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The Influence of Processing Variables on the Physical Properties of a Wet-Spun Modacrylic Fiber*

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INTRODUCTION

Although acrylic fibers have been commercially available since 1948, comparatively little has been published concerning the influence of spinning variables on their properties. Most of the studies reported to date have been rather limited in scope, as they treat the effects of a restricted number of process variables either on fiber porosity and cross section[1–6] or on the mechanical properties of the fibers.[3,4,6,7] Some information on the dry spinning of polyacrylonitrile is also recorded.[1,8,9] The most comprehensive study involving process variables was made by Morbey,[10] who examined the effect of ten variables on the wet spinning of polyacrylonitrile–cellulose acetate mixtures by a discontinuous three-step process.

The present paper reports the influence of eleven spinning variables on the mechanical and dyeing properties of modacrylic staple fibers produced on an experimental continuous spinning unit. The fibers were spun from resin–acetonitrile solutions into a water–acetonitrile coagulating bath. The study of a large number of variables on a continuous system (as contrasted with a batch system) is somewhat complicated, and new techniques were developed for treating the information obtained. Therefore, in addition to reporting the physical results, an important purpose of this work is to illustrate the procedures that were found helpful in the study of continuous systems. The new technique, moreover, is also applicable to other experimental areas in which the independent variables can be considered in a number of different ways.

SPINNING SYSTEM AND VARIABLES

A sketch of the spinning system used during the course of these experiments is shown in Figure 1; this arrangement is fairly typical of any staple wet spinning process. The system (1) extrudes a solution of fiber resin through a multihole spinnerette into a coagulating bath where solvent is

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removed from the filaments, (*2*) withdraws the coagulated fiber bundle (called a "tow") from the bath and passes it through a wash bath, (*3*) stretches the tow to orient the fiber and thereby increase its strength, and (*4*) dries the fiber either with or without relaxation following the stretching operation. If staple fiber is desired, the tow is then cut into required lengths. For the present study, only the properties of the uncut tow were determined.

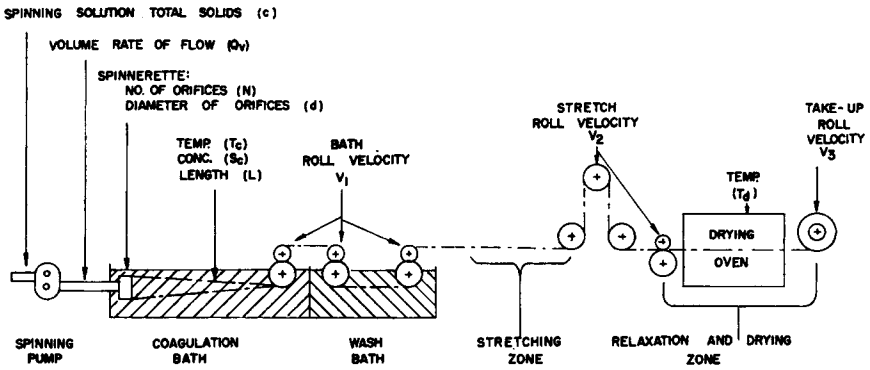

Fig. 1. Schematic diagram of experimental wet-spinning system.

The spinning process described is governed by a great many variables including the following:

(*1*) Volume rate of flow at which the spinning dope is pumped through the spinnerette, Q_v
(*2*) Number of orifices in spinnerette, N
(*3*) Diameter of spinnerette orifice, d
(*4*) Bath roll velocity, V_1
(*5*) Stretch roll velocity, V_2
(*6*) Relaxation roll velocity, V_3
(*7*) Concentration of the resin in spinning solution, c
(*8*) Length of coagulating bath, L
(*9*) Temperature of coagulating bath, T_c
(*10*) Concentration of solvent in coagulating bath, S_c
(*11*) Drying temperature, T_d
(*12*) Temperature of spinning dope
(*13*) Shape and arrangement of orifices in spinnerette
(*14*) Stretching temperature and conditions
(*15*) Chemical variables such as resin composition, solvents, pigments, stabilizers, etc.
(*16*) Drying time

These "basic" variables may be classified as follows. The first six will be considered mechanical variables since they define the velocity of the

fiber at different points in the manufacturing process. With the exception of the number and dimensions of the orifices in the spinnerette, they are all time dependent. The other variables will be classified as physical or chemical variables. All the variables listed are truly independent since, by an adjustment of their values, the spinning conditions are precisely defined. However, it will be immediately apparent that these independent variables are functionally related to other terms that may be treated as independent variables and that may be more suitable for defining the experimental spinning conditions. Some examples of these new expressions follow.

(*17*) Stretch ratio, $\lambda = V_2/V_1$

(*18*) Weight of resin extruded per unit time, $Q = Q_v c$

(*19*) Size of finished tow as measured by its "denier" (the linear density of the fiber expressed in grams per 9000 meters), $D \propto Q/V_3$

(*20*) Denier per filament of the finished fiber, $\delta \propto Q/NV_3$

(*21*) Draw down of the filaments in the coagulating bath, which is proportional to Nd^2V_1/Q_v

(*22*) Denier per filament in the coagulating bath, δ_c, which is proportional to Q/NV_1

(*23*) Per cent relaxation after stretching, $R = (1 - V_3/V_2)100$;

(*24*) Exposure time of the fiber in the coagulating bath, $t \propto L/V_1$

(*25*) Extrusion velocity through spinning orifice, which is proportional to Q_v/Nd^2

(*26*) Shear rate through the spinning orifice, $\dot{\gamma} \propto Q_v/Nd^3$

The fact that the combined variables 17 to 26 (which may actually be the basic factors controlling the spinning process and the fiber properties) are functions of the independent variables 1 to 16 is rather disconcerting since it complicates the selection of independent variables to be studied in an experiment. For example, if it is decided to treat the two velocities V_2 and V_1 as independent variables, neither one can be changed without changing the intermediate variable V_2/V_1 (stretch ratio); therefore, it will be difficult to ascertain whether an observed change in a property results from a velocity change or a stretch change.

To resolve this difficulty, a new technique was developed for studying variables that can be expressed in several different functionally related forms. It was found that the coefficients of a linear regression equation based on one set of independent variables can be treated in such a way as to generate coefficients for new variables functionally related to the original ones. By means of this procedure, which is developed and described in detail elsewhere,[11] it is possible to interpret the experiment in terms of alternative sets of independent variables. These alternative interpretations provide insights into the process that are very helpful in guiding further experimentation.

TIME-DEPENDENT VARIABLES

Experiment and Results

In the first set of experiments, the following time-dependent properties were selected as independent variables in a complete two-level factorial design,[12] 2^{4-0}: weight of resin extruded per unit time, Q (variable 18), bath roll velocity V_1 (variable 4), stretch roll velocity V_2 (variable 5), and relaxation after stretching, R (variable 23). (These time-dependent variables of course, could have been expressed by several other functionally related sets consisting of four independent variables.) In a 2^{4-0} design, each independent variable is assigned a high (+1) and low (−1) value (or level) equally spaced about a mean value (0 level). Half of the 16 required experiments are then made at the high level, and half are made at the low level, of each variable. In addition, five fibers were produced at the 0 level of all variables in order to estimate the reproducibility and linearity of the system.

The experimental conditions selected are given in Table I, which also lists the tenacity θ, elongation ϵ, stiffness modulus E, dyeability D_{ab}, and denier per filament $\delta = D/N$ of the resulting tows. The measurements of the physical properties were made by weighing a 1-m. length of tow to obtain the denier. This sample was then cut in half, and the tenacity, stiffness, and elongation to break of each half was measured on a tensile testing machine with a constant rate of extension. The stiffness modulus was defined as 100 times the stress, in grams per denier (gpd), required to strain the tow 1%. The standard deviation of the duplicate measurements made on the adjacent sections of the tow is given in Table II. The dyeability was determined by dyeing the fiber with a cationic dye, dissolving the dyed fiber in dimethylformamide to provide a solution of fixed concentration, and measuring the optical density (OD) of the solution.

Linear regression equations were then fitted to the experimental data by standard techniques.[12] The coefficients of the resulting equations are listed in Table II, in which the significant values as judged from a Daniel half-normal plot[13] are enclosed in parentheses. The coefficients represent the average change in a property produced by a change in the independent variable from the −1 level to the 0 level or from the 0 to the +1 level.

Thus Table II indicates that the fiber tenacity decreases with increasing extrusion rate Q and with increasing coagulation bath exit velocity V_1. At the same time the fiber strength increases when the stretch roll velocity V_2 is increased, and it is not affected by the amount of relaxation R. The stiffness modulus shows similar effects but, numerically, the changes in stiffness are approximately ten times greater than the changes in tenacity. The only variable which had a significant effect on elongation was the stretch roll velocity (increasing its value reduces the elongation). The effects of the spinning variables on the denier and dyeability will be considered later.

