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ULTRALOW DENIER POLYBENZIMIDAZOLE (PBI) YARNS

By Marshall Tan and Joseph R. Leal

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16. Abstract

A study to determine the feasibility of preparing ultralow denier polybenzimidazole (PBI) yarns was undertaken utilizing technology previously developed under various NASA and Air Force contracts. Conditions that presently yield multifilament yarns with bundle deniers ranging from 75 to 15,000 were used as a baseline. From this starting point, process parameters were identified that give 5-filament yarns with yarn deniers as low as 0.80. Physical properties from such ultralow denier yarns were at levels that would permit subsequent fabrication into fabrics.

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FOREWORD

The research described herein was conducted by the Celanese Research Company, a division of Celanese Corporation, and performed under NASA Contract NAS2-9575. The National Aeronautics and Space Administration technical monitor was Demetrius Kourtides, Ames Research Center, Moffett Field, California.

At Celanese, the work was accomplished under the direction of Marshall Tan, Research Engineer. Joseph R. Leal, Senior Staff Associate, served as project coordinator and contract administrator.

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ABSTRACT

A study to determine the feasibility of preparing ultralow denier polybenzimidazole (PBI) yarns was undertaken utilizing technology previously developed under various NASA and Air Force contracts. Conditions that presently yield multifilament yarns with bundle deniers ranging from 75 to 15,000 were used as a baseline. From this starting point, process parameters were identified that give 5-filament yarns with yarn deniers as low as 0.80. Physical properties from such ultralow denier yarns were at levels that would permit subsequent fabrication into fabrics.

SUMMARY

Processing parameters are well established for the extrusion of polybenzimidazole (PBI) solutions into multifilament yarns with filament deniers of 1.5. Fabrics made from such yarns, however, would exceed the weight constraints placed upon the Solar Sail and lower deniers than had previously been experienced were needed. By appropriate adjustment of the many variables, which control fiber spinning processes, conditions were identified which yielded yarns with filament deniers as low as 0.17. Despite this order of magnitude reduction in denier, the physical properties of the yarns were not degraded materially.

Polymer solutions (dopes) were made in dimethylacetamide (DMAc) solvent at concentrations of 23% by weight. The dry jet/wet spinning process was demonstrated with the extrusion of spinning dopes from 10-hole and 5-hole spinnerettes into air gaps of 13 - 18 cm (5 - 7 inches). The extruded filaments, fully coagulated in cool water, were capable of being processed at rates of 10 m/min or more. The resulting yarns had filament deniers as low as 0.17. Physical properties of the ultralow deniers ranged from 5 - 7 g/d tenacity, 5 - 15% elongation and 130 - 160 g/d modulus. These properties are roughly comparable to those obtained with 1.5 denier per filament (dpf) PBI fibers.

INTRODUCTION

Polybenzimidazole (PBI), or more properly, poly-2, 2' (m-phenylene)-5, 5'-bibenzimidazole, is a non-flammable polymer and textile fiber which was developed at the Celanese Research Company under Air Force and NASA contracts over the past fourteen years. Of the several thousand pounds of polymer made, most was converted into textile fibers and yarns for test and evaluation in Air Force and NASA applications requiring non-flammable woven, knitted, or braided flexible structures such as flight clothing and lanyards. PBI is characterized by outstanding thermal, physical, and chemical stability, properties which make it attractive for applications involving hostile or extreme environments. The space environments in which the Solar Sail would be deployed can be considered to be relatively harsh.

The Solar Sail concept envisions the use of a large sail which will reflect the sunlight that impinges upon it. In reflecting the sunlight, a small propulsive force will occur which, when integrated over a sufficiently large area, will result in a significant thrust. The area density for the substrate material was set at about $3 g/m^2$. A temperature capability up to 370°C was considered necessary as was a long term resistance to radiation. Although PBI in fibrous form was not considered feasible for the entire sail, it seemed attractive as an accessory in joining segments of the sail together and as a rip-stop material.

The inherent properties of PBI would meet the temperature and radiation requirements, but state-of-the-art yarns were considered too big to be used in conjunction with a 2.5nm (0.1 mil) thick film. Typically, PBI yarns consist of multiple filaments which have an effective diameter equivalent to about 15-17nm (1.5 denier per filament - dpf). Experimentally, some filaments had been spun and drawn to a cross-sectional dimension approximately 10-11nm (1.0dpf) but it was evident that something closer to 1-2nm was desired. To achieve such ultralow deniers, it would be necessary to examine the many spinning process parameters and to find those conditions that would permit continuous extrusion of the polymer into very fine filaments.

OBJECTIVES AND STATEMENT OF WORK

The objective of the contract was to determine the feasibility of making ultralow denier PBI yarns. This objective was to be met by the performance of the following tasks:

Task I. A preliminary study and calculation will be conducted as to the fiber and yarn required to fabricate fabric with an area density of $3 g/m^2$. The voids or pinholes present in this fabric will be defined.

Task II. Conditions leading to low denier spun yarn will be defined. The spun yarn will then be drawn and again the conditions leading to the minimum possible denier will be defined.

Among the important variables in fiber formation are solvent and non-solvent selections, polymer concentration, solvent-non-solvent ratio, jet-hole size, and shear rate during coagulation. A considerable background exists in the dry spinning of PBI and the dry spinning method will be examined preferentially over the wet spinning technique. A series of experiments in which each of the important variables is considered will be conducted.

PBI is soluble up to about 23% solids level in dimethylacetamide. Other solvents include dimethylformamide, dimethylsulfoxide, concentrated sulfuric acid, and glacial formic acid, but DMAc is the preferred solvent and will be used exclusively. Most other liquids are non-solvents.

Task III. In the unexpected event that dry spinning does not reach deniers below 1 dpf, wet spinning methods will be examined. In wet spinning, coagulation occurs in a non-solvent. In general DMAc solutions are used with water as the coagulant. Other coagulants, such as dilute DMAc or dilute sulfuric acid, should be explored.

Task IV. Physical properties will be determined on selected samples of fiber and yarn. In particular, the denier, tenacity, elongation and modulus will be determined. Other properties as may be determined to be meaningful to the Solar Sail application will be made only with the concurrence of the NASA Technical Project Manager.

Task V. Both fiber and yarn samples of the lowest denier achieved (a minimum of 20 gms) will be supplied to NASA.

