JOURNAL OF APPLIED POLYMER SCIENCE VOL. 13, PP. 817–826 (1969)

Spin Orientation during Acrylic Fiber Formation by Wet-Spinning

D. R. PAUL,* *Chemstrand Research Center, Inc., Durham, North Carolina 27702*

Synopsis

The molecular orientation acquired during fiber formation of acrylic fibers by wet-spinning has been studied. Orientation was detected by measurements of sonic modulus which were converted into an orientation factor. The orientation correlates very well with the ratio of take-up velocity to the freely extruded velocity. Several mechanisms for the origin of spin orientation are discussed.

INTRODUCTION

Nearly all synthetic fibers are prepared by extruding a polymer melt or solution through a spinneret hole to form a viscous but fluid filament which must be solidified in some way. The filaments are collected on a rotating roll and subsequently transferred to other rolls for stretching to reduce the denier and to give molecular orientation. The events that occur during fiber formation, i.e., between the spinneret and the first roll, are very influential in establishing the properties of the final fiber. For example, the solidification is of extreme importance, as it directly controls the polymer morphology. In melt-spinning, solidification occurs by crystallization from the melt, while in wet-spinning the polymer is precipitated from solution. The two processes give fibers with entirely different structures. Mechanical or rheological processes also play a very important role in fiber formation through both the extrusion step and the attenuation that occurs between the spinneret and the first roll. Ziabicki has made an extensive study of the mechanics of fiber formation by melt-spinning. Very little has been published on similar studies of wet-spinning.

An important consequence of these mechanical processes is a premature molecular orientation acquired during the fiber formation step itself before any intentional orientation stretch is taken. This is frequently called spin orientation. The level of this orientation influences the later drawing processes and the final fiber properties quite drastically. Ziabicki and Kedzierska[1–3] studied the response of spin orientation to various spinning variables in melt-spinning of several polymers Haskell and Owens[4] have

* Present address: Department of Chemical Engineering, The University of Texas, Austin, Texas 78712.

reported on the occurrence of this phenomenon in the formation of cellulose films from viscose. Some results are reported here on a similar mechanical study of acrylic fiber formation by wet-spinning.

Ziabicki used birefringence as a measure of orientation. Unfortunately, this is not a good tool for the acrylic fibers studied here, primarily because the maximum birefringence (perfect orientation) is quite low and the measurements are subject to large relative errors. Also the porous structure of wet-spun fibers[5,6] leads to form a birefringence contribution when the usual techniques are used. Charch and Moseley[7,8] have shown that the sonic modulus of a fiber is often a very sensitive indicator of molecular orientation. This stems from the fact that sound travels faster along a polymer chain than from one chain to another. Thus, as more chains become oriented in the direction of the fiber axis, the faster sound travels down the fiber and the higher the sonic modulus, since the modulus is proportional to the square of the sonic velocity. The orientation encountered here can be observed by x-ray diffraction, but it is difficult to make the results quantitative. Since the velocity of sound along a fiber is relatively easy to measure, this device has been used exclusively.

EXPERIMENTAL AND RESULTS

Sample Preparation and Testing

The polymer used was a copolymer of acrylonitrile and vinyl acetate containing about 7.7% by weight of the latter with a weight-average molecular weight of about 115,000. The polymer was dissolved in dimethylacetamide (DMAc) to give a solution containing 25% polymer by weight. This solution was pumped to a 100-hole spinneret immersed in a liquid bath containing 55% DMAc and 45% water by weight maintained at 55°C. The aqueous DMAc solution coagulates the filaments as they emerge from the holes.[9] These filaments were removed from the bath continuously at a velocity V_1 by a rotating roll or godet. The flow rate of spinning solution per hole Q was established by a positive displacement pump. The fiber samples were washed with water on the godet and then wound on a bobbin by hand such that there was essentially no slack but no tension either. The bobbins of wet yarn were dried at 50°C for 24 hr in a forced air oven. This gives complete drying without extensive collapsing of the fibrillar structure characteristic of wet spun fibers at this point of processing.[5,6]

The velocity of sound along the axis of each one hundred filament yarn sample produced was measured by a KLH Pulse Propagation Meter at a frequency of 10 kcps. The samples were stretched taut during testing. The sonic modulus E (in grams/denier) was calculated from the velocity of sound by

$$E = 11.3V^2 \tag{1}$$

where V has the units of kilometers/second.

