

Direct Fiber Formation and Fiber Properties of Aromatic Polyoxadiazoles

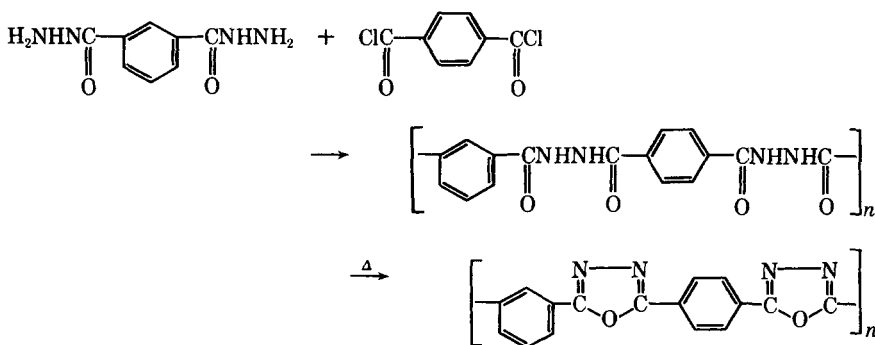
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Synopsis

A novel and simple fiber formation process has been developed to fabricate aromatic polyoxadiazoles. The aromatic copolyoxadiazole solution prepared from terephthalic acid, isophthalic acid, and hydrazine sulfate in fuming sulfuric acid was utilized directly as spinning solution and was successfully wet-spun to form fiber into a coagulating bath containing sulfuric acid. In the wet-spinning process, selection of the coagulating bath was the most important factor, and the best results were obtained by the use of approximately 50 wt-% aqueous sulfuric acid. It was easy to prepare a polyoxadiazole fiber having a tenacity of more than 4 g/den. and an elongation of more than 10%. In addition, the fiber properties reached to a tenacity of 6 g/den. and an elongation of 12% under optimum spinning conditions. The wet-spun polyoxadiazole fiber showed an almost round cross section and a clear skin-core structure by microscopic observation. The fiber had a high level of thermal and dimensional stability and a high proportion of property retention at elevated temperatures, as well as all-round general fiber properties.

INTRODUCTION

Fiber formation of thermally stable high polymers has been the subject of steadily increasing research and development in the past few years.¹ Among others, attention has been drawn to aromatic polyoxadiazoles by Frazer et al.²⁻⁵ as a new class of thermally stable fiber formers. Their preparation of the polyoxadiazole fiber is, however, rather complicated. The process involves synthesis of a soluble polyhydrazide from isophthalic dihydrazide and terephthaloyl chloride, fabrication into fiber by dry-spinning, and thermal conversion of polyhydrazide into polyoxadiazole in the form of fiber.



On the other hand, Iwakura, Uno, and Hara⁶ recently reported a simple preparative method for aromatic polyoxadiazoles from terephthalic acid and hydrazine sulfate by using fuming sulfuric acid as a solvent as well as a condensing agent.

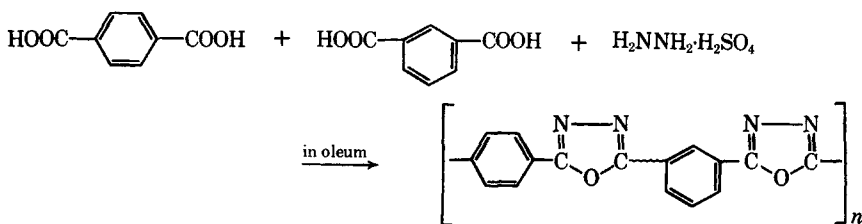
It is known that infusible intractable polymers, such as polyterephthalamide^{7,8} and polybisbenzimidazobenzophenanthroline,⁹ are wet-spun from solutions in concentrated sulfuric acid. This procedure was applied to fiber formation of aromatic polyoxadiazoles.

The present paper is concerned with a successful direct fiber formation of the fuming sulfuric acid solution of the polyoxadiazole prepared by Iwakura's method.⁶ In the preliminary wet-spinning studies, poly-*p*-phenyleneoxadiazole provided with two intractability problems; that is, (a) extremely high viscosity of the spinning solution made spinning a uniform filament difficult, and (b) only brittle fiber was obtained, presumably because of the high crystallizability of the polyoxadiazole. Delicate and tedious searches for conditions would be required for obtaining a better fiber from the polyoxadiazole. Meanwhile it was found that a random copolyoxadiazole quite readily gave a fiber of better quality. Therefore, the random copolyoxadiazole prepared from terephthalic acid and isophthalic acid was used for the following studies. The physical properties of the polyoxadiazole fiber so obtained are also described.

