JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 2399-2425 (1964)

Influence of Melt Spinning Variables on the Tensile Properties of High Density Polyethylene Fibers*

T. D. HIGGINS and G. M. BRYANT, *Union Carbide Chemicals Division, Research and Development Department, South Charleston, West Virginia*

Synopsis

The tenacity and stiffness modulus of yarns melt-spun from high density polyethylene are functions of the sum of the logarithm of the take-up velocity in melt drawing and the true (logarithmic) deformation imparted in the cold-drawing process (i.e., stretching at a temperature below the polymer melting temperature). Thus, for the conditions investigated the effective melt drawing deformation is independent of the calculated velocity of the melt in the spinneret orifices. The maximum cold draw ratio is shown to be a function of the production rate, increasing to a maximum value and then decreasing as the production rate is increased. The maximum cold draw ratio at a given production rate is found to be a function of the yarn temperature and the deformation introduced in melt drawing. The tenacity and stiffness modulus of yarns melt-spun from polypropylene may also be expressed as functions of the summation of the logarithm of the take-up velocity of melt drawing and the true deformation imparted in cold drawing. The orientation, as measured by birefringence, of yarns spun from an experimental polyester are a function of the ratio of the take-up velocity and the orifice velocity, whereas the same measurement of the orientation of polyethylene is a function of the extrusion velocity alone. Equations of state for the tenacity and stiffness modulus of melt-spun polyethylene yarns were found to be of the same form as for a wet-spun modacrylic fiber.

INTRODUCTION

Among the family of natural fibers, the properties of a particular fiber class can be attributed primarily to its chemical structure. Although variations in morphological features such as molecular orientation and crystallinity have been observed within a particular chemical type, and can be correlated with fiber properties, it has not been possible to control these factors very effectively.

With the advent of man-made fibers, it became possible to control the morphological structure and hence the properties of fibers through the variables of the spinning process. A number of papers have been written describing the effects of processing variables on the properties of polyamide[1-9] and poly(ethylene terephthalate)[10-14] fibers; however, there is apparently little if any literature pertaining to the effect of processing variables on the properties of polyethylene fibers.

* Paper presented at the Spring meeting of the Fiber Society, Charlottesville, Va., May 10, 1963.

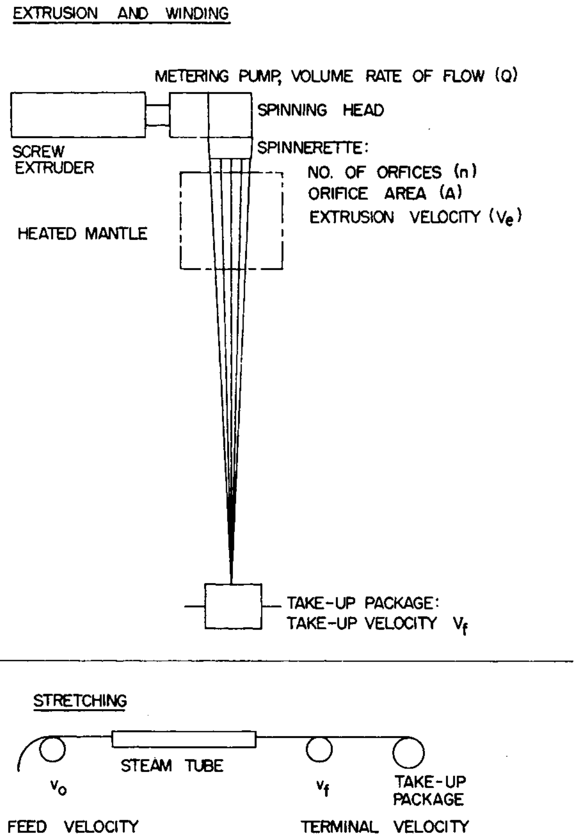

Fig. 1. Schematic diagram of melt-spinning and steam-stretching process.

The present paper reports the influence of nine melt-spinning variables on the properties of high density polyethylene fibers. The ethylene polymer employed throughout the major portion of this work was a high density resin with a melt index of 5.5 dg./min. at 190°C., corresponding to a weight-average molecular weight of about 50,000.

The objectives of the melt-spinning process are to reshape the raw material and modify its molecular structure to give a more or less highly oriented continuous filament textile yarn (Fig. 1). The polyethylene spinning process to be discussed consists of two steps: (*1*) extrusion and winding, followed by (*2*) stretching. In the extrusion-winding step, polymer chips are fed to the barrel of a screw extruder and are melted; the melt is transported to the spinning head by means of a metering pump and is forced through a plate containing a multiplicity of orifices to form filaments. The filaments leave the orifices with a velocity (V_e) which is directly proportional to the volume rate of flow of the melt (Q), and inversely proportional to the product of the number of orifices (n) and the orifice area (A). The cooling rate of the filaments emerging from the spinneret may be decreased by encircling the thread line with a heated mantle or accelerated by a directed air flow. The amount of draw-down from the melt is governed by the velocity of the take-up package (V_f).

In the stretching step, the denier of the filaments is reduced further, and the molecules of the polymer are oriented. In the present polyolefin stretching process, attenuation and orientation is accomplished by drawing the yarn in an atmosphere of steam. The amount of attenuation may be expressed by the ratio of the output and the feed velocities of the stretching process; this ratio is termed the stretch ratio. No effort is made to localize the point at which the yarn stretches.

RESULTS AND DISCUSSION

Melt Spinning of Polyethylene

True Stress–True Strain Concept

An initial investigation was conducted to determine the effect of the stretch ratio on the strength of polyethylene fibers. It was noted that the breaking stress increased with increasing stretch ratio. As shown in Figure 2, it was also observed that stress-strain curves for yarns stretched to low stretch ratios were characterized by a yielding at high stress, that is, by the stress passing through a maximum with increasing strain. The strain at which the maximum occurred decreased with increasing stretch ratio. Tensile tests on single filaments demonstrated that, in general, highly stretched filaments also "yield" before breaking. The yield strain for these fibers occurred at a stress level essentially equal to the apparent ultimate strength of the yarn.

The ultimate strength of the yarn is defined as the maximum stress exhibited in the stress–strain curve. The ultimate elongation is defined as the elongation at which the stress passes through a maximum.

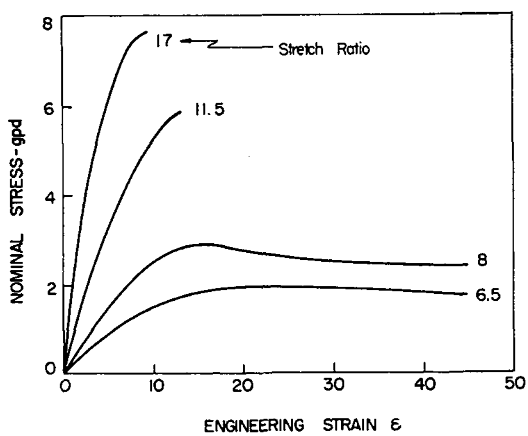

Fig. 2. Stress–strain curves for yarns of various stretch ratios.

In a conventional textile evaluation of tensile properties, one measures the ultimate stress based on the cross-sectional area or denier of the unstrained specimen. In the present case, where the ultimate strengths of materials having a wide range of ultimate elongations are to be compared, it is preferable to use the true stress, that is the stress calculated from the actual denier or area at a given level of strain.

The difference between conventional tenacity and true tenacity based on the instantaneous denier during tensile testing may be seen in Figure 3.

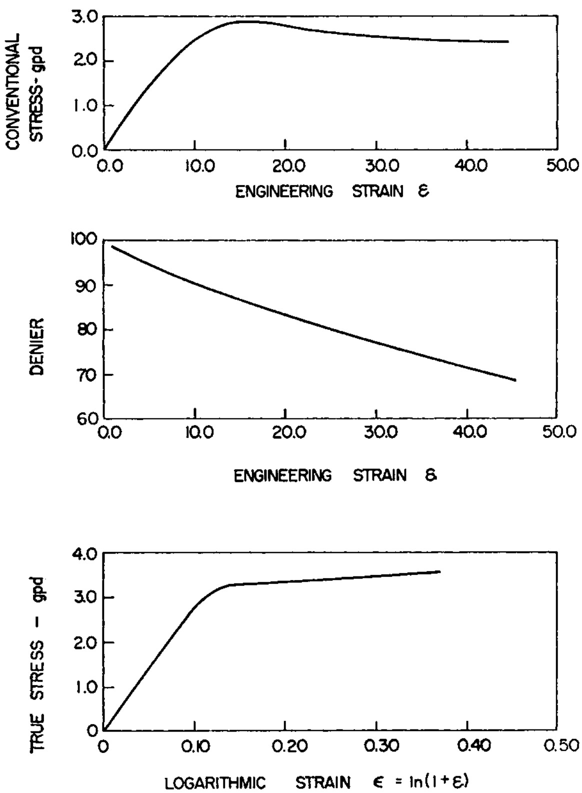

Fig. 3. Contrast of conventional and true stress.

The conventional stress, calculated from the denier of the fiber prior to testing, increases to a maximum and then decreases. However, the denier decreases continuously with increasing strain so that in contrast to conventional stress, the true stress increases to the point of rupture.