The effects of the mechanical variables on spin orientation were determined from samples prepared according to an experimental design that helped minimize the amount of data required. The variables studied were spinneret hole diameter D, spinning solution flow rate per hole Q, godet speed V_1, and the denier per filament of the fiber (dpf). Of course the last three are not independent, as they are related by the following material balance:

$$\text{dpf} = 2.95 \times 10^4(CQ/SV_1) \tag{2}$$

where C is the polymer concentration in grams/cubic centimeter of the spinning solution. For this equation, V_1 has the units of feet/minute and Q has units of cubic centimeters/minute. An orientation stretch is normally taken after the first godet, and the stretch ratio is designated as S. Here an orientation stretch of 6× will be assumed so dpf does not refer to the actual denier on the first roll, but instead it is the final denier after a 6× stretch. Samples were prepared at constant Q and variable dpf and then at constant dpf and variable Q for both 3.0 and 5.0 mil spinneret hole diameters. By proper design each sample could be used in more than one data set. In this manner the entire region of stable spinning was studied.[10]

Several other samples were prepared by freely extruding filaments into the bath without being removed by the godet, i.e., no external stresses were imposed on the filaments while they were being formed. A filament prepared in this way will leave the spinneret with a certain velocity, V_f, called the "free velocity" which is primarily a function of Q, D, bath conditions, and the properties of the spinning solution.[10] These filaments were removed from the spin bath afterwards by hand and dried as before.

Sonic Modulus Response to Spinning Variables

The results of the experiments outlined earlier are shown in Figures 1–3. In the first two figures the sonic modulus is plotted versus the flow rate Q while the denier remains constant along a given line. This illustrates an increase in sonic modulus or orientation as the production rate is increased while producing a filament of a given denier. As the denier becomes smaller, the level of spin orientation increases. A comparison of Figures 1 and 2 shows that in general the level of spin orientation is higher for the 5.0-mil spinneret than the 3.0-mil spinneret. The slopes of the constant denier lines are larger for the 3.0-mil spinneret.

The results for the freely extruded filaments are also shown in Figures 1 and 2. In general it must be concluded that these data do not depend on either the flow rate or the spinneret hole size, since the data in both figures fall more or less randomly about a common value of 20 g/den. These samples were examined by very sensitive x-ray methods and no indication of a preferred orientation could be found, thus indicating 20 g/den as the sonic modulus of the unoriented fiber prepared by these spinning and drying conditions.

Figure 3 shows in another manner the influence of denier on sonic

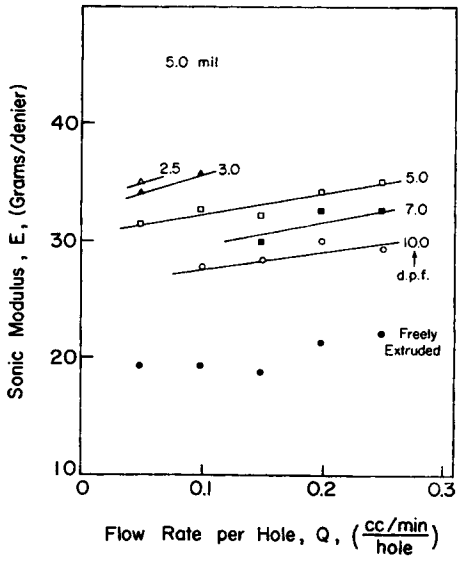

Fig. 1. Effect of flow rate for a 5.0-mil spinneret.

