

Wet Spinning of Aliphatic and Aromatic Polyamides

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Synopsis

Bench-scale equipment for wet spinning was designed and built. An experimental study of the wet spinning of several polyamides has been carried out. The polymers studied include nylon 6, nylon 66, redissolved Nomex, and redissolved Kevlar. The superstructure of the wet-spun fibers were studied by optical and scanning electron microscopy as well as small- and wide-angle x-ray diffraction. Mechanical properties were measured and related to the spinning variables. For nylon 6 and nylon 66, the coagulation bath composition was found to be of major importance in determining fiber superstructure. For the case of the redissolved Kevlar, anisotropic spinning dopes were obtained from redissolved fiber, and the wet-spun filaments produced from such solutions were investigated. These fibers proved to have relatively high modulus and strength as spun. They had even greater strengths after hot drawing.

INTRODUCTION

Fibers may be spun from a polymer melt (melt spinning) or from a solution of the polymer. In the latter case, the solvent must be removed by diffusion to leave a solid polymeric filament. Solvent removal in solution spinning may be carried out by either evaporation (dry spinning) or extraction with a nonsolvent for the fiber (wet spinning). In wet spinning, a polymer solution is extruded as a filament into a coagulating bath through which it is pulled by a take-up roll (see Fig. 1). Wet spinning is an important industrial process, with cellulose (viscose rayon), polyacrylonitrile, and aromatic polyamide fibers being commercially wet spun. The scientific literature on wet spinning, though significant,¹⁻¹⁵ is far less extensive and much less quantitative than that for melt spinning. In this paper, we will examine the wet spinning of polyamides.

While nylon 6 and nylon 66 are melt spun commercially, there has been some interest through the years in wet spinning of these polymers also. Ucci and Knudsen¹⁶ have told us that Chemstrand in the 1950's developed nylon 66 wet-spun fibers using a formic acid solvent and supplied a specimen of high-quality fabric made from these fibers. More recently, Epstein and Rosenthal¹⁷ have noted the wet spinning of nylon 66 from H₂SO₄. The wet spinning of nylon 6 from several solvents has been investigated by Kiyotosukuri, Hasegawa, Imamura^{18,19,20} and by Kiyotosukuri and Hirasa.^{21,22}

Aromatic polyamide fibers are of relatively recent vintage, and their commercial development together with other high temperature-resistant fibers has been reviewed by Black and Preston.^{23,24} The wet spinning of poly(hexamethyleneterephthalamide) was studied by Epstein and Rosenthal,¹⁷ but fully

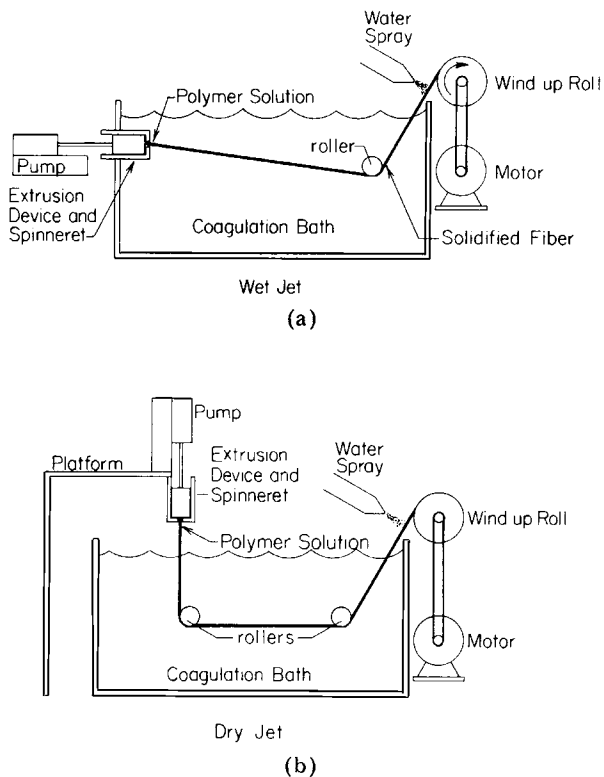


Fig. 1. Wet spinning operation; (a) wet jet; (b) dry jet.

aromatic polymers are only described in the patent literature, notably by King²⁵ for poly(*m*-phenyleneisophthalamide) and by Kwolek²⁶ and Blades²⁷ for poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide). The patent of Kwolek is striking in that the spinning dopes are anisotropic liquids with liquid crystal characteristics, and very high-strength and high-modulus fibers are produced. A recent paper by Ciferri²⁸ reviews the Kwolek patent and related work. Some of the same problems are briefly discussed by Northolt and van Aartsen.²⁹

In recent years at the University of Tennessee, we have developed a research program on fiber spinning and processing. The early work, which was recently reviewed,^{30,31} largely concerned melt spinning. Recently, we have turned our attention to the formation of fibers from polyamides by both melt spinning and wet spinning methods. Studies of melt spinning nylon 6 by our group have recently been reported elsewhere.³² In this paper, we will describe our wet spinning studies of nylon 6, nylon 66, and various aromatic polyamides.

EXPERIMENTAL

Materials

Several nylon 6 [polycaprolactam] and nylon 66 [poly(hexamethyleneadipamide)] polymers were supplied to us by four industrial concerns. du Pont

TABLE I
Polyamides Wet Spun in This Study

Material designation	Chemical type	$[\eta]$	Molecular Weight (from $[\eta]$)	$M_n \times 10^3$ outside laboratory	M_w/M_n outside laboratory	Supplier
N6 1	nylon 6	1.06	13.9 ^c	17.76 ^a	—	American Enka
N6 2	nylon 6	1.95	32.5 ^c	27.55 ^a	2.16	Allied Chemical
N6 3	nylon 6	2.05	34.8 ^c	32.68	2.43	Allied Chemical
				34 ^b		
N66 1	nylon 66	0.98	12.5 ^c	22.9 ^a	—	Monsanto
				28.4 ^a		
N66 2	nylon 66	1.85	30.6 ^c	28 ^b	2.9	du Pont
Nomex	<i>m</i> -linked aromatic polyamide	2.5	89.1 ^d	—	—	du Pont
Kevlar	<i>p</i> -linked aromatic polyamide	—	—	—	—	du Pont

^a Endgroup analysis.