EXPERIMENTAL

A. Polymer, Dope and Equipment.

Polybenzimidazole (PBI) is a polymer made by the melt condensation of 3, 3', 4, 4'-tetraaminobiphenyl and diphenylisophthalate. Typical polymer is a tan to light brown powder with an inherent viscosity of 0.7 to 0.8 dl/g (0.4g per 100 ml of 97% sulfuric acid). Besides acid, PBI is soluble in highly polar solvents such as dimethylformamide, dimethylacetamide, and dimethylsulfoxide. Dimethylacetamide (DMAc) containing 2% LiCl is the preferred solvent which has been used at Celanese to spin textile fibers from PBI.

Polymer solutions (dopes) were made by solutioning PBI polymer in DMAc solvent. Generally, polymer concentrations of 23% by weight were used. In all cases, 2% lithium chloride was added as a stabilizer.

The equipment used throughout the experimental work is conventional fiber producing equipment. Schematic diagrams of the processes used are shown in figures 1 and 2. Photographs of the dry jet/wet spinning process with its individual components is shown in figures 3 through 5.

B. Single Stage Process.

The so-called dry jet/wet spinning process is characterized as being a single stage or one-step process since spinning and drawing are accomplished continuously in-line. As practiced in this project, the spin dope (polymer solution) was placed in a pressure vessel (bomb) and heated to 120°C. To spin, the dope was fed under 0.10MPa (15 psi) nitrogen pressure to a metering pump driven by a variable speed D.C. motor. The pump speed, and hence the dope flow rate, was maintained constant by an electronic controller. In order to remove the last traces of particulate matter, the dope was passed through a heated candle filter and finally, just before entering the spinnerette, through a stainless steel sintered disc filter. The spinnerettes used had either 5 or 10 holes with diameters of 40nm. The faces of the spinnerettes were heated at about 130°C during the extrusion of the dope.

In the dry jet/wet spinning technique, the spinnerette is positioned vertically at some distance above the coagulating bath. The coagulating bath consisted of water. A slight flow of fresh water was continuously fed into the coagulating bath to prevent a build up of solvent as the spinning progressed.

The coagulated fibers leaving the coagulating bath were passed around a set of skewed rolls, the bottom one of which was partially immersed in hot water. By wrapping the yarn several times around the skewed rolls, the yarn remains for sometime on the rolls, during which it is washed free of solvent.