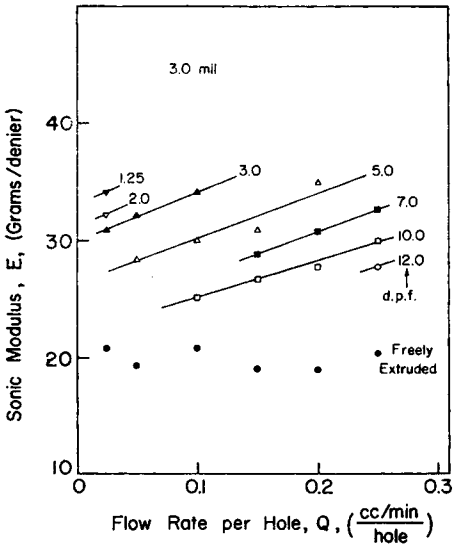

Fig. 2. Effect of flow rate for a 3.0-mil spinneret.

modulus or orientation. Here E is plotted versus the reciprocal of the denier (1/dpf) with lines of constant Q. The rationale for such a plot can be seen in eq. (2), which shows

$$(1/\text{dpf}) \propto V_1/Q \tag{3}$$

At constant Q, this amounts to a plot of E versus V_1. Ziabicki[1-3] shows similar plots of birefringence versus roll speed for melt-spun fibers; of

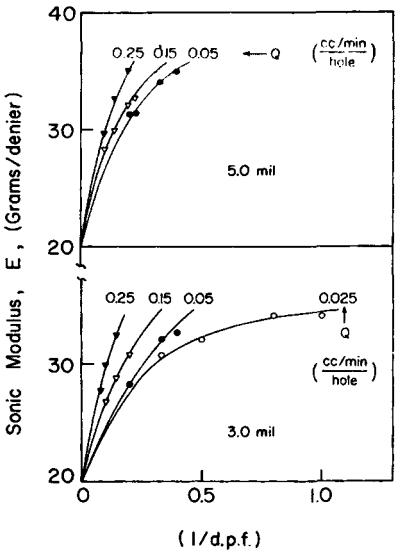

Fig. 3. Effect of denier.

course, E is not directly equivalent to birefringence. In this plot all of the curves are drawn through $E = 20$ (unoriented state) and infinite dpf. This is not quite correct, as the denier of a freely extruded filament is quite large but not infinite. Actually each curve intersects $E = 20$ at some different value of (1/dpf) that is very small but not identically zero. This plot shows the response to godet velocity V_1 is quite large at first but then levels out. The response for each curve is also quite dependent on Q and D.

Correlation of Results

The plots shown earlier indicate trends in a useful manner, but it would be more appealing if all of this data could be correlated into a more general form that might perhaps be more indicative of the fundamental mechanisms involved. Solution spinning technology frequently uses the term "jet stretch ratio," defined as $V_1/\langle V \rangle$, where $\langle V \rangle$ is the average solution velocity in the spinneret hole, i.e.,

$$\langle V \rangle = 4Q/\pi D^2 \tag{4}$$

This ratio implies a stretch or an attenuation from velocity $\langle V \rangle$ to V_1 and thus would have the significance of the draw ratio used to describe an orientation stretch. The term, jet stretch, commonly implies stretching the fluid portion of the filament only. At this point, one might wonder if the present data could be correlated in terms of this parameter. Arguments can be given to show that this parameter has no real fundamental significance. For example, the spinning solution does not issue from the spinneret with velocity $\langle V \rangle$, but instead it leaves with a velocity V_f which

is normally 4 to 10 times less than $\langle V \rangle$ for the present system. This represents a large increase in diameter of the stream as it leaves the hole. This is the familiar Barus effect which is a consequence of the elastic memory of the spinning solution, normal stresses generated by the shear field, velocity profile rearrangements on leaving the capillary, plus an interaction with the coagulation bath in this case.[10] Actually V_1/V_f would be a more realistic parameter.

