

A New Amorphous Heat-Resistant Aromatic Polyamide Fiber Prepared by Wet-Spinning

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SYNOPSIS

A new amorphous heat-resistant aromatic polyamide was prepared by solution polymerization in *N*-methylpyrrolidone (NMP) from equimolar amounts of 4,4'-methylenedianiline, *p*-phenylenediamine, isophthaloyl chloride, and terephthaloyl chloride. After neutralization of the byproduct HCl, with calcium hydroxide, the as-polymerized polymer solution (15.7% polyamide in NMP) was spun directly on a horizontal wet-spinning device. Yarn drawing of as-spun fibers, near the glass transition temperature of the polymer, was performed on a hot-drawing equipment. To determine the optimal drawing conditions, the influence of the draw ratio on the tensile properties was studied in detail. On the basis of these results, a draw ratio of 1.7 was applied to prepare a larger quantity of drawn polyamide multifilament yarn (f330 and f500). Tensile properties of both fibers and filaments were determined by standard methods. The fibers are characterized by an excellent thermal stability as indicated by temperature-dependent tensile measurements, long-term heat resistance, boiling-water shrinkage, hot-air shrinkage, etc., of the fibers. Despite the amorphous character of the polyamide fiber, it offers an excellent resistance to common organic solvents (except to THF and DMF). Moreover, the fiber exhibits a good resistance toward diluted inorganic acids, salts, and bases. Depending on the specific properties of the polyamide fiber, the material may find applications in, e.g., hot-air filter fabrics, protective clothing, electrical insulation paper, or advanced structural materials. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Over the past few years, a wide variety of new heat-resistant engineering plastics have been developed that are now commonly used in various applications. To find new outlets, several of these new materials have been melt-spun into heat-resistant fibers. Among these engineering plastics are

- polyphenylene sulfide (PPS),^{1,2}
- polyetherimide (PEI),^{1,3,4} or
- polyetheretherketone (PEEK).¹

Because of economic benefits of the melt-spinning process, PPS, PEI, and PEEK fibers offer an attractive price-performance ratio. However, the

unique thermal and viscoelastic properties of these resins often require special precautions (e.g., improved melt-spinning techniques) during processing.

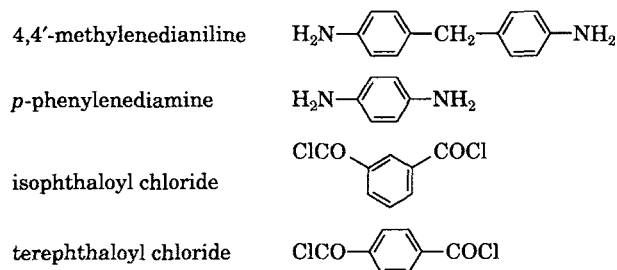
Another aspect of heat-resistant fibers embraces the dissolution of the polymer concerned in a suitable organic solvent, followed by fiber spinning in a hot inert gas in which the solvent evaporates (the so-called dry-spinning process) or, alternatively, in a coagulation bath with a nonsolvent (the so-called wet-spinning process). Some examples of commercially available fibers prepared by the dry-spinning process include

- poly(*m*-phenylene isophthalamide) fibers^{5,6} (e.g., DuPont's Nomex fiber, available since 1967), or
- polybenzimidazole fibers⁷ (e.g. Celazole fibers, manufactured by Celanese).

Kermel fibers, poly (amide imide) (PAI) fibers from Rhône-Poulenc, are prepared by the wet-spinning process.⁸

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In this article, we describe the synthesis of an amorphous heat-resistant aromatic polyamide.⁹ This polymer is prepared by a solution polymerization from equimolar amounts (molar ratio 1 : 1 : 1 : 1) of



After neutralization, the as-polymerized polymer solution was spun directly on a horizontal wet-spinning device. Properties of drawn yarns will be compared with those of PPS and PEI melt-spun fibers.

