The Measurement of Molecular Orientation in Fibers by Acoustic Methods

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INTRODUCTION

It has been known for some time that when polymer molecules in a high polymer sample (fiber or film strip) are oriented by stretching, the sound velocity along the direction of stretch increases progressively with orientation, as measured by x-ray diffraction.[1,2] De Vries[3] has combined acoustic and birefringence measurements on regenerated cellulose fibers to obtain an empirical relationship between molecular orientation and sonic modulus, which is calculated from the sound velocity. These observations have permitted only a qualitative measurement of orientation since the absolute value of sound velocity varies with polymer chemical structure and since, until recently, the general effect of crystallinity on sound velocity was not understood. The present work results in a simple, quantitative procedure for determining the molecular orientation by properly accounting for these two complicating factors. The results of the present work are summarized by Charch and Moseley.[4]

EFFECTS OF CRYSTALLINITY AND POLYMER STRUCTURE

It has been shown in earlier work[2] and in the present study[4] that the sound velocity in polymeric fibers and film strips is relatively insensitive to crystallinity at temperatures substantially below the glass transition temperature T_g. Measurements made in this laboratory show this independence of sound velocity on crystallinity for both oriented and unoriented fibers as well.[4] The present study of orientation effects has been restricted to temperatures below T_g where crystallinity has a negligible effect.

The fact that sound velocity is independent of crystallinity means that sonic modulus[4] is also independent of crystallinity when it is expressed in units of force per unit linear density (or in units of grams per denier), as in eq. (16) below. When linear density (denier) is used as a basis, the moduli of different fibers from the same polymer are compared on the basis of an equal number of molecules passing through the fiber cross-section rather than on the basis of unit cross-sectional area.

The fact that sonic modulus (on a linear density basis) is independent of crystallinity at temperatures below T_g, is interpreted to mean that the intermolecular and intramolecular force constants which control fiber stiffness are not measurably different for crystalline and amorphous regions at these temperatures. As a consequence, the orientation parameter calculated from sound velocity (on sonic modulus) is taken to be a measure of the average orientation of all molecules in the sample regardless of the degree of crystallinity. For this reason, the parameter is called the *total molecular orientation* as contrasted to *crystalline* orientation and *amorphous* orientation.

The influence of polymer structure on the sound velocity of oriented fibers is taken into account by suitable use of the sound velocity in an unoriented (randomly oriented) fiber of film strip. The two experimental quantities used to calculate the molecular orientation are the velocity of sound in the direction of a fiber axis (long dimension of a film strip) and the velocity in a randomly oriented sample. The orientation parameter computed from these two velocities is identical to Hermans' orientation factor,[5,6] and is called the total molecular orientation, α.

DEPENDENCE OF SOUND VELOCITY ON ORIENTATION

A dependence of sound velocity on orientation is indicated in Tables I and II. The unoriented (randomly oriented) fibers have low sound velocities ranging from about 1 to 2 km./sec. (Table I). These velocities are comparable to those found in liquids where the mechanism of sound transmission is largely intermolecular.[7]

TABLE I

Sound Velocity in Unoriented Polymers at a Frequency of
10 Kcycles/sec.

| Polymer | Sonic velocity C_u, km./sec. | |
	Film	Fiber
Dacron[a]	1.4	1.4
Nylon 66	1.3	1.3
Viscose rayon		2.0
Orlon[b]		2.1

[a] Trademark for du Pont polyester fiber.
[b] Trademark for du Pont acrylic fiber.

TABLE II

Representative Sound Velocities in Highly Oriented Fibers
at a Frequency of 10 Kcycles/sec.

Fiber	Sonic velocity change during stress–strain tests, km./sec.
Dacron	3.4–5.9
Nylon 66	2.3–5.7
Viscose rayon	3.5–6.1
Orlon	4.2–5.1
X-36[a]	5.3–6.9

[a] Celanese saponified acetate fiber.

Higher sound velocities in highly oriented fibers range from about 2.3 to 6.9 km./sec. (Table II). In the case of each fiber, the lower velocity in Table II was measured under a small tension of about 0.1 g./den., while the larger value was obtained after stretching the sample to near the breaking load.

The relatively high sound velocities in Table II in partially oriented fibers are presumed to result from the participation of partially oriented molecular chains in the processes of sound transmission. This can be shown to be a reasonable hypothesis by computing a theoretical sound velocity associated with stretching highly oriented polymer molecules. Such theoretical velocities were calculated for several polymer types in a manner similar to that described by Meyer and Lotmar[8] and Lyons.[9] These calculations made use of approximate infrared and Raman derived force constants for bond stretching and bond bending.[10] Values of theoretical velocities for stretching various polymer molecules ranged from 12 to 14 km./sec., which is substantially above the highest values observed for most fibers, i.e., 5.1 to 6.9 km./sec. (Table II). In the case of certain highly oriented fibers from linear polyethylene, experimental sound velocities of 11 km./sec. approach the theoretical maximum values. As expected, x-ray diffraction indicates an

unusually high level of orientation in fibers with this high level of sound velocity.

In summary, the magnitude of experimental sound velocities in fibers is appropriately explained by the partial contribution of intermolecular and intramolecular force constants. The high sound velocities associated with high levels of molecular orientation apparently result from a large contribution of the stiff intramolecular bonds to the process of sound transmission. The low sound velocities of randomly oriented fibers are comparable to velocities of liquids where the mechanism of sound transmission is largely intermolecular. This point will be developed more fully in a later section.