Table II also lists the standard deviations of the replicate experiments

TABLE I. Design and Response Matrix for Experiments Involving Time-Dependent Variables

		Independent Variables				Responses				
Run no.	Level	Production rate Q, lb./hr.	Bath roll velocity V_1, fpm	Stretch roll velocity V_2, fpm	Relaxation R, %	Tenacity Θ, gpd	Elongation ϵ, %	Stiffness modulus E, gpd	δ, denier/filament	Dyeability D_{ab}, OD
	+	10.80	40.0	160.0	6.0					
	0	9.45	35.0	140.0	4.0					
	−	8.10	30.0	120.0	2.0					
	% Change	14.0	14.0	14.0	100.0					
1		−	−	+	+	3.00	21.2	57.7	2.55	0.282
2		−	+	−	−	2.34	26.0	48.0	3.22	0.455
3		−	+	+	−	2.94	21.5	51.0	2.41	0.288
4		−	−	−	−	2.65	23.3	53.8	3.21	0.387
6		+	−	+	+	2.77	21.5	50.3	3.25	0.285
7		+	−	−	+	2.24	22.7	51.0	4.29	0.416
8		+	+	−	−	1.94	23.9	44.7	4.07	0.490
9		+	+	+	−	2.38	20.7	50.5	3.05	0.303
11		−	+	−	+	2.11	27.4	52.2	3.31	0.830
12		−	−	−	+	2.57	25.4	51.8	3.33	0.459
13		−	+	+	+	2.73	23.6	58.0	2.50	0.525
14		−	−	+	−	3.14	21.5	60.0	2.41	0.303
16		+	−	−	−	2.25	26.7	49.5	4.22	0.519
17		+	+	+	+	2.36	23.4	54.3	3.26	0.571
18		+	−	+	−	2.99	21.0	60.2	3.09	0.324
19		+	+	−	+	1.83	28.7	44.3	4.30	0.742
0		0	0	0	0	2.68	23.9	52.4	3.12	0.243
5		0	0	0	0	2.54	22.0	48.9	3.22	0.310
10		0	0	0	0	2.56	25.0	50.0	3.26	0.430
15		0	0	0	0	2.55	24.0	56.5	3.21	0.395
20		0	0	0	0	2.45	23.6	52.2	3.22	0.395

[a] Fixed experimental conditions: $S_c = 16\%$, $N = 5000$, $c = 25\%$, $T_d = 170°C.$, $T_c = 65°C.$, $L = 108$ in.

TABLE II. Coefficients for Regression Equations Including Time-Dependent Variables

	Variables			Responses				
Coefficient	Effect of:	0 Level	% Change per level	Tenacity θ gpd	Elongation ϵ, %	Stiffness modulus E, gpd	δ, denier/filament	Dyeability D_{ab}, OD
b_0	—	—	—	2.515	23.66	52.33	3.278	0.448
b_1	Production rate	Q, 9.5 lb./hr.	14.0	(−0.170)	−0.08	(−1.73)	(0.412)	0.007
b_2	Bath roll velocity	V_1, 35 fpm	14.0	(−0.186)	0.74	(−1.96)	−0.014	(0.077)
b_3	Stretch roll velocity	V_2, 140 fpm	14.0	(0.274)	(−1.86)	(2.92)	(−0.463)	(−0.088)
b_4	Relaxation	R, 4%	50.0	−0.064	0.58	0.12	(0.070)	(0.065)
b_{12}	Interactions			−0.031	−0.14	−0.19	−0.006	−0.006
b_{13}	"			0.006	−0.07	0.31	(−0.065)	0.003
b_{14}	"			0.019	−0.08	−0.74	0.016	−0.018
b_{23}	"			0.000	−0.24	0.16	0.004	−0.015
b_{24}	"			−0.008	0.79	(1.71)	0.009	(0.076)
b_{34}	"			−0.010	0.04	−0.29	0.005	−0.010
b_{123}	"			−0.038	0.04	0.57	0.009	0.011
b_{124}	"			0.020	0.58	−0.23	0.018	0.006
b_{134}	"			−0.005	0.26	−0.61	0.003	0.019
b_{234}	"			0.024	−0.22	1.17	−0.008	0.006
b_{1234}	"			0.014	−0.61	0.78	−0.006	0.000
			σ_0	0.082	0.93	2.92	0.053	0.076
			$4\sigma_b$	0.095	1.80	2.40	0.044	0.047
			σ_t	0.066	0.50	1.72	—	—

made at the 0 level, σ_0, of the coefficients as obtained from a Daniel replot eliminating the significant coefficients, σ_b, and of the duplicate mechanical measurements made on adjacent sections of tow, σ_t. Another estimate[12,13] of σ_0 is obtained from $\sqrt{16}\sigma_b$.

Deriving Alternative Models

Principles

Thus, by using standard experimental design procedures, the effects of the four independent variables selected (Q, V_1, V_2, R) on the fiber properties were determined. The question remains, however, whether the results could be explained more simply in terms of some other variables functionally related to the original set, such as stretch (V_2/V_1) or denier (Q/V_2). In other words, could an alternative mathematical model (equation) better describe the system under study than the simple linear models expressed in Table II? A better model might be one which requires fewer parameters, involves terms having some theoretical significance, and/or predicts more closely the properties of fibers spun under a wider range of experimental conditions.

The first step required for developing suitable alternative models is to "normalize" the coefficients of the regression equation. For two-level factorial designs, this is accomplished by dividing the coefficient by the fractional change made in the corresponding independent variable in going from the 0 to the +1 level. For example, the coefficient b_2 for the tenacity response in Table II is −0.186 gpd. This represents the change in tenacity produced by increasing the corresponding independent variable V_1 by one coded unit from 30 to 35 feet per minute (fpm) or from 35 to 40 fpm. Therefore, the fractional change in V_1 per unit level change is 5/35 or 0.142, and the normalized coefficient $\mathbf{b_2}$ is $-0.186/0.142 = 1.31$. In this manner the coefficients are made independent of the actual spread in values between the +1 and −1 levels selected for the experiment and are now equal to the change in response produced by increasing the independent variable 100% from its 0 level.

Expressing the coefficients in normalized form permits a direct comparison between the coefficients for any given response that suggests alternative models which will fit the observed data. For example, if the variables A and B can be expressed as a new variable functionally related to each other in the form of a product AB, the normalized coefficients of A and B will be equal. Alternatively, if they are related in the form of a quotient A/B, the normalized coefficients of A and B will be equal but of opposite sign. For example, the variables V_1 and V_2 may be combined to represent a dependence of the process on stretch, V_2/V_1, if their coefficients are equal in magnitude but opposite in sign. An example of this type of relationship will be considered in the section on dyeability. One other characteristic of normalized coefficients will be required to develop some of the models considered later: a coefficient may appear in more than one term of

the new model, provided the algebraic sum of the new terms equals the total value observed experimentally.

The application of this technique to nonlinear models (i.e., exponential, power, etc.) and to the interaction terms of the linear model will not be considered here; a complete description is available elsewhere.[11]

Example of Alternative Model Applied to Denier

The technique of combining variables is, in effect, an attempt to construct the actual relationship that exists between a set of variables from a knowledge of the coefficients of an experimentally determined linear model. A good illustration of developing an alternative model is offered by the denier response shown in Table II. Since the normalized coefficient of $Q(+0.41/0.142 = +3.08)$ is equal and opposite to that of V_2 $(-0.46/0.142 = -3.26)$, an equation in which $\delta \propto Q/V_2$, i.e.,

$$\delta = b_0 + b_4 (Q/V_2) \tag{1}$$

might be an acceptable replacement for the linear model

$$\delta = b_0 + b_1 Q + b_2 V_2 + b_3 (QV_2) \tag{2}$$

Confirmation that $\delta \propto Q/V_2$ is an acceptable form of the true model is obtained when the QV_2 interaction of -0.065 is considered. It can be shown[11] that an equation in the form of eq. (1) will generate a QV_2 interaction in eq. (2) equal to minus the coefficient of Q times the fractional change in V_2 per design level $(-0.41 \times 0.14 = -0.058)$ or the coefficient of V_2 times the fractional change in Q $(-0.46 \times 0.14 = -0.065)$. These predicted values are consistent (within experimental error) with the observed value in Table II.

The validity of this treatment can be demonstrated because the theoretical relationship between the denier and the mechanical spinning variables is known. By equating the mass of resin extruded per unit time (dm/dt)

$$dm/dt = Q \tag{3}$$

with the mass of fiber delivered per unit time (dm'/dt) at the end of the spinning machine

$$dm'/dt = DV_3/(9 \times 10^5) \tag{4}$$

the denier can be expressed as an explicit function of the spinning variables:

$$D = 9 \times 10^5 \, Q/V_3 \tag{5}$$

In terms of the variables actually used in the experiment,

$$D = \frac{9 \times 10^5 \, Q}{V_2 (1 - R/100)} \tag{6}$$

The denier per filament, δ, is obtained by dividing eq. (6) by the number of holes in the spinnerette, N:

$$\delta = \frac{9 \times 10^5 Q}{V_2 (1 - R/100)N} \tag{7}$$

Thus, this example in which the true relationship is known confirms that a linear equation can be analyzed so as to predict the form of possible alternative models.

An Alternative Model for Dyeability

The usefulness of alternative models in interpreting experimental results when the true model is unknown can be illustrated by considering the dyeing properties of the spun fibers. The data in Table II show that the dyeability increases with increasing bath roll velocity, increasing relaxation, and the interaction of these two quantities. In addition, dyeability decreases with increasing stretch roll velocity. Dyeability is therefore a function of three of the four independent variables studied, and a three-dimensional graph would be necessary to show the results. If, however, the main-effect coefficients are normalized as indicated in Table IIa, a simpler alternative model is suggested.