^b Gel permeation chromatography.

^c Mark-Houwink equation established with endgroup determination molecular weight (M_n).

^d Mark-Houwink equation established with light-scattering molecular weight (M_w).

TABLE II
 Mark-Houwink Parameters and Conditions Used in Characterizing Polyamides

Polymer	Solvent	Temperature, °C	$K \times 10^5$	a	Ref.
Nylon 6	90% HCOOH, 10% H ₂ O	20	110	0.72	33
Nylon 66	90% HCOOH, 10% H ₂ O	20	110	0.72	33
Nomex	N,N'-dimethylacetamide with 5% LiCl	20	38.6	0.77	36

 TABLE III
 Polymer-Solvent Systems Considered as Spinning Dopes

Polymer	Solvent system	Polymer wt %
Nylon 6	HCOOH/H ₂ O	30
	H ₂ SO ₄ /H ₂ O	
Nylon 66	HCOOH/H ₂ O	25
	H ₂ SO ₄ /H ₂ O	
Nomex	N,N'-dimethylacetamide with 5% LiCl	20
Kevlar	H ₂ SO ₄ /H ₂ O	1.0
	H ₂ SO ₄	2, 4.5, 12

Nomex, a *m*-linked aromatic polyamide [probably poly(*m*-phenyleneisophthalamide)], and du Pont Kevlar, a *p*-linked aromatic polyamide [probably poly(*p*-phenyleneterephthalamide)], were obtained from du Pont and other sources. These materials are listed in Table I.

Intrinsic viscosities were determined for all of the polymers studied using the conditions listed in Table II. The data were converted to molecular weights using the Mark-Houwink equation³³⁻³⁵

$$[\eta] = KM^a \quad (1)$$

The K and a values of Taylor³⁴ were used for both nylon 66 and nylon 6, although they were established for nylon 66 alone. This would seem, though, to be a very reasonable approximation because of the similarity of the structural units. Molecular weight distributions were measured on some of the polyamides by an outside laboratory. The molecular weights are summarized in Table I.

Various polymer-solvent systems were considered as spinning dopes, as summarized in Table III. Specifically, formic acid (HCOOH), sulfuric acid (H₂SO₄), and their solutions with water were used as well as dimethylacetamide. The formic acid was Fischer 90% purified A119. Two grades of H₂SO₄ were used. These were Fischer concentrated reagent-grade 95-98% and 100% level prepared by mixing 30% excess fuming H₂SO₄ with the 95-98% material. N,N'-Dimethylacetamide was obtained from the Aldrich Chemical Company, and the lithium chloride, from Fischer ("certified" grade).

Solution Properties

The properties of the polymer solutions summarized in Table III were investigated especially with regard to solubility. The most extensive study was with

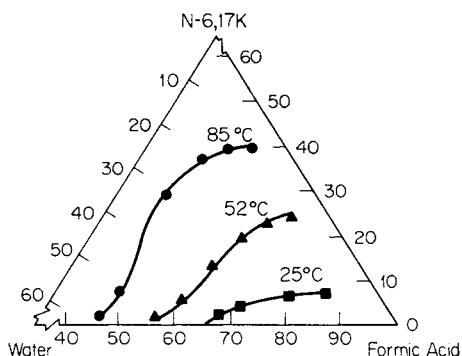


Fig. 2. Ternary phase equilibrium of N61 nylon 6/HCOOH/H₂O at 20°C, 52°C, and 85°C.

regard to nylon 6 with HCOOH/H₂O solvent where spinning bath coagulation rates could be adjusted. It was difficult to obtain concentrated enough initial solutions to make the spinning operation rheologically feasible. Ternary equilibrium phase diagrams were constructed for the N61 nylon 6/HCOOH/H₂O system at 20°C, 52°C, and 85°C. These are summarized in Figure 2. The maximum solubility of nylon 6 at 20°C is about 7%. To obtain more concentrated spinning dopes, solutions were prepared at 65°C and cooled to room temperature. Spinning was then carried out before precipitation occurred. In this manner, polymer concentrations of 30% could be used.

Nylon 6 was soluble in H₂SO₄ at room temperature up to about 20%.

The nylon 66 solutions were prepared in the same manner as the nylon 6 solutions. The nylon 66 appeared to be slightly less soluble than the nylon 6 in the HCOOH/H₂O solvent and had about the same solubility in H₂SO₄.

The Nomex fiber was readily dissolved in dimethylacetamide containing 5% LiCl by adding the fiber to the solvent and letting the suspension sit at room temperature for five to six days.

The Kevlar fiber was insoluble in most solvents. As suggested by Kwolek,²⁶ H₂SO₄ was found to be the best solvent. Only 1.0 wt % of the Kevlar fiber was dissolved in 95–98% H₂SO₄ at room temperature after five to six days without agitation. When H₂SO₄ in concentrations in excess of 100% was used, the fiber dissolved to 2 wt % at room temperature without agitation. It was found that gentle heating of the fuming H₂SO₄ to 65°C increased the solubility to 4.5 wt %. A 12% solution was prepared using a high-speed four-bladed blender. The components were mixed and allowed to stand at room temperature for one to two days forming a viscous liquid with suspended solids. The mixture was heated to 70–80°C and placed in the blender. The heat of viscous dissipation was sufficient to maintain the temperature at 70–80°C. The mixing was continued for 2–4 hr until the solution appeared homogeneous.