MECHANISM OF SOUND TRANSMISSION

If sound is sent across an array of parallel molecules (Fig. 1a), sonic energy is presumed to be transmitted from one molecule to another by stretching of intermolecular bonds. On the other hand, if sound is sent along the length of a bundle of parallel polymer molecules (Fig. 1b), the sonic energy is presumed to be transmitted principally by stretching of the chemical bonds in the backbone of the polymer chain. In the case of partially oriented polymer molecules (Figure 1c), the molecular motion due to sound transmission is presumed to have right-angle components, along and across the direction of the molecular axis. The magnitude of either of these two components is taken to be a function of the angle between the molecular axis and the direction of sound propagation θ (Fig. 1c).
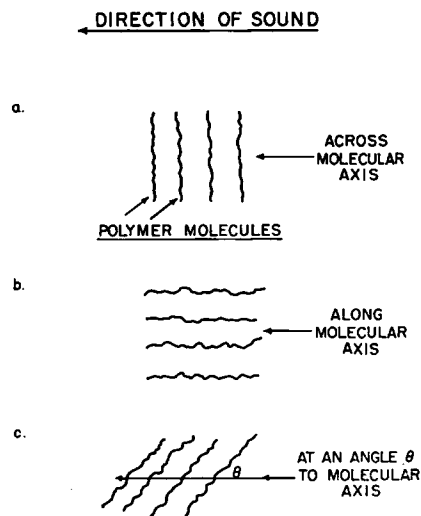

Fig. 1. Possible modes of sound transmission in polymers.

As discussed in the Appendix, the above considerations lead to an equation that relates the sound velocity in a sample to its molecular orientation in terms of certain constants characteristic of the polymer structure. To develop such an equation, it appears necessary to make one of the two following extreme assumptions.

(1) Any fiber deformation which occurs during sound transmission is the sum of the intramolecular and intermolecular deformations. This assumption results in a *series* addition of the intramolecular and intermolecular force constants, weighted by an average orientation function.

(2) Any force on the fiber resulting from a sound wave is the sum of the forces exerted on the intramolecular and intermolecular bonds. This assumption results in a *parallel* addition of the intramolecular and intermolecular force constants, weighted by an average orientation function.

As shown in the Appendix, these two extreme assumptions lead to two equations which relate the sound velocity in a fiber to an orientation function averaged over all molecular segments in the fiber.

Series case:

$$\frac{1}{C^2} = \frac{1 - \overline{\cos^2 \theta}}{C_t^2} + \frac{\overline{\cos^2 \theta}}{C_m^2} \qquad (1a)$$

Parallel case:

$$C^2 = (1 - \overline{\cos^2 \theta})\, C_t^2 + (\overline{\cos^2 \theta})C_m^2 \qquad (1b)$$

Here, C denotes the sonic velocity along a fiber axis; C_t is the sonic velocity for a hypothetical sample in which all molecular segments are transverse to the direction of sound transmission, C_m is the sonic velocity for a hypothetical sample in which all segments are pointed in the direction of sound transmission; and θ is the orientation angle of any segment, i.e., the angle between a segment and the direction of sound transmission (Fig. 1c).

SELECTION OF A REALISTIC EQUATION

In this section, two different approaches are used to examine whether eq. (1a) (series model) or eq. (1b) (parallel model) is the more realistic one. These two approaches involve application of the series and parallel equations to fiber sonic velocity data and consideration of Urick's equation for mixtures.[11,12]

Test of the Series and Parallel Equations by Application of Fiber Sound Velocity Data

It is possible to show that only the series model leads to a realistic result when eqs. (1a) and (1b) are applied to sonic velocity data obtained on fibers. This point was established in the following manner.

The value of $\overline{\cos^2 \theta}$ for a randomly oriented sample can be shown to be $^1/_3$ by the methods outlined by Kennard.[13] Setting $\overline{\cos^2 \theta}$ equal to $^1/_3$ in eqs. (1a) and (1b), we obtain:

Series case

$$1/C_u^2 = (2/3C_t^2) + (1/3C_m^2) \qquad (2a)$$

Parallel case

$$C_u^2 = (2C_t^2/3) + (C_m^2/3) \qquad (2b)$$

where C_u is the sonic velocity in a randomly oriented (unoriented) fiber.

Solving both equations for C_t^2 yields:

Series case

$$C_t^2 = 2C_u^2 C_m^2/(3C_m^2 - C_u^2) \qquad (3a)$$

Parallel case

$$C_t^2 = (3C_u^2 - C_m^2)/2 \qquad (3b)$$

Values of C_t were approximated from fiber sound velocity data, the typical values of C_u in Table I and certain estimates of C_m being used. Two different estimates of C_m were used: (a) the maximum values of velocity commonly encountered in fibers (Table II) and (b) the theoretical maximum value discussed earlier (12–14 km./sec.).

For the series model, eq. (3a), two values of C_t were calculated for each of several polymers (Table III). These two values result from the two estimates used for C_m. It is particularly interesting to note that the value of C_t is virtually insensitive to the estimate chosen for C_m. This point is discussed further in the next section and results from the fact that, when $3C_m^2$ in the denominator of eq. (3a) is much greater than C_u^2, the equation reduces to

$$C_t^2 \doteq 2/3\, C_u^2 \qquad (3c)$$

which is independent of the actual value chosen for C_m.

All values of C_t in Table III are similar to sound velocities commonly encountered in liquids,[7] where the mechanism of sound transmission is largely intermolecular. Since C_t is the velocity characteristic of sound transmission across polymer molecules (Fig. 1), the values in Table III seem reasonable.

