Relationship Between Molecular Orientation and Draw Ratio of Polypropylene Monofilaments

W. C. SHEEHAN and R. E. WELLMAN, *Southern Research Institute Birmingham, Alabama*

Synopsis

The following empirical equation was derived for the relationship between molecular orientation α and permanent extension ratio λ of polypropylene monofilaments: $\alpha = 0.91(1 - 1/\lambda)$. The permanent extension ratio λ is the measured draw ratio adjusted to 1 when the orientation is zero. The standard deviation of the data points for 44 experimental filaments having different molecular weights, molecular weight distributions, and isotacticities about the line described by the equation was only 0.03. This equation is similar to a general empirical relationship between birefringence and draw ratio for several synthetic fibers derived by De Vries.

Introduction

Kordes et al.[1] derived an empirical equation for the relationship between birefringence and draw ratio of nylon 6 fiber. De Vries[2] found similar relationships for nylon 66, polyethylene, polystyrene, poly(ethylene terephthalate), and viscose rayon fibers; and he showed that all of the different relationships could be expressed by the following differential equation:

$$d(\Delta\eta)/d(\ln \lambda) = \mu + \rho\Delta\eta \tag{1}$$

In this equation, $\Delta\eta$ is the specific birefringence of the fiber, λ is the permanent extension ratio, and μ and ρ are constants that are characteristic of the type of fiber. The permanent extension ratio λ is defined as the measured draw ratio λ_e divided by the draw ratio when the specific birefringence is zero λ_0. In other words, the permanent extension ratio is the measured draw ratio so adjusted that it has a value of 1 when the specific birefringence is zero.

We have determined the relationship between the molecular orientation and the draw ratio for polypropylene monofilaments and have found it to be similar to the general empirical relationship between birefringence and draw ratio of synthetic fibers derived by De Vries. The relationship for the polypropylene monofilaments was apparently independent of the molecular weight, molecular weight distribution, and isotacticity of the filaments.

Methods

Nine sets of polypropylene monofilaments, a total of 44 experimental fibers, were prepared and characterized for use in the determination of the relationship between molecular orientation and draw ratio. The mono-filaments were prepared on laboratory melt-spinning and drawing equipment from eight polymers of different molecular weights and isotacticities. They were extruded at 235–280°C. through a single-hole spinneret into a water bath at 10–50°C., with the surface of the bath about 4 in. from the face of the spinneret. The monofilaments were taken up at a speed 3.1 times the extrusion speed. The spun filaments were drawn at 135°C. and then annealed at 100°C. for 15 min. The molecular weights and molecular weight distributions of the fibers depended on the molecular weights and molecular weight distributions of the polymers and on the extent of degradation of the polymers during extrusion. The extent of degradation was controlled by adjustment of the extrusion temperature. The isotactic contents of the fibers were independent of extrusion conditions and, hence, were the same as for the polymers from which the fibers were prepared.

Weight-average molecular weights $\bar{M}_w$ of the filaments were calculated from intrinsic viscosities in decalin at 135°C. [η] with eq. (2) given by Chiang.[3]

$$[\eta] = 1.00 \times 10^{-4} \bar{M}_w{}^{0.80} \tag{2}$$

The molecular weight distributions for the filaments, as expressed by the ratios of weight-average molecular weights $\bar{M}_w$ to the number-average molecular weights $\bar{M}_n$ of the filaments, were calculated with eq. (3)[4,5]:

$$\bar{M}_w/\bar{M}_n = 10([\eta]/[\eta]_0)^{1.22} \tag{3}$$

where [η]$_0$ is the intrinsic viscosity of the polymer before extrusion and [η] is the intrinsic viscosity of the polymer after extrusion. The content of isotactic polypropylene in the polymers was determined by extraction with n-heptane.[6] A 10-g. sample of chopped filaments was extracted with 350 ml. of n-heptane in a Soxhlet extractor for 48 hr., and the heptane-insoluble fraction was taken as the isotactic polymer.

Draw ratios of the drawn filaments were calculated from the deniers of the undrawn and drawn filaments, which were determined with a Vibroscope at 70°F. and 65% R. H. by ASTM method D204-57T. The molecular orientations of the filaments were determined from sonic-velocity measurements with the aid of eq. (4), which was developed by Moseley.[7]

$$\alpha = 1 - C_u{}^2/C^2 \tag{4}$$

In this equation, α is the molecular orientation in the sample; C_u is the sonic velocity in an unoriented filament, which was found to be 1.80 km./sec.; and C is the sonic velocity in the sample. The sonic velocities in the

filaments were measured with a KLH Pulse Propagation Meter, Model 5, equipped with a Nesco Graphic Recorder, Model JP100-2. Measurements were made at $-18°C$. to eliminate effects of crystallinity. The unoriented filament used for the determination of C_u was prepared by melt extruding a sample of polypropylene with a theoretical spin–draw ratio (ratio of take-up speed to extrusion speed) of one. The x-ray diffraction pattern of the filament showed no crystallite orientation.