The 1% and 2% Kevlar solutions were yellowish in color and had low viscosities. The 4.5% solution was brownish and more viscous. The 12% solution was very viscous and possessed rather unusual properties. Its color at rest was found to be a dark brown, but upon stirring it showed streaks of opalescent white. The 12% solution was also found to rotate light when examined between crossed polarizers in an optical microscope. This behavior is characteristic of "anisotropic" or liquid crystal solutions. Kevlar spinning dopes were reported to exhibit

similar anisotropic behavior in certain composition ranges in the Kwolek and Blades patents.^{29,30}

No quantitative rheological measurements were made because of the corrosive character of the solvents. Viscosity values were estimated for the nylon and Nomex solutions with a Brookfield viscometer. Qualitative judgments of solution, elasticity, and spinnability were made.

Wet Spinning Apparatus

A schematic drawing of the wet spinning apparatus is shown in Figure 1. It consists of (i) a solution delivery system, (ii) a capillary spinneret, (iii) a coagulation bath, and (iv) a take-up device. After investigating different possible delivery systems, it was finally decided to use a Harvard apparatus infusion withdrawal pump, a positive displacement pump which delivers a constant steady rate independent of pressure. The solution was extruded at a rate of 1.35 cm³/min through a cylindrical reservoir made of Type 316 stainless steel and then through a single-hole spinneret with diameter 0.015 in. and a length-diameter ratio of one. The coagulation bath used was fabricated from sheet metal and was 72 in. long and 8 in. deep. The bath was fabricated so that the extrusion device could be attached to it with an O-ring seal. The take-up device was a variable-speed Bodine electric 1/20 horsepower motor with a specially built spool attachment. Because of the fiber tackiness, a solution spray was applied to the fiber as it was taken up. Otherwise, the wet-spun fibers would have stuck together. The fibers were usually taken up at a rate of 7.5 meters/min.

Solutions were either wet-jet or dry-jet wet spun (see Fig. 1a and b).

Coagulating Bath Conditions

Several different coagulating bath liquids were used for each spinning dope. They are summarized in Table IV. The purpose of studying the different bath conditions was to vary the rate of coagulation of the wet-spun fiber traversing it.

Optical Microscopy

A Leitz Wetzler Ortholux microscope was used to obtain optical micrographs of fiber cross sections. The samples were prepared by embedding the fiber in an epoxy mixture and slicing the solidified mass to a thickness of 10 to 20 microns using a microtome knife. The slices were mounted on glass slides using heat and Canada balsam in xylene. The porosity of many of the fibers made them weak, and they tended to break and fall out of the embedding medium.

Scanning Electron Microscopy (SEM)

An AMR Model 900 high-resolution scanning electron microscope was used to study the wet-spun fibers. Surface features and cross sections were observed. A primary advantage of the SEM is the great depth of field. The samples were coated with a gold-palladium alloy to avoid charging in the microscope.

X-Ray Diffraction

Wide-angle x-ray diffraction (WAXS) measurements were obtained using a Phillips x-ray generator with Ni-filtered $\text{CuK}\alpha$ radiation of 1.542 Å wavelength at 35 kV and 15 mA. Small-angle x-ray diffraction measurements (SAXS) were obtained using a Rigaku-General Electric rotating-anode x-ray generator operated at 55 kV and 80 mA with an evacuated camera and a sample-to-film distance of 400 mm.

Mechanical Testing

The tensile properties of the fibers were tested in an Instron Table Model tensile tester. Because of the moisture sensitivity of the fibers, the tests were carried out at 65% relative humidity and 24°C after being conditioned in this environment for 48 hr. The initial fiber lengths were 1 in., and the tests were carried out at 0.5 in./min cross-head speed.

NYLON 6

Results

Qualitative studies were carried on the spinnability of solutions of nylon 6 with both $\text{HCOOH}/\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solvents by pulling filaments from the solution and observing their stability. At equivalent concentrations, the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions were more viscous and apparently more viscoelastic than the $\text{HCOOH}/\text{H}_2\text{O}$ solutions, and stable filaments could more readily be drawn from

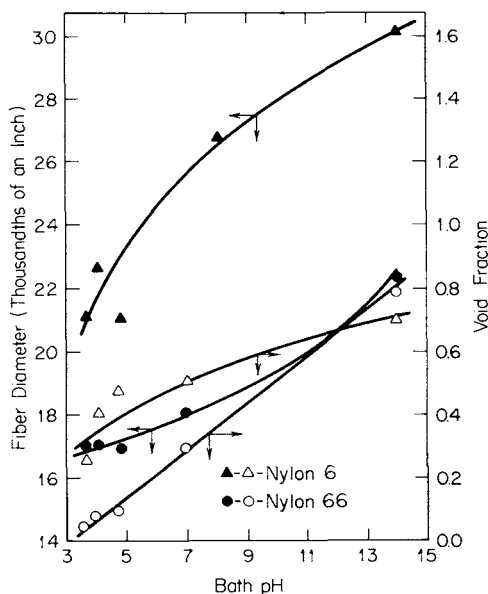


Fig. 3. Fiber diameter and void fraction of the N63 and N662 fibers as a function of coagulation bath pH ($\text{NaOH}/\text{H}_2\text{O}$ and $\text{HCOOH}/\text{H}_2\text{O}$ baths).

TABLE IV
 Coagulating Bath Conditions

Spinning solution	Coagulation bath
Nylon 6 (90% HCOOH/10% H ₂ O)	5% NaOH/H ₂ O H ₂ O 5% HCOOH/H ₂ O 10% HCOOH/H ₂ O 15% HCOOH/H ₂ O 4% CH ₃ OH/H ₂ O 4% CH ₃ OH/4% NaOH/H ₂ O
Nylon 6/(90% H ₂ SO ₄ /H ₂ O)	5% NaOH/H ₂ O H ₂ O
Nylon 66/(90% HCOOH/H ₂ O)	5% NaOH/H ₂ O H ₂ O 5% HCOOH/H ₂ O 10% HCOOH/H ₂ O 15% HCOOH/H ₂ O
Nomex/(dimethylacetamide/5% LiCl)	H ₂ O 5% DMAc/H ₂ O 10% DMAc/H ₂ O 15% DMAc/H ₂ O 5% NaOH/H ₂ O
Kevlar/H ₂ SO ₄	5% NaOH H ₂ O 5% H ₂ SO ₄ 10% H ₂ SO ₄ 15% H ₂ SO ₄

them. However, the coagulation rates were found to be much slower, and this made wet spinning very difficult. For this reason, our most extensive studies were made using the more rapidly coagulating HCOOH/H₂O solutions.