TABLE III

	C_t, km./sec.	
Polymer	C_m taken as maximum observed velocity (data of Table II)	C_m taken as 13 km./sec.
Dacron	1.15	1.15
Nylon 66	0.98	0.98
Viscose rayon	1.66	1.64
Orlon	1.76	1.72
X-36	1.66	1.64

On the other hand, eq. (3b), the equation for the parallel model, leads to a physically meaningless result. In order for C_t^2 in eq. (3b) to be positive it is necessary that C_m^2 be less than $3C_u^2$. An examination of the data in Tables I and II show that this condition is not fulfilled. The square of the maximum observed velocity greatly exceeds the quantity $3C_u^2$ in the case of every polymer studied.

In summary, the series case, eq. (3a), leads to a realistic result in which calculated values of C_t approximate values commonly encountered in liquids, whereas the parallel case, eq. (3b), leads to a physically meaningless result.

Consideration of Urick's Equation for Mixtures

Equation (1a) for the series case is analogous to Urick's equation[11,12] which is known to hold for mixtures consisting of solid particles in a fluid medium.

By this analogy, a fiber is considered to be comparable to a dispersion of solid particles in a fluid medium. Various molecular segments with a compressibility K_2 are thought of as particles dispersed in a medium with a compressibility K_1. K_2 is analogous to the intramolecular force constant, and K_1 is analogous to the intermolecular force constant discussed earlier.

Urick's equation[11,12] may be written in the form:

$$1/C^2 = [\rho_2\beta + \rho_1(1 - \beta)][K_2\beta + K_1(1 - \beta)] \quad (4)$$

where C is the sonic velocity of the mixture, ρ_2 and K_2 are the density and volume compressibility, respectively, of the suspended particles; ρ_1 and K_1 are the density and volume compressibility, respectively, of the medium; and β is the volume concentration of particles.

For simplification, eq. (4) may be rewritten as

$$1/\rho C^2 = K_1(1 - \beta) + K_2\beta$$

where

$$\rho = \rho_2\beta + \rho_1(1 - \beta)$$

The particles considered in Urick's equation are implicitly assumed to be randomly oriented in space. If directional properties are given to both the segments and the medium, an argument analogous to that given in the Appendix leads to the result:

$$1/C^2 = (1 - \overline{\cos^2\theta}/C_1^2) + \overline{\cos^2\theta}/C_2^2$$

This is the equation for the series case, eq. (1a), where C_1 is analogous to C_t and C_2 is analogous to C_m.

In the two approaches described above, the series model is consistent with data given in this work for fibers and given by Urick[11,12] for mixtures. The parallel relationship, on the other hand, is inconsistent with the data.

SIMPLIFICATION OF THE SERIES EQUATION

In Figure 2, $\overline{\cos^2\theta}$ is plotted against sound velocity from eq. (1a) for C_m values of 7 km./sec. (approximate maximum value observed, Table II), 12 km./sec. (approximate maximum calculated from bond force constants), and infinity. In all cases C_t was taken to be 1.0 km./sec., which is near the calculated values of Table III. From the similarity of the curves in Figure 2, it is concluded that values of $\overline{\cos^2\theta}$ calculated from eq. (1a) are not sensitive to variations in C_m above 12 km./sec. That is, for any measured value of velocity, approximately the same $\overline{\cos^2\theta}$ will be calculated, regardless of whether C_m is taken as 12 km./sec. or infinity.

On the basis of the above consideration, C_m values are conveniently taken as infinity, and the reciprocal of C_m^2 in eq. (1a) is taken as zero. The calculations from which Figure 2 was constructed
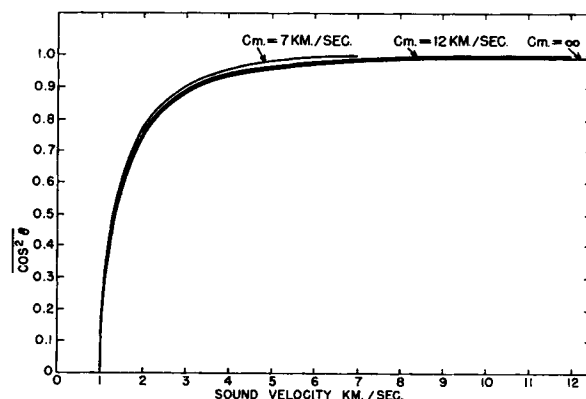

Fig. 2. Theoretical relationship between $\overline{\cos^2\theta}$ and sound velocity for series case.

show that this would lead to an error of about 0.01 in $\overline{\cos^2 \theta}$ at values of $\overline{\cos^2 \theta}$ greater than 0.98. Thus, for a perfectly oriented sample, a value of about 0.99 would be calculated for $\overline{\cos^2 \theta}$ if C_m were assumed to be infinity. Thus, eq. (1a) reduces to

$$C_t^2/C^2 = 1 - \overline{\cos^2 \theta} \qquad (5)$$

As mentioned earlier, the value of $\overline{\cos^2 \theta}$ for a randomly oriented sample is $^1/_3$. Substitution of this value into eq. (5) yields

$$C_t^2 = 2C_u^2/3 \qquad (6)$$

where C_u is the sonic velocity for an unoriented sample. (Values are listed in Table I.) Eliminating C_t between eqs. (5) and (6), one obtains

$$\overline{\cos^2 \theta} = 1 - (2C_u^2/3C^2) \qquad (7)$$

This is the final simplified equation that results from the series model. This equation may be used to calculate $\overline{\cos^2 \theta}$ from the two experimental quantities, C_u and C.