EXPERIMENTAL

Spinning Solution

A random copolyoxadiazole having inherent viscosity of approximately 2.0 was prepared by the use of fuming sulfuric acid from terephthalic acid (T), isophthalic acid (I), and hydrazine sulfate, where the ratio of the two acid components, T/I, was 75/25.



A typical procedure for preparing the polyoxadiazole is as follows. To a solution of 10.46 g of hydrazine sulfate in 100 g of 30% fuming sulfuric acid there was added a mixture of 9.96 g of T and 3.32 g of I all at one time with stirring at 120°C. The reaction mixture was stirred at that temperature for 2 hr. It became very viscous as reaction proceeded. Stirring was continued at 140°C for an additional 2 hr and an amber-colored clear solution of the polyoxadiazole was obtained. The inherent viscosity in concentrated sulfuric acid was 2.11 (concentration: 0.2 g/100 ml at 30°C).

In this polycondensation reaction, most of the free sulfur trioxide in the fuming sulfuric acid is consumed as a condensing agent, and thereby the amount of remaining sulfur trioxide in the polymer solution is usually of the order of a few per cent.

The fuming sulfuric acid solution containing 10 wt-% of the polyoxadiazole obtained here was utilized directly for wet-spinning studies.

Fiber Formation

A monofilament was prepared for exploratory studies. The spinning solution was extruded through a spinneret immersed in a coagulating bath by means of a mechanically driven stainless steel syringe of 20 ml capacity. The filament formed was passed in the bath of the length of 1.6 m and was taken up onto the first roller. The wet, acid-containing filament was then passed in a washing bath of 1.8 m in length and simultaneously drawn to several times of the original length. The filament, now free from traces of sulfuric acid, was wound onto a bobbin and dried in an air oven.

Throughout the spinning experiments, the conditions shown in Table I were fixed, while other factors were varied to see their effects on the resultant fiber properties.

TABLE I
Fixed Spinning Conditions

Spinneret, mm ϕ \times hole*	0.2 \times 1 or 0.3 \times 1
Coagulating bath temperature, °C	15 ~ 20
Speed of first roller, m/min	1.1 or 2.2
Washing bath	water
Washing bath temperature, °C	50 ~ 60

* mm ϕ denotes diameter of spinneret.

RESULTS AND DISCUSSION

Preparation of Polyoxadiazole Fiber

Preliminary Wet-Spinning Studies. Initial attempts were made to extrude the fuming sulfuric acid solution of the polyoxadiazole into a coagulating bath consisting of water, only to obtain a filament without difficulty. Despite a few variations in the wet-spinning conditions, the undrawn filament was found to have rather consistent tensile properties; it exhibited tenacity of 0.9 ~ 1.0 g/den., elongation of 40% ~ 130%, and initial modulus of 30 ~ 35 g/den. The filament was, however, too brittle to be drawn by conventional hot-stretching at a temperature below 300°C.

To improve the tensile properties of the polyoxadiazole fiber, it was necessary to pass the coagulated filament directly into a hot water bath to stretch before winding. This spinning method consequently offered a polyoxadiazole fiber having sufficient tensile properties without further hot-stretching. The results of wet-spinning studies will be hereafter described in some detail.

TABLE II
Selection of Coagulating Bath

Coagulating bath (aqueous soln)	Spinning conditions				Fiber properties			
	Spinneret, mm ϕ \times hole	Speed of first roller, m/min	Draft ratio*	Draw ratio	Denier	Tenacity, g/den.	Elonga- tion, %	Initial modulus, g/den.
50% ZnCl ₂	0.2 \times 1	1.1	1.5	3	10.0	3.05	13.5	93
50% ZnBr ₂	0.2 \times 1	1.1	1.5	3	9.1	2.91	9.0	97
45% Zn(NO ₃) ₂	0.2 \times 1	1.1	1.5	3	9.2	3.34	21.4	101
40% H ₂ SO ₄	0.2 \times 1	1.1	2	4	7.4	3.82	9.9	118
47% H ₂ SO ₄	0.3 \times 1	1.1	3	4	9.9	5.10	7.7	153
50% H ₂ SO ₄	0.3 \times 1	2.2	4	4	6.8	5.24	12.2	143
52% H ₂ SO ₄	0.3 \times 1	2.2	4	4.5	6.6	6.17	12.2	150

* Draft ratio stands for the ratio of the speed of the first roller to the extrusion speed of the spinning solution at the spinneret.

