Note

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PREPARATION AND PROPERTIES OF HIGHLY DYEABLE ARAMID FIBER

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ABSTRACT: In order to obtain a highly dyeable aramid fiber having good dimensional stability at high temperature, poly [*m*-phenyleneterephthalamide/isophthalamide (mole ratio 90/10)] was wet-spun, drawn 2.4 times in *N*-methylpyrrolidone/water (volume ratio 60/40) at 98 °C and washed with hot water. The dried fiber had moderate tensile property and could be dyed to heavy shade with disperse dyes at 135 °C without carrier. Its shrinkage at 450 °C was 18%.

1. INTRODUCTION

Nomex® [poly(*m*-phenyleneisophthalamide)](MI) has gained acceptance in several end-use applications because of its high heat durability and flame resistance. In industrial applications, the natural color fiber is used, but most of the applications for apparel, carpet and drapes require colored fiber. However, Nomex fiber is extremely difficult to dye and dyeing of the fiber is very expensive because of the treatment of waste dyebath containing high concentration of a dye carrier. Moreover, dyeable type Nomex (T455) is highly shrinkable at high temperatures and this is unfavorable in view of protection against fire. Poly(*m*-phenyleneterephthalamide) (MT) is a higher melting aramid polymer as compared with MI (melting point of MT measured by differential thermal analysis is 510 °C and that of MI is 425 °C) [1]. Therefore, MT is dimensionally more stable at high temperatures than MI by nature. However, its solution obtained by polycondensation is quite unstable to apply for industrial spinning. The more soluble MT/MI copolyamide fibers were also prepared, but their properties have not been investigated sufficiently [1]. In this work, MT/MI copolyamide fiber was prepared by wet-spinning, in order to obtain highly dyeable aramid fiber having good dimensional stability at high temperatures. The key point was not to treat it at high temperatures. The limiting oxygen index of the copolymer was also measured.

2. EXPERIMENTAL

2.1 Materials

m-Phenylenediamide (M) and isophthaloyl chloride (I) (each, E. P. grade) were distilled under vacuum before use. Terephthaloyl chloride (T) purchased from Mitsubishi Kasei Co. was used without further purification. *N*-Methylpyrrolidone (NMP) purchased from Mitsubishi Kasei Co. was dried over molecular sieves.

2.2 Preparation of the Spinning Dopes

By a conventional method, M was reacted with T/I mixtures (which were previously co-melted, cooled and pulverized) in NMP to form the aramid solution. It was then neutralized by adding calcium acetate monohydrate.

2.3 Preparation of the Copolyamide Fibers

2.3.1 Wet-spinning

Dopes obtained in 2.2 were wet-spun into 52 wt.% calcium chloride aqueous solution at 90 °C. Typical spinning conditions were as follows.

Spinnerets: 0.08 mm in diameter/20 holes, Take up velocity: 10 m/min. The coagulated fiber taken on a glass bobbin was washed with water at room temperature and then drawn 2.1 - 2.2 times in hot water (95 °C) and dried at 80 °C. Denier per filament was about 2.

As one method for obtaining the highly dyeable fiber having good dimensional stability at high temperatures, the washed coagulated fiber was drawn in NMP/H₂O (volume ratio 60/40) at 98 °C. It was then

Table 1 Preparation of MT/MI Copolyamides

MT/MI (mole ratio)	Polymer concentration ^{a)} (%)	η_{inh} ^{b)}	Viscosity (Pa·s, 25 °C)	Comments
100/ 0	12.4	1.27	146	Polymer precipitated after standing 2 days at room temperature
95/ 5	14.5	1.01	136	Gelled after 1 week
	15.5	1.10	272	Gelled after 4 days
90/10	15.8	1.16	675	Stable solution after 1 month
80/20	17.2	0.97	560	Stable solution after 1 month

a) After $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ was added.

b) 0.5 g Polymer/100 mL H_2SO_4 at 25 °C.

washed with hot water.

2.3.2 Heat Treatment

The dried fiber was heat treated at constant length, using the hot plate (30 cm long).

2.4 Dyeing

Dyeing was carried out with disperse dyes with or without carrier, using a Tekusamu Giken Minicolor Type MC 12E. Typical conditions for dyeing are described in the footnote of Table 2.

2.5 Measurements

Inherent viscosities (η_{inh}) of the polymers were determined in sulfuric acid at a polymer concentration 0.5 g/100 mL at 25 °C. η_{inh} were calculated from the equation $\eta_{inh} = \ln \eta_{rel}/C$ (η_{rel} : relative viscosity, C: polymer concentration).

Tensile properties were measured as previously reported [2]. Shrinkage of fibers was determined after keeping them for 10 min at relaxed state in an air oven. The limiting oxygen index (LOI) of the copolymer was measured for the film (about 40 μm thick), using a Suga Sikenki combustion tester ON-1.