TYPICAL BEHAVIOR OF FIBER MOLECULAR ORIENTATION DURING STRETCHING

As discussed in a later section, the sound velocity of yarns was measured continuously while they were stretched. From these data and from the velocity of an unoriented specimen, a continuous plot of $\overline{\cos^2 \theta}$ versus yarn elongation was made with the use of eq. (7). Figure 3 is a plot of $\overline{\cos^2 \theta}$ versus yarn elongation for an undrawn nylon 66 yarn. Plots for drawn yarns are given in Figures 4 and 5. The value of $\overline{\cos^2 \theta}$ is $^1/_3$ for the unoriented yarn before stretching but is higher for the drawn yarns, indicating that the latter have been oriented by the drawing operation. As both the undrawn and drawn yarns were stretched, the value of $\overline{\cos^2 \theta}$ increased.
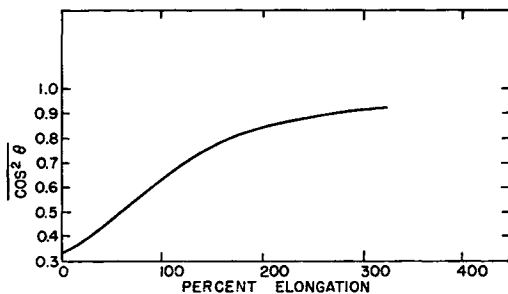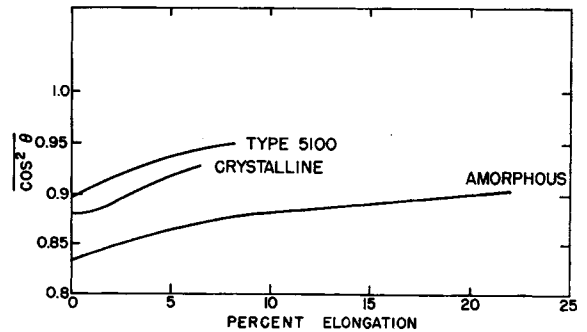
Fig. 4. Plot of $\overline{\cos^2 \theta}$ vs. elongation for drawn polyethylene terephthalate fibers.

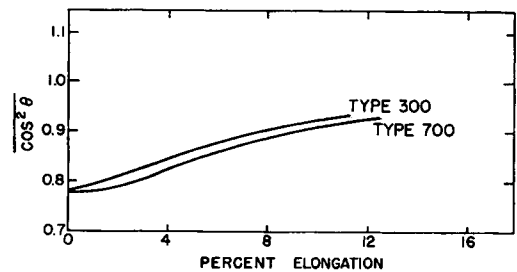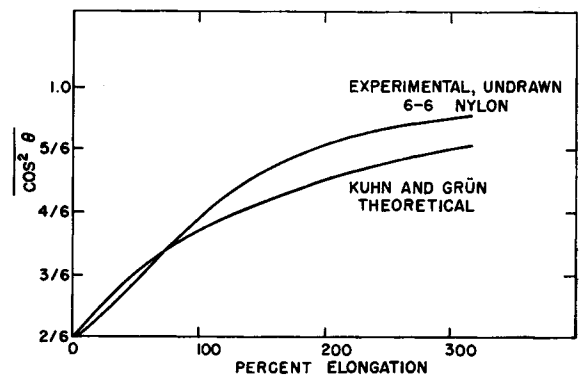Fig. 5. Plot of $\overline{\cos^2 \theta}$ vs. elongation for drawn nylon 66 fibers.

Fig. 6. Theoretical and experimental relationship between $\cos^2 \theta$ and elongation.

It seems instructive to compare the shape of the $\overline{\cos^2 \theta}$ vs. yarn elongation curve with a theoretical curve derived by Kuhn and Grün[14] for crystallite orientation. The Kuhn and Grün development amounts to a mathematical transformation leading to a relationship between $\overline{\cos^2 \theta}$ and yarn elongation. The development, as discussed by Kuhn and Grün, is for crystallite orientation. However, it is not unreasonable to expect a completely analogous behavior for total molecular orientation in the case of glasslike polymers, i.e., for measurements below the glass transition temperature.

Fig 3. Plot of $\overline{\cos^2 \theta}$ vs. elongation for undrawn nylon 66 fiber.

In Figure 6, the Kuhn and Grün curve is compared to the experimental curve for an undrawn nylon 66 yarn. The two curves are similar in shape, even though there are certain real differences at high elongations. Actually, Kuhn and Grün predicted that such deviations might occur at high extensions.

SELECTION OF AN ORIENTATION FUNCTION

As discussed earlier and in the Appendix, the value of $\overline{\cos^2 \theta}$ varies from one-third for a randomly oriented material to unity for a theoretically perfectly oriented sample. For purposes of convenience, an orientation parameter α has been selected which will vary from zero to unity as $\overline{\cos^2 \theta}$ varies from one-third to unity. This parameter is identical to Hermans' orientation factor[5,6] and is defined as

$$\alpha = (3 \overline{\cos^2 \theta} - 1)/2 \qquad (8)$$

α is termed the total molecular orientation. As mentioned earlier, the term *total* is used to indicate that the measured orientation is an average for all molecular segments, both crystalline and amorphous.

Next, $\overline{\cos^2 \theta}$ is eliminated between eqs. (7) and (8); this yields

$$\alpha = 1 - (C_u^2/C^2) \qquad (9)$$

For a theoretically completely oriented sample, the value of C^2 will be finite, and α will not be unity. This discrepancy results from the assumption that C_m is infinite. As discussed earlier, calculated values of C_m range from 12 to 14 km./sec. Substitution of these values for C in eq. (9) and the use of reasonable values of C_u (Table I) yields a calculated value of α of 0.97–0.99, instead of unity, for a completely oriented sample. However, the error in α due to this assumption is less than 0.01 for values of α less than about 0.90.