Results and Discussion

Morgan[8] has shown that the degree of molecular orientation α of polypropylene fibers determined by sonic velocity is linearly related to birefringence $(\Delta\eta)$. Thus, the substitution of α for $\Delta\eta$ in De Vries' eq. (1) for the relationship between birefringence and draw ratio of synthetic fibers changes only the constant μ and gives eq. (5):

$$d\alpha/d(\ln \lambda) = \mu' + \rho\alpha \tag{5}$$

Under the condition that $\lambda = 1$ when $\alpha = 0$, eq. (5) has the following two solutions:

$$\alpha = \mu \ln \lambda \qquad\qquad \text{For } \rho = 0 \tag{6}$$

and

$$\alpha = \mu(\lambda^\rho - 1)/\rho \qquad\qquad \text{for } \rho \neq 0 \tag{7}$$

Since α must approach a maximum value of 1 or less as λ increases without limit, ρ for polypropylene fibers, as well as other fibers, must be less than zero. When ρ is equal to or greater than zero, no maximum value of α is reached. De Vries found that ρ in eq. (1) can be assigned a "preferred" value for each type of fiber, which is a multiple of $1/2$, and we assumed this would also be true in eq. (7) for polypropylene monofilaments.

With the limitation that ρ is a negative number and a multiple of $1/2$, we determined that the best value of ρ in eq. (7) for our data on polypropylene filaments was -1. In determining this value, we determined the least-squares lines for the relationship between α and λ_e^ρ for each of the nine sets of monofilaments prepared with ρ equal to $-1/2$, -1, and $-3/2$, and then we calculated the variances of the data from these lines. The variances calculated for the several sets of filaments with each of the values of ρ were combined to determine which value of ρ yielded the minimum variance. The combined variance with $\rho = -1$ was only 0.00103, compared with a combined variance of 0.00245 for $\rho = -1/2$ and a combined variance of 0.00182 for $\rho = -3/2$.

In the determination of the best value of ρ in eq. (7), it was possible to use the measured draw ratio λ_e rather than the permanent extension ratio λ. As noted earlier, λ is equal to λ_e/λ_0. λ_0, the draw ratio when α is zero, is a constant for a polymer spun under a specific set of conditions.

With $\rho = -1$, eq. (7) becomes

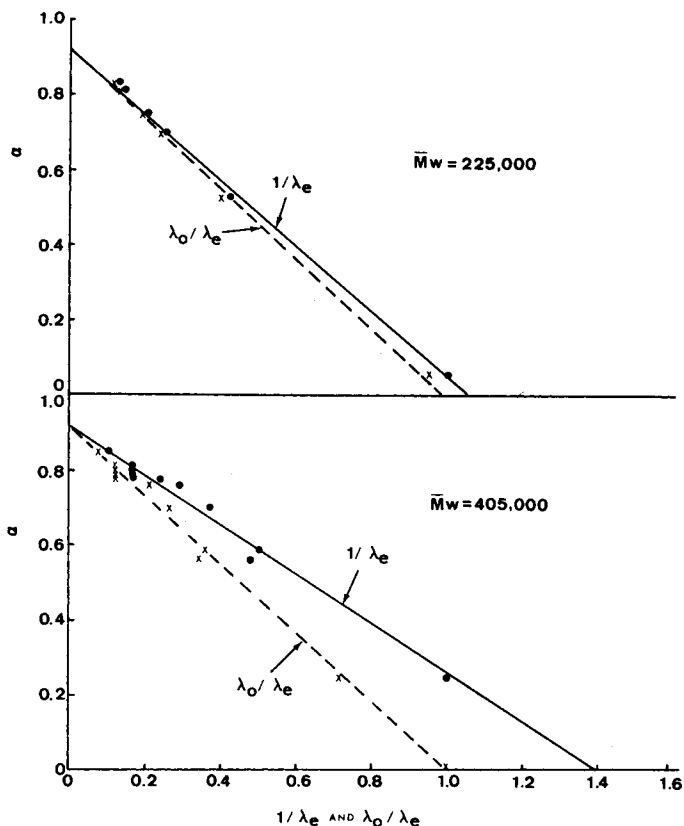$$\alpha = \mu(1 - 1/\lambda) = \mu(1 - \lambda_0/\lambda_e) \tag{8}$$

Fig. 1. Relationship between molecular orientation α and draw ratio of polypropylene filaments of different molecular weights. (λ_e is measured draw ratio, λ_0 is draw ratio when $\alpha = 0$, and λ_0/λ_e is the reciprocal of the permanent extension ratio $1/\lambda$.)