Figure 1. Schematic of Dry Jet/Wet Spinning Process

Single Stage Operation

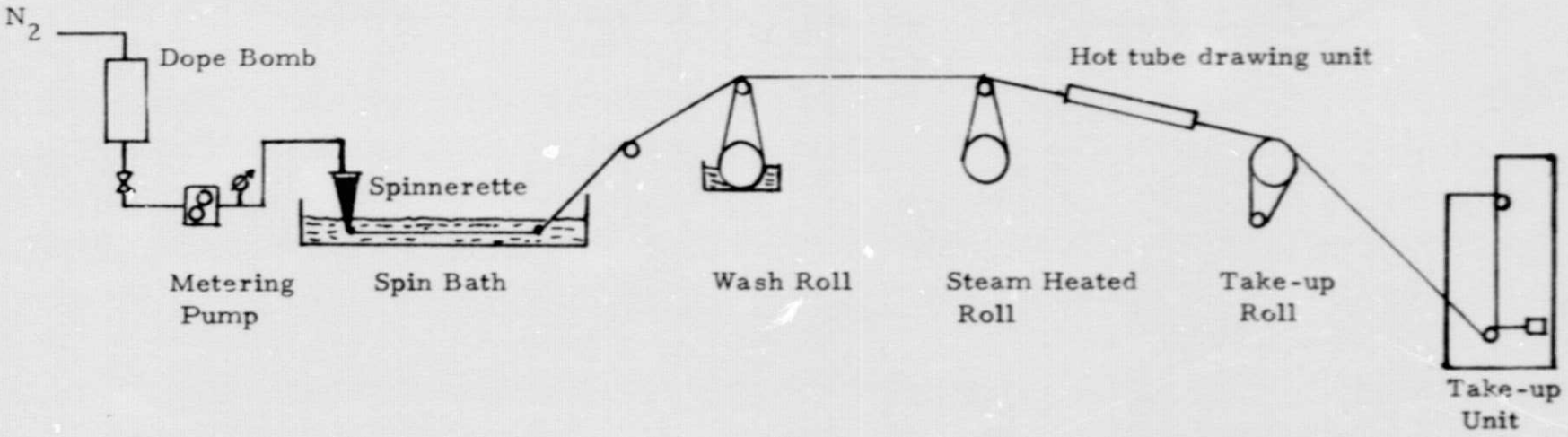


Figure 2. Diagram of Hot Drawing Process

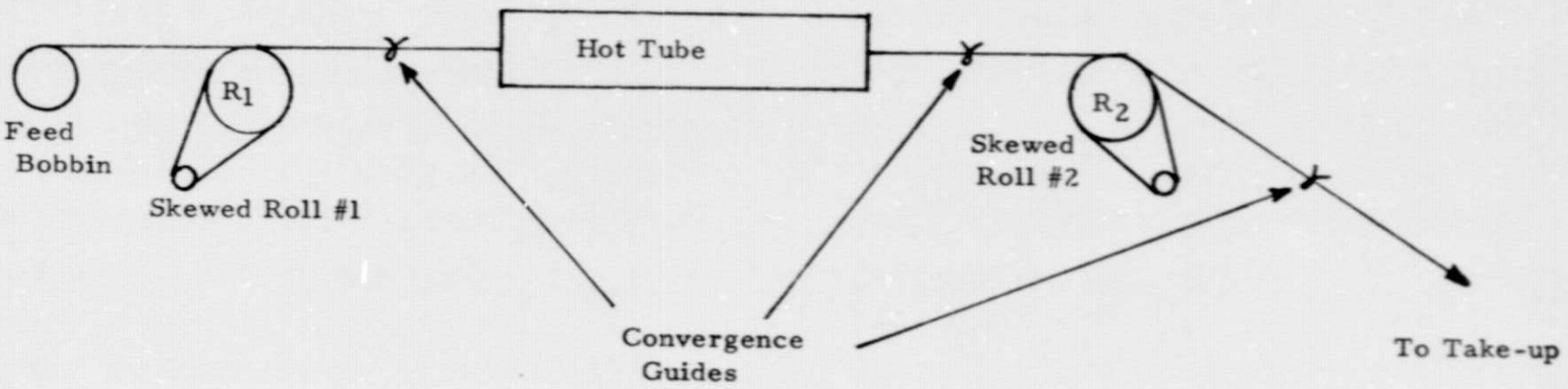


Figure 3. Dry Jet/Wet Spinning Line

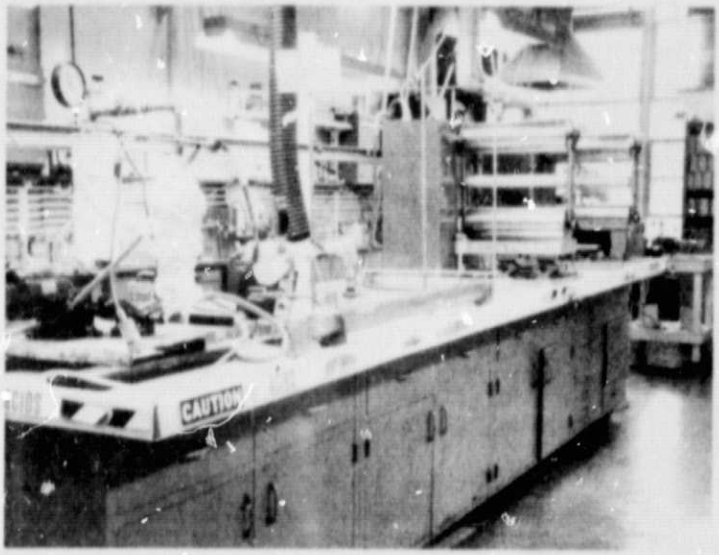


Figure 4. Hot Air Draw Tube

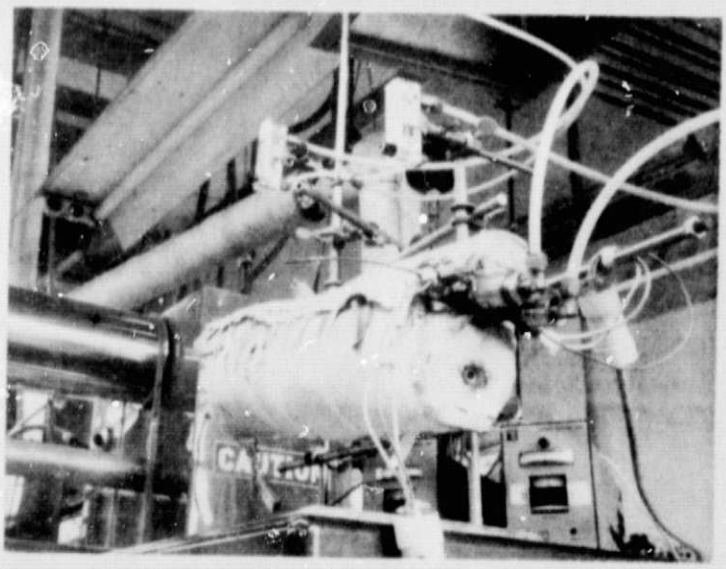
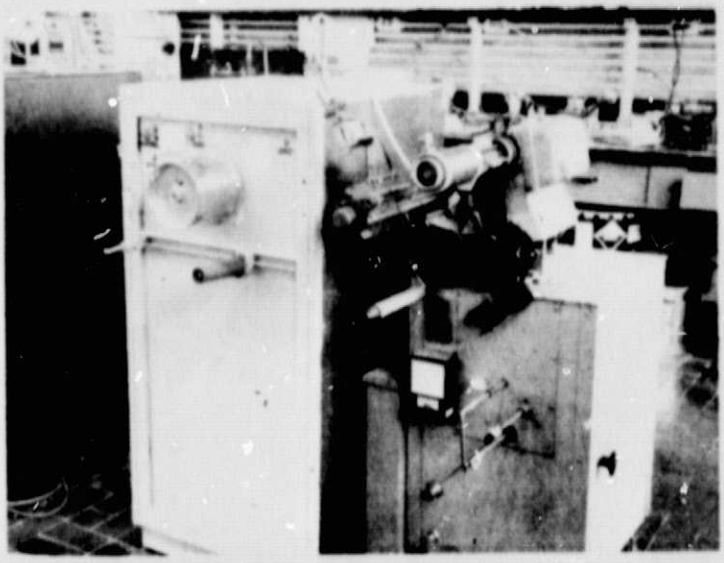
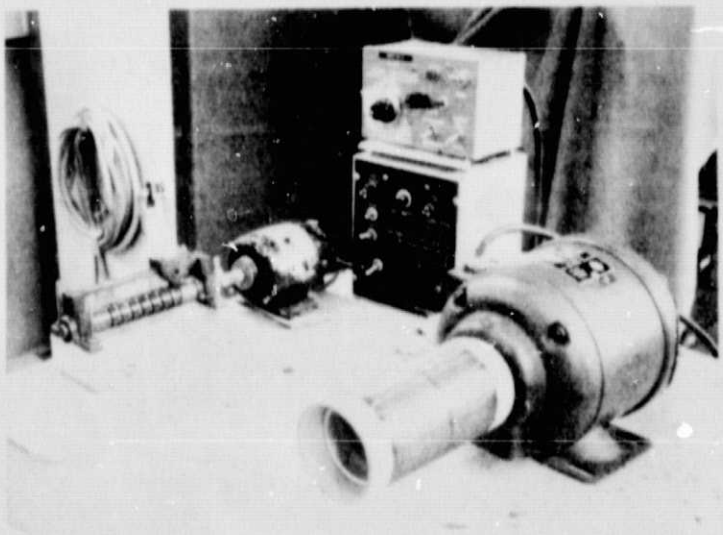


Figure 5. Take-up Units



a. Leesona Take-up



b. D.C. Motor-Driven Take-up

The PBI filaments from the first set of skewed rolls (wash rolls) were dried by passing over a set of steam-heated skewed rolls. Again, the number of wraps given the yarn determines the length of time on the rolls. In this case, sufficient time was provided to assure that the filaments were thoroughly dried before they were subjected to the high temperature drawing step of the process.

Drawing of the yarn was accomplished by passing the dried yarn through a heated muffle furnace at 400°-500°C. Skewed rolls before and after the muffle furnace are accurately maintained at differential speeds such that the yarn is under a given degree of tension. The combination of the spin line tension and the muffle furnace temperature cause the yarn to elongate. In so doing, the polymeric structure within the filaments becomes somewhat better organized and the physical properties of the yarn are developed. The drawn yarn was collected by either of two pieces of equipment. One such unit is a commercial unit which was found to be primarily suited for yarns of more conventional deniers. The other unit was assembled from a d.c. motor, the speed of which could be precisely controlled, and a transverse winder. This set-up provided less tension during take-up and permitted longer continuous operation without breaking the yarn.