Figure 4 shows all of the sonic modulus data plotted versus the jet stretch ratio for the two hole sizes. Note that E should be 20 g/den when this ratio becomes $V_f/\langle V \rangle$, which is a different value for each flow rate; thus, even in principle, a single curve should not describe the results. It is plainly evident from Figure 4 that this term is not adequate to correlate all the information shown in Figures 1, 2, and 3.

One shortcoming of the jet stretch ratio can be remedied as indicated earlier by replacing $\langle V \rangle$ in the ratio by V_f. The resulting ratio, V_1/V_f, might properly be called the filament attenuation, since it represents the actual denier reduction the filament undergoes because of the take-up process. In other words, if no tension were applied to the filaments, they would leave the spinneret at a velocity of V_f, whereas by applying the tension the filaments eventually attain a velocity of V_1. Experimental values of V_f are shown in Table I for the conditions used here.[10] A plot of E versus V_1/V_f is shown in Figure 5. This ratio correlates the results much better than the jet stretch ratio. A single curve is quite adequate. The scatter present is probably no larger than the inherent experimental errors. A part of the reason for this improved correlation is that at constant denier, $V_1/\langle V \rangle$ does not depend on Q, whereas V_1/V_f does in just the right way. For free extrusion V_1/V_f is unity, so the curve in Figure 5 was drawn through this point at a modulus of 20 g/den.

It is easy to understand that V_1 and V_f are the two important velocities involved in this attenuation, but it is not apparent why the ratio is sig-

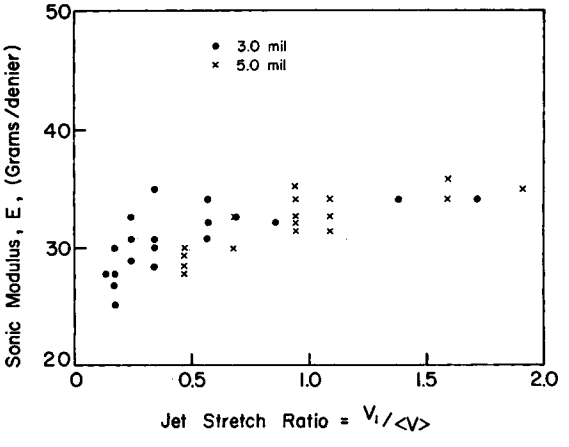

Fig. 4. Correlation with jet stretch ratio.

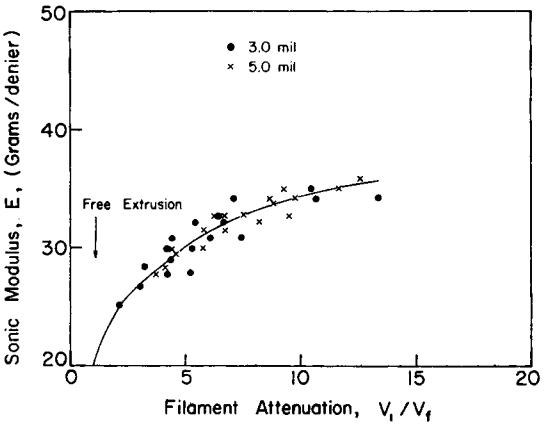

Fig. 5. Correlation with filament attenuation.

TABLE I
Free Velocity Data

	V_f, ft/min	
Q, cc/min/hole	D = 3.0 mil	D = 5.0 mil
0.025	2.30	—
0.050	4.15	2.10
0.100	5.85	3.25
0.150	5.65	4.45
0.200	4.70	5.60
0.250	6.10	6.60

nificant. For example, one might expect the difference to be a key parameter. A thorough rheological analysis of spinning would probably reveal the answer to this important question, but this will not be attempted here.