EXPERIMENTAL

Polymerization

The aromatic polyamide was prepared by solution polymerization in *N*-methylpyrrolidone (NMP) on a 160 L Drais reactor using polymer-grade raw materials. Dry NMP (90 L) was pumped into the Drais reactor. Both diamines, 4,4'-methylenedianiline (MDA; 4930 g, 24.8 mol), and *p*-phenylenediamine (PPD; 2680 g, 24.8 mol), were added carefully. After dissolving with continuous stirring for 45 min, both acid dichlorides, isophthaloyl chloride (IDC; 5050 g, 24.8 mol) and terephthaloyl chloride (TDC; 5050 g, 24.8 mol), were added to the reactor at a stirrer speed of 100 rpm. Stirring was continued for another 2 h while cooling the reactor. The maximum solution temperature was about 65°C; at the end of the polymerization, the temperature was 60°C. During the entire polymerization, the Drais reactor was purged with nitrogen. To minimize corrosion of the wet-spinning equipment, the acidic polymerization solution was neutralized with calcium hydroxide, Ca(OH)₂. After stirring for 75 min, the neutralized polymer solution (15.7% polyamide in NMP) was discharged from the Drais reactor.

Wet Spinning

Multifilament wet spinning of the above-mentioned as-polymerized aromatic polyamide solution was carried out (without the so-called air gap) on hor-

izontal wet-spinning equipment. A schematic representation of this equipment is shown in Figure 1.

A plastic container, filled with the polyamide spinning dope, was placed in a pressure vessel that was pressurized with nitrogen (5 bar) to transfer the spinning dope to the booster pump. The spinning dope was then pumped through a filter pack to the spinning pump, which forced the spinning dope through the spinneret. The pressure developed by the booster pump was about 40 bars. The first filter pack contained several filters down to a 25 μm pore size. The spinneret (diameter 20 mm; containing 330 capillaries with a diameter of 50 μm or 500 capillaries, 65 μm in diameter) was placed in the first coagulation bath (length 5 m) filled with hot water (65°C). At the end of the bath, the yarn was wound with the aid of a winding device having a speed of 18 m/min. By placing a cylindrical yarn guide at the end of the bath, a well-opened bundle could be obtained over the entire length of the bath. Next, the yarn was fed to a second bath (length 5.5 m) also filled with hot water (65°C). The yarn was dried on a heated drum (at 220°C, 12 wraps) and collected on a winding spool using a Barmag winder. The as-spun polyamide yarn, produced in this particular way, had a dull white appearance. The count of the as-spun yarn was 790 dtex (790f330) for the 330 filament yarn and 1100 dtex (1100f500) for the 500 filament yarn.

Yarn Drawing

Both as-spun polyamide yarns (790f330 and 1100f500) were drawn on hot-drawing equipment. The best drawing results were obtained in a two-step drawing process using two hot plates (at 310°C, total length: 2 m) near the glass transition temperature of the polymer (DSC: $T_g = 293^\circ\text{C}$). At lower temperatures, nonsignificant drawing occurred; when the temperature of the plates was too high, the filaments stuck to one another. In all experiments, the unwinding speed of the as-spun polyamide fiber was 4.0 m/min. To prevent static charging of the yarns during drawing, a spin finish was applied to the fiber.

ANALYSIS

Tensile Properties

Yarn counts were estimated on a Mettler balance. Tenacity and elongation at break of conditioned yarns were measured according to a standard method