TABLE IIa
Normalized Coefficients for Dyeability from Table II

(1) Independent variable	(2) Coefficient for D_{ab} from Table II	(3) Mean value (0 level)	(4) Fractional change in (1) per level	(5) = (2)/(4) Normalized coefficient
V_1	+0.077	35	5/35 = 0.142	+0.54
V_2	−0.088	140	20/140 = 0.142	−0.62
R	−0.065	4	2/4 = 0.500	+0.13

The normalized coefficient for bath roll velocity (V_1), except for sign, is the same within experimental error as the normalized coefficient for stretch roll velocity (V_2). If one now stops to consider that when V_1 increases, stretch decreases, and that as V_2 increases, stretch increases, it is reasonable to conclude that the apparent velocity effects are actually manifestations of stretch effects. A 100% increase in stretch from its mean value of 4 (or 140/35) decreases dyeability by 0.58 OD, the average of the absolute values of the normalized coefficients for V_1 and V_2.

The argument presented above suggests that the data might be treated as a function of stretch and relaxation rather than as a function of V_1, V_2, and R. When this is done as shown in Figure 2, a simple interpretation of the results is possible. The dyeability decreases with increasing stretch

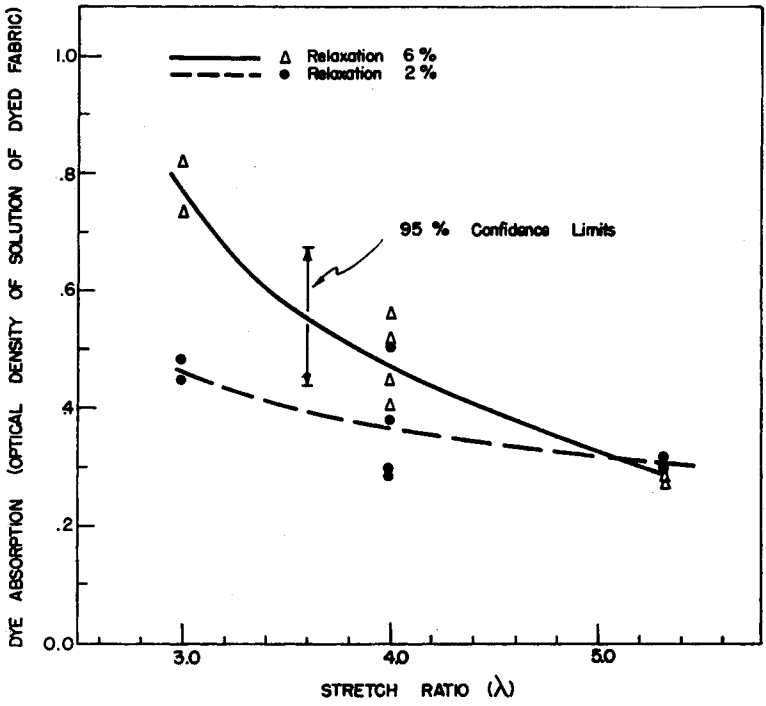

Fig. 2. Dye absorption of fiber as a function of stretch and relaxation.

and decreasing relaxation because of the resulting increase in fiber orientation. However, a given amount of relaxation applied to fibers of low stretch has a much greater effect on orientation and dyeability than the same amount applied to highly stretched samples. A comparison of the coefficients of the original model has thereby provided an insight into the form of a possible alternative model that lends itself to a logical interpretation of the results.

Alternative Models for Tenacity

The empirical results presented in Table II indicate that tenacity depends on Q, V_1, and V_2. Naturally, one might suspect that the true variables controlling tenacity are actually related to one or more of the nine other variables listed which are functionally related to Q, V_1, and V_2. By means of the technique outlined above, five alternative models have been developed which are compatible with the data found in the first experiment and involve terms that might have some theoretical significance. (These five models, of course, do not exhaust all the possibilities; they do represent what is felt to be the most likely explanations of the experimental results.) The five proposed models, the significance of each term in the model, and the calculated normalized coefficient of each term is shown in Table III. Since the normalized coefficient represents the change in tenacity (in

TABLE III. Alternative Models for Expressing Results of First Set of Experiments

Alternative model no.	Variable		Possible significance	Normalized coefficient
	Symbol	Mean		
Original	Q	9.45	—	−1.19
	V_1	35	—	−1.30
	V_2	140	—	+1.92
I	V_1/Q	3.78	Draw-down in coagulation bath	+1.19
	V_2/V_1	4.08	Stretch ratio	+2.49
	V_2	140	Strain rate of stretching	−0.57
II	V_1/Q	3.78	Draw-down in coagulating bath	+1.19
	$1/V_1$	0.0292	Coagulation time	+2.49
	V_2	140	Strain rate of stretching	+1.92
III	Q	9.45	Shear rate through spinnerette	−0.57
	V_1/Q	3.78	Draw-down in coagulating bath	+0.62
	V_2/V_1	4.08	Stretch ratio	+1.92
IV	Q/V_2	0.069	Final denier	−1.00
	V_2/V_1	4.08	Stretch ratio	+1.11
V	Q/V_1	0.276	Denier in coagulating bath	−1.00
	V_2/V_1	4.08	Stretch ratio	+2.11

grams per denier) produced by increasing the indicated variable 100% from its mean value, it is possible to express the models presented in Table III mathematically. For example, the mathematical equivalent of model I is

$$\theta = 2.52 + 1.19\,\frac{(V_1/Q - 3.78)}{3.78} + 2.49\,\frac{(V_2/V_1 - 4.08)}{4.08} - 0.57\,\frac{(V_2 - 140)}{140} \quad (8)$$

Selection of Proper Model

First Set of Additional Experiments

Each model in Table III fits the data obtained in the first experiments equally well. In order to determine which model comes closest to describing the mechanism governing fiber strength, additional experiments covering a larger area of experimental conditions will have to be made.

The first set of additional experiments consisted of five runs made at increasing production rates but constant ratios of Q/V_2 and V_2/V_1. Hence, while the absolute values of Q, V_1, and V_2 increased proportionally, their relative values remained constant. No difference in the measured physical properties of the tows resulted from these changes (Table IV and Figure 3). This finding leads one to the conclusion that the model involved is one in which the three independent variables Q, V_1, V_2 occur only as ratios, as in models IV and V. This point is illustrated by Column 4 of Table V which shows the change in tow tenacity predicted by each of the six models when the production rate is increased from the lowest to the highest value

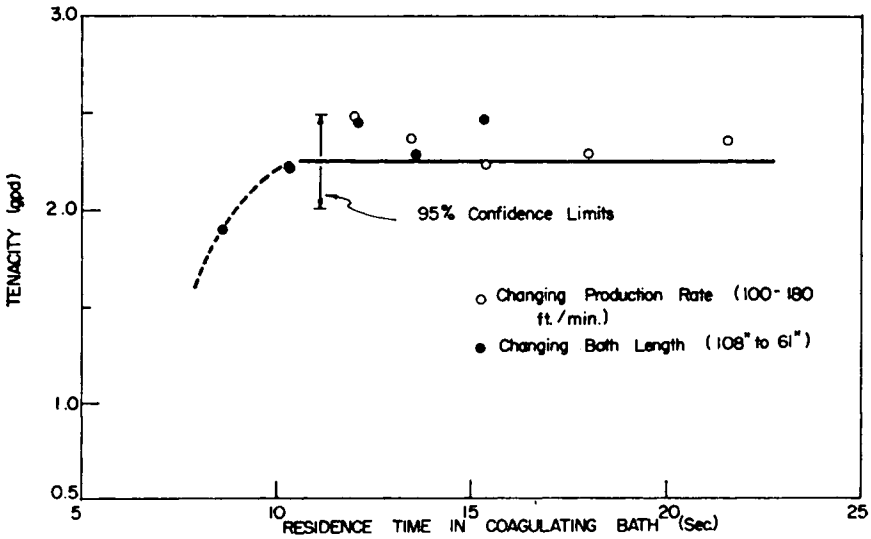

Fig. 3. Tenacity as a function of fiber residence time in the coagulating bath.

TABLE IV. Mechanical Properties of Fiber Spun with Varying Residence Time in the Coagulating Bath[a]

Expt. No.	Production rate Q, lb./hr.	Bath roll velocity V_1, fpm	Stretch roll velocity V_2, fpm	Transit time, t, sec.	Bath length L, in.	Tenacity θ, gpd	Stiffness modulus E, gpd	Elongation s, %
1	8.10	30	120	18	108	2.30	48.0	23.5
2	12.15	45	180	12	108	2.48	52.0	20.0
3	10.80	40	160	13.5	108	2.37	48.0	22.1
4	6.75	25	100	21.6	108	2.36	52.0	25.8
5	9.45	35	140	15.4	108	2.22	49.0	21.5
6	9.45	35	140	13.6	95	2.29	55.0	23.7
7	9.45	35	140	12.1	85	2.23	52.6	21.8
8	9.45	35	140	15.4	108	2.06	49.2	20.2
9	9.45	35	140	8.7	61	1.90	48.7	24.2
10	9.45	35	140	10.4	73	2.22	52.8	23.2
11	9.45	35	140	15.4	108	2.48	53.4	22.8

[a] Fixed experimental conditions: $\delta = 20\%$, $N = 5000$, Si = 16%, Tt = 170°C.