DISCUSSION

Calculation of An Orientation Factor

Moseley[7,8] has related the sonic modulus of solid polymers to molecular orientation. In his calculations he recognized that sound travels with a certain velocity down the molecular axis while it travels at a different (slower) velocity between chains, i.e., perpendicular to the chain axes. By considering a series addition of deformations, he showed that the observed sonic modulus of a partially oriented fiber could be related to the two velocity components and the average angle that a chain segment makes with the fiber axis. Through this approach, the orientation factor α, defined by

$$\alpha = {}^1/_2(3\ \langle\cos^2\theta\rangle - 1) \tag{5}$$

can be calculated from the sonic modulus using the following approximate equation

$$\alpha = 1 - (E_u/E) \tag{6}$$

The term E_u is the sonic modulus of a sample having completely random molecular orientation. The orientation factor α ranges from 0 for random orientation to 1 when all chains are oriented perfectly with the fiber axis. Radial orientation would give a negative α. Thus α gives one a better feel for the amount of orientation than E does.

Equation (6) was derived for a solid polymer with no porosity. It was pointed out earlier that the samples prepared here have a porous, fibrillar network structure since the polymer is precipitated from solution in the spin bath.[5,6,9] Orientation can consist of fibril orientation with respect to the fiber axis and molecular orientation within fibrils. Now there is some question as to how applicable eq. (6) is for such a system, but since no other approach is available this will be used. The resultant α may not have the precise meaning implied by eq. 5, but it should still give a useful relative measure of orientation. The curve drawn in Figure 5 is thus used to construct the plot of α versus V_1/V_f shown in Figure 6 by using eq. (6) with E_u = 20 g/den. The orientation factor increases very rapidly as the stretch is initially increased then changes very little thereafter. Ziabicki has noted a similar response for some melt-spun systems using birefringence as a measure of orientation. The birefringence can be used to calculate an orientation factor as discussed by Morgan.[11] When Ziabicki's results are compared on this basis with those in Figure 6, one finds interestingly enough that the saturation of orientation occurs at roughly 50% of maximum orientation for this wet-spinning system and several melt-spinning systems.

The acrylic fibers prepared here had a pore volume of about 50% of the total fiber volume. There are no good theories to indicate how the sonic

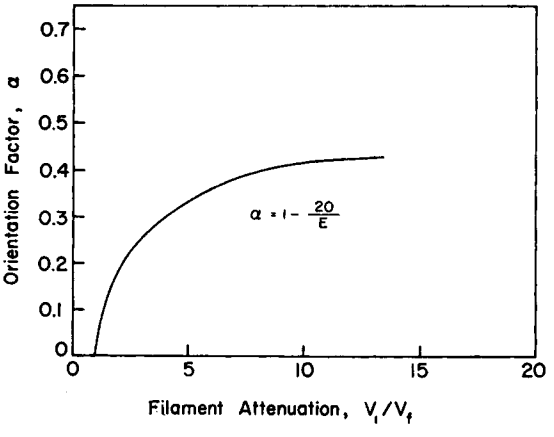

Fig. 6. Orientation factor.

modulus for even unoriented fibers should depend on porosity and fibrillar morphology. Measurements made during this work revealed a sonic modulus of 50 g/den for the nonporous, unoriented polymer, which agrees exactly with values given by Moseley[7,8] for another polymer of similar composition. While there are uncertainties in applying eq. (6) to fibrillar networks, the experimental results of Craver and Taylor[12] on paper (also porous and fibrillar on a different scale of magnitude) can be used as a basis to indicate that this approach probably yields reasonable values for α.

Mechanism of Orientation

There are several mechanisms commonly considered as potential sources of orientation during fiber formation. All of them can be divided into two classes. One group says the source is in the fluid region before solidification and the other points to the solid region. In the first mechanism the molecules are preferentially oriented by the perpendicular (shear) velocity gradient in the spinneret capillary and/or the parallel (axial) velocity gradient in the fluid outside the capillary and then solidified in this state. In the second, the thread-line tension is considered to cold draw the solidified filaments and thus orient the polymer chains. The thread-line tension is due to the elastic and viscous tensions generated within the fluid filament due to the attenuation from velocity V_f to V_1 plus a contribution from the hydrodynamic drag in the bath for wet spinning. Ziabicki and Kedzierska proposed a mechanism of the first type caused by the axial gradient as the source of spin orientation in melt-spinning.