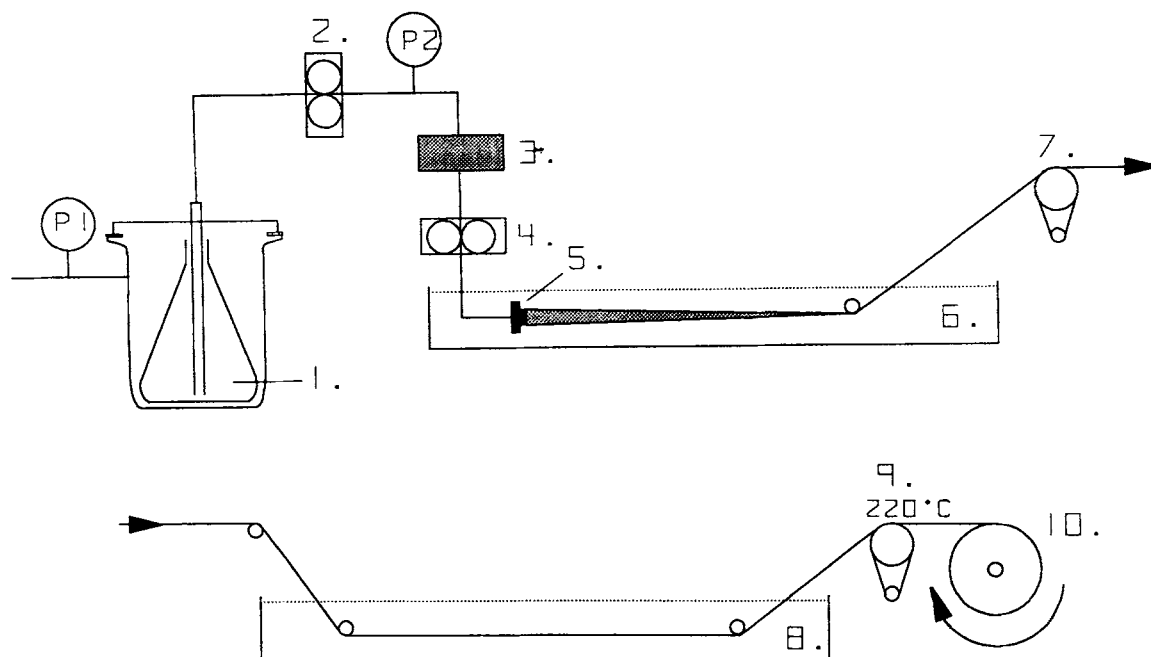


Figure 1 Scheme of the multifilament wet-spinning machine: (1) container with polyamide spinning dope; (2) booster pump; (3) filter pack; (4) spinning pump; (5) spinneret; (6) first coagulation bath filled with hot water; (7) winding device; (8) second coagulation bath filled with hot water; (9) heated drum; (10) Barmag winder.

(ASTM D2101, yarn test length 500 mm, clamp speed 100%/min, and applied twist Z 250 tpm) on an Instron tensile tester using 4C-type clamps. The tensile modulus of the yarns was determined according to ASTM method D885.

Chemical and Solvent Resistance

The chemical and the solvent resistance of the drawn amorphous polyamide yarns was measured according to standard methods. About 10 m of conditioned yarn was wound on standard glass frames that were immersed in several test liquids. After 1 week of immersion at room temperature, the yarns were dried (or, if necessary, thoroughly washed with water and dried) and tested for their tensile properties and free yarn shrinkage.

TMA Analysis

A thermal mechanical analysis (TMA) of yarns was performed by a Mettler TMA 40 apparatus. The free yarn shrinkage was determined up to a temperature of 400°C in a helium atmosphere, using 13 mm pieces of yarns. A small continuous load of 0.4 cN/tex and a heating rate of 10°C/min were applied.

RESULTS AND DISCUSSION

Yarn Drawing

Small-scale preliminary yarn drawing trials have been carried out, using the 790f330 as-spun polyamide yarns to determine the necessary draw ratio (λ) for obtaining polyamide drawn yarns with an elongation at break of 12–15%. These data are presented in Table I.

Table I Drawing of 790f330 As-spun Polyamide Fibers at 310°C

λ^a	Yarn Count (dtex)	Tenacity (mN/tex)	Elongation at Break (%)	E_{init}^b (N/tex)
1.5	475	345	14.7	5.88
1.7	462	400	14.3	6.02
1.9	390	454	12.1	7.24
2.1	349	517	11.4	7.67
2.3	317	575	10.6	8.58

^a Draw ratio.

^b Initial modulus.

In Figure 2, both yarn count (in dtex) and tenacity (in mN/tex) are provided as a function of the applied draw ratio (λ). Furthermore, the dependence of elongation at break (in %) and the initial modulus (in N/tex) on the draw ratio (λ) is shown in Figure 3.

As expected, drawing of the 790f330 as-spun polyamide yarn results in both an increase of tenacity and of initial modulus, whereas a decrease in yarn count and elongation is obtained. Based on these results, we decided to draw the as-spun yarns applying a draw ratio of 1.7, which means an unwinding speed of 4.0 m/min and a winding speed of 6.8 m/min.