TABLE V
Tenacities Predicted by Models of Table III for Experiments Run at Highest and Lowest Machine Speeds

Alternative model no.	Predicted tenacity, gpd, at:		Predicted change in tenacity, gpd
	Low speed,[a]	High speed,[b]	
Original	2.67	2.35	0.32
I	2.60	2.27	0.33
II	2.92	2.50	0.42
III	2.62	2.30	0.32
IV	2.51	2.51	0.00
V	2.49	2.49	0.00
Observed	2.36 ± 0.24[c]	2.48 ± 0.24[c]	−0.12 ± 0.35[c]

[a] Run 4 in Table IV.
[b] Run 2 in Table IV.
[c] 95% confidence limits based on σ of 0.12 gpd for tenacity with 28 degrees of freedom obtained from σ_0 and $4\sigma_b$ of Table II and $4\sigma_b$ of Table VII.

studied. Thus, three of the proposed five models, along with the original linear model, have been eliminated since they do not predict the behavior observed in these five additional experiments.

Second Set of Additional Experiments

Six more experiments were run in which the length of the coagulating bath was varied at a constant machine speed in order to determine the possible effect of filament residence time in the coagulating bath, t, a derived variable of model II. As the time in the coagulating bath is reduced from 15.4 to 8.7 sec., this model predicts a drop in tenacity of 1.14 gpd at constant spinning speed. The actual tows show no dependence of tenacity, stiffness modulus, or elongation on bath length (i.e., filament residence time in the bath). These experiments, therefore, also eliminate II as a valid model. Still, Figure 3 does suggest that the tenacity might be lowered if the time could be made even shorter either by increasing the spinning speed beyond the range covered or by shortening the coagulating bath further, or both.

PHYSICAL AND CHEMICAL VARIABLES

Experimental

The previous experiments point to the conclusion that the tow physical properties must be governed by the stretch ratio and final denier (model IV), or by the stretch ratio and the denier per filament in the coagulating bath (model V). The latter combination suggests the possibility that the mechanical properties of the fiber might be functions of the solvent content of the filament as it is stretched. It was for this reason that a fourth set of

TABLE VI. Design and Response Matrix for Experiments Involving Physical Variables[a]

Run no.	Level	Independent Variables: Production Q, lb./hr.	Spinnerette no. of holes N	Coagulation bath: Length L, in.	Coagulation bath: Temp. T_c, °C.	Coagulation bath: Concn. S_c, %	Dope total solids c, %	Drying temp. T_d, °C.	Responses: Tenacity Θ, gpd	Elongation ϵ, %	Stiffness modulus E, gpd	δ, denier/filament	Residual solvent after stretching, S_f, %
	+	12.54	7500.0	108.0	70.0	16.0	28.0	170					
	0	9.40	5000.0	95.0	65.0	14.0	25.0	155					
	−	6.27	2500.0	82.0	60.0	12.0	22.0	140					
	% Change	33.00	50.0	13.7	7.7	20.0	12.0	9.7					
1		−	−	−	−	−	−	−	2.44	22.6	47.0	3.86	8.73
2		+	−	−	+	+	−	+	1.08	17.3	35.0	8.34	13.98
3		−	+	+	+	+	−	−	3.20	23.6	55.0	1.38	7.39
4		+	+	+	−	−	−	+	2.46	24.0	47.9	2.74	8.06
5		−	+	−	+	−	+	+	3.06	22.7	46.5	1.50	7.20
6		+	+	−	−	+	+	−	2.64	24.0	41.9	2.79	8.69
7		−	−	+	−	+	+	+	2.02	17.5	45.4	4.07	9.37
8		+	−	+	+	−	+	−	1.96	22.4	39.9	8.19	11.20
9		−	+	+	−	−	+	−	3.01	20.6	53.0	1.43	6.74
10		+	−	−	−	−	+	+	1.48	17.7	43.9	8.27	12.17
11		−	−	−	+	+	+	−	2.20	18.7	53.3	3.92	9.63
12		+	+	+	+	+	+	+	2.00	22.5	46.2	3.15	10.18
13		+	−	+	−	+	−	−	1.54	20.1	44.8	7.30	12.85
14		−	−	+	+	−	−	+	1.93	17.7	55.0	4.10	9.87
15		+	+	−	+	−	−	−	2.62	25.6	48.8	2.42	8.61
16		−	+	−	−	+	−	+	2.94	23.0	57.7	1.33	8.01

[a] Fixed experimental conditions: $V_1 = 35$ fpm, $V_2 = 140$ fpm, $V_3 = 134$ fpm.

TABLE VII. Coefficients for Regression Equations Involving Physical Variables

Variables				Responses				
Coefficient	Effect of:	0 Level	% Change Per Level	Tenacity θ, gpd	Elongation E, %	Stiffness modulus ϵ, gpd	δ, denier/filament	Residual solvent after stretching, S_t, %
b_0	—	—	—	2.286	21.25	47.58	4.049	9.54
b_1	Production rate Q, lb./hr.	9.4	33.0	(−0.314)	0.45	(−4.03)	(1.351)	(1.18)
b_2	Spinnerette holes N	5,000	50.0	(0.455)	(2.00)	(2.04)	(−1.957)	(−1.43)
b_3	Coag. bath length L, in.	95	14.0	−0.021	−0.20	0.82	−0.004	−0.09
b_4	Coag. bath temp. T_c, °C.	65	7.7	−0.030	0.06	−0.12	0.076	0.22
b_5	Coag. bath concn. S_c, %	14	20.0	−0.084	−0.41	−0.17	−0.014	(0.47)
b_6	Dope total solids c, %	25	12.0	0.010	−0.49	−1.32	0.116	−0.15
b_7	Drying temp. T_d, °C.	155	9.7	(−0.165)	(−0.95)	−0.38	0.138	0.31
$b_{12}, b_{37}, b_{56}, b_{48}$	Two-way interactions			0.003	0.33	0.61	(−0.668)	−0.40
$b_{13}, b_{29}, b_{46}, b_{58}$				0.039	0.75	0.33	−0.051	−0.06
$b_{14}, b_{36}, b_{57}, b_{28}$				−0.028	0.19	−0.96	0.049	0.06
$b_{15}, b_{26}, b_{47}, b_{38}$				−0.074	−0.31	−1.41	0.009	0.24
$b_{16}, b_{25}, b_{34}, b_{78}$				0.038	0.44	0.74	0.084	−0.01
$b_{17}, b_{23}, b_{45}, b_{68}$				−0.053	−0.38	0.08	0.087	0.07
$b_{18}, b_{24}, b_{35}, b_{67}$				0.009	0.29	−0.38	−0.056	0.02
b^{s} [a]				−0.071	−0.51	(2.76)	−0.059	0.22
			$4\sigma_b$	0.200 [b]	1.70	1.90	0.280	0.96
			σ_t	0.066	0.50	1.72	—	—

[a] Runs 1–8 and 9–16 of this experiment were made in separate blocks with two different batches of raw material. This coefficient represents the difference between blocks produced by the use of different batches of raw materials.

[b] When b_5 is eliminated, this value becomes 0.16 gpd.

experiments was devoted primarily to a study of those variables which might govern the amount of solvent in the tow. This set consisted of a $^1/_8$ replicate of a 2^7 factorial design (2^{4-7}) involving the seven variables Q, N, L, T_o, S_c, c, and T_d.

The fixed experimental conditions, the values of the independent variables, and the fiber properties obtained are listed in Table VI. The coefficients of the resulting regression equations are given in Table VII. As before, the significant coefficients are enclosed in parentheses. The solvent content of the stretched fiber was measured by extracting a sample of the two with boiling ethyl Cellosolve and analyzing for the solvent content by gas chromatography. (The solvent content of the tow was also measured before stretching, with results showing the same trends as those made before stretching. Only the values determined after stretching are reported, because they were more reproducible. The presence of entrained water and solvent is probably responsible for the greater error associated with measurements of the solvent content before stretching.)

Relationship Between Tenacity and Solvent Content

The results given in Table VII indicate that the tenacity and solvent content of the tow are significantly influenced by the same variables, i.e., the pumping rate Q and the number of orifices in the spinnerette, N. This suggests that tenacity and solvent content are interrelated responses and that tenacity depends on the solvent content of the tow as it is stretched. The relationship between these two variables is shown in Figure 4. For this plot, the tenacities were adjusted to a common drying temperature

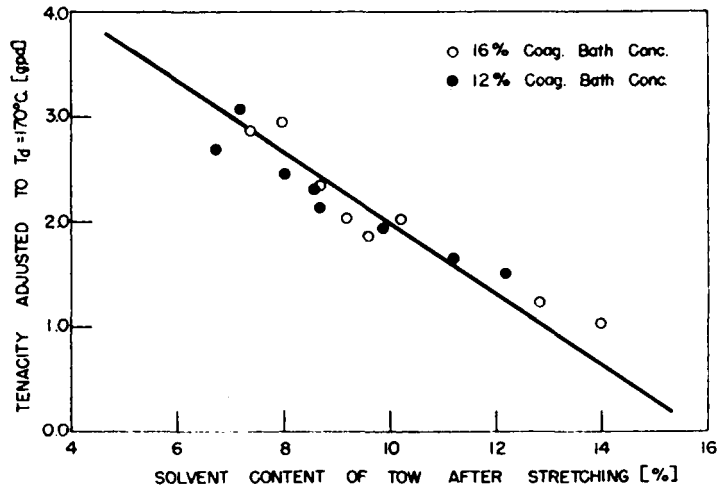

Fig. 4. Tenacity of finished tow versus solvent content of tow measured after stretching. (Draw ratio 4×.)

