientation effect is still strong and significant orientation should still be developing in the majority of the fluid.⁵ The major resistance to flow through the semi-hyperbolic die is due to the body forces of the polymer molecules resisting orientation. A momentum balance suggests that this orientation related body force is orders of magnitude larger than the forces related to either velocity gradients, shear at the wall, or gravitational effects.^{4,5}

Fiber Orientation Factor

Measuring the birefringence of a fiber can be used in the determination of the fiber orientation factor. This measurement method was used as a validation that the orientation number calculation does represent orientation within the cellulose fiber. The angle of rotation, $2i$, was measured and used to find the phase difference, Γ , which also incorporates the constant values of the compensator used in the angle measurements. Therefore, the birefringence, Δn , was calculated based on eq. (6) and used to calculate the Herman's orientation factor, f_H shown in eq. (7).

$$\Delta n = \Gamma/d \quad (6)$$

$$f_H = \Delta n/\Delta^\circ \quad (7)$$

where d is the diameter of the fiber being tested and Δ° is the maximum or intrinsic birefringence of cellulose.⁸ A Herman's orientation factor equal to one indicates that the fiber is perfectly oriented, whereas a factor of zero indicates that there is no orientation within the fiber.

EXPERIMENTAL

Materials

The cellulose used in this study was a dissolving pulp with a degree of polymerization of 670 (Buckeye Technologies, Memphis, TN) and the IL used was [Bmim]Cl (Fisher). The thermal properties are listed in Table I.⁹ Three cellulose/IL solutions of 8, 10, and 12% cellulose by weight were studied at temperatures of 80, 90, and 100°C.

Instruments and Experimental Technique

Dissolution of cellulose in the IL solvent was carried out in a Brabender internal mixer (C.W. Brabender Instruments, Inc., South Hackensack, NJ). The wet spinning was done using the Advanced Capillary Extrusion Rheometer 2000 (ACER 2000, formerly Rheometric Scientific, Piscataway, NJ) and a semi-hyperbolic die of three Hencky strains of 5, 6, and 7. A schematic of the ACER illustrated in Figure 2.

The sheets of the dissolving pulp were ground to a fine powder and dried in an oven to constant weight. The IL [Bmim]Cl was

Table I. Thermal Properties of 1-Butyl-3-Methylimidazolium Chloride, [Bmim]Cl

Melting Point Temperature (°C)	41
Glass Transition Temperature (°C)	-69
Start Temperature of Thermal Decomposition (°C)	150
Heat Capacity @ 25°C (J mol ⁻¹ K ⁻¹)	322.7
Heat Capacity @ 50°C (J mol ⁻¹ K ⁻¹)	333.7

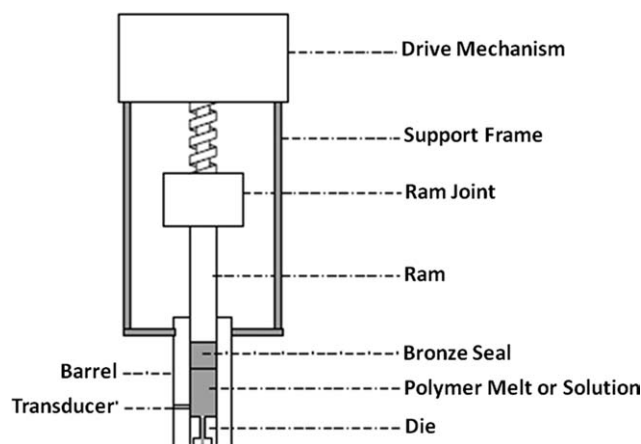


Figure 2. Advance Capillary Extrusion Rheometer (ACER).⁴

melted first in the Brabender mixing chamber and then cellulose powder and propyl gallate (1 wt% on cellulose) were added under continuous mixing at 90°C and 60 RPM rotors speed. Dissolution was performed until a clear viscous solution was obtained. The time of dissolution varied for different concentration solutions, ranging from 30 min to 2 h. After dissolution, the samples were removed from the mixing chamber and stored in glass jars at room temperature.

The IL/cellulose solution was preheated to load into the barrel due to the solutions viscosity. Once the IL/cellulose solution reached thermal equilibrium with the set temperature, the ram was attached and moved to a position in the barrel where it was in contact with the solution. The elongational strain rates were then set from lowest to highest based on the experimental parameters. The solution was then extruded into the coagulation bath of water and drawn under two submerged stationary spools before being spun onto the collection spool. The spinner was set to the desired experimental parameters. The collection spool was then soaked in water for approximately 2 days before being rinsed and dried. All the spinning parameters of concentration, temperature, and draw ratio are shown in Table II. The draw ratio is calculated from the elongational strain rate and the take-up velocity of the spinner.