C. Two Step Process.

The two step process used was very similar to that described above except that the drawing step was conducted off line, separately, rather than on-line, continuously. This method was tried first so that properties could be measured on the as-spun yarn. In this way, progress toward the ultralow denier targets could be monitored at an early stage. However, it was found that the relatively weak as-spun fibers were easily damaged during the take-up operation. This resulted in frequent breaks during collection and it was decided to try an in-line draw. Once it was demonstrated that an in-line draw was feasible, the two step method was abandoned.

A. Task I.

Before any spinning was attempted, a preliminary study and calculation was made as to the fiber and yarn required to weave a fabric with an area density of $3 g/m^2$. As a first approach, we assumed the possibility of spinning a 1.0 dpf/10 filament yarn. Such a yarn has an overall denier of 10. By definition, a 9000 meter length of such a 10-denier yarn weighs 10 grams. A 3-gram length of this yarn would equal 2700 meters. If we assume a plain weave fabrice with equal numbers of yarns in the x and y directions (warp and filling), a square meter of such a fabric would have 1350 meter-long yarns in each of the two directions. The distance between yarns would then be 1/1350 meters (=0.74 mm). In this first case, the effective diameter of the yarns was neglected.

When the effective diameter of the yarn is considered, a 10 denier yarn provides a plain weave fabric with 91.4% voids or 0.71 mm of space between adjacent yarns. Extrapolated to 1.0 denier, such a fabric would have 74.1% open space and 0.06 mm between yarns. This calculation is based on the assumption that the yarn filaments have a perfectly round cross-section, that the yarn denier is equivalent to that of a monofilament and that the fabric yarns are perfectly parallel in both the lengthwise and crosswise directions. The density of the PBI was taken as $1.33 g/cm^3$.

Table I shows the calculated spacing and percent voids in a $3 g/m^2$ plain weave fabric using PBI yarns of various deniers. Figure 6 shows the data graphically.

B. Tasks II and III

A review of conventional spinning technology disclosed that there are advantages and disadvantages to both dry and wet spinning methods when very fine deniers are to be produced. In the typical dry spinning techniques, the polymer solution is permitted to drop in a free fall through a considerable vertical distance. As the viscous dope falls, it encounters a hot stream of dry gas (nitrogen in the case of PBI) which serves to evaporate the solvent and coagulate the polymer. With super fine filaments, the height (5-8 m) may be a controlling factor since the filaments may not have sufficient strength to maintain integrity all the way to the bottom.

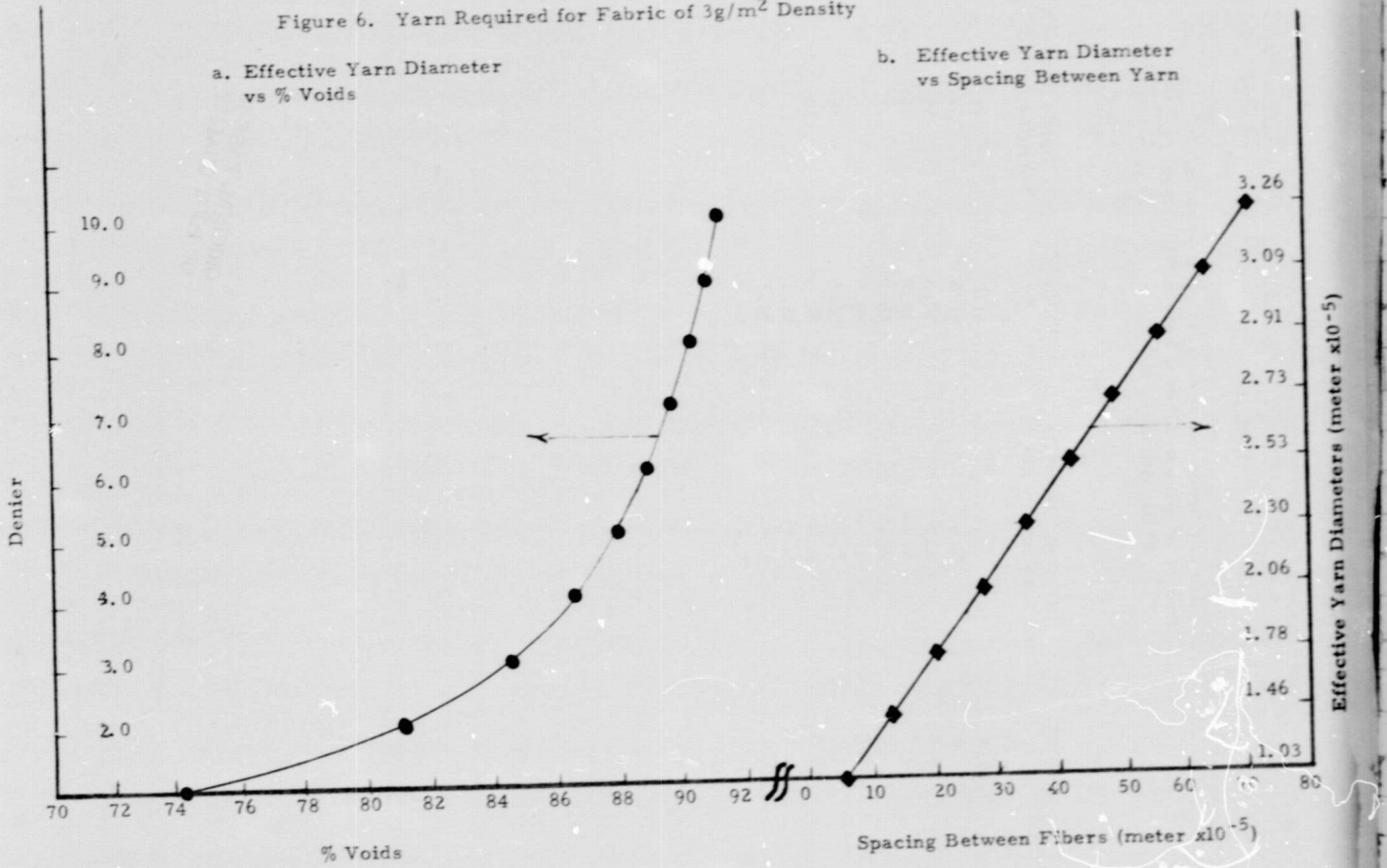
Wet spinning, on the other hand, is generally carried out in a horizontal position with extrusion of the polymer solution directly into a liquid coagulant. However, the unavoidable currents formed in the liquid as the