Selection of Coagulating Bath. In the wet-spinning process, selection of the coagulating bath is considered to be one of the most important factors. In early wet-spinning runs, water was used as the coagulant; however, the filament formed was opaque and had rather poor tensile properties. The phenomenon was attributed to too fast a coagulation of the polyoxadiazole solution by water. Therefore, it was expected that conditions for the formation of transparent and tough filament would be attained by the use of an aqueous, neutral, inorganic salt solution or aqueous sulfuric acid as the coagulating agent which would slow down the coagulation speed of the spinning solution.

Calcium chloride and barium chloride were omitted as bath components because of precipitation of insoluble salts by the reaction with sulfuric acid from the polyoxadiazole solution. Sodium sulfate had some effect on the transparency of the filament formed, mainly because of its limited solubility in water, while ammonium sulfate was a little more effective than sodium sulfate. As is shown in Table II, zinc chloride, zinc bromide, and zinc nitrate, having greater solubility in water than the above, gave better results among the neutral inorganic salts examined; the best tensile properties of the polyoxadiazole filament thus obtained were tenacity of 3.3 g/den., elongation of 21%, and initial modulus of 100 g/den.

It has been known⁸ that extrusion of sulfuric acid solutions of polymers into aqueous sulfuric acid is one of the most effective wet-spinning process for fibers from polyterephthalamides.

In the present study, the sulfuric acid concentration in the coagulating bath was varied in order to find an optimum condition. As is shown in Table II, the fiber properties depended greatly on the coagulating bath concentration, and spinnability and drawability of the polyoxadiazole fiber were improved by increasing the sulfuric acid concentration in the bath. It was found that by the use of approximately 50 wt-% aqueous sulfuric acid as the coagulant, a polyoxadiazole fiber having the best transparency and tensile properties was formed. The fiber properties reached a tenacity of 6.1 g/den., elongation of 12%, and initial modulus of 150 g/den.

Effect of Spinning Conditions on Fiber Properties. On the basis of the above results, draft ratio (cf. footnote of Table II) and draw ratio were varied in the next wet-spinning runs in which 47 ~ 50 wt-% aqueous sulfuric acid was used as the coagulant. Data on the fiber properties and the spinning conditions under which the fibers were derived are given in Table III.

The table shows that the fiber properties are highly dependent on the draw ratio, but only slightly on the draft ratio. When a fiber is drawn, in general the tenacity and the initial modulus increase and the elongation at break decreases in accordance with the increase in the degree of molecular orientation and of crystallization. For continuous wet-spinning of the polyoxadiazole fiber, a draw ratio of approximately 4 was chosen from the observed maximum draw ratio of 4.5 ~ 5; and it was found easy to prepare

TABLE III
Effect of Spinning Conditions on Tensile Properties of Fiber

Spinneret, mm ϕ \times hole	Spinning conditions				Fiber properties			Initial modulus, g/den.
	Speed of first roller, m/min	Draft ratio	Draw ratio	Denier	Tenacity, g/den.	Elonga- tion, %		
0.2 \times 1	1.1	2.0	3.0	8.0	3.12	9.6	98	
			3.5	6.0	4.30	8.3	131	
			4.0	5.1	5.80	9.2	165	
0.3 \times 1	2.2	3.0	4.4	4.3	7.00	5.6	207	
			3.5	11.1	3.68	15.5	105	
			4.0	9.2	4.48	12.3	110	
0.3 \times 1	2.2	4.0	4.5	7.5	6.19	9.5	151	
			3.5	7.1	4.61	17.0	145	
			4.0	6.1	5.77	12.7	148	
0.2 \times 5	1.1	4.0	4.5	5.8	6.10	9.9	154	
			3.0	14.0	3.25	12.8	104	
			3.5	16.5	3.84	12.2	138	
			4.0	15.7	4.93	12.6	136	