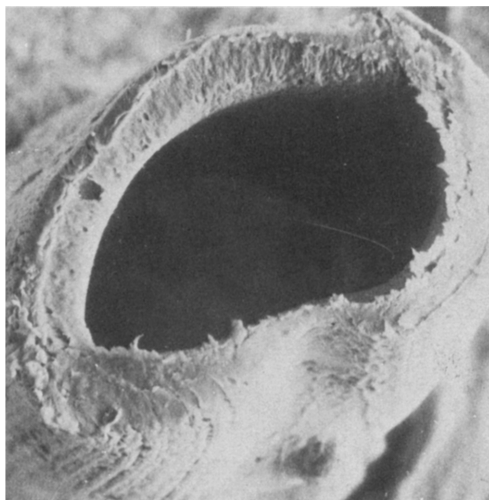
The spinnability also depended strongly on both the concentration of the solutions and the molecular weight of the nylon 66. Spinnability increased with concentration and polymer molecular weight. Solutions of the N61 polymer (lowest molecular weight nylon 6, see Table I) were barely spinnable, with the emerging filaments easily breaking up as they moved through the bath from the spinneret. The higher molecular weight nylon 6 polymer solutions were more readily wet spun. Our most extensive experiments were carried out on the N63 polymer.

The diameters of the wet-spun fibers were determined as a function of coagulation bath conditions which are summarized in Table IV. For the NaOH/H₂O and HCOOH/H₂O baths, these are plotted as a function of pH in Figure 3. Generally, the fiber diameter decreased with decreasing pH.

Lengths L of fibers produced were weighed. This allowed computation of the fiber denier. The void fraction ϵ was determined from the mass M through the relation

$$\epsilon = 1 - \left(\frac{M}{\rho AL} \right) \quad (2)$$

where ρ is the crystalline density and A is the cross-sectional area. We also plot ϵ as a function of pH in Figure 3. Increasing the pH increases the void fraction. We summarize fiber diameters, denier, and void fraction in Table V.



(a)



(b)

Fig. 4. SEM photomicrographs of wet-spun N63 nylon 6 fibers: (a) 100 \times , 5% NaOH, 30.63×10^{-3} in. fiber diameter; (b) 100 \times , 15% formic acid, 21.06×10^{-3} in. fiber diameter.

The general features of the superstructure of the fibers was best revealed in the SEM photomicrographs. Photomicrographs for the 5% NaOH and 15% HCOOH baths are shown in Figure 4. The fibers spun into the alkaline, high pH, bath have a hollow core and the skin has a generally porous appearance. The fibers become more compact and the tendency toward hollow cores decreases as the bath becomes more acidic.

The SAXS patterns for these fibers all exhibit dense diffuse scattering symmetrically distributed about the incident beam. A typical pattern is shown in Figure 5a. The WAXS patterns of the wet-spun nylon 6 fibers in the acid baths

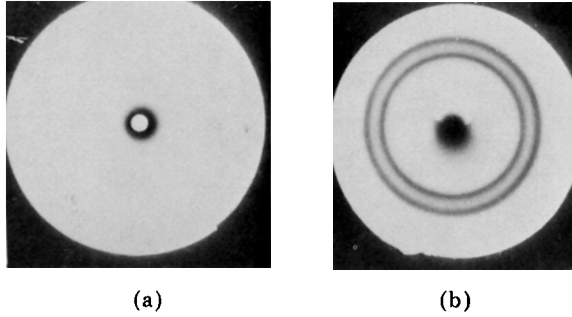


Fig. 5. X-Ray diffraction patterns for wet-spun N63 nylon 6 fibers: (a) SAXS pattern; (b) WAXS pattern.

are all identical, and Figure 5b is representative. It indicates the fiber is crystalline and unoriented. From the occurrence of sharp rings corresponding to 3.71 Å and 4.51 Å, it was the α -monoclinic structure of Brill³⁷ and Holmes, Bunn, and Garner.³⁸ The fibers spun into the NaOH bath contained a faint third ring with d spacing of 6.15 Å. These observations would seem to indicate that a small amount of the γ phase was present in fibers spun into the NaOH bath.³⁹

Observations of microtomed sections from the wet-spun fibers in the polarized light microscope with a first-order red-wave plate showed a microstructure which appeared to contain very small spherulites and numerous voids.

Instron force-elongation measurements were mainly interpreted in terms of tensile strengths and elongations to break. Tensile strengths in terms of engi-

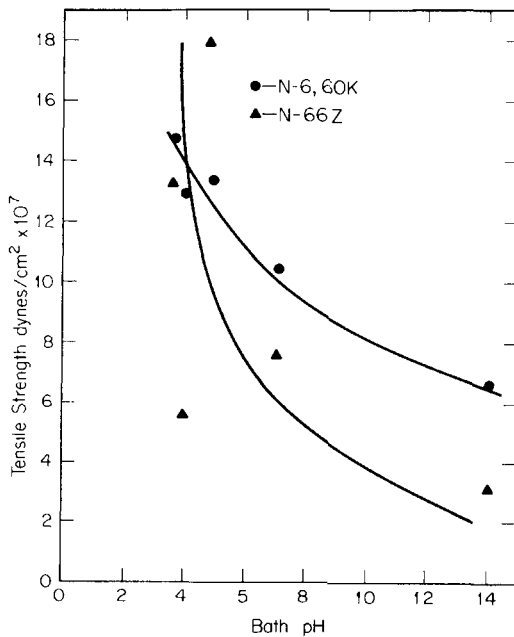


Fig. 6. Tensile strength as engineering stress as a function of bath pH for wet-spun nylon 6 N63 and nylon 66 N662 fibers.