Table I

% Voids and Space Between Yarns for Various Deniers of Yarn to Make a Fabric With Area Density of $3 g/m^2$

Denier	Effective Diameter of Yarn (meter $x10^{-5}$)	Voids %	Space Between Yarns(meter $x10^{-5}$)
10.0	3.26	91.4	71
9.0	3.09	91.0	64
8.0	2.91	90.4	56
7.0	2.73	89.8	49
6.0	2.53	89.0	42
5.0	2.30	88.0	35
4.0	2.06	86.6	28
3.0	1.78	84.6	20
2.0	1.46	81.3	13
1.0	1.03	74.1	6
0.5	0.73	64.5	4

Figure 6. Yarn Required for Fabric of $3g/m^2$ Density



polymer is extruded into it, can disrupt the filaments when they are extremely fine. Once the filaments are at least partially coagulated, on the other hand, the liquid surrounding the yarn serves to envelope the filaments and protect them to some extent. Such protection is particularly desirable as the filaments become more and more fragile.

In order to exploit the desirable features of both spinning methods, it was decided to extrude the polymer solution vertically into the air, permitting it to drop freely for a short distance before it enters a liquid coagulating bath. In this way, a certain amount of draw down occurs before the polymer meets the liquid. At the same time, some coagulation is initiated and the fine filaments are better able to withstand passage through the liquid and any slight turbulence that may be generated there.

A spinning dope was made up by solutioning PBI polymer in dimethylacetamide (DMAc) solvent. A 23% by weight concentration was used, with 2% lithium chloride added as a stabilizer. A schematic diagram for the preparation of PBI spinning dope is shown in Figure 7. This scheme follows the prodecure outlined by Conciatori et al (1).

In the initial experiments, a two step operation was used. The polymer was spun into the coagulant and collected. Then, in a separate operation, the spun yarn was made to pass through a hot furnace while being stretched. There was considerable difficulty in handling the yarn and in collecting it. It is quite weak until it undergoes the hot stretching step (draw) and the handling and collection of the spun yarn remained a problem. Moreover, the handling problem persisted in the second step during the stringing up. The two-step process is summarized in Table II.

As shown in Table II, the maximum draw ratio achieved by the two stage method was 5.08X at 500°C. At this temperature, a filament denier of 0.92 was realized. Since a 10-hole jet was used, the yarn denier would calculate to about 9.2. Although the physical properties of the 0.92dpf yarn were satisfactory, slightly higher tenacity and elongation were observed when the draw ratio was reduced to 3.41X at 450°C. The physical properties resulting from these experiments are detailed under Task IV.

In order to minimize the handling of the yarn, a single stage operation was tried. An in-line hot air drawing unit was incorporated in the spinning line and the spun yarn, taken directly out of the coagulant, was made to pass through the hot air drawing unit. This method proved to be significantly better than the two step method and was used exclusively during the remainder of the study.

The one-step process is summarized in Table III.

Figure 7.

PBI DOPE PREPARATION

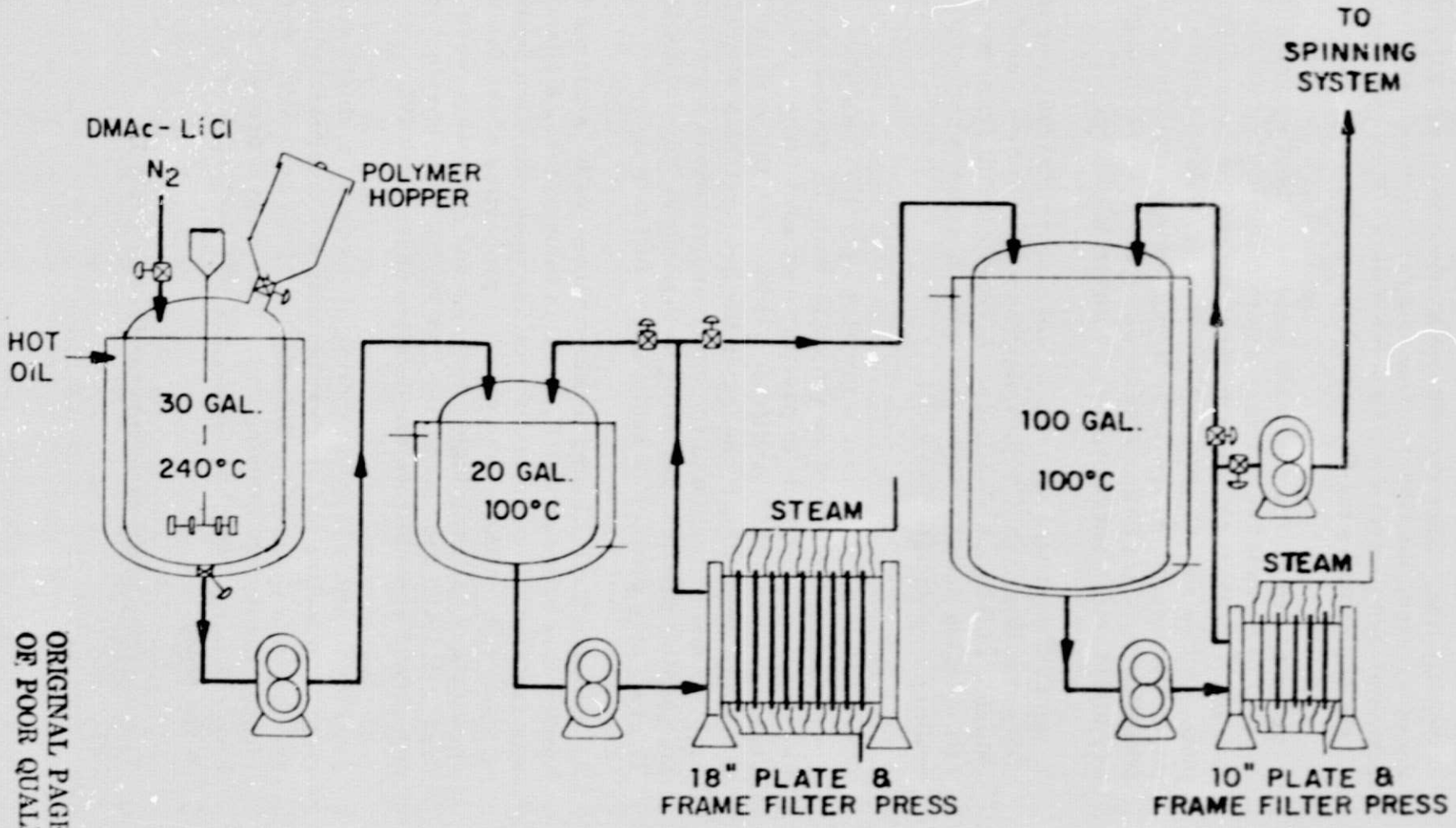


Table II

Two Stage Process

Spinnerette : 10 hole x 40 nm (microns)
Spinnerette Temperature : 423°K (150°C)
Bath Composition: Water
Bath Temperature: Room temperature (296°K - 23°C)
Wash Roll Temperature: 328 - 338°K (55° - 65°C)