(the high temperature) since this variable affects tenacity but not the solvent content of the yarn. This was done by subtracting 0.33 gpd ($2b_7$) from the tenacity of tows produced at the low temperature. The relationship between tenacity θ and solvent content S_t shown in Figure 4 is

$$\theta = 4.70 - 0.270S_t \tag{9}$$

with a standard error of estimate (or residual standard deviation) of 0.19 gpd and a correlation coefficient squared (r^2) of 0.904. Equation (9) indicates that at a stretch ratio of 4 an increase of 1% (absolute) in the tow solvent content causes a decrease in tenacity of 0.27 gpd. This result is not unexpected, since the mobility of the fiber macromolecules will increase as the solvent content of the fiber increases. Therefore, less orientation will be imparted by a given amount of stretch.

Factors Governing Solvent Content of the Tow

Having established the dependence of tenacity on solvent content, it becomes of interest to identify the factors which influence the solvent content of the tow, S_t. Table VII shows that S_t depends on the solvent content of the coagulating bath, Q, and N. According to eq. (7), Q and N control the filament size. By plotting S_t against various functions of the filament size in the coagulating bath δ_c (i.e., δ_c, $1/\delta_c$, $\delta_c^{1/2}$, and $1/\delta_c^{1/2}$) it was found empirically that S_t correlates best with $\delta_c^{1/2}$, which is proportional to the reciprocal of the specific surface s of the filament. The specific surface is defined as the area of surface per unit volume of fiber through which the solvent can diffuse out into the coagulating bath, i.e.,

$$s = \frac{2\pi r_f l}{\pi r_f^2 l} = \frac{2}{r_f} \tag{10}$$

where r_f is the radius of a cylindrical filament of length l. Consequently, the specific surface is inversely proportional to the radius of the fiber.

The specific surface of the fibers at the end of the coagulating bath can be related to fiber denier from a consideration of the relationship between fiber denier and its radius

$$r_f = \sqrt{\frac{\delta_c}{9 \times 10^5 \rho\pi}} \tag{11}$$

and between the tow denier as it leaves the coagulating bath and its final denier

$$\delta_c = D\lambda(1 - R/100)/N \tag{12}$$

Combining eqs. (10), (11), and (12) gives

$$1/s = 2.65 \times 10^{-4} \sqrt{\frac{D\lambda(1 - R/100)}{N}} \tag{13}$$

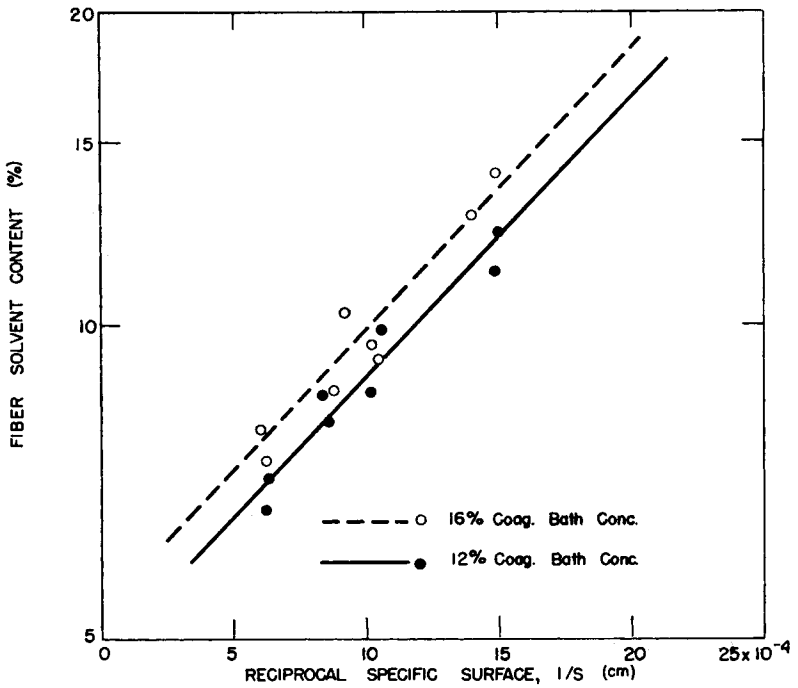

Fig. 5. Solvent content of tow measured after stretching versus the reciprocal specific surface of the fiber at the end of the coagulating bath. (Draw ratio 4×.)

for a fiber having a density ρ of 1.26. The relationship between the filament size and its solvent content is shown in Figure 5 in which $1/s$ as defined by eq. (13) is plotted against the log of S_f. The least-squares regression equations of Figure 5 are

$$S_f = K \exp \{615/s\} \tag{14}$$

where $K = 5.31$ for filaments coagulated in a bath containing 16% solvent and $K = 4.84$ for filaments coagulated in a 12% bath. The correlation coefficient squared of these combined equations is 0.936.

The actual value of the specific surface differs from that calculated from eq. (14) for three important reasons: (1) The fibers are not of circular cross section, (*2*) because of the contained solvent, the fiber is swollen in the coagulating bath which changes the fiber density and surface area, and (*3*) the specific surface changes with draw and solidification as the fiber travels through the coagulating bath.

Factors one and three, however, probably effect the calculated results only by introducing a proportionality constant, and the second introduces only a 3% difference when the solvent content changes from the highest to the lowest values observed. Thus, in spite of these difficulties, eq. (13) probably represents a valid method of calculating a fiber specific surface proportional to the real quantity. Actual measurements of the ratio of

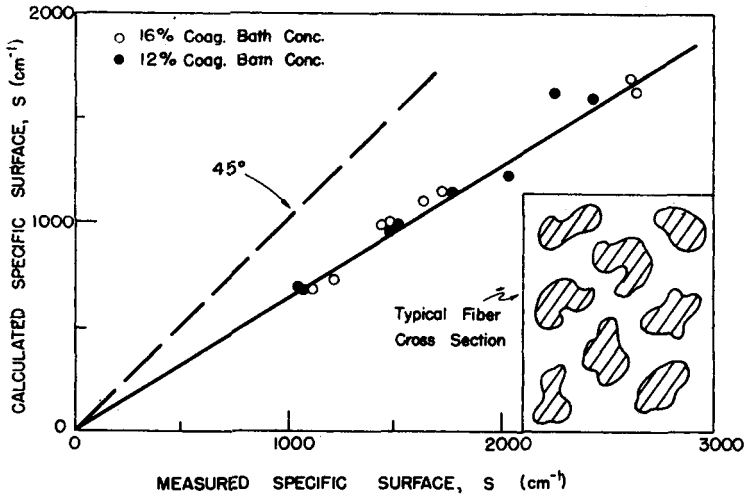

Fig. 6. Calculated versus measured specific surface.

fiber perimeter to fiber cross-sectional area made on photomicrographs of the finished fiber show the specific surface to be 50% greater than that expected for a perfect circular cylinder (see Fig. 6).

Solvent Diffusion and Specific Surface

Solution of Fick's laws for radial diffusion out of an isotropic cylinder predicts[14a] that the solvent content will vary with radius r_f and time t as $\exp\{-t/r_f^2\}$. For diffusion out of a "case-hardened" cylinder having a thin skin of constant thickness and fixed diffusing constant and an internal core having no resistance to the diffusion medium, the solvent content would vary[14b] as $\exp\{-t/r_f\}$. The empirically determined dependence of solvent content on the radius of the filament fits neither of these relations, although the similarity with the case-hardened cylinder is close ($S_f \propto \exp\{r_f\}$ rather than $\propto \exp\{-1/r_f\}$).

A second discrepancy with the diffusion equation is also apparent. The results cited in Table IV and Figure 3 show that the tenacity of the fibers does not change with residence time in the coagulating and wash bath. This observation implies that solvent content of the tow during stretching also does not depend on these factors (at least during the times covered in these experiments). For a closer check on the effect of bath residence time on fiber solvent content, three additional runs were made. The results given in Table VIII show that the fiber solvent content increases somewhat as the coagulating bath is shortened, but that this difference is largely eliminated after extraction in the wash bath (which was held at constant length). Even when exposure time in the wash bath varied (the experiments made at changing production rates, Table IV and Figure 3), the solvent content apparently did not vary enough to affect the measured

TABLE VIII
Solvent Content of Tows at Different Points in the Spinning Process as a Function of Coagulation Bath Length

Solvent Content of Tow (%, Average of 3 Measurements)					
	Coagulation bath length			Std. dev. of measurement, (df = 6), %	Signif. difference at 95% confid. level, %
Point measured	61 in.	85 in.	108 in.		
After coagulation bath	26.8	27.1	21.6	1.40	2.8
After wash bath	16.9	15.6	14.1	1.08	2.2
After stretching	11.4	11.3	10.0	0.70	1.4

tenacity. These experiments therefore appear to be carried out at "infinite" time, where the diffusion laws predict that the fiber solvent content will no longer depend on the time or the radius of the fiber but will have a concentration of solvent equal to the concentration of solvent in the external bath. This conclusion is not compatible with the observed results which show a dependence on radius.