As discussed by Charch and Moseley,[4] the sonic modulus in units of grams per denier is directly proportional to the square of the sonic velocity and is given by

$$E = 11.3C^2 \qquad (10)$$

where C is in units of kilometers per second. Substitution into eq. (9) yields

$$\alpha = 1 - E_u/E \qquad (11)$$

where E_u is the sonic modulus of an unoriented specimen.

Equation (11) provides a basis for quantitative structure–property studies. In this equation a fundamental structural parameter, orientation, is related to a common mechanical property, modulus.

APPARATUS FOR MEASURING SOUND VELOCITY

In practice, yarns and film strips are held in contact with two piezoelectric crystals which are Rochelle salt twister bimorphs (Fig. 7). Pulses of sonic energy are sent from one bimorph (transmitter) down the yarn to the receiving bimorph and the time of travel measured. The sound velocity is computed from the pulse travel time and the distance between the bimorphs.
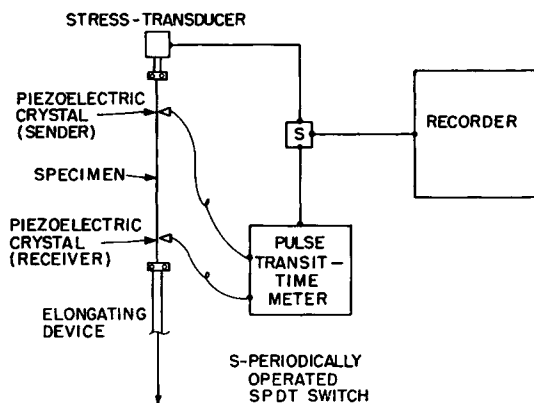

Fig. 7. Schematic of apparatus for measuring stress and pulse time during stress–strain tests.

The pulse apparatus is used to shock excite the transmitting bimorph into oscillation at its natural frequency of 10 kcycles/sec. These pulses occur at a rate of 160/sec., and the pulse travel time is measured continuously by the instrument. This apparatus (Pulse Propagation Meter) was manufactured by the Jenszen Laboratories (69 Harvey Street, Cambridge 40, Massachusetts) and has been described by Hamburger.[15]

This technique of measuring sound velocity is essentially instantaneous and continuous. In the present work, the method was used to determine changes in sound velocity during conventional yarn stress–strain tests[15] and to measure sound velocity as a function of distance along the length of yarns during windup. These applications are discussed in a later section.

DETERMINATION OF SOUND VELOCITY IN UNORIENTED MATERIALS

Selection of an Unoriented Sample

The sound velocity C_u characteristic of an unoriented polymer may be determined on either an unoriented film strip or fiber. It has been found that fibers, in general, can be more easily manipulated than film strips. Unfortunately, "as-spun" fibers may possess a small amount of spin orientation which will lead to an incorrect value of C_u. Consequently, before C_u is determined on an as-spun fiber, it is advisable to examine it for any possible orientation by x-ray,[6,16,17] birefringence, or other suitable measurements.

If a film strip is used to determine C_u, it is also necessary to exercise care to prevent orientation from being developed during the sample preparation. If the film is cast from a solvent, the solution should be poured slowly onto an evaporating plate, and no casting knife should be used to smooth the surface. Excessive shearing forces (e.g., from the use of a casting knife) are believed to introduce small amounts of orientation. It is not necessary to obtain a film of uniform thickness since the sound velocity measurement is not dependent on the sample cross section.

Polymers with More than one Value of C_u

Fibers and film strips from some unoriented polymers show little change in sonic velocity when they are strained up to 1–2%. Then, at higher extensions the sonic velocity increases, and this increase is taken as evidence of an increase in molecular orientation. In such cases, the sonic velocity near zero strain is the proper value of C_u to use in eq. (9) for calculating the molecular orientation α.

In certain cases, however, the sonic velocity has been observed to decrease by a small amount during the initial straining until a minimum value is reached. This small decrease is actually predicted by the theory of elasticity.[18] Calculations made in this laboratory have indicated that the observed decrease can be accounted for entirely by the theory of elasticity, and that little or no orientation occurs before the minimum velocity is reached. After the minimum, samples have been observed to orient as evidenced by an increase in velocity and by x-ray diffraction measurements.

It is to be emphasized that the total decrease in sound velocity before the minimum is extremely small in comparison to the increase after the minimum. In the present work, the minimum value of the sound velocity has been selected for calculating the molecular orientation.

APPLICATIONS

There are at least two applications in which orientation measurements by sound velocity have a considerable advantage over conventional techniques. These are (a) the continuous measurement of orientation during a stress–strain test performed at ordinary testing rates and (b) the rapid continuous measurement of uniformity of orientation along the length of a yarn during windup. Typical results of each of these measurements are discussed below.

Continuous Measurement of Orientation During Conventional Stress–Strain Tests

Samples were held between two sets of yarn clamps (Fig. 7). The top clamp was attached to a Statham strain gauge, (manufactured by Statham Laboratories, Inc., 12401 West Olympic Boulevard, Los Angeles 64, California), while the bottom clamp was moved downward at a uniform speed. The output of the strain gauge was used to determine tension, while the output of the pulse apparatus was used to determine sound velocity. The data given earlier in Figures 3–6 were calculated from sound velocities measured in this way.