Sample No.	Extrusion Rate m/sec(m/min)	Bath Stretch Ratio	Heat Draw Temperature °K (°C)	Heat Draw Stretch Ratio
42077-1	0.32 (19.4)	2.6	No Draw	
42077-2	0.46 (27.3)	1.8	No Draw	
-2-D3	Post Drawn	-	723 (450)	3.55
-2-D6	" "	-	723 (450)	3.41
-2-D7	" "	-	773 (500)	5.08
-2-D8	" "	-	773 (500)	4.06
-1-D1	" "	-	773 (500)	3.04
-1-D2	" "	-	773 (500)	2.36

As shown in Table III, a maximum draw of 6.5 was reached. In the single stage technique, there is a certain degree of easier control in the overall draw of the filament. Since the process is a continuous one, variations can be made in the amount of draw occurring during coagulation simultaneously with variations in the stretching taking place in the hot draw tube. In general, it was demonstrated that the one-step process yielded filament deniers as low as those observed with the two-stage process and lower. This is shown in Table IV.

Since the efforts toward ultralow denier yarns were encouraging with 10-filament yarns, it was decided to try spinning yarns with only five filaments. Even if the filament denier remained the same, the effect of reducing the filament count would be to decrease the yarn denier by a factor of two. Essentially the same conditions that were successfully used with the 10-hole spinnerette were employed with a 5-hole jet. Results of the 5-hole trials are shown in Table V.

As is shown in Table V, overall draw ratios as high as 9.1 were possible. However, this was possible only at a very low extrusion rate. Such low extrusion rates become impractical for the production of any substantial quantities of yarn. Moreover, even at the high draw ratios and low extrusion rates, the denier per filament was not as low as was possible with draw ratios of around 6X at much higher extrusion rates.

Several spinning parameters were evaluated. These included air gap, bath stretch, bath composition and temperature, heat stretch and extrusion rate. However, because of limitations in time and resources, a thorough evaluation leading to ultimate process/ property optimizations was not possible.

The distance between the face of the spinnerette and the surface of the coagulant bath, the air gap, is known to influence the quality of the yarn when some polymers are spun by the dry jet/wet spinning process. Accordingly, the air gap was varied between 14 cm (5.5 in.) and 22 cm (8.75 in.). The physical properties of the yarns obtained indicated that there was relatively little difference between 14 and 18 cm (7 in.) but there was some apparent loss in properties, especially elongation, at air gap distances in excess of 18 cm. There results are shown in Table VI.

The extrusion rate is a measure of the quantity of polymer being extruded. If too little polymer is available, the take-up speed and draw ratio may be affected. The development of fiber properties is greatly influenced by draw r atio and thus the interrelationship with extrusion rate. On the other hand, too great a rate can lead to insufficient coagulation unless the residence time in the bath is increased. Because a larger amount of polymer is being coagulated, the washing and drying times usually need to be extended. If a

Table III

One Stage Process

Spinnerette : 10 hole x 40 nm (microns)
Spinnerette Temperature : 403°K (130°C) or 423°K (150°C)
Bath Composition : Water
Bath Temperature : Room temperature (296°K - 23°C)
Wash Roll Temperature : 328° - 338°K (55° - 65°C)
Drying Roll Temperature : Steam-heated (>373°K - 100°C)

Sample No.	Extrusion Rate m/sec(m/min)	Bath Stretch Ratio	Heat Draw Temperature °K (°C)	Heat Draw Stretch Ratio
5677-4*	0.39 (23.6)	1.3	773 (500)	1.9
-5*	0.39 (23.6)	1.3	773 (500)	2.3
-7*	0.39 (23.6)	1.3	773 (500)	3.2
6977-1	0.39 (23.6)	1.4	773 (500)	3.1
-2	0.39 (23.6)	1.4	773 (500)	3.9
51877-1*	0.39 (23.6)	1.7	773 (500)	3.8
-2*	0.39 (23.6)	1.7	773 (500)	3.6
52077-7	0.34 (20.5)	2.0	773 (500)	4.0
-9	0.34 (20.5)	2.0	773 (500)	4.5

* Spinnerette Temperature: 423°K (150°C)

Table IV

Filament Deniers from Two Stage vs One Stage Processes

Sample No.	Process	Draw Ratio	Denier/filament*
42077-D3	Two-Stage	3.55	1.22
-D8	Two-Stage	4.06	1.19
-D7	Two-Stage	5.08	0.92
5677-4	One-Stage	3.20	1.13
5	One-Stage	3.60	0.93
7	One-Stage	4.50	0.77
6977-2	One-Stage	5.30	0.54
51877-2	One-Stage	5.30	0.53
52077-9	One-Stage	6.50	0.50

* The weight in grams of a 9000 meter length of a single filament

Table V

5- Filament Yarns

Spinnerette : 5-hole x 40 nm (microns)
Spinnerette Temperature : 403°K (130°C)
Bath Composition: Water
Bath Temperature : Room temperature (296°K - 23°C)
Wash Roll Temperature : 328° - 338°K (55° - 65°C)
Drying Roll Temperature : Steam-heated (>373°K - 100°C)

Sample No.	Extrusion Rate m/sec(m/min)	Bath Stretch Ratio	Heat Draw Temperature °K (°C)	Heat Draw Stretch Ratio	DPF*
71377-1	0.06 (3.6)	3.3	773 (500)	3.3	0.33
71377-6	0.06 (3.6)	3.3	773 (500)	4.2	0.32
71377-8	0.06 (3.6)	5.6	773 (500)	3.0	0.32
6177-5	0.04 (2.1)	7.1	773 (500)	2.0	0.31
8577-2	0.18 (10.7)	3.0	773 (500)	3.1	0.31
8577-3	0.16 (9.7)	3.3	773 (500)	3.1	0.18
8477-1	0.17 (10.4)	3.1	773 (500)	3.0	0.17