The reason these solutions of Fick's laws do not agree with the experimental observations may be that they involve several assumptions not realized in the spinning experiments. For example, the diffusion constant, radius, skin thickness, and concentration of the external bath are not constant, as required by the cited solutions.

Empirical Deviation of Equation for Tenacity

The experiments covering the time-dependent variables reported in Tables I and II were reduced to models which show that tenacity is a function of stretch and filament size, either in the coagulating bath (model V) or at the end of the process (Model IV). When eqs. (9) and (14) are combined, the last set of experiments (Table VII) then reveal a dependence of tenacity on the specific surface of the fiber in the coagulating bath, which is a function of the fiber size at that point:

$$\theta = 4.70 - 0.270\, K \exp\{615/s\} \tag{15}$$

It should thus be possible to find the relationship between tow tenacity, specific surface, and stretch ratio by plotting the log of tenacity versus $1/s$ for each value of the stretch ratio which occurs. This has been done in Figure 7, which includes all the data obtained in Table VI, the data in Table I made at stretch ratios of 3 and 5.33, and the data obtained in a set of thirteen additional experiments in which fibers having varying stretch ratios and deniers were spun. (Since drying temperature effects tenacity,

the tenacity of all tows produced at the −1 level of temperature were adjusted as before to the +1 level by subtracting 0.33 gpd.) The results confirm the dependence of fiber tenacity on these two factors.

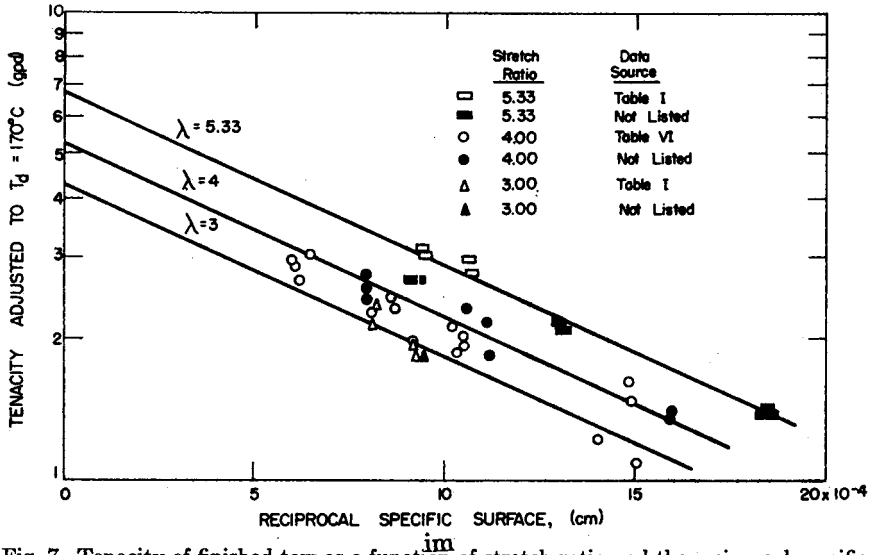

Fig. 7. Tenacity of finished tow as a function of stretch ratio and the reciprocal specific surface of the fiber at the end of the coagulating bath.

The relation shown by Figure 7 can be solved empirically to yield the following equation applicable to yarns dried at the high temperature:

$$\theta = 2.44 \exp\{0.19\lambda - 863/s\} \tag{16}$$

Replacing s by the variables controlled in the spinning operation (eq. 13) yields:

$$\theta = 2.44 \exp\{0.19\lambda\} \exp\left\{-0.229 \sqrt{\frac{D\lambda(1-R/100)}{N}}\right\} \tag{17}$$

The standard error of estimate of eq. (17) is 0.20 gpd (coefficient of variation of 9%) and $r^2 = 0.861$. Since the standard error of estimate of this equation corresponds closely to the experimental error for tenacity shown in Tables II and VII, it is apparent that stretch ratio and fiber size in the coagulating bath are responsible for virtually all the variations in tenacity encountered in these spinning experiments.

Although changing the concentration of solvent in the coagulating bath from 12 to 16% increases the solvent content in the tow, the change is so small (less than 1.0%) that the resulting change in tenacity is not great enough to be detected by present test methods. For this reason, the coagulating bath concentration does not appear in eq. (17).

Selection of Best Model for Tenacity

From the derivation of eq. (17), it is evident that the tenacity of the fiber depends only on the drying temperature, the stretch imparted to the fiber, and its solvent content during stretching. The solvent content is in turn governed by the denier per filament of the fiber in the coagulating bath. By making use of eq. (6), eq. (17) can be expressed in terms of the original controlled variables as:

$$\theta = K \exp\{K'V_2/V_1\} \exp\{K''(Q/V_2)(V_2/V_1)(1/N)\} \quad (18)$$

$$\theta = K \exp(K'V_2/V_1) \exp\{K''(Q/V_1)(1/N)\} \quad (19)$$

where the K's are constants. Eq. (19) contains the same combination of variables proposed in model V, and eq. (18) contains the same variables as model IV except that V_2/V_1 occurs twice. In this manner, the relation between models IV, V, and eq. (17) is shown.

Although eq. (17) was developed on quasitheoretical grounds, there is no assurance that it is a better model than IV or V. All the data available were therefore fitted to equations of the form of the models listed in Table III (the coefficients were recalculated to give the least-squares fit). Two additional models were also tested:

$$\theta = 2.30 + 0.421\lambda - 1730(1/s) \quad (20)$$

and

$$\theta = 1.74 \exp\{0.794 \ln \lambda\} \exp\{-865\ (1/s)\} \quad (21)$$

Equation (20) was selected because it is the simple linear model involving terms in λ and $1/s$ (i.e., the regression equation of the data shown in Figure 7 if plotted linearly against tenacity rather than logarithmically). Equation (21) is similar to eqs. (16) and (17) except that the stretch term appears as $\ln \lambda$, which is theoretically a more valid measure of large deformations taking place as a result of viscous or plastic flow.[15] The results

TABLE IX
Correlation Coefficients for Various Models of Tenacity and Stiffness

Model	r^2 for Tenacity	r^2 for Stiffness
Original	0.09	0.23
I	0.65	0.33
II	0.66	0.34
III	0.65	0.40
IV	0.86	0.48
V	0.85	0.47
Eq. (17)	0.86	0.45
Eq. (20)	0.86	0.46
Eq. (21)	0.86	0.45

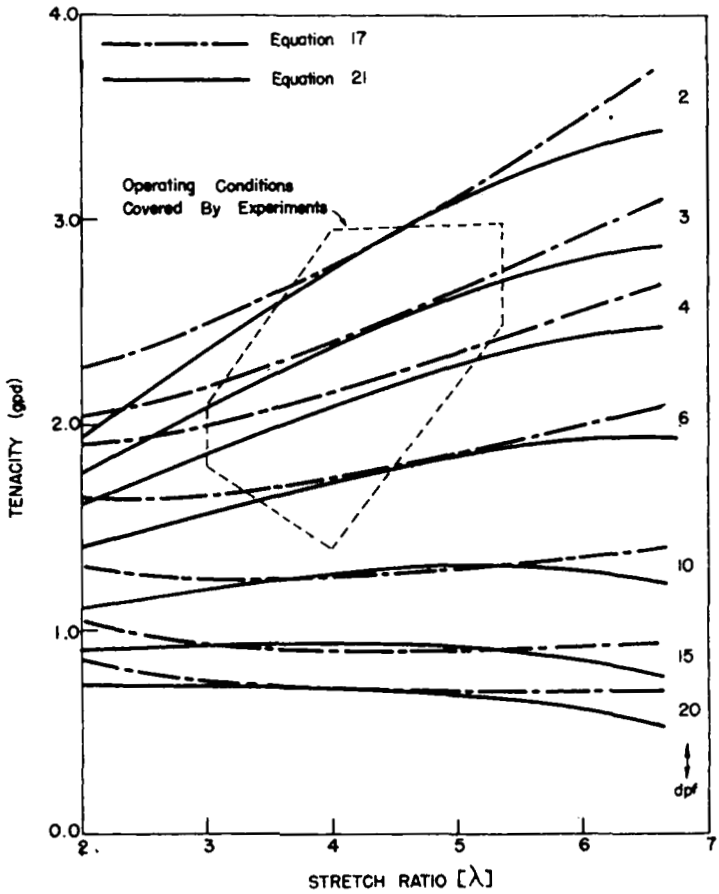

Fig. 8. Tenacity of tow predicted by eqs. (17) and (21) as a function of stretch ratio and finished denier per filament (assuming 4% relaxation and a drying temperature of 170°C.).

summarized in Table IX show that models IV and V and eqs. (17), (20), and (21) represent the data equally well. Again a choice between several acceptable models is called for.