Fiber Tensile Properties

Tensile properties of conditioned drawn polyamide fibers (f330 and f500) are collected in Table II. The tensile properties of these drawn polyamide yarns, as given in this table, can be compared with the literature data of melt-spun amorphous PEI and crystalline PPS filament yarns—170f72 PEI: tenacity 270 mN/tex and elongation at break 31%,³ and 200f72 PPS yarn: tenacity 470 mN/tex and elon-

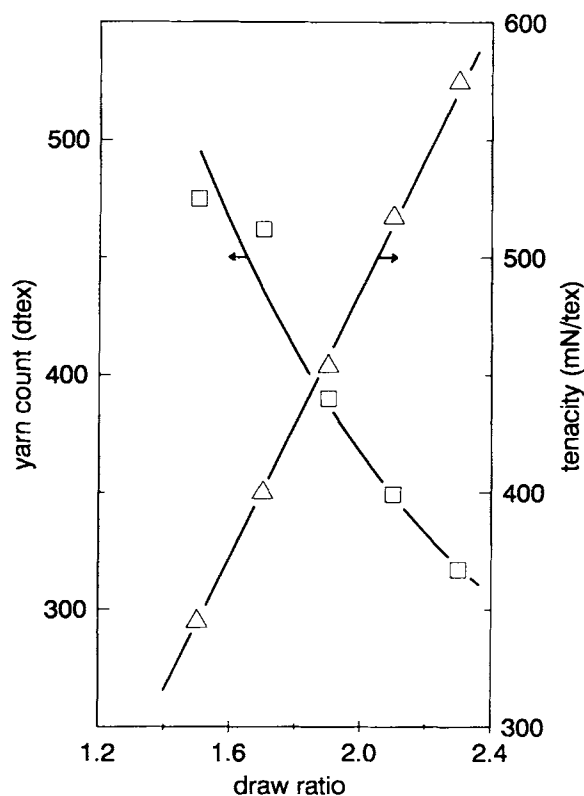


Figure 2 Yarn count and tenacity as a function of the draw ratio of 790f330 as-spun polyamide fibers.

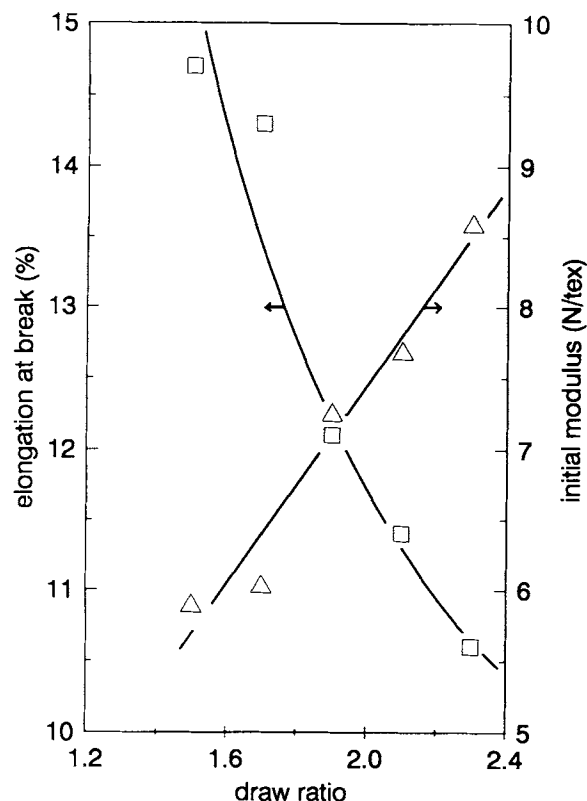


Figure 3 Elongation at break and initial modulus as a function of the draw ratio of 790f330 as-spun polyamide fibers.

gation at break 28%.¹ Clearly, at about the same tenacity, the amorphous polyamide yarn is characterized by its relatively low elongation at break.