In the present work, the output of the Statham strain gauge and the output of the pulse apparatus were sent alternately (every 2–4 sec.) to a single Brown electronic recorder to give an intermittent
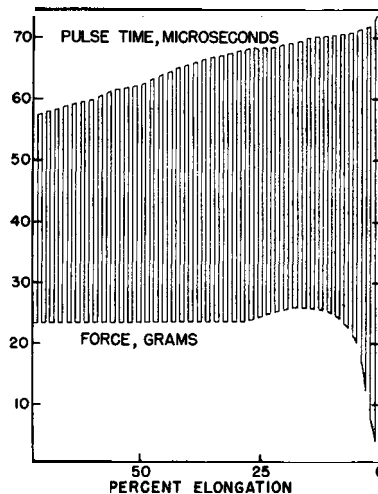

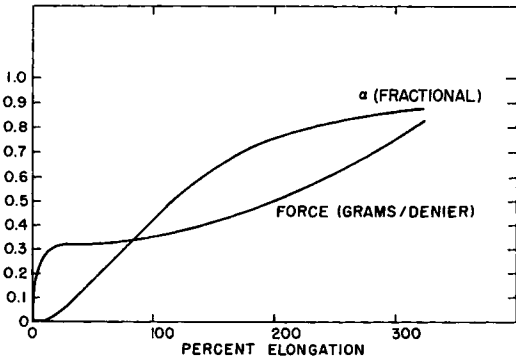Fig. 8. Simultaneous measurements of force and pulse time.

Fig. 9. Force–elongation and orientation–elongation curves for undrawn nylon 66.

measurement of force and pulse time. A tracing of a typical recorder chart is shown in Figure 8.

From these data the tension, in grams per denier, and the orientation α were computed and plotted against the percent elongation (Fig. 9). It is interesting to note that the orientation gradually increases during the stress–strain test and that the slope (orientation efficiency, $d\alpha/de$) decreases at increasing elongations.

Similar data in Figures 4 and 5 for initially oriented yarns show that the orientation change occurring during the stress–strain test is an appreciable portion of the total orientation at break. In some cases the orientation at break reaches very high values, greater than 0.90.

These data were obtained with a minimum of difficulty and have proved to be of great value in studying the molecular processes which occur during the mechanical deformation of fibers. This method of determining orientation during

stretching operations is virtually an instantaneous method which can be conducted without interrupting the stretching process.

Measurement of Uniformity of Orientation Along the Length of Yarns

The uniformity of orientation along the length of yarns was studied by passing them over two bimorphs held 4 in. apart (Fig. 10). A yarn sample was taken from a bobbin through a tension gate, across two bimorphs, through a second tension gate, and finally onto a windup. The sample length in contact with the bimorph was held under a constant small tension and the yarn was wound up at a constant rate of about 2 ft./min. The output of the pulse apparatus was sent to a
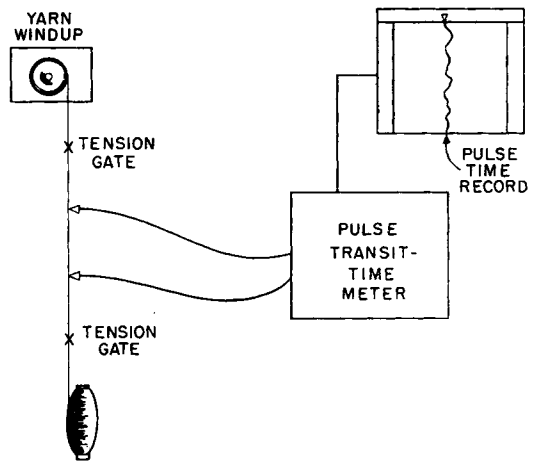

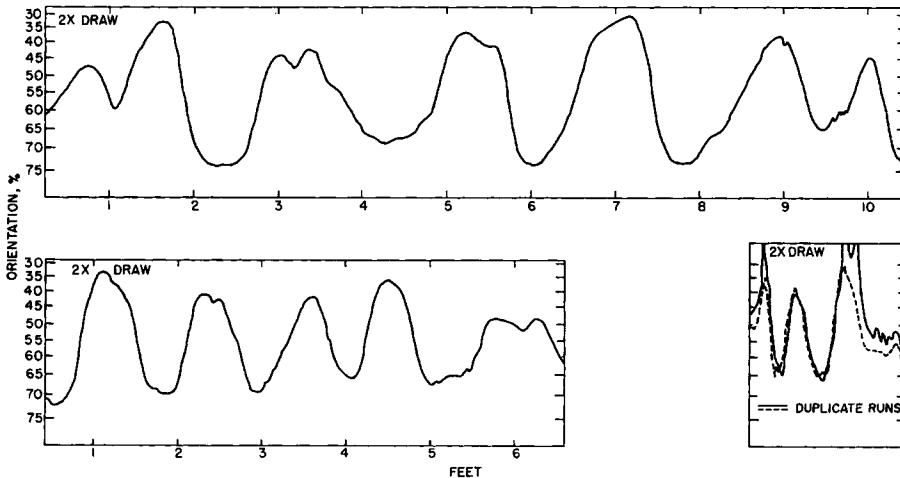Fig. 10. Schematic of apparatus for measuring orientation uniformity.