The crystallinity measurements of the fibers were determined using Wide Angle X-Ray Diffraction (WAXD) equipment (Phillips X Pert Pro X-ray diffraction system, Mahwah, NJ) as well as the curve fit software called Pro Fit®. To prepare each sample for testing, the fibers were overlapped to form a small rectangular bundle where the layers of the fibers added up to several millimeters in thickness. Each sample bundle was attached to the aluminum stage, and the x, y, and z coordinates were measured for correct scanning to occur. The WAXD was run at 45 kV and 40 mA. The beginning angle was 5° and the stopping angle was 35°. The birefringence was determined by measuring the polarimetry using an optical microscope with crossed polarizing filters (Leitz-Ortholux polarizing light microscope). Between the crossed polarizers, the fiber sample appeared bright against the isotropic background. A

Table II. Fiber Crystallinity and Orientation Results

Run #	Conc. (%)	Temp. (°C)	Draw Ratio	Crystallinity (%)	Herman's orientation factor (f_H)	N_{OR}
1	10	100	39.1	82.6	0.497	0.112
2	10	100	18.2	69.9	0.581	0.155
3	10	100	28.2	74.6	0.646	0.155
4	10	100	38.9	76.8	0.526	0.155
5	10	100	22.0	70.4	0.593	0.199
6	10	94.1	26.7	76.4	0.656	0.177
7	10	94.1	41.9	82.4	0.548	0.177
8	10	94.1	19.0	70.0	0.630	0.248
9	10	94.1	29.9	77.6	0.652	0.248
10	10	105.9	26.7	72.8	0.531	0.102
11	10	105.9	41.9	86.6	0.585	0.102
12	10	105.9	19.0	76.9	0.586	0.143
13	10	105.9	29.9	76.6	0.590	0.143
14	10	90	28.2	74.0	0.732	0.282
15	10	110	28.2	82.6	0.445	0.107
16	8	100	36.7	79.2	0.540	0.082
17	8	100	26.7	69.1	0.291	0.089
18	8	100	41.9	78.4	0.509	0.089
19	8	100	19.8	64.9	0.522	0.107
20	8	100	28.2	69.6	0.460	0.107
21 ^a	8	100	37.7	-	-	-
22	8	100	19.0	73.1	0.553	0.125
23 ^a	8	100	29.9	-	-	-
24	8	100	22.8	74.0	0.541	0.132
25	12	100	36.7	89.6	0.672	0.152
26	12	100	26.7	76.8	0.749	0.165
27	12	100	41.9	81.7	0.674	0.165
28	12	100	19.8	73.9	0.664	0.198
29	12	100	28.2	76.0	0.382	0.198
30	12	100	37.7	74.1	0.647	0.198
31	12	100	19.0	75.0	0.539	0.231
32	12	100	29.9	71.3	0.550	0.231
33	12	100	22.8	75.9	0.587	0.245

^aNote: There were not enough fibers spun for Run 21 and 23 to test for crystallinity and orientation.

compensator was then used to determine the angle or rotation for each fiber which was a key variable in the calculation of the birefringence.

RESULTS

Crystallinity

The comparative crystallinity of the fibers for the 33 experimental runs was calculated using a peak integration method and the results are shown in Table II. Using the intensity curves for the WAXD, the two peaks as well as the amorphous peak were determined with curve fitting software and corrected for background noise. The area under the two main

peaks as divided by the total area under the curve, this included the amorphous region, to obtain the crystallinity index. The peak fitting software runs a minimum of three times in the same X-ray scan to obtain the peak areas for the crystallinity calculations. The calculated crystallinity was then averaged for each sample and ranged from 64.9 to 89.6%. This method was used as a sample to sample comparative measure to determine which processing parameters had the greatest effect on crystallinity; it is not an exact representation of the fiber crystallinity. Based on the crystallinity calculations, the highest and lowest runs were Run #25 and Run #19, respectively.

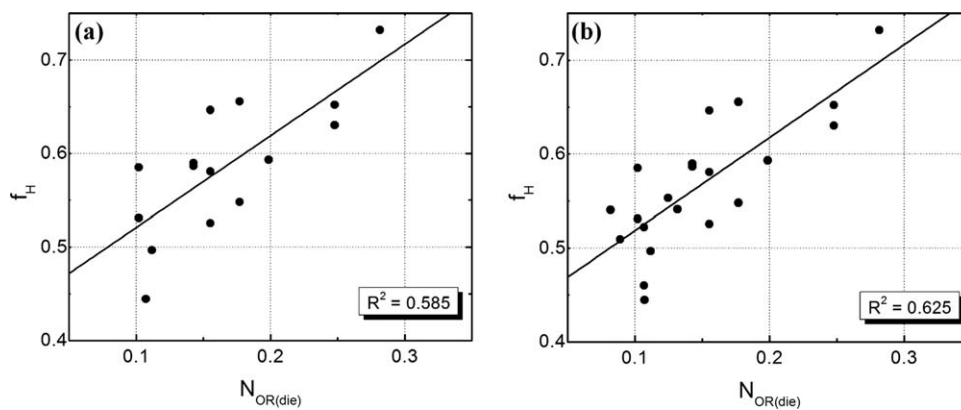


Figure 3. Herman's orientation factor versus the die orientation number for (a) 10% solution (b) 8% and 10% solutions.