TABLE V
Nylon 6 Fiber Characteristics as a Function of Coagulation Bath Conditions

Coagulation bath	Denier, g	Diameter, 10^{-3} in.	Void fraction ϵ	Remarks
5% NaOH/H ₂ O	1560	36.6	0.68	hollow core surrounded by porous skin
H ₂ O	1930	26.7	0.48	small hole with skin and core structure
5% HCOOH/H ₂ O	1220	21.0	0.46	more uniform
10% HCOOH/H ₂ O	1540	22.4	0.40	more uniform
15% HCOOH/H ₂ O	1710	21.1	0.25	most uniform and compact

neering stress (force/initial cross section) are plotted versus bath pH in Figure 6.

Interpretation and Discussion

Most of the variations of fiber superstructure may be directly interpreted in terms of the influence of coagulation rates. The H₂SO₄ solutions coagulate more slowly than the HCOOH solutions, and this prevents them from solidifying with the present bath length and spinning speeds. For the case of the HCOOH spinning dope, the coagulation rate varies with bath conditions. In an alkaline bath, the reaction between OH⁻ and HCOOH causes very rapid coagulation rates. This results in a fiber of large diameter, with a high void fraction and a central hollow core. As one reduces OH⁻ and adds HCOOH to the bath, the neutralization reaction rate decreases and disappears, and diffusion rates decrease. This lowers the coagulation rate, and smaller-diameter, more compact fibers are obtained.

The diffuse SAXS measurements indicate that voids of small size exist in all the nylon 6 fibers spun. The general superstructures of our fibers are similar to those reported by Kiyotosukuri et al.^{18,19,20} who indicate porous structures.

The WAXS measurements indicating α -monoclinic crystallinity in most of the wet spun fibers are of considerable interest, especially in that melt-spun nylon 6 does not crystallize in the spinline³² and forms a pseudohexagonal γ structure on the bobbin.^{39,40,32} A similar development of α -crystalline form in wet-spun nylon 6 is reported by Kiyotosukuri et al.²⁰

NYLON 66

Results

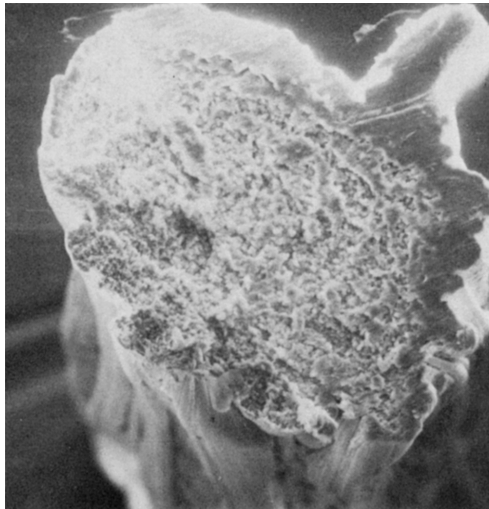
The spinnability of nylon 66 solutions and the character of the wet-spun fibers were similar to those of nylon 6. Spinning dopes of HCOOH/H₂O and H₂SO₄/H₂O were prepared, with the latter being more viscous and elastic. The HCOOH/H₂O were preferred because of the low coagulation rates of the H₂SO₄/H₂O solutions. Solutions of the N661 polymer were very difficult to spin, but solutions of the higher molecular weight N662 polymer in HCOOH/H₂O were readily spun.

TABLE VI
Nylon 66 Fiber Characteristics as a Function of Coagulation Bath Conditions

Coagulation bath	Denier, g	Diameter, 10^{-3} in.	Void fraction ϵ	Remarks
5% NaOH/H ₂ O	526(?)	22.4	0.80	hollow core surrounded by porous skin
H ₂ O	1170	18.1	0.31	small hole with skin and core structure
5% HCOOH/H ₂ O	1140	16.8	0.10	more uniform
10% HCOOH/H ₂ O	1380	28.0	0.08	more uniform
15% HCOOH/H ₂ O	1440	17.1	0.05	most uniform



(a)



(b)

Fig. 7. SEM photomicrographs of wet-spun nylon 66 N662 fibers: (a) 200 \times , 5% NaOH, 22.37×10^{-3} in. fiber diameter; (b) 200 \times , 15% formic acid, 17.14×10^{-3} in. fiber diameter.

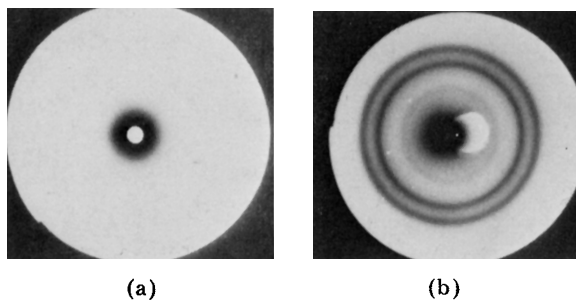


Fig. 8. X-Ray diffraction patterns for wet-spun nylon 66 N662 fibers: (a) SAXS pattern; (b) WAXS pattern.

The diameters and void fractions ϵ of the nylon 66 fibers were determined as described for the nylon 6 fibers and considered as a function of the nature of the coagulation bath pH. These are plotted in Figure 3 and summarized in Table VI.

The fiber superstructure was best seen in SEM photomicrographs. Examples are presented in Figure 7. The fibers were found to be rough, porous, and fibrillar. Those spun in alkaline baths exhibited hollow cores. Generally, as pH decreased, the fibers appeared less porous and more compact.

The SAXS patterns were similar to those of nylon 6 samples. They exhibited intense diffuse scattering uniformly distributed about the incident beam. A typical pattern is shown in Figure 8a.