TABLE IV
Effect of Heat Aging on Tensile Properties of Fiber

	Denier	Tenacity, g/den.	Elongation, %	Initial modulus, g/den.
Before heat aging	9.8	3.58	20.2	113
After heat aging	9.3	4.12	23.6	112

TABLE V
Effect of Polymer Molecular Weight on Tensile Properties of Fiber^a

Inherent viscosity of poly- oxadiazoles ^b	Viscosity of spinning solution, ^c poise	Fiber properties			
		Denier	Tenacity, g/den.	Elongation, %	Initial modulus, g/den.
0.88	900	unspin- nable			
1.33	2700	undraw- able			
1.68	7010	7.3	4.21	11.5	138
2.11	13250	6.5	4.72	13.6	128

^a Wet-spinning conditions are as follows: coagulating bath of 52 wt-% aqueous sulfuric acid, draft ratio 4, and draw ratio 4.

^b Measured at a concentration of 0.2 g/100 ml in concentrated sulfuric acid at 30°C.

^c Solution of 10 wt-% concentration was measured at 20°C by using a Brookfield rotary viscosimeter.

a fiber having a tenacity of more than 4 g/den. and elongation of more than 10%.

The polyoxadiazole fibers of both monofilament and multifilament were wet-spun to develop equally good characteristics.

Effect of Heat Aging on Fiber Properties. Further improvement of the tensile properties of the polyoxadiazole fiber was achieved by heat aging; the filaments obtained above were aged in an unrestricted state in an air oven at 200°C for 30 min. The results are shown in Table IV. By the heat aging at elevated temperatures, the polyoxadiazole fiber increased its tenacity and elongation, with its initial modulus remaining unchanged.

Effect of Polymer Inherent Viscosity on Fiber Properties. In the wet-spinning experiments described above, a uniform filament was easily obtained from polyoxadiazole having an inherent viscosity ranging from 1.8 to 2.6. In order to see the correlation between the fiber properties and the inherent viscosity of the polymer, monofilaments were wet-spun from each of the polyoxadiazoles, of which the inherent viscosity was 0.88, 1.33, 1.68, and 2.11, respectively. The results are given in Table V.

The polyoxadiazoles with inherent viscosity higher than 1.7 gave tough filaments having a tenacity of more than 4 g/den., while polymers with inherent viscosity lower than 1.3 could not be wet-spun or the wet filament obtained was not stretchable at best.

Viscosity of 10 wt-% solutions of the polyoxadiazole showed a reasonable dependence on the inherent viscosity of the polymer. Thus, it was concluded that the most appropriate polymers for fiber formation are those having an inherent viscosity higher than 2.0 or those showing a solution viscosity higher than 10,000 poises in a 10 wt-% solution.

Structural Studies on Polyoxadiazole Fiber

Residual Acid in Fiber. A spot test for sulfur in the fiber was negative. This is enough to show that the residual sulfuric acid in the fiber was so low that the fiber does not require further washing.

Microscopic Observation. The cross section and longitudinal views of the fiber, shown in Figures 1 and 2, were observed under a photomicroscope and an electron microscope of a stereoscanning type. The cross section is almost round and shows a clear dual structure of skin and core. The longitudinal view indicates a striated surface in contrast to the smooth surface of most melt-spun fibers.

X-Ray Diffraction Study. An x-ray diffraction diagram of the polyoxadiazole fiber, given in Figure 3, shows that the fiber is moderately oriented.