Such a choice can be made when the implications of eqs. (17) and (21) are considered. The tenacities predicted by these equations are plotted as a function of stretch and finished denier per filament (at 4% relaxation) in Figure 8. In this figure, the section within the diamond includes the experimental area actually covered by the experiments already described. The rest of the area therefore represents values of tenacities predicted by eqs. (17) and (21) extrapolated to conditions not actually covered. Figure 8 shows that the effectiveness of a given amount of stretch in increasing tenacity decreases as the finished filament denier increases, and for filament deniers of about 10 or more, stretch has very little effect on tenacity. This implies that high-denier fibers contain so much solvent that little orien-

TABLE X. Tenacity of High Denier Fibers Predicted by Various Models

Model	Predicted tenacity, gpd		Predicted change on stretching, gpd	Predicted tenacity, gpd		Predicted change on stretching, gpd
	Den. 11.9, Stretch 3.0	Den. 11.8, Stretch 5.33		Den. 16.8, Stretch 3.0	Den. 14.4, Stretch 5.33	
IV	0.38	0.89	+0.51	−0.62	0.38	+1.0
V	0.91	0.55	−0.36	0.23	−0.06	−0.29
(17)	1.13	1.13	0.00	0.88	0.94	+0.06
(20)	0.88	0.97	+0.09	0.38	0.61	+0.23
(21)	1.10	1.12	+0.02	0.86	0.93	+0.07
Observed[a]	1.14	1.03	−0.11	0.78	0.84	+0.06
95% Confidence limits[b]	±0.24	±0.24	±0.35	±0.24	±0.24	±0.35

[a] Corrected to +1 level of drying temperature by subtracting 0.33 gpd.

[b] Based on σ of 0.12 gpd with 28 degrees of freedom obtained from σ_0 and $4\sigma_b$ of Table II and $4\sigma_b$ of Table VII.

tation takes place during stretching. At even higher deniers, strength decreases with increasing stretch!!

Although this is a rather surprising result, it is easy to rationalize on the basis of the mechanism developed above and defined by eq. (17), (20), or (21). A fiber of a given final denier produced at a high stretch ratio has a larger cross-sectional area in the coagulating bath before stretching than a fiber produced at low stretch. Even though the high stretch tends to increase the strength (by $\exp\{0.19\lambda\}$ in eq. (17)), the greater fiber size in the coagulating bath tends to decrease it (by $\exp\{-0.229\sqrt{D\lambda}\}$ in eq. (17)) because of the higher solvent content during stretching. When the finished denier becomes large enough, the latter effect becomes greater than the former, and the strength of the fiber decreases on stretching.

To check this prediction, 12- and 17-denier fibers were prepared at stretch ratios ranging from 3 to 5.33. Unfortunately, it was not possible to make the 17-denier fiber at the high stretch ratio because the spinning solution could not be pumped fast enough. The tenacity of the tows produced are presented in Table X together with the results predicted by the models under consideration. A comparison of the observed and predicted values shown in this table eliminates IV and V as valid models. Although eq. (20) is somewhat better, it gives a relatively poor fit, particularly at the high deniers, and predicts that a 20-denier fiber made using a draw ratio of four will have zero tenacity.

A choice between (17) and (21) is more difficult to make since both equations fit all the experimental data equally well. Logically, however, a function yielding a maximum tenacity, eq. (21), rather than a minimum, seems more reasonable. The location of the maximum predicted by eq. (21) can be obtained by differentiating with respect to λ and equating the derivative to 0. This gives

$$\delta\lambda = 50.6 \tag{22}$$

Since the product $\delta\lambda$ is the denier per filament in the coagulating bath, the surprising conclusion is reached that no matter what size of finished fiber is desired, the maximum tenacity will be obtained when the stretch ratio is selected so as to produce a denier of 50 in the coagulating bath. Obviously, the high stretches required to produce optimum small-size fibers cannot be achieved in practice. For the manufacture of 10-denier fibers and higher, however, the concept of an optimum fiber size (OFS) in the coagulation bath becomes important. Thus, if eq. (21) can be accepted as valid, it may be possible to characterize a wet spinning process in terms of one parameter, the OFS. No doubt, its value will be a function of the specific resin, solvent, coagulation, and stretching systems employed. In any event, the fact that these two models, which are both based on the specific surface of the fiber in the coagulating bath, do fit is strong evidence that the influence of specific surface on fiber solvent content is the key variable controlling fiber strength.

The best model found relating fiber stiffness with the spinning variables is of the same form as eq. (21):

$$E = 38.3 \exp\{0.358 \ln \lambda\} \exp\{-0.061 \sqrt{D\lambda(1 - R/100)/N}\} \quad (23)$$

The standard error of estimate is 3.8 gpd and $r^2 = 0.45$. Although eq. (23) does not fit the stiffness data as well as (21) fits the tenacity, it is fairly good considering the high experimental error associated with the stiffness measurement ($\sigma = 2.9$, Tables II and VII).

DISCUSSION

These results illustrate the fundamental role of filament size and stretch ratio in determining the tenacity and probably the stiffness of wet-spun fibers. The effect of stretch is not at all unexpected. The importance of filament size, however, has not been previously recognized. For instance, as Morbey[10] has mentioned, draw ratio and spinnerette hole size are the most significant variables influencing the fiber mechanical properties. He ascribed the great effect of spinnerette hole size on fiber tenacity to the higher shear rate of extrusion through the smaller holes and the consequent greater orientation expected to take place under these conditions. However, his experiments were conducted at constant pumping rate and at a constant extrusion velocity which was maintained by changing the number as well as the diameter of the orifices so as to keep the total extrusion area constant. Consequently, not only the shear rate was changed with the hole diameter, but also the size of the filaments. Considering these possibilities, the results described here would attribute the dependence of fiber tenacity to the filament size rather than to the effect of hole size on shear rate.

The shear rate through the spinnerette orifice indicated by variable (26) is $\dot{\gamma} \propto Q_v/Nd^3$. Table VII indicates that tenacity varies inversely with Q and directly with N, a result opposite to what would be expected if the resulting increase in shear rate were the controlling factor. A second point indicating that shear rate is not an important variable is the fact that model III, which involves a term dependent on shear rate, was shown to be invalid. In addition to the experimental results already described, direct measurements of the effect of shear rate made by varying the spinnerette

TABLE XI
Effect of Spinnerette Hole Diameter on Fiber Mechanical Properties

Spinnerette		Relative		Fiber properties[a]			
No. of holes	Diam., mm.	Area	Shear rate	Tenacity, gpd	Elongation, %	Stiffness, gpd	Denier/ filament
1250	0.140	1	2.9	1.83	16.6	62.8	6.7
1250	0.200	2	1	1.85	17.0	61.0	6.8

[a] Average of 4 tow breaks.

hole diameter did not show any dependence of the fiber mechanical properties on shear rate (Table XI); consequently, the important feature controlling tenacity appears to be filament size rather than shear rate. Since the number of holes in a spinnerette influences the filament size (eq. (7)), this factor affects the fiber properties.

The greater influence of fiber solvent content over extrusion shear rate in controlling the fiber strength is also confirmed by some results of Gröbe.[3] He reported that the tenacity of fibers spun from a 19% total solids solution was 4.4 gpd while that spun from a 13% solution at equal resin mass throughput was 2.5 gpd in spite of the 46% higher shear rate to which this solution had to be subjected. The solution of lower concentration would contain more solvent during stretching, however, and this would explain the drastic drop in the tenacity. Gröbe was spinning polyacrylonitrile from dimethylformamide into a coagulant of hexanetriol.

It also should be pointed out that "draw-down" in the coagulation bath (variable (21)), which is often considered a major characteristic of wet-spinning systems, does not appear to have any significant effect on the fiber physical properties. This conclusion is reached because the models containing draw-down as one of the variables were shown to be invalid. In addition, all results could be explained by eq. (21) which does not involve draw-down.

Although eq. (23) relating stiffness with the spinning variables explains only 45% of the observed variance, it fits nearly as well as can be expected. It appears, therefore, that stiffness is controlled by the same mechanism operating for tenacity.

The influence of molecular orientation in reducing the elongation is seen in the significant effect of stretch roll velocity and the relatively high (although insignificant) regression coefficients of bath roll velocity V_1 and relaxation R (Table II). These effects are opposite in sign to those for the tenacity, as expected for variables which influence the orientation of the fiber. On the other hand, the mechanism governing elongation is not completely analogous to the orientation mechanism already described for tenacity, since the effect of the number of spinnerette holes on these properties is in the same direction (Table VII) rather than the opposite. Because of the relatively large experimental variability associated with elongation, the mechanism controlling this property remains obscure.

The only other effects shown by the work reported here are decreases in tenacity and elongation with increases in drying temperature. This behavior can be explained by a flaw mechanism. At the beginning of the drying cycle, excess moisture and solvent is driven out of the fiber, and the rate at which this is done is critical. Extremely fast evaporation, as would be expected at higher temperatures, would cause cracks or flaws in the fiber structure and thereby reduce both the fiber elongation and tenacity. Such an effect might also explain the decrease in elongation as the number of spinnerette holes decreases (filament size increases) because more flaws would develop in the larger fibers, which have a greater quantity of liquid to be evaporated.