*Denier per Filament

Table VI

Effect of Air Gap on Physical Properties

Spinnerette: 10 hole x 40 nm (microns)
Spinnerette Temperature: 403°K (130°C)
Bath Composition: Water
Bath Temperature: Room temperature (296°K - 23°C)
Wash Roll Temperature: 328-338°K (55 - 65°C)
Drying Roll Temperature: Steam-heated (373°K - 100°C)
Drawing Temperature: 773°K (500°C)

Sample No.	Air Gap m (in)	Extrusion Rate m/sec (m/min)	Draw Ratio	Physical Properties Tenacity GPa (g/d)	Elongation %	Modulus GPa (g/d)	DPF
52077-1	0.14 (5.5)	0.35 (21.2)	5.5	0.735 (6.18)	10.5	19.3 (164)	0.55
52077-6	0.18 (7)	0.34 (20.5)	5.6	0.714 (6.08)	16.6	16.2 (138)	0.68
52077-7	0.18 (7)	0.34 (20.5)	6.0	0.705 (5.99)	13.1	16.3 (139)	0.60
51877-1	0.22 (8.75)	0.39 (23.6)	5.5	0.637 (5.41)	4.31	20.6 (175	0.58

constant denier (diameter) is desired, the draw ratio may have to be increased, unless it has already reached the point at which the physical properties of the filaments are exceeded, the so-called "draw-break" point. The results of a short span of extrusion rates indicate that a relatively wide range of conditions exist within which the tenacity and modulus are little affected. The effect on elongation, however, is not clear cut. This data is tabulated in Table VII.

The bath composition and bath temperature generally are related to the coagulation rate. It is preferred that the polymer coagulates at such a rate as to minimize inhomegeneities from the outer surface to the inner core. A brief examination of two bath temperatures and two compositions pointed to cool temperatures as being preferable. Little or no obvious differences in yarn properties were shown by water over a 50/50 mixture of water/DMAc. These data are displayed in Table VIII.

Among the most important variables to be considered in this project was the draw ratio. This parameter was considered key to reaching ultralow deniers, while at the same time, providing respectable physical properties. For these reasons, a relatively close inspection was given to the draw ratio. While the overall ratio is the primary factor, the draw that occurs in the coagulant bath, as well as that imposed during passage through the tube furnace, were examined. The data collected is shown in Table IX.

As the work progressed, it became apparent that ultralow denier PBI yarns could be made by appropriate adjustment of the various spinning process parameters. Furthermore, the physical properties of the ultralow denier yarns were not so severely degraded as to preclude their use in the fabrication of textile structures.

C. Task IV

To measure the progress of the work, physical properties were measured on selected samples of fiber and yarn. Using standard ASTM test methods tenacity, elongation, modulus and denier were determined. Some values have already been shown on preceding pages. However, to illustrate how the yarn properties served to guide the work, Tables X and XI set forth the values obtained during the initial phases of the project, at a time when there was a question as to which spinning technique would be used.

From the tabulated data, it is readily seen that the one-stage process gave lower deniers at about the same overall draw ratio and at comparable physicals. This was one of the factors that led to the decision to concentrate upon the single stage dry jet/wet spinning process.

Table VII

Effect of Extrusion Rate on Physical Properties

Spinnerette : 10 hole x 40 nm or 5 hole x 40 nm
Spinnerette Temperature : 403°K (130°C)
Bath Composition : Water
Bath Temperature : Room temperature (296°K - 23°C)
Wash Roll Temperature: 328 - 338°K (55 - 65°C)
Drying Roll Temperature: Steam-heated (>373°K - 100°C)
Drawing Temperature: 773°K (500°C)
Air Gap : 0.18 m (7 in.)

			Physical Properties		
Sample No.	Extrusion Rate m/sec(m/min)	Draw Ratio	Tenacity GPa(g/d)	Elongation %	Modulus GPa(g/d)
52077-6	0.34 (20.5)	5.6	0.714 (6.08)	16.6	16.2 (138)
52577-7	0.16 (9.5)	6.6	0.651 (5.55)	4.11	20.9 (178)
61777-2	0.06 (3.3)	5.7	0.622 (5.30)	10.9	15.0 (128
61777-3	0.04 (2.1)	6.5	0.566 (4.82)	4.51	16.8 (143)
62177-7*	0/20 (11.7)	6.5	0.630 (5.37)	4.51	18.7 (159)

*5-Filaments (5 hole x 40 nm jet)

Table VIII

Effect of Bath Composition and Temperature on Physical Properties

Spinnerette : 10 hole x 40 nm
Spinnerette Temperature : 403°K (130°C)
Wash Roll Temperature : 328 - 338°K (55 - 65°C)
Drying Roll Temperature : Steam-heated (373°K - 100°C)
Drawing Temperature : 773°K (500°C)
Air Gap : 0.18 m (7 in.)

Sample No.	Extrusion Rate m/sec(m/min)	Bath Composition	Bath Temperature °K (°C)	Draw Ratio	DPF	Physical Properties Tenacity GPa(g/d)	Elongation %	Modulus GPa(g/d)
52577-1	0.16 (9.5)	H_2O	288 (15)	5.9	0.47	0.707 (6.03)	8.38	19.6 (167)
52777-1	0.19 (11.6)	H_2O	347 (74)	6.4	0.31	0.706 (6.02)	4.06	21.9 (187)
6177-4	0.20 (11.7)	DMAc/H_2O	298 (25)	5.8	0.48	0.678 (5.77)	6.64	18.7 (159)
6377-1	0.09 (5.2)	H_2O	288 (15)	6.5	0.36	0.776 (6.60)	16.6	15.3 (130)
62177-5	0.20 (11.7)	H_2O	288 (15)	5.9	0.34	0.705 (5.99)	7.13	18.8 (160)

Table IX

Effect of Draw Ratio on Physical Properties

Spinnerette : 10 hole x 40 nm or 5-hole x 40 nm (micron)
Spinnerette Temperature : 403°K (130°C) or 423°K (150°C)
Wash Roll Temperature : 328-338°K (55 - 65°C)
Drying Roll Temperature : Steam-heated (>373°K - 100°C)
Drawing Temperature : 773°K (500°C)
Air Gap : 0.18 m (7in.)