The WAXS patterns of the wet-spun nylon 66 fibers were all identical and are shown in Figure 8b. The pattern has sharp Debye rings corresponding to interplanar spacings of 4.41 Å, 3.68 Å, and 6.52 Å. These would seem to correspond to the 100, 010 and 002 reflections of the triclinic α structure of Bunn and Garner.⁴¹

The polarized-light microscope observations show the existence of spherulites.

The force-elongation curves were mainly interpreted in terms of tensile strengths and elongations to break. These results are summarized in Figure 6. In terms of engineering stress (dynes/cm²), the tensile strength increases with bath acidity and decreasing void fraction. The tensile strength, in terms of grams per denier units, is constant at about 0.15. The elongation to break is of the order of 24%.

Interpretation and Discussion

The observations on the wet-spun nylon 66 fibers are similar to those for the nylon 6 fibers and may be likewise interpreted in terms of coagulation rates. The H₂SO₄/H₂O spinning dopes proved unsuccessful because of low coagulation rates. The variation in fiber porosity with bath pH would seem to be due to decreasing coagulation rates with increasing acidity.

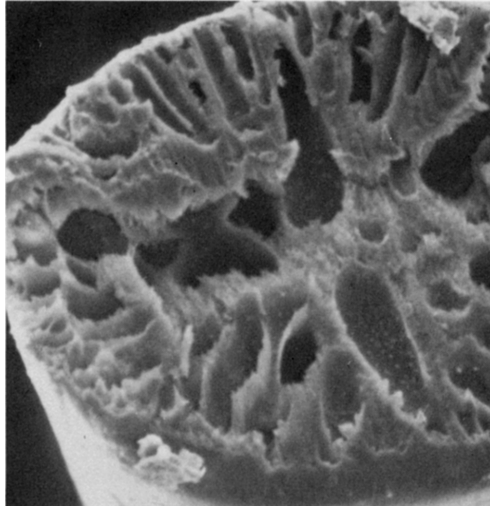
The mechanical properties of the wet-spun fiber are considerably inferior to those of melt-spun fiber in terms of both tensile strength and elongation to break. While the values vary for melt-spun fibers depending upon spinning conditions,

they are generally about an order of magnitude higher. This would certainly seem to be due to the porous structure of the wet-spun fibers.

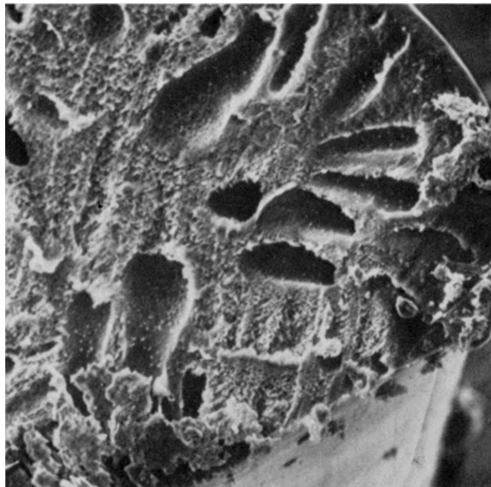
NOMEX

Results

The spinnability of the Nomex solutions in 5% LiCl/dimethylacetamide (DMAC) was superior to that found in the aliphatic polyamide solutions.



(a)



(b)

Fig. 9. SEM photomicrographs of wet-spun redissolved Nomex fibers: (a) 200 \times Nomex, water, 25 $^{\circ}$ C, 16.8×10^{-3} in. fiber diameter; (b) 200 \times , Nomex, 15% DMAc, 25 $^{\circ}$ C, 20.71×10^{-3} in. fiber diameter.

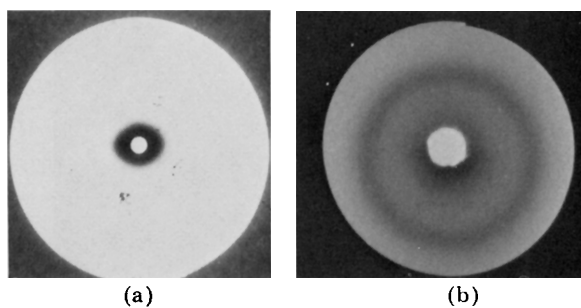


Fig. 10. X-Ray patterns for wet-spun redissolved Nomex fibers: (a) SAXS pattern of spun fiber; (b) WAXS pattern for spun fiber.

The Nomex solutions were spun through five different coagulation baths at 25°C and 43°C. Some experiments were also carried out at temperatures in the range of 0–10°C. The void fractions ϵ defined by eq. (2) and fiber diameter were determined. Generally, these show no real trend with bath composition or temperature. The denier was of the order of 700 g, the diameter about 0.02 in., and the void fraction apparently about 0.7.

The superstructure of the wet-spun Nomex fibers was studied by optical microscopy and by SEM. SEM photomicrographs are shown in Figure 9. The fiber is seen to be compact, with a smooth outer surface except for occasional inscribed rings. The fibers spun into the 5% DMAC seemed to show elliptical or oval cross sections unlike those spun into water or at higher DMAC concentrations.

The SAXS patterns (see Fig. 10a) showed diffuse scattering similar to the nylon 6 and nylon 66. However, the oval shape of the patterns suggests that the microvoids are slightly elongated parallel to the fiber axis.

The WAXS patterns (Fig. 10b) of the wet-spun fibers exhibit only a single diffuse halo, indicating that they are noncrystalline, glassy materials in the as-spun condition.