It was found that, for the range of stretches studied, the true tenacity equivalent of the maximum conventional stress was a linear function of the natural logarithm of the steam stretch ratio *d*. The natural logarithm of an extension ratio is called natural strain or true strain. It is the sum of all the strain increments of deformation, referred to the initial unstrained state (l_i).

$$\epsilon = \int_{l_i}^{l} dl/l = \ln (l/l_i) \qquad (1)$$

The phenomenon of the linear increase in true tenacity with increasing true strain of stretching polyethylene yarns might be considered to be analogous to that discovered by Bridgman[15] in his studies of the effect of tensile strain on metals subjected simultaneously to intense hydrostatic pressure. His investigation demonstrated that, when expressed as true stress, the ultimate strength of metals is a linear function of the logarithm of the tensile prestraining from the isotropic state.

In the example at hand the isotropic length (l_0) was not known. The material had been deformed in the melt spinning process. However, the integral of eq. (1) can be split into two parts: the first representing the deformation imparted in spinning, the second representing the deformation imparted by the stretching process.

$$\epsilon_T = \int_{l_0}^{l_s} dl/l + \int_{l_s}^{l_d} dl/l \qquad (2)$$

$$= \ln (l_s/l_0) + \ln (l_d/l_s) \qquad (3)$$

$$= \epsilon_s + \epsilon_d \qquad (4)$$

In these equations ϵ_T is the total true prestrain to which the material has been subjected before tensile testing, l_0 is the length of the isotropic material, l_s is the length after spinning, l_d is the length after cold drawing, ϵ_s is the true strain of spinning, and ϵ_d is the true strain of stretching.

The length before drawing is equal to the product of the input velocity (v_0) and time; the length after drawing (stretching) is equal to the product of the terminal velocity of drawing (v_f) and time. Therefore, the true strain of stretching may be expressed as a function of the ratio of the take-up velocity to the input velocity of drawing.

$$\epsilon_d = \ln (v_f/v_0) \qquad (5)$$

This expression ignores the fact that the actual yarn stretch is somewhat less than the amount indicated by the ratio of the velocities. Release of tension after stretching results in a decrease in the length and an increase in the diameter of the filaments of the yarn. In the process studied this effect was found to be small.

If melt drawing is considered to be an analogue of the cold draw in the stretching process, one may write for the true deformation of spinning:

$$\epsilon_S = \ln (V_f/V_0) \qquad (6)$$

where V_f is the take-up velocity of the spinning process and V_0 is the velocity of the extrudate at the point at which melt drawing commences.

Polyethylene Spinning Experiments

A series of yarns were spun and stretched to determine how the tensile properties of stretched yarns are influenced by the extrusion and take-up velocities of spinning. The spinning conditions are listed in Table I. One will note that the yarns spun in this study were produced under two conditions: first, at constant melt draw V_f/V_e and constant spun yarn denier but increasing productivity $\dot{m}$ and extrusion velocity V_e; second, at constant extrusion velocity and productivity but decreasing spun yarn denier and

TABLE I
Spinning Conditions, Polyethylene Spinning Experiments[a]

Spun yarn no.	Yarn denier $\propto \dot{m}/V_f$	Melt draw ratio V_f/V_e	Extrusion velocity $V_e(=\dot{m}/\rho nA)$, ft./min.	Take-up velocity, V_f, ft./min.	Productivity $\dot{m}$, g./min.
1	800	100	12	1200	32
2	800	100	18	1800	48
3	800	100	24	2400	64
4	1600	50	12	600	32
5	530	150	12	1800	32
6	400	200	12	2400	32

[a] Processing variables held constant: spinning temperature, 290°C.; spinneret 15/.040 in. D, $L/D = 15$; mantle temperature, 290°C.

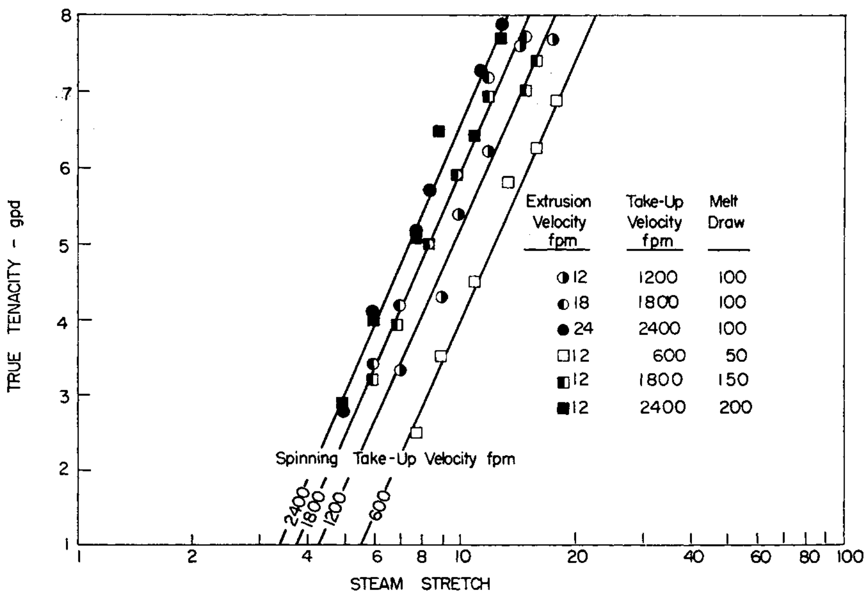

Fig. 4. True tenacity as a function of true strain of steam stretching and take-up velocity of spinning.

increasing melt draw ratio. The number of orifices n and the area of the spinning orifices A were constant in both cases.

Tenacity, Function of Total Prestrain. The tenacities of yarns stretched from the yarns spun in this study are plotted in Figure 4 versus the true strain of stretching. The true tenacity of a yarn stretched from a given

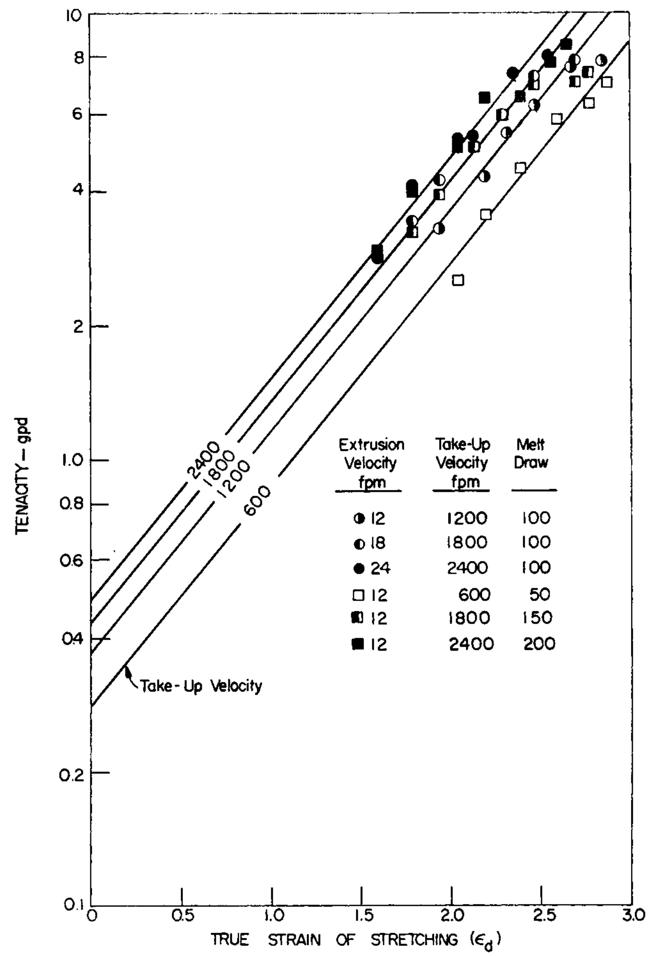

Fig. 5. Logarithm of true tenacity as a function of true strain of stretching and take-up velocity of spinning.

spun yarn increases linearly with increasing true strain of stretching. However, the level of tenacity realized from a particular amount of stretching is also a function of some other variable. Inspection of the symbols in the legend and the family of curves in Figure 4 reveals that for any particular degree of cold drawing, tenacity varies with the take-up velocity, regardless of the value of the nominal melt draw ratio or orifice velocity.

Figure 4 also suggests that the phenomenon studied may not be analogous to that studied by Bridgman,[15] in that the tenacity intercept values for the condition $d = 1$ are all negative. Furthermore, the linearity exhibited is perhaps fortuitous. Highly stretched yarns were observed to be "blushed," that is, they were opaque due to the presence of voids. One would expect that voids would reduce the apparent strength of the material.

Negative values of strength at $d = l(\epsilon_d = 0)$ may be avoided by plotting the logarithm of true tenacity versus the true strain of cold drawing (Fig. 5). This manner of plotting the data yields reasonable values of tenacity (0.3–0.5 g./den.) for the condition $\epsilon_d = 0$. It also implies that the strength of a highly drawn, nonvoided yarn would be greater than that of a yarn drawn to the same degree but blushed. The experimental strength of a highly drawn yarn is seen in Figure 5 to be less than that predicted by the curve for the velocity at which it was spun.