Sample No.	Overall Draw Ratio	DPF	Physical Properties Tenacity GPa(g/d)	Elongation %	Modulus GPa(g/d)
5677-4*	3.2	1.13	0.601 (5.11)	34.8	12.3 (105)
5677-5*	3.6	0.93	0.727 (6.19)	21.4	15.7 (134)
5677-7*	4.5	0.77	0.761 (6.48)	22.1	14.8 (126)
6977-1	4.5	0.60	0.667 (5.69)	9.61	18.0 (153)
6977-2	5.3	0.54	0.705 (6.00)	7.15	20.3 (173)
51877-2*	5.3	0.53	0.565 (4.73)	4.54	19.4 (165)
51877-1*	5.5	0.58	0.636 (5.41)	4.31	20.6 (175)
52077-7	6.0	0.60	0.705 (5.99)	13.1	16.3 (139)
8577-1**	6.1	0.31	0.785 (6.69)	9.52	19.6 (167)
52077-9	6.5	0.50	0.764 (6.50)	8.89	20.1 (171)
52577-7	6.6	0.34	0.651 (5.55)	4.11	20.9 (178)
71377-1**	6.6	0.33	0.626 (5.33)	8.77	16.3 (139)
6277-4	8.1	0.33	0.329 (2.80)	16.7	8.70 (74)
71377-8**	8.6	0.32	0.389 (3.31)	6.88	10.5 (90)
61777-5**	9.1	0.31	0.414 (3.52)	5.63	10.8 (92)

*Spinnerette temperature: 423°K (150°C)
**5-Filament yarn (5 x 40 nm jet)

Table X

Physical Properties from the Two Stage Process

Spinnerette : 10 hole x 40 nm (micron)
Spinnerette Temperature : 423°K (150°C)
Bath Composition : Water
Bath Temperature : Room temperature (296°K - 23°C)
Wash Roll Temperature : 328 - 338°K (55 - 65°C)

Sample No.	Overall Draw Ratio	DPF	Physical Properties Tenacity GPa(g/d)	Elongation %	Modulus GPa(g/d)
42077-1*	2.6	4.74	0.150 (1.28)	87.5	5.3 (45)
42077-2-D3	5.4	1.22	0.646 (5.50)	3.11	23.1 (197)
-2-D6	5.2	1.28	0.703 (5.97)	9.04	18.8 (160)
-2-D7	6.9	0.92	0.630 (5.35)	8.40	15.8 (134)
-2-D8	5.9	1.19	0.690 (5.88)	8.04	18.9 (161)
-1-D1	5.6	0.76	0.666 (5.68)	7.13	18.8 (160)
-1-D2	5.0	0.97	0.642 (5.46)	6.26	18.8 (160)

*As-spun, draw only in the coagulant bath

Table XI

Physical Properties from the One Stage Process

Spinnerette : 10 hole x 40 nm (micron)
Spinnerette Temperature : 403°K (130°C) or 423°K (150°C)
Bath Composition : Water
Bath Temperature : Room temperature (296°K - 23°C)
Wash Roll Temperature : 328 - 338°K (55° - 65°C)
Drying Roll Temperature : Steam-heated (>373°K - 100°C)

Sample No.	Overall Draw Ratio	Physical Properties DPF	Tenacity GPa(g/d)	Elongation %	Modulus GPa(g/d)
5677-4*	3.2	1.13	0.600 (5.11)	34.8	12.3 (105)
-5*	3.6	0.93	0.727 (6.19)	21.4	15.7 (134)
-7*	4.5	0.77	0.761 (6.48)	22.1	14.8 (126)
6977-1	4.5	0.60	0.667 (5.69)	9.61	18.0 (153)
-2	5.3	0.54	0.705 (6.00)	7.15	20.3 (173)
51877-1*	5.5	0.58	0.636 (5.41)	4.31	20.6 (175)
-2*	5.3	0.53	0.565 (4.73)	4.54	19.4 (165)
52077-7	6.0	0.60	0.705 (5.99)	13.1	16.3 (139)
-9	6.5	0.50	0.764 (6.50)	8.89	20.1 (171)

*Spinnerette Temperature: 423°K (150°C)

D. Task V

In fulfillment of the contract requirements, samples were delivered. In total, the samples amounted to about 20 grams. A listing of the samples delivered is shown in Table XII.

Table XII

Properties of Delivered Samples

Sample No.	Denier		Tenacity	Elongation	Modulus
	Filament	Yarn	GPa(g/d)	%	GPa(g/d)
5677-4	1.13	10.9	0.600 (5.11)	34.8	12.33 (105)
5677-5	0.93	7.87	0.727 (6.19)	21.4	15.73 (134)
5677-6	0.77	7.0	-	-	-
5677-7	0.77	7.0	0.761 (6.48)	22.1	14.79 (126)
5677-8	0.77	7.0	-	-	-
5677-10	0.80	7.75	-	-	-
5677-11	0.80	7.75	-	-	-
5677-12	0.80	7.75	0.751 (6.40)	23.7	14.79 (126)
51177-2	0.67	6.26	0.656 (5.59)	6.6	19.02 (162)
52077-2	0.55	4.98	0.726 (6.18)	10.5	19.25 (164)
52077-3	0.68	6.26	-	-	-
52077-4	0.68	6.26	-	-	-
52077-5	0.68	6.26	-	-	-
52077-6	0.68	6.26	0.714 (6.08)	16.6	16.32 (139)
52077-7	0.60	5.40	-	-	-
52077-8	0.60	5.40	0.703 (5.99)	13.1	16.32 (139)
52077-9	0.50	5.42	0.763 (6.50)	8.9	20.08 (171)
8377-6	0.28	1.45	0.660 (5.62)	6.78	18.31 (156)
8377-3	0.18	1.05	0.881 (7.50)	12.9	19.37 (165)
8377-4	0.17	0.80	0.815 (6.94)	9.52	19.61 (167)

CONCLUSIONS

State-of-the-art technology for the production of 1.5 dpf PBI fibers and yarn was pushed forward to yield ultralow denier PBI yarns without the need for the development of new equipment or unique processing techniques. An order of magnitude reduction in denier was achieved with little sacrifice of fiber physical properties. Because of its inherent resistance to combustion, chemicals and radiation, as well as its low and relatively non-toxic smoke generation, ultralow denier PBI yarns can be recommended for weight critical applications in hostile and hazardous environments.

REFERENCES

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