3. RESULTS AND DISCUSSION

3.1 Preparation of MT/MI Copolyamide Solutions

Table 1 shows the results of preparation of MT/MI copolyamide solutions. The solutions of MT homopolymer and MT/MI (mole ratio 95/5) were quite unstable as described in Ref. 1, but the solutions of copolymers containing MI component ≥ 10 mole% were stable even after 1 month. In view of dimensional stability at high temperatures, the copolymers containing less MI component are preferable. Therefore, MI/MT (90/10) was chosen for the preparation of fibers.

3.2 Wet-spinning of MT/MI (90/10) Copolyamide

Wet-spinning was carried out, using 52 wt.% calcium chloride aqueous solution (90 °C) as a coagulant as described in 2.3.1, where lustrous coagulated fibers were obtained. If the concentration of calcium chloride in the coagulant bath was lower than 50 wt.%, the coagulated fiber was dull and contained many voids. The coagulation is supposed to proceed with desolvation by salting out through the semi-permeable membrane which was formed initially on the surface of the fiber. Therefore, the polymer solution used here which contained calcium chloride up to nearly half the concentration of polymer needs the coagulant bath containing higher concentration of calcium chloride.

3.3 Dyeability and Dimensional Stability at High Temperatures of MT/MI (90/10) Copolyamide Fiber

Dyeability and dimensional stability at high temperatures of MT/MI (90/10) copolyamide fiber were evaluated and are shown in Table 2. Dyeability was evaluated quite qualitatively. The dried and not heat-treated fiber had moderate tensile property as shown in the footnote of Table 2 and could be dyed to heavy shade with disperse dyes at 135 °C without dye carrier. Its dimensional stability at 400 °C, however, was poor. Dyeability decreased and dimensional stability at high temperatures increased with elevating temperature of heat treatment, probably because of the increase in crystallinity. Nomex T455 which was described to be dyeable with cationic dyes in Ref. 3 could not be dyed with the disperse dyes, and its shrinkage at high temperatures was quite

Table 2 Dyeability and Dimensional Stability at High Temperatures of MT/MI (90/10) Copolyamide Fiber^{a)}

Heat treatment				Dyeability ^{b)}	Shrinkage	
Temperature (°C)	Time	Condition			(%)	
					400 °C	450 °C
Not heat-treated				◎	49	—
250	5 s	in air,	at constant length	○	40	>40
270	5 s	in air,	at constant length	△	24	30
300	5 s	in air,	at constant length	×	22	18
135	20 min	in water, free		◎	31	36
135	20 min	in water, at constant length		◎	19	21
cf. Nomex T455				△~×	47	51

a) The coagulated fiber was drawn 2.1 times in water (95 °C) and dried at 80 °C. Its tensile property is as follows: Tenacity 3.1 g/d, Elongation 14%, Initial modulus 73 g/d.

b) Conditions of dyeing

Dye: Dianix Brilliant Red BS-E, Dianix Navy Blue ER-FS, and Resolin Orange 3GL (each, 6% owf) were used as received. Carrier: Acetophenone. Liquor ratio, 1:50; Temperature 135 °C; Time, 90 min. ◎, dyed to heavy shade without carrier; ○, dyed to heavy shade with carrier 20% owf; △, dyed to pale shade with carrier 20% owf; ×, not dyed with carrier 20% owf.

Table 3 Properties of the Dried Fiber of MT/MI (90/10) Copolyamide Treated with NMP/H₂O Mixture

Conditions of treatment		Tenacity	Elongation	Initial modulus	Dyeability ^{a)}	Shrinkage (%)	
		(g/d)	(%)	(g/d)		400 °C	450 °C
Drawn 2.2 times in water (95 °C)	→ NMP/H ₂ O (20/80) at 100 °C for 10 min at constant length	3.7	22	75	◎	9	18
Drawn 2.1 times in water (98 °C)	→ NMP/H ₂ O (30/70) at 100 °C for 10 s at constant length	3.3	16	64	◎	14	16
Washed coagulated fiber	→ Drawn 2.4 times in NMP/H ₂ O (60/40) at 98 °C	3.9	15	84	◎	15	18

a) Dyes and measure of dyeability are the same as described in Table 2.

high. In order to estimate the dimensional stability at high temperatures of the as-spun dried fiber treated under the conditions of dyeing, it was heat-treated in water at 135 °C under pressure freely or at constant length. The results are also shown in Table 2. Shrinkage at high temperatures of the fiber treated at constant length decreased remarkably while its dyeability did not change. This result suggests that if the fiber which was coagulated and hot-drawn in water is treated with a swelling agent at constant length at atmospheric pressure, it may have excellent dimensional stability at high temperatures, keeping its good

dyeability. From this point of view, the fiber which was coagulated and hot-drawn in water was heat-treated with NMP/H₂O mixture under several conditions. The results shown in Table 3 are as expected. In order to obtain the same effect, the coagulated and washed fiber was conveniently drawn in NMP/H₂O mixture (volume ratio 60/40) at 98 °C as shown in Table 3.

3.4 The Limiting Oxygen Index (LOI) of MT/MI (90/10) Copolyamide

LOI of MT/MI (90/10) copolyamide was measured for the film (about 40 μm thick) which was prepared

by casting the solution, drying and washing with water. Its LOI was 31%, which was similar to that of MI homopolymer (30%).

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