For fibers prepared from a given polymer under a specific set of conditions, λ_0 is equal to the reciprocal of the value of the intercept on the $1/\lambda_e$ axis in a plot of α versus $1/\lambda_e$. Knowing λ_0, a plot of α versus λ_0/λ_e can be made. Figure 1 shows plots of α versus $1/\lambda_e$ and of α versus λ_0/λ_e for experimental filaments made from two polymers of different molecular weights. Similar results were obtained for the experimental filaments made from the other polymers investigated. The plots were reasonably linear, but the intercepts on the $1/\lambda_e$ axis often occurred at values considerably greater than 1.0. This was probably due to some orientation in the undrawn filaments, which occurred during spinning, since, as pointed out by De Vries, intercepts greater than 1.0 occur when the measured draw ratio of the fiber is less than the permanent extension ratio. No quantitative expression was found for the variation of the orientation during spinning with the molecular weight of the polymer; but, qualitatively, the orientation increased with increasing molecular weight under a given set of spinning conditions.
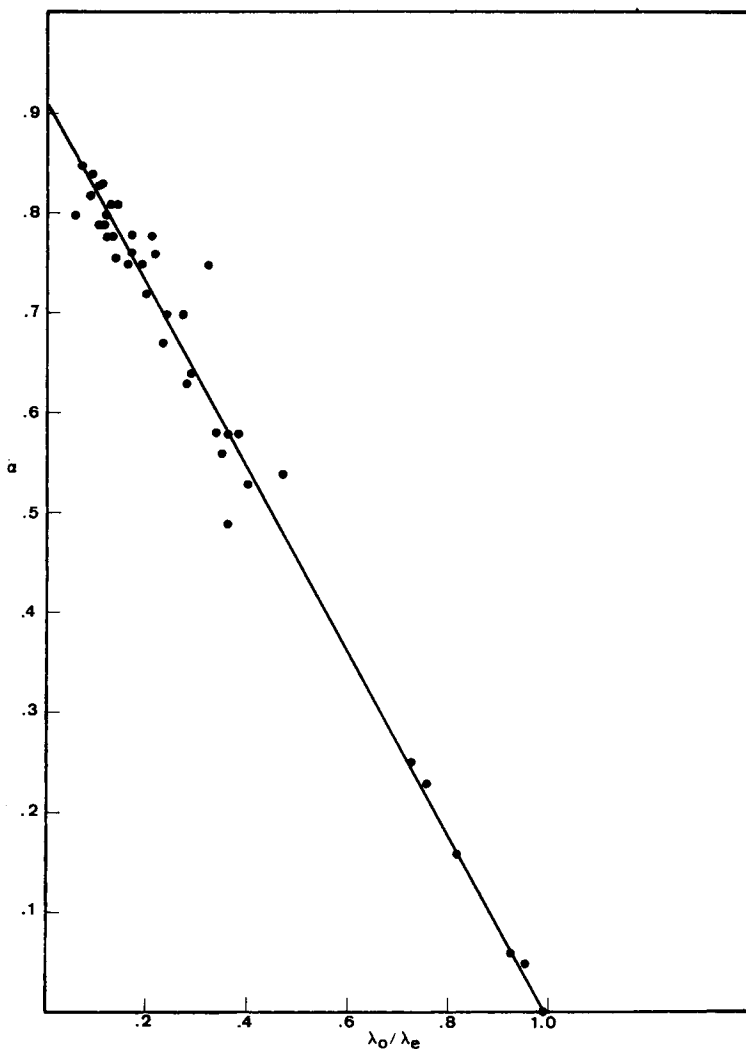
Fig. 2. Relationship between molecular orientation α and the reciprocal of the permanent extension ratio λ_0/λ_e for 44 experimental polypropylene monofilaments.

The constants μ and λ_0 in eq. (8) and the standard deviation of the data from the least-squares line defined by eq. (8) are given in Table I for each of the nine sets of experimental polypropylene monofilaments. The values of the constant μ are equal to the maximum degree of orientation α_{max}. As shown in this table, the values of μ ranged from 0.86 to 1.00, the values of λ_0 ranged from 0.69 to 1.08, and the standard deviations from the least-squares lines ranged from 0.00 to 0.06. Differences in molecular weight, molecular weight distribution, and isotacticity of the filaments would not account for the variations in the values of μ or the deviations from eq. (8).