Chemical and Solvent Resistance

The effect of various chemical agents on the 615f500 drawn polyamide yarns, as measured by fiber tensile

Table II Tensile Properties of Drawn Polyamide Fibers

Yarn	f330	f500
Number of filaments	330	500
Applied draw ratio	1.7	1.7
Yarn properties		
Yarn count (dtex)		
As-spun yarn	790	1100
Drawn yarn	429	615
Tenacity (mN/tex)	398	319
Elongation at break (%)	13.3	10.5
Filament properties		
Filament linear density (dtex)		
Drawn filaments	1.38	1.31
Tenacity (mN/tex)	350	310
Elongation at break (%)	12.0	9.7

Table III Chemical and Solvent Resistance of 615f500 Polyamide Fibers

Medium	Tensile Properties ^a			Free Yarn ^b Shrinkage (%)
	Count (dtex)	Tenacity (mN/tex)	Elongation (%)	
Blank	615	319 (16)	10.5 (0.4)	—
Toluene	621	336 (14)	10.7 (0.7)	0
Tetrahydrofuran	664	270 (20)	10.5 (1.4)	11
Acetone	637	300 (7)	11.8 (0.4)	5
Methanol	629	290 (7)	11.0 (0.4)	4
Dichloromethane	635	290 (18)	9.9 (1.0)	2
Cyclohexane	610	340 (40)	10.4 (1.5)	0
Tetrachloroethylene	634	337 (10)	10.6 (0.6)	0
<i>N,N</i> -Dimethylformamide	648	242 (1)	14.2 (0.3)	41
White spirit	618	325 (12)	10.3 (0.6)	0
Sulfuric acid (10%)	662	301 (9)	10.5 (0.5)	0
Nitric acid (10%)	642	254 (4)	9.6 (0.3)	1
Hydrochloric acid (10%)	634	312 (2)	10.2 (0.2)	0
Sodium hydroxide (10%)	632	315 (7)	10.4 (0.4)	0
Sodium chloride (10%)	624	326 (12)	10.9 (0.6)	0

^a Values in the parentheses denote the standard deviation of five measurements.

^b Free yarn shrinkage of 1 m of yarn, immersed for 1 week in the medium.

properties and free yarn shrinkage, is shown in Table III. Standard deviations of tensile properties are given in parentheses.

Despite its amorphous character, the polyamide yarn exhibits an excellent resistance to most organic solvents, except, to a minor extent, tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF). In fact, the polyamide yarn proves to be far superior to other known amorphous yarns.

Moreover, the polyamide yarn has a good resistance to aqueous solutions of inorganic acids, base, and salt. At a glance, the polyamide yarn seems to be well suited for applications under extreme environmental conditions.

Heat Resistance

The polyamide fiber has an excellent performance at high temperatures. Table IV shows the tensile properties of 429f330 drawn polyamide fibers at temperatures up to 185°C. For comparison, some data are listed for a 150 dtex PEI melt-spun fiber (internal experimental sample) and a 1360 dtex PPS melt-spun fiber (experimental sample received from the Phillips Fibers Corp.).

Measuring the tensile properties of the amorphous polyamide and PEI fibers at temperatures below their glass transition temperature (polyamide: $T_g = 293^\circ\text{C}$, and PEI: $T_g = 215^\circ\text{C}$) results in an

Table IV Heat Resistance of Polyamide, PEI, and PPS Fibers

Temperature (°C)	429 dtex Polyamide Yarn			150 dtex PEI Yarn			1360 dtex PPS Yarn		
	T (mN/tex)	RS (%)	TE (%)	T (mN/tex)	RS (%)	TE (%)	T (mN/tex)	RS (%)	TE (%)
21	397	100	12.7	302	100	28.2	376	100	29.2
100	333	84	12.5	218	72	26.3	306	81	31.6
150	277	70	13.3	159	53	26.0	277	74	34.0
185	237	60	13.4	116	38	29.0	—	—	> 40%

T = tenacity; RS = residual strength; TE = tensile elongation.