Figure 4 suggests that an equation of state for the tensile strength of polyethylene yarns should have the form

$$\sigma = C_1 + C_2\epsilon_d + f_1(V) \tag{7}$$

whereas Figure 5 suggests that the form should be

$$\ln \sigma = C_3 + C_4\epsilon_d + f_2(V) \tag{8}$$

where σ is the true tenacity and the C_i are constants.

TABLE II

Tenacity of Yarns of Low Draw Predicted by Models of Eqs. (9) and (10)

		True tenacity predicted, g./den.			
Stretch ratio	Observed	Eq. (9)	95% Confidence limits[a]	Eq. (10)	95% Confidence limits[b]
1.60	0.60	−3.22	−3.83 to −2.61	0.83	0.74 to 0.94
2.12	0.80	−1.72	−2.33 to −1.11	1.15	1.00 to 1.29

[a] Based on a standard deviation of 0.306 g./den. with 30 degrees of freedom.

[b] Based on a standard deviation of ln(1.062695) with 30 degrees of freedom.

Constants and the form of $f(V)$ to fit eqs. (7) and (8) to the experimental data were obtained by multiple regression analysis. The data represented by the eight points which deviated from their expected positions in Figure 5 were not utilized in the regression analysis.

$$\sigma = 5.32\ (\epsilon_d + 0.32 \ln V_f - 3.60) \tag{9}$$

$$\ln \sigma = -3.8241 + 1.139\epsilon_d + 0.3988 \ln V_f \tag{10}$$

$$\sigma = 0.022 \exp \{1.139\epsilon_d + 0.399 \ln V_f\} \tag{11}$$

Both the linear model [equation of state eq. (9)] and the exponential model [eq. (10) or (11)] represent the data equally well, in that both account for 97% of the variation in the experimental data. A choice between

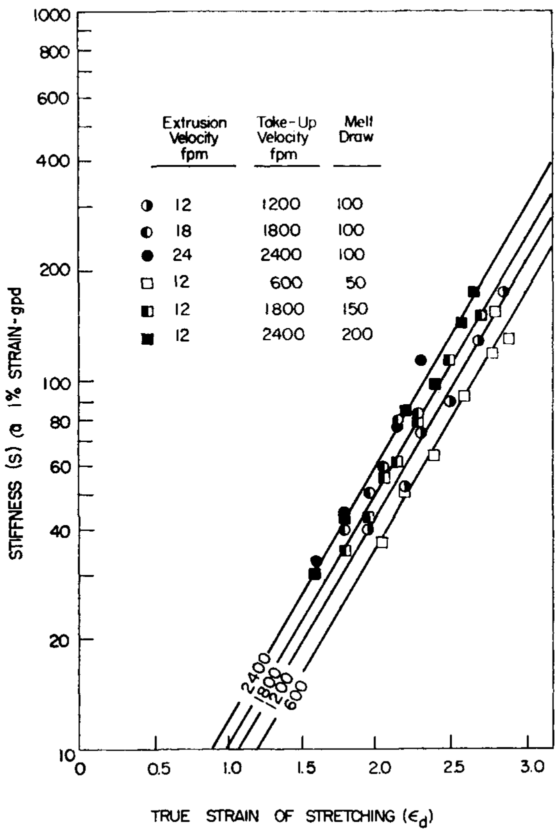

Fig. 6. Stiffness modulus as a function of true strain of stretching and take-up velocity of spinning.

the two equations of state can be made on the basis of experimentation outside of the area for which these equations were fitted.

Two additional yarns were stretched from spun yarn sample 3 of Table I. Table II compares the true tenacity of the experimental yarns with the values predicted by eqs. (9) and (10), and demonstrates the greater validity of eq. (10) at low draw ratios.

Stiffness Modulus. Figure 6 is a plot of the logarithm of the stiffness modulus at 1% strain versus the true strain equivalent of steam drawing. Inspection of the figure will reveal that stiffness S is a function of the spinning velocity and the true strain of stretching. The family of parallel lines was found to be characterized by the following model:

$$\ln S = -1.631 + 1.563\epsilon_d + 0.328 \ln V_f \tag{12}$$

An equivalent form of this equation is

$$S = 0.196 \exp\{1.563\epsilon_d + 0.328 \ln V_f\} \tag{13}$$

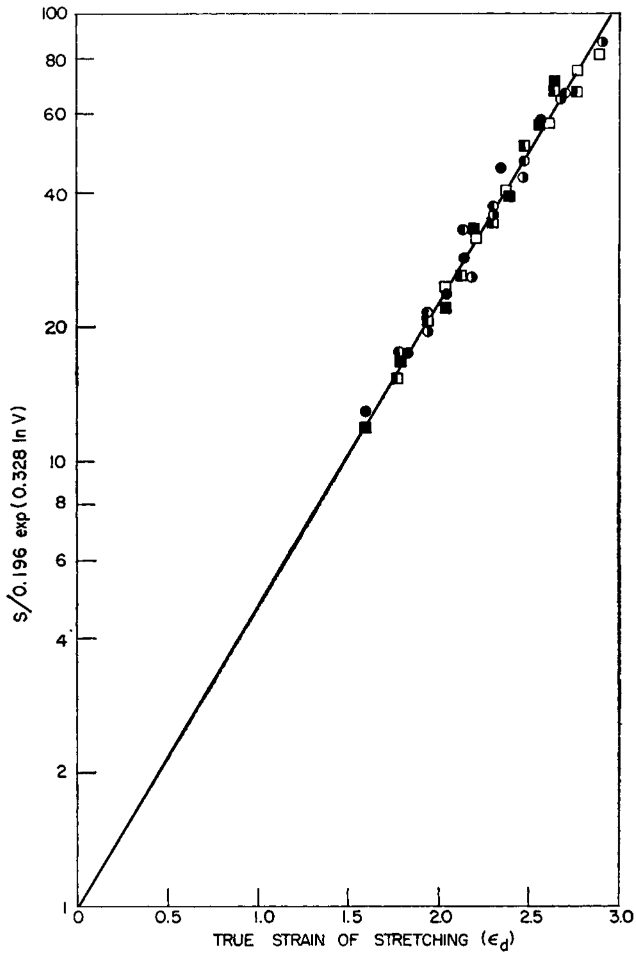

Fig. 7. Normalized stiffness as a function of true strain of stretching.

Experimental values of stiffness, corrected for prestrain in spinning were plotted versus the true strain equivalent of steam drawing (Fig. 7). The scatter of points is less than in the figure depicting corrected tenacity as a function of the true strain of steam drawing (Fig. 8). This may be due to the fact that tenacity is a sensitive function of flaws whereas stiffness is not. The more highly drawn yarn would be expected to contain more flaws and thus exhibit greater scatter in tensile strength than yarns of low draw ratios.

Comments on the Equations of State. One would expect that the effect of the deformation of spinning on the tensile properties of a stretched yarn should depend upon the temperature of the molten polymer and the temperature of the environment into which the melt is extruded.

Figure 9 illustrates the finding that the constant (0.022) of eq. (11) depends upon the temperature of the melt and the quenching conditions.

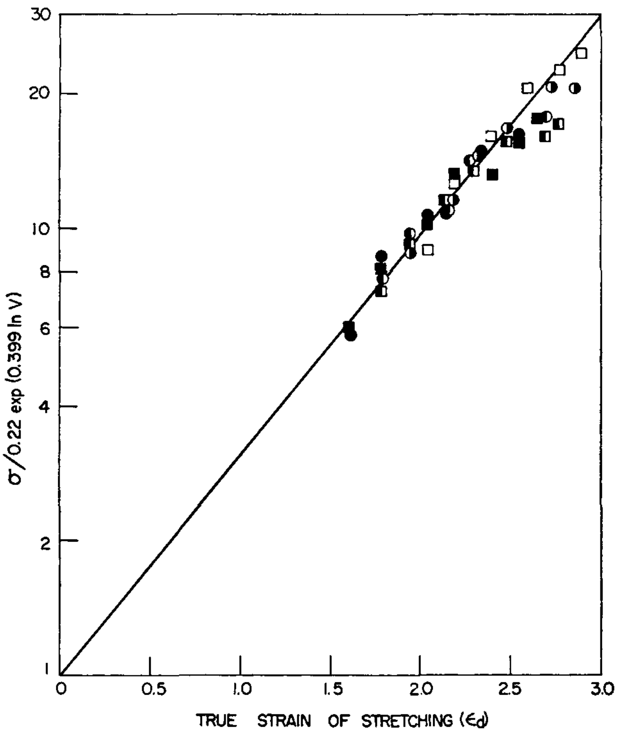

Fig. 8. Normalized tenacity as a function of true strain of stretching.

The temperature of the air used to quench the yarns was less than that employed in the main investigation. These curves show that yarns spun at higher spinning temperatures must be stretched more to achieve the same tensile strength as yarns spun at lower temperatures. This means that the magnitude of the constant (0.022) must decrease with increasing spinning temperature. The curves also show that there is a threshold value of spinning velocity below which the deformation of spinning does not influence the amount of stretching necessary to achieve a particular level of tenacity. This suggest that the empirical models should be so modified as to contain a built-in warning as to their range of general usefulness.