It was found that hot drawing (250°C) of the respun Nomex fiber to 3 \times produces a crystalline filament (see Fig. 11). Three Debye rings corresponding to

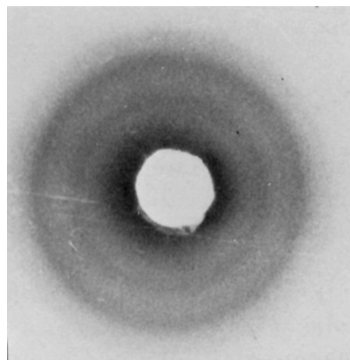
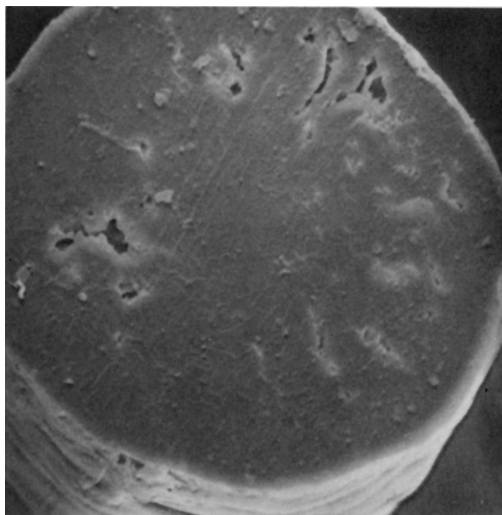
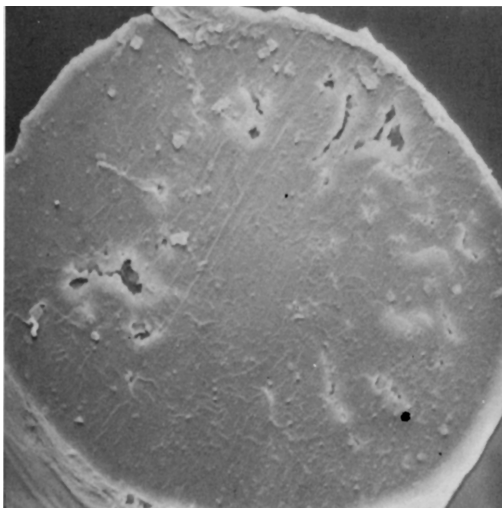


Fig. 11. WAXS pattern for wet-spun redissolved Nomex fiber drawn to 3 \times .



(a)



(b)

Fig. 12. SEM photomicrograph of wet-spun redissolved Kevlar fiber: (a) 500 \times , 5% NaOH, 6.2×10^{-3} in. fiber diameter; (b) 500 \times , 15% H₂SO₄, 7.5×10^{-3} in. fiber diameter.

d spacings of 3.77 Å, 4.55 Å, and 6.302 Å were obtained. Similar reflections were obtained when measurements were carried out on the original staple fiber. These correspond to the d spacings obtained by Lee³⁶ in our laboratories on poly(*m*-phenyleneisophthalamide) polymerized by Fellers, Zdrahala, and Firer.⁴²

The tensile strengths of the fibers show little variation with coagulation bath conditions, being of the order of 7×10 dynes/cm² (or 0.3 g/denier). The elongations to break are of the order of 55–70%.

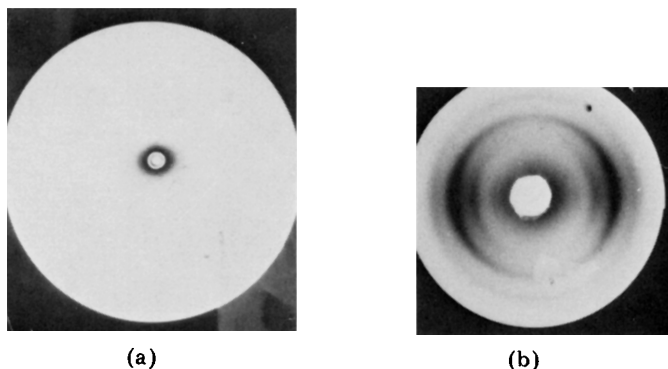


Fig. 13. X-Ray patterns for wet-spun redissolved Kevlar fibers: (a) SAXS pattern; (b) WAXS pattern.

Interpretation and Discussion

In contrast to those of nylon 6 and nylon 66, the fiber superstructure and mechanical properties of Nomex are insensitive to the coagulation bath at least in the range of conditions studied. The formation of glassy rather than crystalline fibers would seem to indicate that crystallization kinetics for Nomex are much slower than for the aliphatic nylons in the range of conditions studied.

KEVLAR

Results

A remarkable feature of the Kevlar solutions is their spinnability. Filaments could readily be pulled from the 1% and 2% solutions, and the solutions could readily be dry-jet wet spun into fibers.²⁷ No capillarity instabilities were observed in these filaments, even with a 1-in. air gap. The 4.5% solution showed improved spinnability. The 12% solution, apparently an anisotropic solution as referred to by Kwolek,²⁶ showed excellent spinnability and, unlike most of the spinning dopes studied, readily allowed considerable variations in the take-up velocity.

The coagulation bath was varied from conditions of acidity to alkalinity. For the 12% spinning dope, the fiber diameters and void fractions of the fibers studied were determined and are summarized in Table VII. The diameters of the fibers were roughly constant, while the void fraction decreased with increasing pH.

The appearance of the fibers was of considerable interest. The fibers were a bright yellow when coagulated in an alkaline bath but were brown when coagulated in other baths. The SEM photomicrographs of the spun fibers (see Fig. 12) indicate the presence of a skin and core structure and of the occurrence and distribution of microvoids. There were, however, no hollow cores or large voids in any of the Kevlar fibers. The fibers spun into the alkaline baths seemed to be rough and wrinkled, while those spun into the acid bath were less rough and more rounded and regular.