Orientation Number (N_{OR})

The orientation number for each run was calculated using the relaxation time, Hencky strain of 5, 6, or 7, and the elongational strain rate, an experimental parameter that was derived from the draw ratio. The relaxation time of each solution concentration was calculated in a previous study.¹⁰ The orientation number calculation results are shown in Table II. Overall, the orientation number ranged from 0.082 to 0.282. Based on the calculations the highest and lowest runs were Run #14 and Run #16, respectively.

Orientation Factor (f_H)

The maximum birefringence for cellulose was found to have several values; 0.056, 0.061, and 0.081.¹¹⁻¹³ For the calculation of the orientation factor, maximum birefringence of the cellulose used was 0.061. The results for Herman's orientation factor are shown in Table II. The orientation factor ranged from 0.291 for Run #17 to 0.749 for Run #26. This indicates that the fibers obtained were slightly oriented to moderately oriented. Also observed was a small increase in the level of orientation as the concentration increased, however this was a general trend and there were exceptions. The orientation factor calculation was used as a validation method for the prediction of fiber orientation using the N_{OR} calculations which is further discussed in Figure 3.

Figure 3 represents the correlations of the Herman's orientation factor with the orientation number for the die. Part (a) of the figure represents the correlation for the 10% solution data, and part (b) represents the correlation for the 8 and 10% solution data. This graph indicates that as the orientation number increases the orientation factor also increases. This supports the definition of the orientation number as being an indication of the level of orientation induced in the die. Also represented are the R^2 values, where the best correlation of the orientation factor to the die orientation number includes both the 8 and 10% solutions. The correlation with the orientation number in the die also indicates that inclusion of the 12% solution data significantly decreases the correlation. This suggests that the level of orientation in the fiber is strongly affected by the die as indicated for the R^2 values.

Figure 4 represents the response surface of the Herman's orientation factor for the fibers, as a function of the temperature and the die orientation number. Figure 4(a) represents the results of just the 10% solution and Figure 4(b) represents the results for the 8 and 10% solutions. The graphs indicate that in general lower temperatures increase the orientation of the fiber. The comparison of the two reveals that the correlation using just the 10% solution was better than using both the 8 and 10% solutions. The addition of temperature to the correlation of orientation factor and orientation number increased the R^2 value for

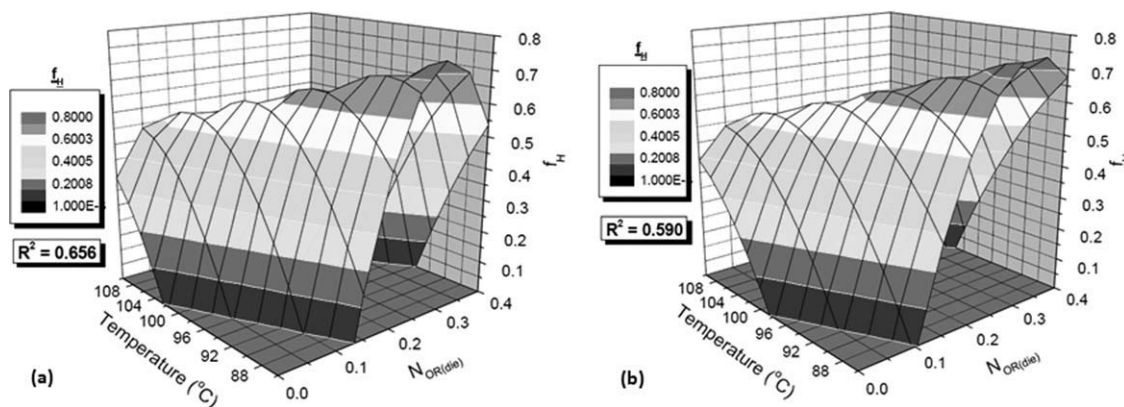


Figure 4. Effect of temperature and die orientation number on the Herman's orientation factor for (a) 10% solution (b) 8% and 10% solutions.

the 10% solution. This suggests that temperature plays a significant role on the level of orientation of the fiber.