Assume that the constants, 0.022 and 0.196, respectively, in equations (11) and (13) each represents the sums of two constants: one to account for a shift in the origin of the spinning velocity coordinate axis, a second equal to the value of the tensile property for an isotropic resin. Then the models may be modified to denote the departure from the linear relationship between ϵ_d and $\ln V_f$ for spinning velocities less than 900 ft./min. by a simple arithmetic separation of the constants into their two components. For example,

$$\ln (0.022) = -3.8241 = \ln \sigma_0 + 0.3988 \ln V_f \tag{14}$$

and therefore $\sigma_0 = 0.328$ g./den.

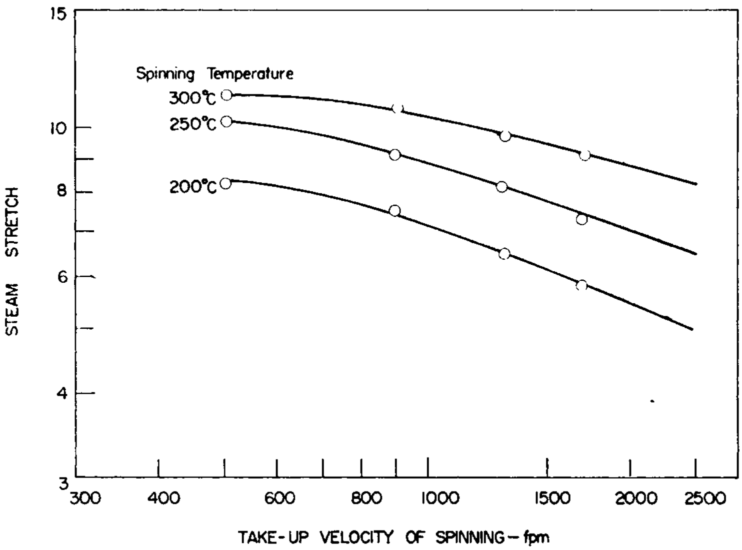

Fig. 9. Stretch ratio to achieve a tenacity of 5 g./den. as a function of take-up velocity and spinning temperature.

The modified forms of equations (11) and (13) are:

$$\sigma = 0.328 \exp \{1.139\epsilon_d + 0.399 \ln V_f - 2.71\} \tag{15}$$

$$S = 4.97 \exp \{1.532\epsilon_d + 0.328 \ln V_f - 2.23\} \tag{16}$$

The values of the constants (0.328 and 4.97) are in reasonable agreement with values[16] of strength (0.257–0.445 g./den.) and stiffness (4.98–12.1 g./den.) for high density polyethylene resins. The assumption that the constants 0.022 and 0.196 represent the sums of two constants appears to be a reasonable one.

It was postulated originally that if the melt deformation of spinning was to be considered an analog of the stretch ratio of the steam-stretching process, then the true strain of spinning would be expressed by the ratio of the take-up velocity of spinning and the velocity of the extrudate at the point that the melt begins to draw. Equations (10) and (13) do not contain a term relating to the extrusion velocity. This suggests either that the postulate is incorrect or that there are other factors implicit in the hypothesis that the tensile properties of yarns can be related to the true strain history of the yarn. It has been demonstrated that one additional factor is the thermal history of the spun yarn. The effect of deformation in the spinning line depends upon both the temperature gradient down and across any single filament in the spinning line. Andrews[17] has derived an expression for both gradients for a single filament, which would be even further complicated if it took into account the interaction between a number of filaments. With reference to the present study it is necessary only to note that the temperature of the yarn is a function of not only the extrusion temperature and the environmental temperature but also depends upon the product of the volume rate of flow and the instantaneous velocity of the yarn. One cannot differentiate, in this study, between volume flow rate and extrusion velocity because the number and size of the orifices were kept constant. An additional complication is added by the fact that the velocity of the melt at the point at which it starts to draw is significantly less than the extrusion velocity. As polyethylene is extruded from an orifice it balloons, that is, increases in diameter. The extent of ballooning is known to increase with increasing rates of extrusion.[18,19] In order that the mass rate of flow be constant an increase in diameter must be accompanied by a decrease in velocity.

The most that can be said at this time is that the influence of the extrusion velocity is very complicated. It may be that in this investigation the contributions of orifice velocity to cooling rate, ballooning and melt draw tend to cancel each other out. It is very likely that the term ln V_f includes a contribution due to the effect of velocity on cooling rate as well as a contribution due to the effect on the deformation of the melt.

Orientation of Spinning. It is reasonable to suspect that the more rapid increase in tenacity with stretching exhibited by yarns spun at the higher take-up velocities is due to a higher degree of orientation in the spun yarns. This hypothesis was tested by making birefringence and high-temperature shrinkage measurements of the spun yarn. The birefringence results in

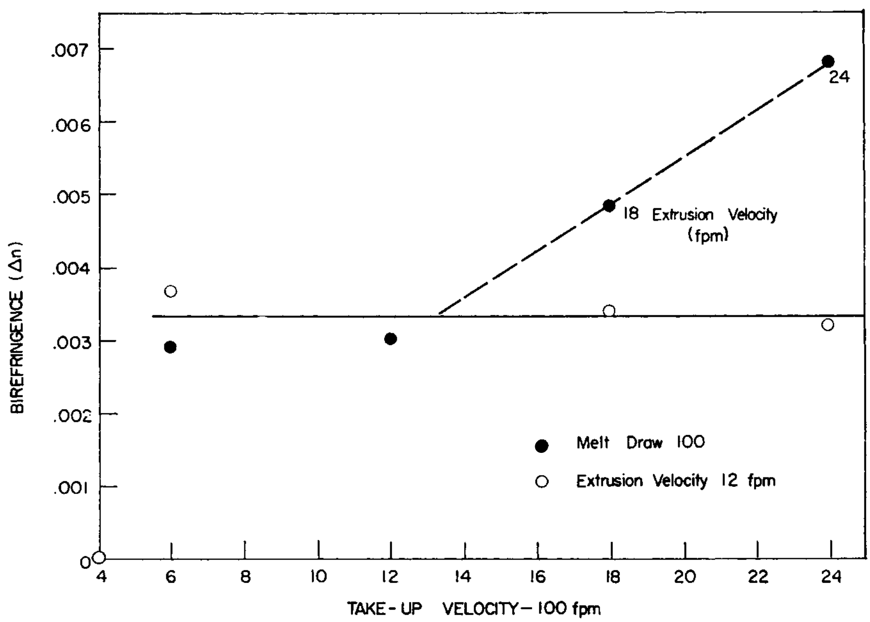

Fig. 10. Birefringence of spun yarns as a function of take-up velocity and extrusion velocity.

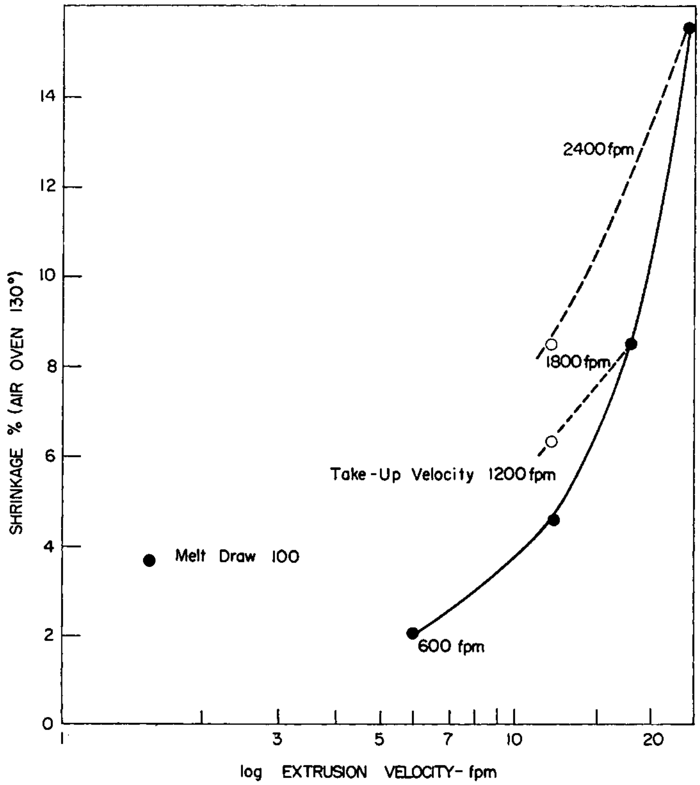

Fig. 11. Yarn shrinkage in 130°C. air as a function of extrusion velocity and take-up velocity.

Figure 10 indicate that the birefringence, and hence the orientation, of the spun yarn increases with increasing extrusion velocity (solid circles), but is independent of take-up velocity when the extrusion velocity is held constant (open circles).