The SAXS patterns (Fig. 13a) all showed a dense, slightly elliptical distribution of diffuse scattering. Again, this scattering would seem due to microvoids. The SAXS pattern of commercial Kevlar fiber (Fig. 13a) also exhibited such diffuse

TABLE VII
Wet-Spun Kevlar Fiber Characteristics

Spinning solution	Coagulation bath	Denier, g	Diameter, in.	ϵ	Tensile strength		Modulus, g/denier	Elongation to break
					g/denier	dynes/cm ² $\times 10^{-8}$		
1.0%/95% H ₂ SO ₄	H ₂ O	—	—	—	—	—	—	—
2.0%/fuming H ₂ SO ₄	H ₂ O	—	—	—	—	—	—	—
4.5%/fuming H ₂ SO ₄	H ₂ O	142	0.0045	0.13	0.295	3.2	14.1	3.8
12%/fuming H ₂ SO ₄	5% NaOH	245	0.0062	0.03	1.95	24.1	14.4	22.9
	H ₂ O	283	0.0072	0.16	1.79	19.2	28.3	16.1
	5% H ₂ SO ₄	224	0.0069	0.3	2.33	21.1	29.8	19.6
	10% H ₂ SO ₄	224	0.0055	0.05	2.68	32.3	34.3	21.7
	15% H ₂ SO ₄	295	0.0075	0.2	1.38	20.6	22.6	20.0

scattering, but it was more elongated in the direction perpendicular to the fiber axis. This effect presumably results from elongation of the microvoids parallel to the fiber axis.

WAXS patterns for the fibers (Fig. 13b) indicated the presence of crystallinity. Four well-defined rings were apparent with d spacings of 3.22 Å, 3.92 Å, 4.97 Å, and 7.59 Å. The fiber spun from the 4.5% solution showed little or no orientation, while the fiber spun from the 12% solution exhibited considerable orientation. WAXS patterns for wet-spun poly(*p*-phenyleneterephthalamide) fibers have been investigated by Northolt and van Aartsen^{29,43} who have proposed a monoclinic (pseudoorthorhombic) unit cell. A comparison between the reflections found by these authors and those obtained by us on the original and redissolved wet-spun Kevlar fibers is summarized in Table VIII. One set of fibers, those wet spun into 5% H₂SO₄, were (i) annealed for 7 min at 300°C and (ii) drawn in an oven to 1.5× at 300°C. The WAXS patterns are summarized in Figure 14. Increased orientation may be seen.

The mechanical properties of the as-spun fibers are displayed in Table VII and the annealed and hot drawn fibers, in Table IX. Significant increases in tensile strength and modulus are observed, as are decreases in elongation to break.

Discussion

The WAXS spacings obtained for the as-spun fibers differ from those of the hot-drawn fibers and in turn from the original dissolved commercial Kevlar fiber

TABLE VIII
WAXS Repeat Distances of Kevlar and Poly(*p*-phenyleneterephthalamide)

Fibers wet spun in this study		Commercial Kevlar (measured in our laboratory)	Observations of Northolt ⁴³	Reflection indices ⁴³	I_{obs}^{43}
As-spun	Hot drawn				
3.22	3.19	3.22	3.225	004	30
3.92	3.98	3.92	3.935	200	100
—	4.35	4.48	4.33	110	81
4.97	5.08	—	—	—	—
—	—	6.31	6.45	002	7
7.59	7.59	7.59	—	—	—

TABLE IX
Properties of Annealed and Hot-Drawn Kevlar Fibers

	Tenacity, g/denier	Elongation to break	Modulus, g/denier
As-spun			
Our work	2.32	19.6	30
Kwolek ²⁹	7.0	9.1	173
After treatment			
Heat treatment (our work)	3.04	7.5	53.6
Hot-drawing (our work)	7.1	8.75	100
Kwolek ²⁹	13.7	1.6	888
Blades ²⁷	21	2.8	756

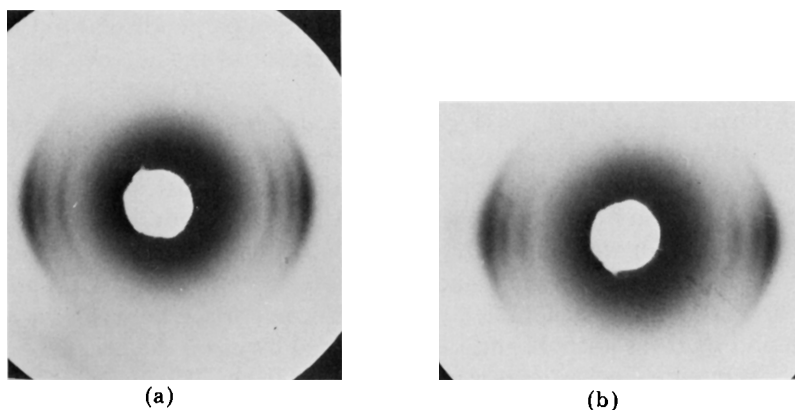


Fig. 14. WAXS patterns for wet-spun redissolved Kevlar fiber: (a) annealed at 300°C for 7 min; (b) drawn 1.5 \times at 300°C.

and from those of Northolt.⁴³ The as-spun, hot-drawn and original Kevlar fiber all possess an extra reflection of 7.59 Å not predicted or observed by Northolt.⁴³ This could be due to an impurity, or perhaps our Kevlar sample is not poly(*p*-phenyleneterephthalamide). Of great interest is the contrast between the redissolved as-spun, hot-drawn, and commercial Kevlar. The as-spun material is missing the 4.48 Å and 6.31 Å reflections observed for the commercial fiber, and it possesses an extra reflection of 4.97 Å. The hot-drawn fiber possesses the reflection at 5.08 (4.97) Å and one at 4.35 (4.48) Å. This suggests that the hot drawing produces a crystal-crystal transformation, and our hot-drawn fiber is intermediate between the as-spun and the commercial Kevlar fibers. It also possesses intermediate orientation (compare Fig. 14 to Fig. 13b).

The mechanical properties are of considerable interest. All the redissolved Kevlar fibers possess a much higher tensile strength than any of the other fibers which were spun. The annealing and hot drawing processes produce a significant increase in these properties. However, these still do not equal those reported by Kwolek,²⁶ Blades,²⁹ and others in du Pont patents. Possible explanations for this include a greater void fraction and size in our fibers than in the commercial fiber, and a lower degree of orientation in our fiber due to different processing conditions.

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