Figure 2 shows a plot of α versus λ_0/λ_e for all of the 44 experimental filaments listed in Table I. The equation for the least-squares line of this plot is:

$$\alpha = 0.91\,[1 - (\lambda_0/\lambda_e)] \tag{9}$$

The standard deviation of our data from the line described by eq. (9) is 0.03. For the 44 filaments, the value of α_{max} from eq. (9) is 0.91 with a standard deviation of 0.01.

There are several possible reasons why the apparent maximum value of α for polypropylene filaments is less than 1.0. One explanation is that ρ is not an exact multiple of $1/2$. Another possible reason for α_{max} being less

TABLE I

Structural Parameters and Equations for Relationship Between Orientation and Draw Ratio of Polypropylene Monofilaments

Set	No. of filaments	Molecular weight $\bar{M}_w$	Molecular weight distribution $\bar{M}_w/\bar{M}_n$	Isotactic content, %	For $\alpha = \mu(1 - \lambda_0/\lambda_2)$		
					μ or α_{max}	λ_0	Std. dev.
6323–A	3	67,000	2.5	94	0.90	1.08	0.00
6423–A	4	78,000	2.1	95	0.86	0.93	0.01
6323–C	6	225,000	9.1	94	0.92	0.96	0.01
6623–C	5	305,000	9.3	97	0.91	0.69	0.03
6723–C	12	405,000	8.5	98	0.92	0.73	0.02
6823–C	4	395,000	9.3	>95	0.87	0.76	0.05
221–C	3	300,000	6.5	85	0.94	0.81	0.06
223–C	3	315,000	7.4	91	0.89	0.72	0.00
224–C	4	315,000	8.1	94	1.00	0.99	0.06

than 1.0 is that the sonic velocity method for determining molecular orientation is not reliable as α approaches 1.0, because α can equal 1.0 only if the sonic velocity becomes infinite. It is also possible that polypropylene can never be completely oriented by drawing, either because of inherent limitations in the method or because, as suggested by Wyckoff,[9] of the few per cent of atactic material present.

De Vries' relation may well be an oversimplification of the true relation between draw and orientation for polypropylene fibers, but it fits our data surprisingly well, and it should prove very useful for estimating the draw needed to provide a desired degree of orientation.

References

1. Kordes, E., F. Gunther, L. Buchs, and W. Goltner, *Kolloid-Z.*, **119**, 23 (1950).
2. De Vries, H., *J. Polymer Sci.*, **34**, 761 (1959).
3. Chiang, R., *J. Polymer Sci.*, **28**, 235 (1958).
4. Davis, T., R. Tobias, and E. Peterli, *J. Polymer Sci.*, **56**, 485 (1962).
5. Sheehan, W. C., and T. B. Cole, *J. Appl. Polymer Sci.*, **8**, 2359 (1964).
6. Gaylord, N. G., and H. F. Mark, *Linear and Stereoregular Addition Polym* Interscience, New York, 1959, p. 160.
7. Moseley, Jr., W. W., *J. Appl. Polymer Sci.*, **3**, 266 (1960).
8. Morgan, J. M., *Textile Res. J.*, **32**, 866 (1962).
9. Wyckoff, H. W., *J. Polymer Sci.*, **62**, 83 (1962).

Résumé

On a établi l'équation empirique suivante pour exprimer la relation entre l'orientat moléculaire α et le rapport d'extension permanente λ de monofilaments de polyprop éne: $\alpha = 0.91(1 - 1/\lambda)$. Le rapport d'extension permanente λ est le rapp d'ètirement mesuré ramené à 1 pour une orientation égale à zéro. Lors d'expérien effectuées sur 44 filaments différents par le poids moléculaire, la distribution des po moléculaires et l'isotacticité, la déviation moyenne des résultats par rapport à la dro décrite par l'équation cidessus n'était que de 0.03. Cette équation est semblabl une relation empirique générale, établie par De Vries, entre la biréfringence et le rapp d'étirement pour plusieurs fibres synthétiques.

Zusammenfassung

Folgende empirische Gleichung wurde für die Beziehung zwischen Molekülorientieru α und permanentem Dehnungsverhältnis λ für Polypropylenmonofils abgeleitet: α $0.91(1 - 1/\lambda)$. Das permanente Dehnungsverhältnis ist gleich dem gemessen Zugverhältnis, wenn es für die Orientierung 0 gleich 1 gesetzt wird. Die Standarda weichung der Punkte für 44 Versuchsfäden mit verschiedenem Molekulargewicl verschiedener Molekulargewichtsverteilung und verschiedener Isotaktizität von d durch die Gleichung beschriebenen Kurve betrug nur 0.03. Diese Gleichung ist ein von De Vries abgeleiteten allgemeinen empirschen Beziehung zwischen Doppelbrechui und Zugverhältnis ähnlich.