The spun yarn shrinkage at 130°C., which should also be proportional to orientation, was measured and is plotted in Figure 11. Orientation, as measured by shrinkage, appears to depend on both the extrusion and take-up velocities. Doubling the take-up velocity from 1200 to 2400 ft./min. at a constant extrusion velocity of 12 ft./min. approximately doubled the shrinkage from 4.6 to 8.5%. Doubling the extrusion velocity from 12 to 24 ft./min. at a constant take-up velocity of 2400 ft./min. increased the shrinkage from 8.5 to 15.6%.

Since the stretching results are unequivocal in demonstrating that tenacity at yield depends only on the take-up velocity, and not on the extrusion velocity, it is concluded that the tenacity after stretching in steam depends on a factor or factors in the spun yarn other than orientation as measured by shrinkage at 130°C. or birefringence at room temperature. A limited x-ray diffraction study revealed differences in the relative orientation of various crystal planes for samples spun at different take-up velocities, which might lead to differences in response to stretch without giving birefringence differences. These data have not been fully interpreted, but do suggest that differences in the crystalline phase may be responsible for the different response to stretch of samples spun at various take-up velocities.

The crystallites in yarns spun at low velocities appear to be disposed toward an orientation of the *a* axis of the crystallites along the fiber direction, whereas in yarns spun at high velocities the *c* axis of the crystallites tends towards orientation in the fiber direction. It has been reported[20,21] that the crystallites in cold-drawn polyethylene are oriented with the *c* axis parallel to the length of the yarn. It is reasonable, therefore, to hypothesize that the more rapid increase in tenacity and stiffness for yarns spun at the higher take-up velocities is due to more of the crystallite structure in the spun yarns having the *c* axis of the crystallites already somewhat oriented with respect to the direction of subsequent stretching. It is thought that an adequate explanation of the anomalous behavior reported here will require consideration of the nature of the crystalline phase at the elevated temperature at which stretching takes place.

Additional Studies of the Influence of Extrusion Velocity. Additional spinning trials were run to determine if the finding that tenacity does not depend on the extrusion velocity was an artifact associated with a particular spinneret or if it was also true for a broad spectrum of spinneret designs. In this additional series the number and the size of the spinneret orifices as well as the length/diameter ratio were changed; the values of total orifice area ranged from 0.016 to 0.116 in.^{2}, with individual orifice diameters ranging from 0.02 to 0.10 in. All other spinning and stretching conditions were maintained at fixed values.

Spinneret parameters, spinning and stretching conditions, and the physical properties of the stretched yarn are listed in Table III.

The tenacity values erred in the limit by only 10.5% from the predicted value of 4.8 g./den. over the extreme range of the spinneret variables covered. Statistical analysis of the results indicates that this range of variation is significant only at a confidence level of 81%. That is, there is approximately one chance in five that a tenacity variation of 10.5% or greater would be observed even when the spinneret parameters have no influence on tenacity. Although the average of the observed values of stiffness (52.8 g./den.) was 9% less than that predicted (58 g./den.), the variation in stiffness modulus observed for the range of spinneret parameters studied was only 8% of the average value. A difference of this magnitude was shown to be statistically significant at only the 62% confidence level. That is, there are approximately two chances in five that a stiffness variation of 8% would be observed even if stiffness did not depend upon the spinneret parameters. The difference between the average of the observed values and the predicted value of stiffness may be due to the difference in the resins employed in the two studies. It is

TABLE III
Additional Study of the Influence of Extrusion Velocity

Spinneret						
No. of orifices	15	50	50	50	15	50
Orifice diameter, in.	0.0995	0.040	0.040	0.030	0.040	0.020
Length diameter ratio	3.77	9.38	9.38	16.66	15.00	9.35
Total orifice area, in.^{2}	0.1160	0.0629	0.0629	0.0354	0.0189	0.0157
Spinning conditions						
Mantle and spinning head temp., °C.	290	290	290	290	290	290
Pump speed (proportional to Q[a]), cpm	60	60	60	60	60	60
Extrusion velocity, ft./min.	4.6	8.5	8.5	15.0	28.8	33.8
Take-up velocity, ft./min.	2000	2000	2000	2000	2000	2000
Melt draw	435	236	236	133	69	59.0
Steam stretch	7.9	7.9	7.9	7.9	7.9	7.9
hysical properties of yarns[b]						
Denier	167	136	156	166	151	141
Stiffness modulus, g./den.	50.5	51.1	54.6	55.8	50.4	54.8
Tenacity, g./den.						
Conventional	4.01	4.32	4.54	4.51	4.26	4.70
True	4.62	4.89	5.10	5.10	4.86	5.30
Elongation, %						
Yield	14.9	—	—	—	14.1	—
Rupture	18.2	12.0	12.4	13.2	16.7	13.2

[a] Q is the volume rate of flow (cc./min.).
[b] Tenacity predicted by eq. (11) 4.8 g./den., 90% confidence limits 4.3–5.3 g./den.; stiffness predicted by eq. (13): 58 g./den., 90% confidence limits 50–66 g./den.

reasonable to conclude from these findings that the total orifice area, thus extrusion velocity, has no significant influence on the tensile properties of the yarn.

One additional point of interest is that the values of tenacity and stiffness are consistently smaller for 15-hole spinnerets than for 50-hole spinnerets. Although the differences between the average values of tenacity and stiffness for yarns produced with dies of 50 and 15 orifices were not statistically significant, further study of this point may be warranted.

It has been demonstrated that the constant in the equation of state depends upon the spinning temperature and the cooling conditions; therefore, a lower tenacity would be expected for yarns of constant total denier spun with a smaller number of filaments, due to the slower cooling of the larger filaments. The empirical equations fitted to the data in the preceding study probably would be in error for spinnerets with significantly less than 15 or more than 50 orifices.

Preliminary Survey of the Steam-Stretching Process. In general, the extent to which a material can be stretched is a function of many variables including initial orientation, crystallinity, and the temperature at which stretching takes place. Figure 12 shows the results of an experiment designed to show the effects of feed rate to the stretching tube (proportional

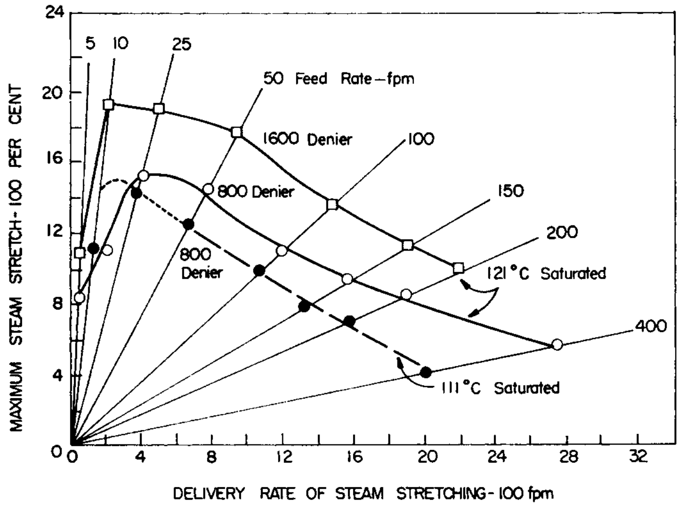

Fig. 12. Maximum steam stretch as a function of delivery rate of steam stretching and stretch aid temperature.

to production rate) and steam temperature on the maximum amount a spun yarn can be stretched, and the tensile properties of yarns stretched a constant amount. One spun yarn was stretched 1000% and samples were collected at increasing production rates. A second yarn of lower denier was stretched to the maximum at increasing rates of production at two different steam temperatures.

It was found that the production rate did not influence the stiffness, ness, tenacity, or elongation of yarns stretched the same amount, although the delivery rate from the stretching tube ranged from 550 to 2200 ft./min. However, the maximum attainable steam stretch and the associated physical properties of tenacity and stiffness modulus go through a maximum as the rate of throughput is increased.

The decrease in maximum stretch with increasing feed rate is probably due to a decrease in the temperature of the yarn. Figure 12 demonstrates that a yarn stretched with 7 psi steam as an aid cannot be drawn as much as yarn stretched in 15 psi steam. Another study demonstrated that, at a constant feed rate of 130 ft./min., decreasing the stretching tube length from 22 to 5 in. decreased the maximum stretch ratio by 35%, from 10.8 to 7.9. Decreasing the tube length is analogous to increasing the input velocity to the tube.