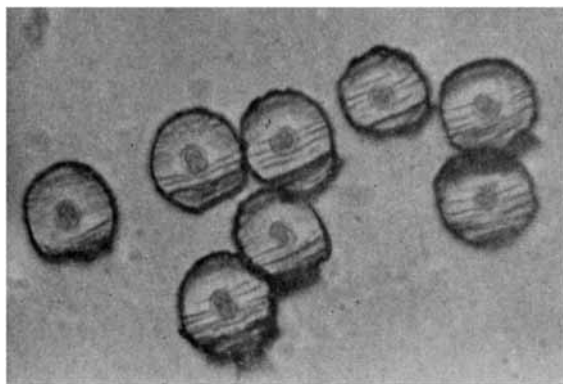
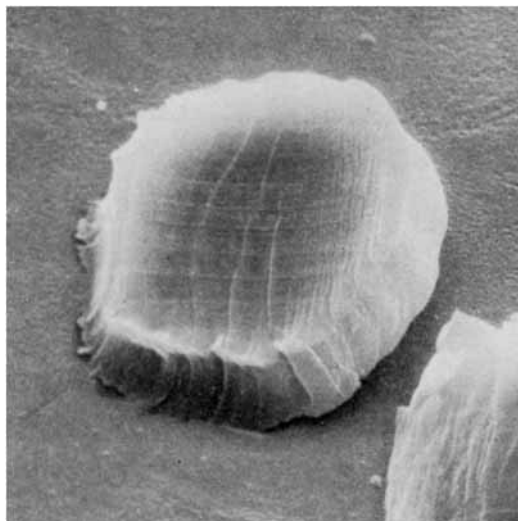


Fig. 1. Photomicrograph of cross section of polyoxadiazole fiber. 400 \times .

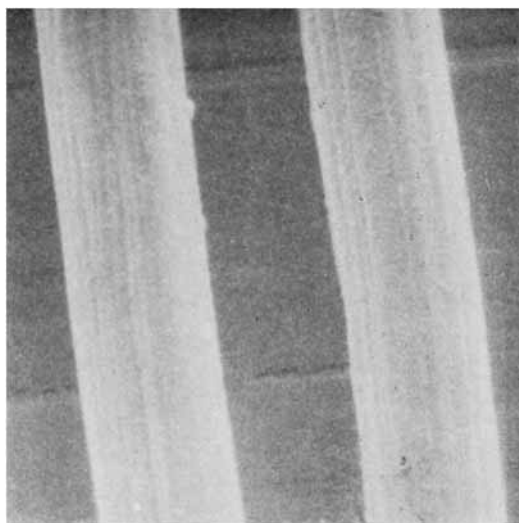
Physical Properties of Polyoxadiazole Fiber

Tensile Properties. A typical stress-strain curve of the polyoxadiazole fiber is shown in Figure 4. It resembles the stress-strain curve of du Pont's Nomex.¹⁰ Other characteristic data are summarized in Table VI. The high value (88%) of the wet-to-dry strength ratio is characteristic for the polyoxadiazole fiber. Brittleness factors of a fiber may be represented by the relation of knot and loop strengths to the straight strength. The values were found to be 71% and 76%, respectively, which together with the high initial modulus reflects the rigid nature of the polyoxadiazole chain.

Density. The polyoxadiazole fiber is slightly heavier than commercialized synthetic fibers such as polyethyleneterephthalate fiber and Nomex nylon¹⁰ (both 1.38 g/cc).



(a)



(b)

Fig. 2. Electron micrograph of polyoxadiazole fiber: (a) cross section 3000 \times ; (b) longitudinal view 1000 \times .

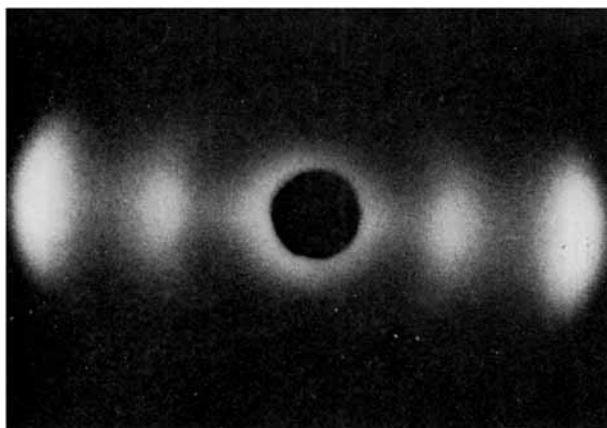


Fig. 3. X-Ray diffraction pattern of polyoxadiazole fiber.