The Young's modulus of the coagulated filaments in the wet state was found to be 1–5 g/den. The thread-line tension is of the order of 5×10^{-3} to 5×10^{-2} g/den for the conditions used.[10] Thus the amount of drawing that will occur in the coagulated filaments is of the order of 1%, which will not yield the orientation indicated here so this mechanism can be essentially ruled out. Ziabicki made similar arguments for melt-spinning.

It was shown earlier that no shear orientation from the capillary is preserved during free extrusion, and probably a good deal of it can still relax out when the filaments are removed by a godet. It is possible that the axial gradient caused by the fluid attenuation does lead to a lot of orientation in the fluid; however, it also seems likely that part of this orientation will have time to relax out before coagulation occurs. The solution used here has a zero shear viscosity of about 400 poise. By using molecular viscoelastic theories[13] one can estimate that the longest relaxation time for this fluid is about 8 msec, which is a rather short time compared to the process speeds and the coagulation rate.

An alternate mechanism of orientation that does not seem to have been considered before lies not in the well defined fluid or solid regions but in the transition zone. It was shown in a previous publication[9] that a distinct boundary between coagulated and uncoagulated solution moves into the filament as the filament proceeds away from the spinneret. The boundary motion is controlled by the solvent and nonsolvent diffusion rates. A

similar boundary might be expected for melt-spun systems, except here the motion would be controlled by heat transfer. The stresses in the threadline must be transmitted across this boundary, and they may actually be higher here than anywhere else. Consideration of this region suggests several possibilities that could lead to orientation. For example, a large shear gradient may be established on the fluid side of the boundary, and in this way the attenuation could occur by shear gradients rather than axial gradients. Due to the diffusion across the boundary, oriented material created very near this boundary could be immobilized very quickly before relaxation thus leading to spin orientation. Another possibility lies on the solid side of this boundary. Since this material is so freshly formed, its modulus may not be as large as that of the completely coagulated filament leaving the bath. This material would be very easy to orient especially if stress concentration occurs in the annular ring.

Another bit of evidence pointing to the importance of this region is that when a certain velocity, $V_{1(\max)}$ is surpassed, the filaments will break.[10] Visual observations show that the break occurs in this zone where coagulation is incomplete. These arguments are by no means conclusive, but they do suggest that this is a crucial zone that must be observed if the mechanism of spin orientation is to be fully understood.

The work reported here has dealt with only one polymer, one set of coagulation conditions, one spinning solution composition, etc. The orientation response will be altered as the coagulation rate, solution viscosity, etc. are changed, but the general ideas discussed here should still be applicable to different systems.

The author expresses his appreciation to the Chemstrand Research Center, Inc., for permission to publish this work.

References

1. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **2**, 14 (1959).
2. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **6**, 111 (1962).
3. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **6**, 361 (1962).
4. V. C. Haskell and D. K. Owens, *J. Appl. Polym. Sci.*, **4**, 225 (1960).
5. J. P. Craig, J. P. Knudsen, and V. F. Holland, *Tex. Res. J.*, **32**, 435 (1962).
6. J. P. Knudsen, *Tex. Res. J.*, **33**, 13 (1963).
7. W. H. Charch and W. W. Moseley, *Tex. Res. J.*, **29**, 525 (1959).
8. W. W. Moseley, *J. Appl. Polym. Sci.*, **3**, 266 (1960).
9. D. R. Paul, *J. Appl. Polym. Sci.*, **12**, 383 (1968).
10. D. R. Paul, *J. Appl. Polym. Sci.*, **12**, 2273 (1968).
11. H. M. Morgan, *Tex. Res. J.*, **32**, 866 (1962).
12. J. K. Craver and D. L. Taylor, *Tappi*, **48**, 142 (1965).
13. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.

Received September 6, 1968