The abrupt decrease in maximum steam stretch with the decrease in feed rate shown in the left-hand side of Figure 12 can also be explained by the hypothesis that the yarn temperature varies with the feed rate. If the drop in maximum steam stretch is caused by the filament temperature exceeding a critical value, one would expect that the maximum point of a curve for a yarn stretched at a colder temperature would be shifted toward

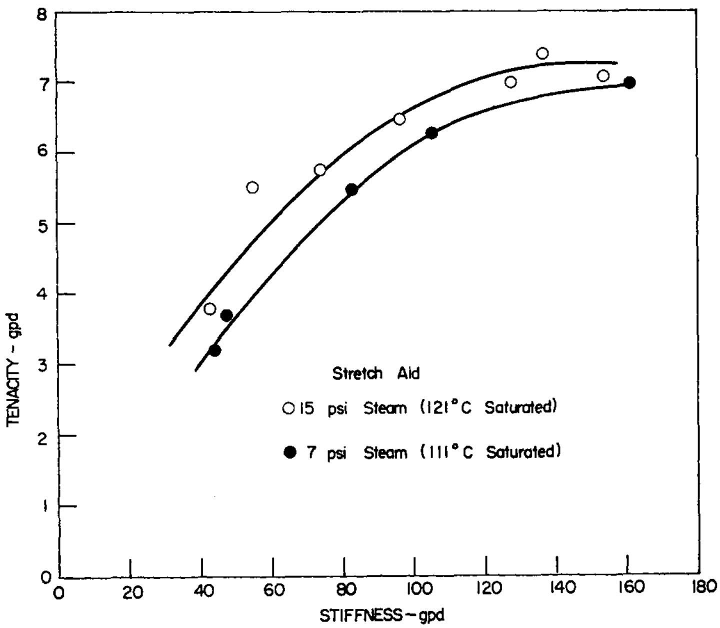

Fig. 13. Tenacity as a function of stiffness modulus and stretch aid temperature.

lower values of feed speed. The 7 psi steam stretch envelope does appear to be shifted toward the slower feed velocity. Being cooler, the 7 psi steam should take longer to heat the yarn to a critical temperature than the 15 psi steam.

Figure 13 illustrates the finding that higher strength yarns were produced with 15 psi steam as a stretch aid. The fact that yarns stretched with 7 psi steam exhibit less strength is thought to be due to greater voiding when drawing at colder temperatures. This finding suggests that the difference between the predicted and experimental values of tenacity for yarns of high stretch (high tenacity) might be decreased by stretching in higher pressure (hotter) steam.

Denier and Tenacity as Functions of Spinning Conditions and Steam Draw. The object of this series of investigations was to characterize the size and tensile properties of polyethylene yarns as functions of some of the variables of spinning and stretching. It can be demonstrated that the yarn denier is an explicit function of the pump displacement, spinning take-up velocity, and steam stretch.[22] The yarn tenacity and stiffness have been expressed as an empirical function of the steam stretch and the take-up velocity. Figure 14 was prepared to show the inter relationship of the metering pump displacement Q, the take-up velocity of spinning V_f, the steam stretch ratio d, the denier, and the stiffness of the stretched yarn. One will conclude from an examination of this figure that although there are five variables, fixing any three determines unique values of the remaining

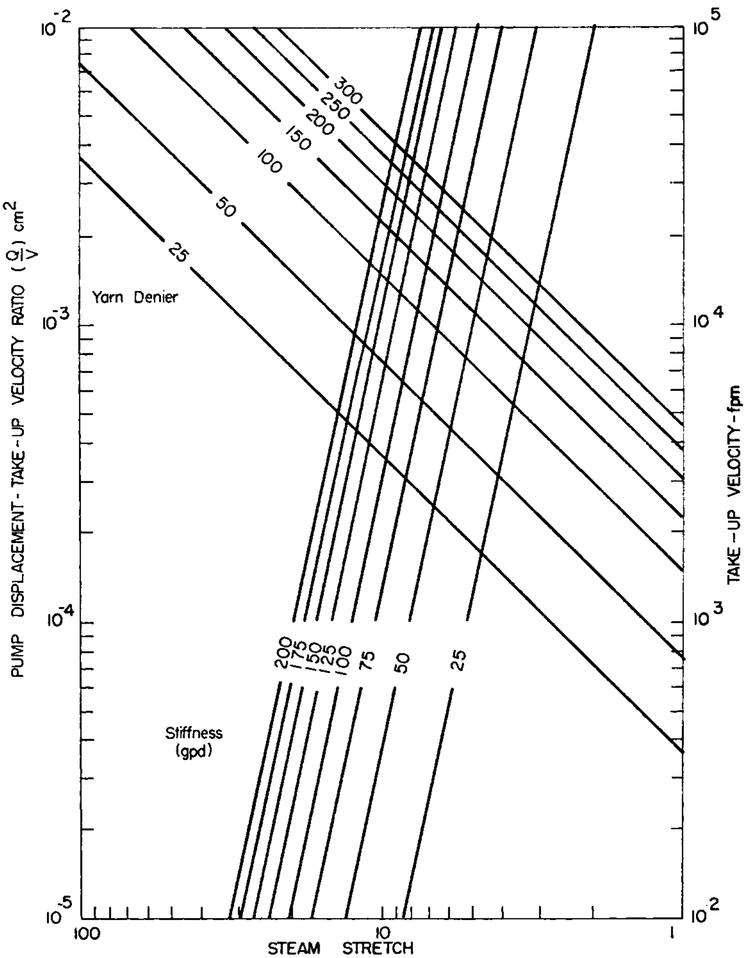

Fig. 14. Stiffness and denier as functions of pump displacement, take-up velocity, and stretch ratio.

two; i.e., selecting a particular value of pump displacement and spinning velocity to obtain a given stretched denier automatically dictates the steam draw and yarn stiffness. Moreover, comparison of Figures 14 and 15 will reveal that selection of particular values of tenacity and stiffness determines unique values for stretch and spinning velocity for this particular process. Figures 14 and 15 are interesting in that they imply that the stiffness modulus and the yarn tenacity may be (within limits) varied independently, since at any particular value of tenacity, increasing the take-up velocity decreases stiffness, or at fixed stiffness level, increasing the take-up velocity increases tenacity. This point has not been confirmed experimentally.

Figures 15 and 16 were prepared to illustrate the implications of the difference in the forms of the two models (equations of state) for tenacity.

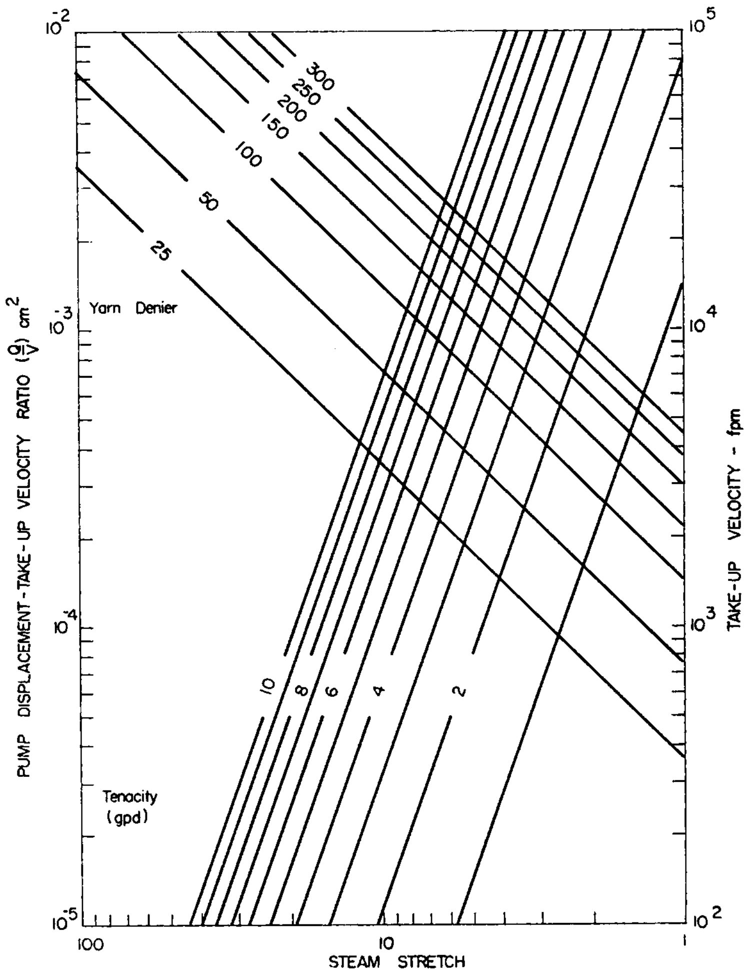

Fig. 15. Tenacity and denier as functions of pump displacement, take-up velocity, and stretch ratio (exponential model).