TABLE VI
Properties of Polyoxadiazole Fiber

Denier	6.7
Tenacity	
dry, g/den.	3.91
wet, g/den.	3.46
ratio of wet/dry, %	88
Elongation at break	
dry, %	10.5
wet, %	10.5
Loop strength, g/den.	2.97
ratio of loop/straight	76
Knot strength, g/den.	2.78
ratio of knot/straight	71
Initial modulus, g/den.	114
Density, g/cc	1.41
Moisture regain, %	4.5

TABLE VII
Light Resistance of Polyoxadiazole Fiber

Light treatment	Fiber properties		
	Tenacity, g/den.	Elongation, %	Tenacity retention, %
Original	4.1	9.7	—
Exposed to xenon lamp for 20 hr	2.3	2.9	56
Exposed in Fade-Ometer for 20 hr	2.7	3.5	66
Exposed in Fade-Ometer for 40 hr	2.7	3.5	66

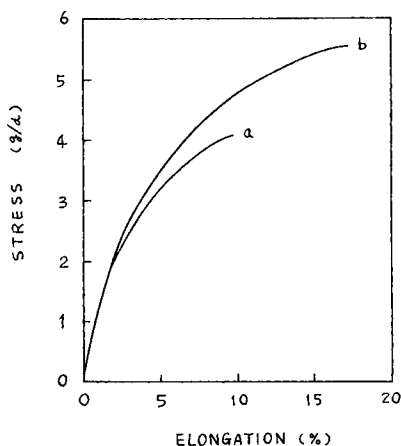


Fig. 4. Stress-strain curves of fiber: (a) polyoxadiazole fiber; (b) du Pont's Nomex nylon.

Moisture Regain. Moisture uptake of the polyoxadiazole fiber was 4.5%, being comparable to that of polyamide fibers.¹¹

Light Resistance. Stability of the polyoxadiazole fiber against exposure to ultraviolet light is fair, as shown in Table VII. The fiber loses one third of its initial strength and two thirds of its initial elongation after 20 hr of exposure in the Fade-Ometer. The stability is comparable to that of Nomex nylon.¹⁰

Thermal Properties of Polyoxadiazole Fiber

Thermal Behavior. Polyoxadiazole fiber carbonizes by heating above 400°C without melting. The fiber supports burning after ignition with an open flame. Figures 5 and 6 give the data of differential thermal analysis (DTA) and thermogravimetric analysis (TGA), respectively, both measured in air. The DTA curve shows no endothermic peak below 400°C and a gradual exothermic shift above this temperature. A sharp peak of exotherm is located at 495°C, indicating thermal decomposition

TABLE VIII
Heat Shrinkage of Polyoxadiazole Fiber

Heat treatment	Shrinkage, %
Exposed to dry air for 30 min at	
150°C	0.4
175°C	0.6
200°C	1.0
225°C	1.0
250°C	1.4
Immersed in water for 30 min at	
100°C	0.5
130°C	1.5

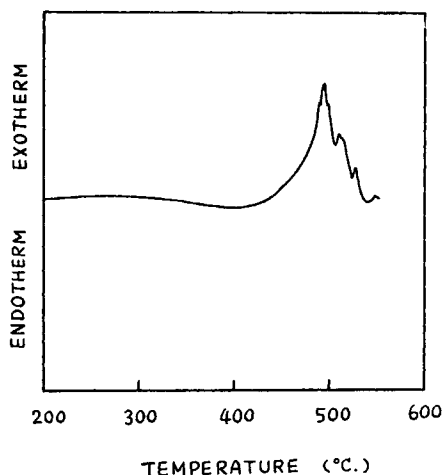


Fig. 5. Differential thermal analysis of polyoxadiazole fiber in air at a heating rate of 10°C/min.

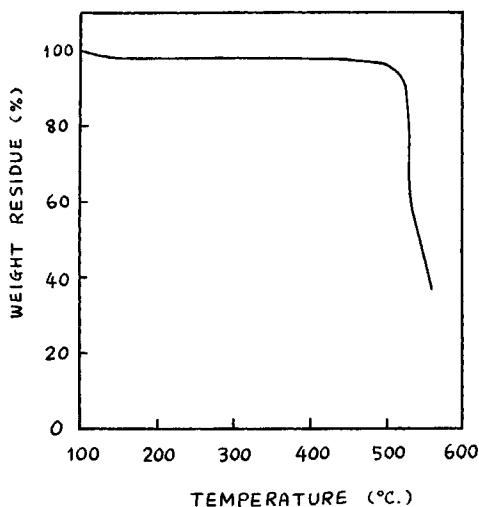


Fig. 6. Thermogravimetric analysis of polyoxadiazole fiber in air at a heating rate of 5°C/min.