Fig. 11. Large variations in orientation: experimental polyacrylonitrile yarn, drawn to a draw ratio of 2.0.
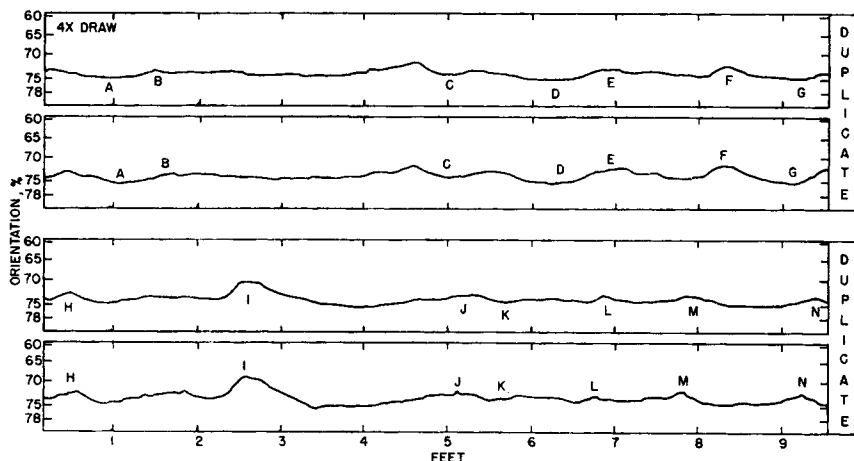
Fig. 12. Small variations in orientation: experimental polyacrylonitrile yarn, drawn to a draw ratio of 4.0.

Brown electronic recorder to give a plot of pulse time against position along the length of the yarn.

Results are given in Figures 11 and 12 for measurements on experimental yarns made from acrylonitrile polymer. These figures are tracings of a Brown electronic recorder chart, and the ordinate is linear in the pulse time for a 4-in. separation between the piezoelectric crystals. The pulse time values were converted to molecular orientation, and a per cent molecular orientation scale was superimposed, i.e., a scale of 100α. This orientation scale will not change so long as one works with the same polymer at a given temperature, and so long as the distance between the piezoelectric crystals is kept constant. Finally the abscissa in Figures 11 and 12 is the length of yarn wound up at any time during the experiment.

One of the advantages of this method is that orientation and orientation nonuniformity resulting from process variables may be easily and rapidly followed. Figure 11 illustrates some large variations in an experimental yarn drawn to a draw ratio of 2.0. Figure 12 illustrates smaller variations in a sample drawn to a draw ratio of 4. As suggested in each figure, duplicate runs were made on the same piece of yarn to establish the reproducibility. In Figure 12 the letters A through N indicate corresponding positions in the duplicate runs.

COMPARISON WITH X-RAY ORIENTATION MEASUREMENTS

As mentioned earlier, the orientation parameter calculated from sound velocity, is taken to be a measure of the *total* molecular orientation as contrasted with *crystalline* orientation and *amorphous* orientation. On the other hand, the usual orientation parameter determined by x-ray measurements on crystalline samples is a measure of the crystallite orientation alone.[6,16,17]

There is a further difference in sampling. The usual technique for x-ray diffraction measurements samples different short lengths along a yarn, whereas in the acoustic technique, a continuous yarn length is measured.

TABLE IV
X-Ray and Acoustic Measures of Orientation

Sample	X-ray orientation angle $\overline{OA}$, degrees		Fractional molecular orientation α (by acoustic measurement)	Range in α (where α varies along yarn length)
	Inner[a]	Outer[a]		
Type 300 nylon 66				
0% strain	15 ± 1	16	0.78	
5% strain	11	12–13	0.89	
10% strain	11	12	0.94	
13% strain	10	11	0.95	
Yarns from experimental acrylonitrile polymer				
1× draw	120 ± 10		0.0	
2× draw	40 ± 2		0.59	0.35–0.73
4× draw	25 ± 1		0.74	0.69–0.75
5× draw	21 ± 1		0.78	0.77–0.80
6× draw	18 ± 1		0.80	0.80–0.81
8× draw	20 ± 1		0.83	0.82–0.84

[a] From inner and outer diffraction rings on x-ray diagram.

Even though these differences exist, large increases in draw ratio are expected to produce an increase in orientation as measured by any suitable technique. In Table IV, both acoustic and x-ray orientation parameters (α and $\overline{OA}$) are tabulated for vzrious values of draw ratio for experimental yarns from acrylonitrile polymer. The x-ray orientation angle $\overline{OA}$ ranges from 180 degrees to nearly zero and decreases with increasing orientation. In cases where the sample was nonuniform, a range was recorded for α.

The same parameters are given for Type 300 nylon 66 strained to various elongations. A more detailed comparison between acoustic and x-ray diffraction data is given by Charch and Moseley.[4]

As expected, the values of α in Table IV increase and $\overline{OA}$ decreases with increasing draw ratio or elongation. Both changes indicate an increase in orientation at higher draw ratios.

APPENDIX

The orientation of any molecular segment is described by the cosine of the orientation angle of the segment, defined as the angle between the segment and the fiber axis. In this work, it is assumed that the force constant for deforming a segment in the direction of the fiber axis is principally determined by the cosine of the orientation angle and two force constants: (a) an intramolecular force constant for a motion along the length of the molecular segment and (b) and intermolecular force constant for a motion perpendicular to the length of a molecular segment.

An expression relating these quantities can be developed by making one of two extreme assumptions. These are discussed in the text and stem from (a) a series weighting of the molecular and intermolecular force constants (b) a parallel weighting.

I. Series Case

A. Equation for Fiber Force Constant

A series addition of the molecular intermolecular force constants for a single segment leads to the expression:

$$1/K_j = \frac{1 - \cos^2 \theta_j}{2K_t} + \frac{\cos^2 \theta_j}{K_m} \qquad (12)$$

where K_j is the force constant in the direction of the fiber axis for the jth molecular segment; θ_j is the angle between the fiber axis and the jth segment; and K_t and K_m are the force constants

for motion across and along any segment, respectively. The occurrence of the factor of 2 in the above expression results from the assumption that molecular segments are cylindrically symmetrical.