Inspection of these figures will reveal that the exponential model predicts less stretch to achieve a low tenacity yarn (<3 g./den.) than the linear model, regardless of the take-up velocity. This has been shown to be correct for a yarn produced at 2400 ft./min. Comparison of the figures also reveals that the exponential model predicts less stretch to achieve high tenacity yarns (>8 g./den.) regardless of velocity. The relationship for intermediate levels (3–8 g./den.) of tenacity is more complex; it depends upon the take-up velocity and the level of tenacity desired. Figure 17 shows that for intermediate values of tenacity the linear model predicts less stretch at low spinning velocities (200 ft./min.), whereas the exponential model predicts less stretch at high spinning velocities (100,000 ft./min.). For intermediate spinning velocities (10^3 and 10^4 ft./min.) the question of which model predicts less stretch depends upon the particular value of

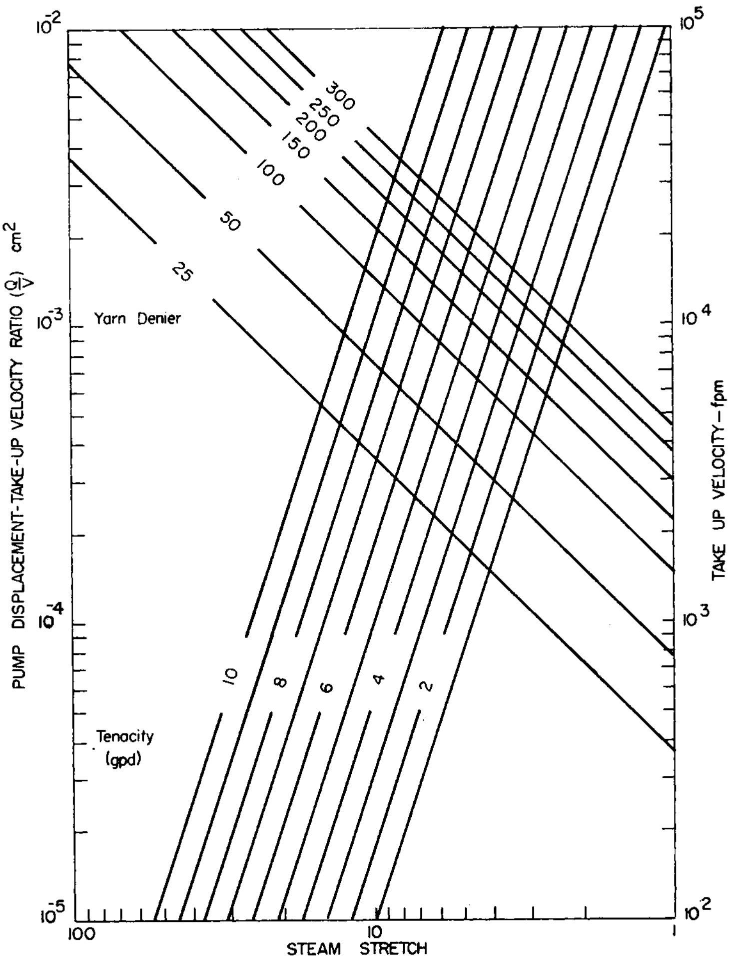

Fig. 16. Tenacity and denier as functions of pump displacement, take-up velocity, and stretch ratio (linear model).

tenacity selected. Unfortunately the difference between the predictions of the two models for the intermediate range of tenacities is so small that one cannot determine which model is better from experiments run in this area. It would require an excessive number of experiments to be able to differentiate between the predictions of the two models. Therefore, both Figures 15 and 16 can be useful in predicting the properties of yarns made made at intermediate velocities. An example follows.

For reasons of economy yarns should be manufactured at high production rates. The graphs facilitate the selection of the appropriate conditions. Consider the production of a 100 den. yarn having a stiffness of 50 g./den. For a high production rate the pumping speed Q and the take-up velocity V_f should be maximized. If a take-up velocity of 4500 ft./min. is selected (approximately twice the maximum velocity used in establishing the figures), all other spinning conditions will be fixed.

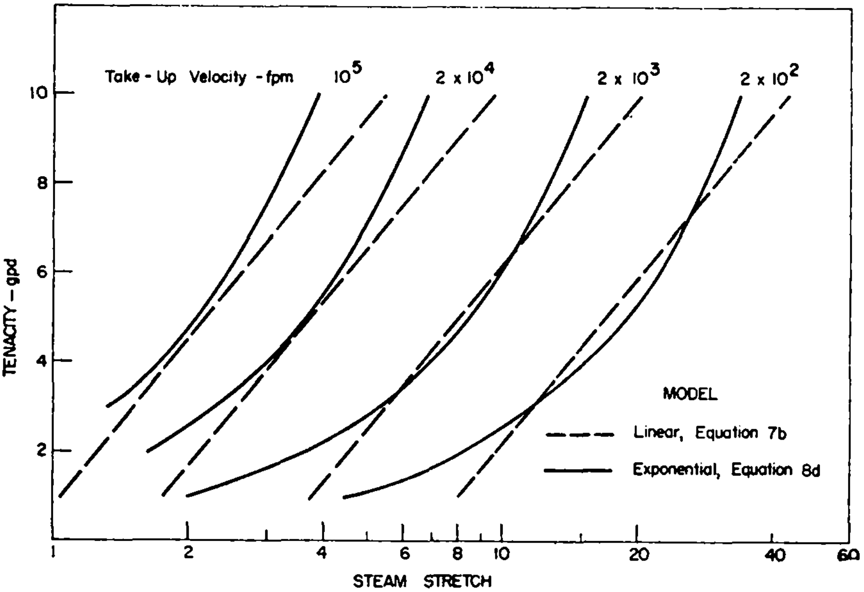

Fig. 17. Contrast of predictions of linear and exponential models for tenacity

These conditions may be found as follows. In Figure 14, the intersection of the right-hand ordinate corresponding to 4500 ft./min. with the constant stiffness line of 50 g./den. takes place at a steam draw ratio of 6. The intersection of the steam stretch ordinate with the desired denier defines the required Q/V ratio to be 8.9×10^{-4} cm.[2] Since V is already fixed, the required value of pump displacement can be calculated. It is found that the pump must displace polymer melt at a rate of 122 cc./min. In order to achieve maximum production in steam stretching, the highest velocity that will allow a draw ratio of 6 to be maintained should be used. The study of steam stretching suggested that the spun yarn could be fed to the

TABLE IV
Comparison of Predicted and Experimental Tensile Data[a]

	Stiffness, g./den.	True tenacity, g./den.	Ultimate elongation, %	Denier
Experimental	50	5.14	13.1	100
Predicted				100
Equation (7)		4.88 ± 0.52		
Equation (15)		4.81 ± 0.50		
Equation (13)	50.7 ± 7.0[b]			
Ultimate elongation			14.0 ± 1.3	

[a] Process Conditions: spinning temperature, 290°C.; spinneret, 15/.040 in.; mantle temperature, 290°C.; metering pump displacement, 122 cc./min. (12.1 lb./hr.); spinning take-up velocity, 4500 ft./min.; stretch aid, 15 psi steam; steam stretch, 6; feed rate to stretching, 400 ft./min.; delivery rate from stretching, 2400 ft./min.

[b] ± values are the 90% confidence limits for the particular variable, 30 degrees of freedom.

steam tube at a rate of 400 ft./min. and be drawn six times its original length.

A yarn was spun and stretched under the conditions indicated. Table IV compares the experimentally determined yarn properties with values calculated from the derived equations of state. The excellent agreement between the predicted and experimental value demonstrates the validity of the empirical equations of state even beyond the range of conditions from which they were derived. The elongation of the yarn was predicted from an equation of state of the same form as eq. (7).

Comparison of Olefin and Polyester Melt Spinning

It may be informative to contrast but briefly the findings of the study of the melt spinning of polyethylene with screening investigations of the melt spinning of the two other resins—polypropylene and an experimental polyester.

Polypropylene Spinning

A three-variable complete factorial experiment[23] was carried out to determine the effect of the extrusion velocity, the take-up velocity of spinning and the steam stretch ratio on the tensile properties of melt-spun polypropylene yarns (Table V).

TABLE V
Polypropylene Spinning Design

	Design level		
	−	0	+
Extrusion velocity ft./min.	2.8	4.2	5.6
Take-up velocity ft./min.	1000	1500	2000
Stretch ratio	2.2	3.0	3.8

Multiple regression analysis of the tensile values for the 11 yarns produced in this study revealed that the tenacity and stiffness of polypropylene yarns could also be expressed as functions of the take-up velocity of spinning and the cold draw ratio:

$$\sigma = 2.74(\ln d + 0.21 \ln V_f - 1.78) \tag{17}$$

with $r^2 = 0.95$, $s = 0.18$ g./den., and

$$\ln S = 0.90 (\ln d + 0.17 \ln V_f + 1.56) \tag{18}$$

with $r^2 = 0.96$, $\ln s = 0.02$, where r^2 is the squared value of the multiple correlation coefficient and s is the standard error of estimate.

These equations of state have the same form as those found for polyethylene spinning and fit the experimental data well. However, the general validity of this form of an equation of state for polypropylene spinning could best be demonstrated by additional spinning experiments outside the experimental surface delineated by the levels of the variables presented in Table V.

Polyester Spinning

A factorial study of some of the variables associated with spinning an experimental polyester resin revealed that in contrast to the spinning of polyethylene, the orientation (as measured by birefringence or sonic modulus[24]) of spun polyester yarns depends upon the melt draw ratio of spinning.

The orientation of the as spun yarns was found to be related to the spinning conditions by an equation of the form:

$$\ln \alpha = a + b \ln R + f(T_c, T_s) \tag{19}$$

where a and b are constants, α is a measure of orientation, $f(T_c, T_s)$ represents an unknown function of the spinning temperature and the cooling conditions, and R is the melt draw ratio.

The polyester study differed from the olefin studies in that all the as spun yarns were stretched to their maximum for one particular value of feed rate to stretching. It was not possible, therefore, to obtain an equation of state relating tensile properties of stretched yarns to the conditions of spinning and stretching and the degree of stretch.