These figures suggest that there is a good connection with the orientation number, especially in the die and with the actual orientation of the fiber. Apparently at the higher temperatures, the effect of relaxation on the orientation induced in the die increases. However, relaxation in the die is inhibited by the constraining walls. The rate of relaxation is apparently dependent on level of orientation, temperature, and physical boundary constraints.

DISCUSSION

Crystallinity

The optimal cellulose precursor for a carbon fiber would have a high crystallinity. The analysis of the crystallinity results indicates that a high draw ratio, a high temperature, and a high solution concentration would yield a fiber with a high crystallinity. The results indicate that as the solution concentration increases, the crystallinity also increases. This suggests that the amount of molecules within the fibers due to the concentration affected the level of crystallinity. The analysis of the crystallinity indicates that this parameter did not correlate as highly as expected which is likely a result of the crystallinity being more affected by fiber orientation, defect structure, and lateral order.

Therefore, based on the results and disregarding the outlier point of 89.6, the crystallinity for all of the runs ranged from 69.6 to 86.6%. Lyocell fibers have a crystallinity in the range of 64.04 to 72.56% calculated using the same methods.¹⁴ This indicates that the crystallinity for the fiber spun from cellulose [Bmim]Cl solutions is comparable with the crystallinity of Lyocell fibers, if not slightly higher.

Orientation

It was found that the fiber orientation ranged from slightly oriented to moderately oriented, indicating that the orientation within the fibers was not as high as anticipated. The analysis of the data revealed several parameters that effected the orientation of the fiber.

First, the increase in the temperature during the spinning process decreased the fiber orientation, thus suggesting that thermal relaxation and perhaps degradation could have affected the orientation of the chain molecules. The thermal degradation of the solution would likely reduce the length of the cellulose chains. This suggests that temperature during the spinning process is a key parameter affecting the properties of the fiber.

The second observation is the increase in orientation number as the Herman's orientation factor increased. This supports the definition of the orientation number being an indication of the orientation of the fiber. A fiber produced with a high orientation number would be expected to have a high orientation factor. However, this is the general trend, and the results obtained from the calculations reveal that there are exceptions.

The analysis of the relationship between crystallinity and the orientation number indicated a decreasing trend overall. This was not expected. Generally, a high level of orientation is an indication that the crystallinity is also high. However, in this case

the opposite is true. Again, this supports the conclusion that the crystallinity measurements were affected by many unforeseeable factors and is not a good indicator of level of orientation within the fiber. Finally, it was observed that as the orientation number of the fiber increased, the tenacity of the fiber also increased. This suggests that fibers with a high orientation number would be stronger as a result of the cellulose molecules being more closely packed.

When temperature was incorporated into the correlations of orientation factor and orientation numbers, the resulting graphs illustrated an arc pattern or what could be described as "folding back." This was most likely an effect of relaxation of orientation imposed predominantly in the die becoming increasingly dominant at higher temperature over induction of additional orientation during draw down in the air gap and in the coagulation bath.

The optimal cellulose precursor would have an orientation number greater than one that indicates that the fiber is in an orientation dominant mode, which results in significant orientation.⁵ However, an orientation number near one, results in a transition region that gives flow instabilities in the semi-hyperbolic die. This causes some data scatter and surface roughening of the fiber.⁵ When the orientation number is less than one, it appears that the elongational flow is in a relaxation dominant mode, in which developing orientation is relaxing as it develops.⁵ The results indicate for all the runs, that orientation number for the die were in a relaxation dominated state due to the orientation numbers being significantly less than one as shown in Table II.

Perhaps, the transition to an orientation dominant regime occurs at a lower orientation number when the fiber is constrained by the die walls than when it is draw down in a free boundary region. All of the data on orientation number previous to this study have been on flow through converging dies. A much smaller die exit diameter with the same entrance diameter or a higher strain rate would increase the orientation number in the die for this material. Also, the orientation number correlated with temperature accounts for the fact that the fiber is cooling and relaxing at different rates in the spinning air gap as well as the coagulation bath for different extrusion temperatures. Relaxation and cooling rates are important to maintaining orientation imposed in the die as well as externally.

CONCLUSIONS

This research was done to determine the effects of cellulose concentration, processing temperature, and draw ratio on the crystallinity and orientation of a wet-spun fiber using a semi-hyperbolically converging die. It can be concluded from the analysis of the cellulose fibers spun from the [Bmim]Cl solutions, that the temperature, solution concentration and the draw ratio had a significant effect on the fiber properties, especially the orientation factor as well as the orientation number. Based upon the analysis of the results, it was determined that fibers spun from a high concentration solution at approximately 90°C at a medium draw ratio would yield the fiber properties desirable for a carbon fiber precursor, that is, a high orientation number. The

final test will be to produce an adequate amount of continuous fiber using the determined parameters for the production of carbon fibers.

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