Table V Hot-Air Shrinkage and Boiling-Water Shrinkage of Polyamide, PEI, and PPS Fibers

	429 dtex Polyamide Yarn	150 dtex PEI Yarn	1360 dtex PPS Yarn
Hot-air shrinkage ^a (%)	0.45	12.0	4.9
Boiling-water shrinkage (%)	1.7	1.5	3.1

^a Heat-treatment at 220°C for 4 s.

unchanged elongation at break, whereas the tenacity drops with increasing temperatures. In this case, the polyamide fiber behaves considerably better than does the amorphous PEI fiber. The residual strength of the PEI fiber at 185°C, just below its glass transition temperature of 215°C, is only 38%. Tensile properties of the crystalline PPS fiber at 185°C could not be determined by the standard procedure because of the rather high elongation at break (> 40%). Indeed, this temperature is well above the glass transition temperature of PPS (DSC: $T_g = 85^\circ\text{C}$).

In addition to this, the aromatic polyamide fiber is also characterized by an outstanding long-term thermal resistance. Heating of the drawn polyamide fibers for 1 h at 250°C or for 40 h at 200°C in air gave no significant changes of the tensile properties of the material. Data on hot air-shrinkage, which means yarn shrinkage after a heat-treatment of 4 s at 220°C, and on boiling-water shrinkage, which

means yarn shrinkage after immersion for 30 min in boiling water, are shown in Table V.

The heat resistance of the 429f330 polyamide fiber, 150 dtex PEI fiber, and 1360 dtex PPS fiber, as measured by a thermal mechanical analysis (TMA), is illustrated in Figure 4. Clearly, the aromatic polyamide fiber is stable up to about 270°C. Near its glass transition temperature ($T_g = 293^\circ\text{C}$), free shrinkage of the fiber occurs. The PPS fiber starts to shrink above its glass transition temperature ($T_g = 85^\circ\text{C}$), whereas up to its melting point ($T_m = 285^\circ\text{C}$), a continuous shrinkage is observed. PEI melt-spun fibers already start to shrink at about 100°C. At about 200°C, the shrinkage amounts to about 10%, and above 200°C, the total free shrinkage may increase to 55%. Above 215°C, near its glass transition temperature, the material starts to flow.

Miscellaneous

Unlike PEI and PPS melt-spun fibers, the amorphous aromatic polyamide fibers are characterized by a significant moisture regain. Conditioning of dried 429f330 polyamide fibers at 20°C at a relative humidity of 65% resulted in a moisture regain of 3.9%. On the other hand, the moisture regain of PEI and PPS fibers is only 1.25%³ and 0.25%,¹ respectively.

Dyeing of the aromatic polyamide fiber was successful using the disperse dyeing technique. The colorfastness of the dyed fibers was demonstrated by extraction with dichloromethane (DCM). In an additional experiment, it was shown that 85–90% of the dye offered was absorbed by the polyamide fiber.

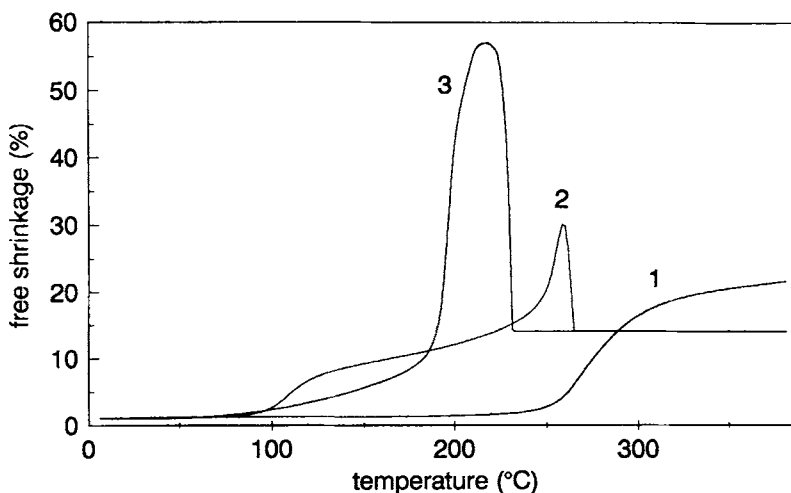


Figure 4 Thermal mechanical analysis (TMA) of (1) 429f330 drawn polyamide yarn, (2) PPS drawn yarn, and (3) PEI drawn yarn.

The amorphous character of the as-spun polyamide fiber was evidenced by X-ray diffraction experiments. During drawing, the polyamide fiber reveals some orientation.

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