It is interesting to note that, for given spinning and stretching conditions, the maximum amount polyester yarns can be stretched decreases with increasing melt draw, that is, spun yarn orientation. The study of polyethylene spinning revealed that the maximum stretch ratio decreased with increasing take-up velocity of spinning; it might be concluded therefore that the orientation of as-spun yarns of polyethylene depends upon a melt draw ratio which is a function of only the take-up velocity of spinning despite the fact that the indices of orientation measured (shrinkage and birefringence depend more significantly upon the extrusion velocity.

Comparison of Melt and Wet Spinning

It is interesting to note that the equations of state [eqs. (11) and (13)] for the tenacity and stiffness of melt-spun polyethylene yarns are identical in form to the equations of state obtained for the tenacity and stiffness of a wet-spun modacrylic fiber.[22] In the case of the wet-spun fiber, the tenacity and stiffness modulus were expressed by an equation of the following form:

$$\sigma \text{ and } S = k_1 \exp\{(-k_2)(1/s)\} \exp\{k_3 \epsilon_d\} \tag{20}$$

where k_1, k_2, and k_3 are constants and $1/s$ is the reciprocal of the specific surface of the fiber in the coagulating bath of the wet-spinning process. The first term in eq. (20) is related to the plasticity of the yarn entering the stretching process. As $1/s$ increases, the solvent content of the yarn entering the stretching process increases so that the amount of orientation imparted by the true deformation of stretching (ϵ_a) decreases.

The similarity in form of eqs. (11), (13), and (20) suggests that the velocity terms in eqs. (11) and (13) may be analogous to exp $\{-k(1/s)\}$ in eq. (20), that is, they may be a measure of the relative ease of orienting the spun yarn.

SUMMARY

Investigations of polyolefin spinning have demonstrated that the tenacity and stiffness of polyethylene and polypropylene are functions of the logarithmic deformation imparted in stretching and the logarithm of the take-up velocity in melt drawing. The tensile properties of stretched yarns do not depend upon the velocity of extrusion of the melt from the spinning orifice, despite the fact that the orientation of the spun yarn, as measured by birefringence and shrinkage, depends more on the extrusion velocity than it does upon the take-up velocity. In contrast, the orientation of yarns spun from an experimental polyester depends equally upon the extrusion velocity and the take-up velocity in that it depends upon their ratio, the melt draw.

Comparison of plots of empirical equations of state for the tensile properties of polyethylene yarns suggests that, for the present process, a yarn exhibiting a particular combination of tenacity and stiffness modulus can be achieved only at a unique combination of spinning velocity and steam stretching. The results suggest that stiffness and tenacity may be varied independently within certain limits; however, this point has not been confirmed experimentally.

The maximum stretch ratio of cold-drawn polyethylene has been shown to be a function of the production rate of stretching, increasing to an optimum value and then decreasing as the production rate is increased. The maximum stretch ratio at a given production rate was found to be a function of the drawing temperature, the length of the stretching tube, and the logarithm of the spinning velocity.

The authors wish to express their appreciation to Dr. S. P. Hersh of the Chemstrand Corporation for his valuable contribution to this work, and to Mr. T. D. Myers for his assistance in obtaining experimental data and preparing the manuscript.

References

1. Meacoch, G., *J. Appl. Chem.*, **4,** 172 (1954).
2. Natus, D., and H. Sauer, *Faserforsch. Textiltech.*, **5,** 431 (1954).
3. Natus, D., and H. Sauer, *Faserforsch. Textiltech.*, **7,** 468 (1956).
4. Yumoto, H., *Bull. Chem. Soc. Japan,* **29,** 45 (1956).
5. Yumoto, H., *Bull. Chem. Soc. Japan,* **29,** 141 (1956).
6. Yumoto, H., *Bull. Chem. Soc. Japan,* **29,** 353 (1956).
7. Griehl, W., and H. Versauemer, *Faserforsch. Textiltech.*, **9,** 226 (1958).
8. Cannon, C. G., and F. P. Chappel, *Brit. J. Appl. Phys.*, **10,** 68 (1959).
9. Ziabicki, A., and K. Kedzierska, *J. Appl. Polymer Sci.*, **6,** 111 (1962).
10. Marshall, I., and A. B. Thompson, *Proc. Roy. Soc. (London)* **A221,** 541 (1954).
11. Marshall, I., and A. B. Thompson, *J. Appl. Chem.*, **4,** 145 (1954).
12. Thompson, A. B., and D. W. Woods, *Trans. Faraday Soc.*, **52,** 1383 (1956).
13. Patterson, D., and I. Ward, *Trans. Faraday Soc.*, **53,** 1516 (1957).
14. Foster, E. L., and H. Heap, *Brit. J. Appl. Phys.*, **8** (1957).
15. Bridgman, P. W., *Large Plastic Flow and Fracture,* McGraw-Hill, New York, 1953.

16. *Mod. Plastics*, **40,** No. 1A (1962). (Encyclopedia Issue for 1963, Plastic Properties Chart, Part I).
17. Andrews, E. H., *Brit. J. Appl. Phys.*, **10,** 39 (1959).
18. Clegg, P. L., *Plastics Inst. Trans.*, **28,** 245 (1960).
19. Middleman, S., and J. Gavis, *Phys. Fluids*, **4,** 963 (1961).
20. Stein, R. S., and F. Norris, *J. Polymer Sci.*, **21,** 381 (1956).
21. Stein, R. S., *J. Polymer Sci.*, **34,** 709 (1959).
22. Hersh, S. P., T. D. Higgins, and H. W. Krause, *J. Appl. Polymer Sci.*, **7,** 411 (1963).
23. Davies, O. L., *The Design and Analysis of Industrial Experiments*, Hafner, New York, 1956.
24. Moseley, W. W., *J. Appl. Polymer Sci.*, **3,** 266 (1960).

Résumé

La ténacité et le module de torsion de fibres filées à partir du polyéthylène à haute densité fondu sont des fonctions de la somme logarithmique de vitesses de filage et de la valeur vraie (logarithmique) de la déformation impartie dans le processus de filage à froid (c.à.d. élongation à une température inférieure au point de fusion du polymère). Donc, dans les conditions expérimentales, la déformation efficace du fondu étiré est indépendante des vitesses calculées de filage dans les orifices des filières. On montre que le rapport maximal d'étirement à froid est une fonction de la vitesse de production, passant par un maximum et diminuant ensuite pour des valeurs croissantes de la vitesse de production. Le rapport maximal de filage à froid pour une vitesse de production donnée s'avère être une fonction de la température de la fibre et de la déformation introduite dans le fondu en étirement. La tenacité et le module de cisaillement de fibres filées à partir de polypropylène fondu peuvent également être exprimés en fonction de la somme logarithmique des vitesses mesurées dans le fondu en étirement et la déformation réelle donné au cours de ce filage à froid. L'orientation des fibres étirées dans un polyester, mesurée expérimentalement par la biréfringence, est une fonction du rapport de la vitesse mesurée à la vitesse à l'orifice, tandis que les mêmes mesures d'orientation du polyéthylène ne sont fonction que de la vitesse d'extrusion. Les équations d'état relatives à la ténacité et le module de cisaillement de fibres filées au départ de polyéthylène fondu, se révèlant être de la même forme que celles relatives à une fibre modacrylique filée à l'état humide.

Zusammenfassung

Zugfestigkeit und Steifheitsmodul von aus Polyäthylen mit hoher Dichte schmelzgesponnenen Fäden sind Funktionen der Summe der Logarithmen der Spannungsgeschwindigkeit beim Ziehen aus der Schmelze und der wahren (logarithmischen) im kalten Dehnungsprozess gegebenen Deformation (d.h. Ziehen bei einer Temperatur unterhalb der Polymerschmelztemperatur). Daher ist unter den untersuchten Bedingungen die effektive Schmelzdehnungsdeformation unabhängig von der berechneten Geschwindigkeit der Schmelze in der Öffnung der Spinndüse. Das maximale Kaltdehnungsverhältnis ist eine Funktion der Produktionsgeschwindigkeit: Sie wächst zu einem Maximalwert und nimmt dann im selben Masse ab, in dem die Produktionsgeschwindigkeit wächst. Das maximale Kaltdehnungsverhältnis bei einer gegebenen Produktionsgeschwindigkeit ist eine Funktion der Garntemperatur und der durch Ziehen aus der Schmelze verursachten Deformation. Zugfestigkeit und Steifheitsmodul von aus Propylen schmelzgesponnenen Garnen kann auch als Funktion der Summe der Logarithmen der Spannungsgeschwindigkeit beim Ziehen aus der Schmelze und der wahren bei kaltem Dehnen gegebenen Deformation ausgedrückt werden. Die durch Doppelbrechung gemessene Orientierung von aus einem experimentellen Polyester gesponnenen Garnen sind eine Funktion des Verhältnisses der Spannungsgeschwindigkeit und der Öffnungsgeschwindigkeit, während dieselbe Messung der Orientierung von Polyäthylen nur eine Funktion der Extrusionsgeschwindigkeit allein ist. Zustandsgleichungen für die Zugfestigkeit und den Steifigkeitsmodul von aus der Schmelze gesponnenem Polyäthylengarn haben dieselbe Form wie die für eine nassgesponnene Modacrylfaster.

Received November 14, 1963