Whatever the mechanism, a similar effect produced by increasing the stretching temperature (rather than the drying temperature) has been observed. Morbey[10] reported that fibers spun from an 80:20 mixture of polyacrylonitrile and cellulose acetate decrease 0.078 gpd in tenacity and 6.44% in elongation when the drawing temperature is increased from 73° to 87°C. For a 60:40 mixture, an increase of 0.078 gpd in tenacity with essentially no change (−0.2%) in elongation was produced. Apparently, the chemical nature of the fiber plays an important role.

CONCLUSIONS

The most important variables controlling the mechanical properties of wet-spun modacrylic fibers are the amount of stretch and the solvent content of the fiber as it is stretched. These are the major factors which would be expected to control the orientation of the fiber. Thus, fiber tenacity and stiffness increase with increasing stretch, and decrease with increasing solvent content. Although the effect of these variables on elongation is not conclusively established, the observed behavior of the elongation shows some analogies with this mechanism: i.e., the elongation decreases as tenacity and orientation increase. No direct measurements of fiber orientation were made, however.

The solvent content of the fiber, in turn, is governed primarily by the size of the filament in the coagulating bath. The smaller the filament, the less the solvent content, because of the corresponding greater surface area per unit volume of solvent to be removed. The size of the fiber in the coagulating bath is governed by the volume of spinning solution extruded per unit time, the concentration of resin in the spinning solution, the number of holes in the spinnerette, and the velocity at which the fiber is withdrawn from the coagulating bath.

The dependence of tenacity upon fiber size in the coagulating bath and upon stretch ratio leads to some unexpected results. For example, the preferred quantitative relationship predicts that the tenacity of a fiber of constant finished denier will pass through a maximum as the stretch ratio is increased. The value of the stretch which produces maximum tenacity depends only on the size of the finished fiber and decreases with increasing fiber size. For fibers ranging in denier from 0 to 9, the optimum stretch is larger than can be realized experimentally, and the tenacity of a fiber always increases as the stretch ratio increases. As the desired fiber size becomes greater than 9 the maximum tenacity passes within the stretch range covered experimentally, and a point is reached where a fiber of constant finished denier will show no change in tenacity with increasing stretch. This prediction was confirmed experimentally. At deniers greater than 15, the maximum shifts to even lower stretches, and the tenacity of a fiber of constant finished denier would be expected to decrease as the stretch increases. This latter effect, however, could not be verified experimentally because of physical limitations of the spinning

equipment. In the spinning system described here, the maximum tenacity is always reached by using a stretch ratio that will produce a denier of 50.6 at the end of the coagulating bath.

The only other variable that influenced the fiber mechanical properties was drying temperature. Higher drying temperatures decrease both the tenacity and elongation of the spun fiber. No change in the fiber properties was observed to result from changes in the velocity or shear rate at which the spinning solution was extruded through the spinnerette holes nor from the diameter of the holes. Other variables, having no effect on fiber properties over the range of the experimental spinning conditions covered, are length, temperature, and solvent concentration of the coagulating bath, residence time of the filaments in the coagulating bath, and relaxation allowed after stretching.

Glossary

b_i	Coefficient of linear regression equation
$\mathbf{b}_i$	Normalized coefficient of linear regression equation
c	Concentration of resin in the spinning solution
D	Total denier of finished tow
D_{ab}	Fiber dyeability
D_c	Total denier of tow at end of coagulating bath
d	Diameter of spinnerette orifice
E	Stiffness modulus of fiber
K	Constant
L	Length of coagulating bath
l	Length of fiber
dm/dt	Mass of resin extruded through spinnerette per unit time
dm'/dt	Mass of fiber collected per unit time at end of spinning machine
N	Number of orifices in spinnerette
Q	Weight of resin extruded per unit time
Q_v	Volume of spinning solution extruded per unit time
R	Relaxation after stretching
r_f	Radius of fiber
r	Correlation coefficient
S_c	Solvent content of coagulating bath
S_f	Solvent content of fiber after stretching
s	Fiber specific surface
T_c	Temperature of coagulating bath
T_d	Drying temperature
t	Transit time of fiber through coagulating bath
V_1	Roll velocity at the end of the coagulating bath
V_2	Roll velocity at end of stretching zone
V_3	Roll velocity after relaxation and at end of spinning machine
$\dot{\gamma}$	Shear rate through spinnerette orifice
δ	Denier per filament of finished fiber
δ_c	Denier per filament at end of coagulating bath

ϵ Elongation of fiber at rupture
θ Tenacity of fiber at rupture
λ Stretch ratio
ρ Resin density
σ Standard deviation

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Synopsis

A study of 11 variables of a modacrylic-fiber wet-spinning process has shown that the tenacity and stiffness modulus of the fiber depend primarily on the amount of stretch imparted during spinning and the solvent content of the tow at the time of stretching. The solvent content governs the degree of plasticity of the fiber during stretching and hence the degree of orientation achieved at a given stretch ratio. The solvent content, in turn, is determined primarily by the specific surface (fiber area per unit volume) through which solvent diffuses out of the fiber into the coagulating bath. As a result, the tenacity and stiffness modulus are inversely related to the denier per filament in the coagulating bath prior to stretching. The denier of the filament in the coagulating bath is determined by the concentration of fiber resin in the spinning solution, the volume of solution extruded per unit time, the velocity with which the fiber is withdrawn from the coagulating bath, and the number of holes in the spinnerette. These fundamental variables, along with stretch, determine the tenacity and stiffness of the spun fiber. The only other variable studied that affected the fiber physical properties was the drying temperature. Increasing the temperature slightly reduces both fiber tenacity and elongation. Variables having no influence on the mechanical properties over the range studied

include length, temperature, and solvent concentration of the coagulating bath, residence time of the filaments in the coagulating bath, relaxation applied after stretching, and shear rate at which the spinning solution is extruded through the spinnerette orifices.

Résumé

Une étude du processus de filature à l'état humide de 11 variétés de fibres modacryliques, a montré que la ténacité et le module de rigidité de la fibre dépend en premier lieu de l'élongation de la fibre durant la filature et du contenu en solvant du fil à l'instant de l'élongation. Le contenu en solvant régit le degré de plasticité de la fibre durant l'élongation et de ce fait le degré d'orientation obtenu pour un rapport, d'élongation donné. Le contenu en solvant est à son tour déterminé en premier lieu par la surface spécifique (surface de fibre par unité de volume) au travers duquel il diffuse dans le bain coagulant. Comme résultat on a obtenu que la ténacité et le module de rigidité sont inversément proportionnels au denier par filament dans le bain coagulant avant l'élongation. Le denier du filament dans le bain coagulant est déterminé par la concentration de la résine dans la solution de filature, par le volume de la solution extrudé par unité de temps, par la vitesse avec laquelle la fibre est soustraite au bain coagulant et par le nombre d'orifices de la filiére. Ces variables fondamentales déterminent avec l'élongation la ténacité et la rigidité de la fibre. L'autre variable, effectuant les propriétés physiques de la fibre, est uniquement la température de séchage. L'augmentation de cette dernière réduit la ténacité de la fibre et, dd façon moins prononcée, l'élongation. Les variables n'ayant aucune influence sur les propriétés mécaniques dans le domaine étudié sont la longueur, la température et la concentration du bain coagulant, le temps de séjour des filaments dans ce dernier, la relaxation appliquée après l'étirement et la vitesse de cisaillement à laquelle la solution est extrudée au travers des orifices de la filière.

Zusammenfassung

Eine Untersuchung von 11 Variablen des Nassspinnverfahrens für Modacrylfasern zeigte, dass Festigkeits- und Steifheitsmodul der Faser hauptsächlich von der Grösse der beim Spinnen angewendeten Streckung und vom Lösungsmittelgehalt des Wergs bei der Streckung abhängen. Der Lösungsmittelgehalt regelt den Plastizitätsgrad der Faser während des Streckens und damit den bei einem bestimmten Streckungsverhältnis erreichten Orientierungsgrad. Der Lösungsmittelgehalt ist seinerseits hauptsächlich durch die spezifische Oberfläche (Faseroberfläche pro Volumseinheit) bestimmt, durch welche das Lösungsmittel aus der Faser in das Fällbad diffundiert. Das führt zu einer umgekehrten Abhängigkeit des Festigkeits- und Steifigkeitsmoduls vom Denier pro Faden im Fällbad vor dem Strecken. Das Denier des Fadens im Fällbad ist durch die Konzentration der Fasersubstanz in der Spinnlösung, das in der Zeiteinheit extrudierte Lösungsvolumen, die Geschwindigkeit, mit welcher die Faser aus dem Fällbad gezogen wird, und der Zahl der Öffnungen der Spinndüse bestimmt. Diese grundlegenden Variablen bestimmen, zugleich mit der Streckung, die Festigkeit und Steifigkeit der gesponnenen Faser. Die einzige andere von den untersuchten Variablen, welche die physikalischen Eigenschaften der Faser beeinflusst, war die Trocknungstemperatur. Zu den Variablen, die im untersuchten Bereich keinen Einfluss auf die mechanischen Eigenschaften haben, gehören Länge, Temperatur und Lösungsmittelkonzentration des Fällbades; Aufenthaltsdauer der Fäden im Fällbad; nach der Streckung angewendete Relaxation und Schergeschwindigkeit beim Extrudieren der Spinnlösung durch die Spinndüsenöffnungen.

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