Averaging $1/K_j$ over all segments leads to the expression:

$$1/K = \frac{1 - \overline{\cos^2 \theta}}{2K_t} + \frac{\overline{\cos^2 \theta}}{K_m} \qquad (13)$$

where K is the force constant for a group of segments with an average orientation characterized by $\overline{\cos^2 \theta}$.

B. Equation for Fiber Modulus

The $1/K$ term in eq. (13) represents a sample with an orientation characterized by $\overline{\cos^2 \theta}$. In contrast, the two terms on the right-hand side of the equation contain force constants characteristic of completely deoriented and completely oriented samples, respectively.

The force constants in eq. (13) may be taken as proportional to corresponding moduli, where the units of modulus are forced per unit linear density (or grams/denier). This restriction on the units of modulus is necessary so that different fibers are compared on the basis of equal number of molecules passing through the fiber cross section rather than on the basis of equal cross-sectional area. Thus:

$$1/E = \frac{1 - \overline{\cos^2 \theta}}{E_t} + \frac{\overline{\cos^2 \theta}}{E_m} \qquad (14)$$

where E is the fiber modulus in units of grams per denier, and E_t and E_m are the moduli of a hypothetical fibers in which all molecules are pointed across and along the fiber axis, respectively.

C. Equation for Sonic Velocity

As discussed by Ballou and Silverman,[1] the sonic modulus of a long, thin, rodlike specimen (e.g., a fiber) is related to the sound velocity by the equation:

$$E = \rho C^2 \qquad (15)$$

where E is the modulus in units of force per unit cross-sectional area, ρ is the volume density, and C is the sound velocity.

If E is expressed in units of force per unit linear density (e.g., grams/denier) the equation becomes:

$$E = kC^2 \qquad (16)$$

where k is a universal constant, dependent only on the units of E and C. Substitution of eq. (16) into eq. (14) yields

$$1/C^2 = \frac{1 - \overline{\cos^2 \theta}}{C_t^2} + \frac{\overline{\cos^2 \theta}}{C_m^2} \qquad (17)$$

which is eq. (1a) in the text.

II. Parallel Case

With the use of the definitions and relations developed for the series case, a parallel addition of molecular and intermolecular force constants leads to the expression:

$$K_j = (1 - \cos^2\theta_j)2K_t + (\cos^2\theta_j)K_m \qquad (18)$$

Averaging over all segments in the sample, one obtains

$$K = (1 - \overline{\cos^2 \theta})2K_t + (\overline{\cos^2 \theta})K_m \qquad (19)$$

Conversion first to moduli and then to velocities yields

$$C^2 = (1 - \overline{\cos^2 \theta})C_t^2 + (\overline{\cos^2 \theta})C_m^2 \qquad (20)$$

which is eq. (1b) in the text.

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Synopsis

In the present work, the sound velocity in polymeric fibers or film strips is related to a quantitative measure of molecular orientation in the sample. It is shown that this measure of orientation can be calculated from two experimental quantities: the sound velocity in an oriented specimen and the velocity in a randomly oriented sample. Both the oriented and unoriented samples must have the same chemical composition, and both measurements must be made at the same temperature, below the glass transition temperature, T_g. Sound velocities were measured by a pulse technique. This method permitted a continuous measurement of orientation changes during conventional stress-strain tests without interrupting the tests. In addition, the uniformity of orientation along the length of fibers was measured continuously during windup. Examples of these applications are given, and a comparison is drawn between acoustic and x-ray measures of orientation.

Résumé

Dans le présent travail la vitesse sonique dans les fibres ou lamelles de films de polymére a été reliée à une mesure quantitative de l'orientation moléculaire dans l'échantillon. Il est démontré que cette mesure de l'orientation peut être calculée au départ de deux grandeurs expérimentales: la vitesse sonique dans un spécimen orienté et la vitesse dans un spécimen orienté au hasard. La composition chimique des échantillons orientés et non-orientés doit être identique et le deux mesures doivent être effectuées à une même température, inférieure à la température de transition vitreuse, T_g. Les vitesses soniques ont été mesurées par une technique à impulsions. Cette méthode permet une mesure continue des variations d'orientation durant des tests tension-élongation conventionnels sans interrompre ceux-ci. De plus l'uniformité de l'orientation le long des fibres a été mesurée en continu durant le filage. Des exemples de ces applications sont donnés et une comparaison est faite entre les mesures d'orientation acoustiques et roentgenographiques.

Zusammenfassung

In der vorliegenden Mitteilung wird die Schallgeschwindigkeit in polymeren Fasern oder Filmstreifen zu einer Grösse in Beziehung gesetzt, die ein quantitatives Mass für die molekulare Orientierung in der Probe bildet. Es wird gezeigt, dass diese Orientierungsgrösse aus zwei experimentellen Grössen berechnet werden kann: aus der Schallgeschwindigkeit in einer orientierten Probe und aus der Geschwindigkeit in einer Probe mit statistisch verteilter Orientierung. Die orientierte und die nichtorientierte Probe müssen beide die gleiche chemische Zusammensetzung haben und beide Messungen müssen bei der gleichen Temperatur, unterhalb der Glasumwandlungstemperatur, T_g, ausgeführt werden. Schallgeschwindigkeiten wurden nach einer Impulsemethode gemessen. Diese Methode erlaubte eine kontinuierliche Messung der Orientierungsänderungen während der normalen Spannungs-Dehnungsbestimmungen ohne diese unterbrechen zu müssen. Ausserdem wurde die Einheitlichkeit der Orientierung entlang dem Faden während des Spannens gemessen. Anwendungsbeispiele werden mitgeteilt und ein Vergleich zwischen der akustischen und der Röntgenstrahl-messung der Orientierung gezogen.