of polyoxadiazole. The weight loss shown in the TGA curve is only slight up to 490°C, but becomes substantial above 500°C, corresponding to the DTA data. These results are in good agreement with the polyoxadiazoles reported by Frazer et al.^{2,12}

Heat Shrinkage. As shown in Table VIII, the polyoxadiazole fiber exhibits a small shrinkage with increase in temperature, for instance, 1.4% at 250°C. However, shrinkage is higher in the wet, being 1.5% in water at 130°C. Thus, the high dimensional stability of the polyoxadiazole fiber is comparable with that of Nomex nylon.¹⁰

TABLE IX
Tensile Properties of Polyoxadiazole Fiber at Elevated Temperatures

Testing temp., °C	Fiber properties		
	Tenacity, g/den.	Elongation, %	Tenacity retention, %
23	4.1	9.7	—
150	3.8	15.9	93
200	3.2	15.0	78

Tensile Properties at Elevated Temperatures. Heat-resistant properties of the polyoxadiazole fiber were studied in two different ways. First, the tensile properties of the fiber were measured at elevated temperatures, with reference to those at room temperature. The results in Table IX and the stress-strain curves in Figure 7 indicate that the fiber is useful at 200°C, with a little loss in the initial modulus and strength but slight increase in the elongation. Thus, it requires more work to break the fiber at 200°C than at room temperature.

Tensile Properties After Heat Aging. Another method to determine the high temperature performance of the polyoxadiazole fiber was conducted by measuring the tensile properties after the fibers were subjected to various high temperature conditions under no external restraint. The results are shown in Figure 8 and Table X. Slight increase in initial modulus and strength was observable when the fibers were treated in the dry for 30 min at temperatures of 200° to 300°C, while no significant change was observed by treating the fiber in the wet.

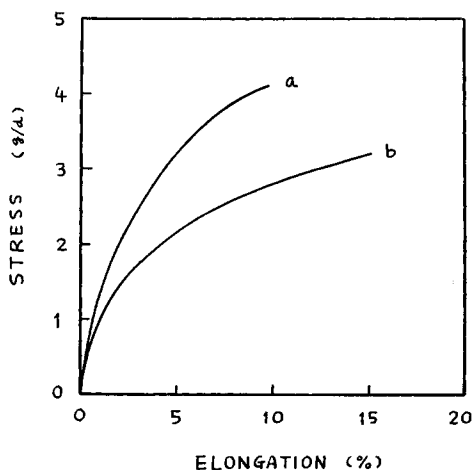


Fig. 7. Stress-strain curves of polyoxadiazole fiber at elevated temperature: (a) fiber measured at 23°C; (b) fiber measured at 200°C.

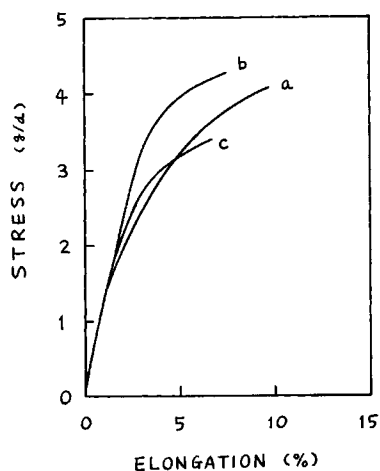


Fig. 8. Stress-strain curves of polyoxadiazole fiber after heat aging. (a) original fiber; (b) fiber aged at 300°C for 30 min in dry air; (c) fiber aged at 130°C for 30 min in steam.

TABLE X
Tensile Properties of Polyoxadiazole Fiber after Heat Aging

Heat aging			Fiber properties		
Atmosphere	Temp., °C	Time, min	Tenacity, g/den.	Elongation, %	Tenacity retention,* %
Dry air	150	30	4.1	8.5	100
	200	30	4.3	9.0	105
	250	30	4.3	8.6	105
	300	30	4.3	7.5	105
	350	30	3.9	5.5	95
	400	30	3.3	2.9	80
Boiling water	100	30	3.9	7.9	95
Steam	130	30	3.4	6.7	83
	170	60	3.4	3.4	83
	200	60	2.2	1.9	53
	250	60	0.1	0.9	3

* Original fiber properties at room temperature are tenacity of 4.1 g/den. and elongation of 9.7%.

Thus, the polyoxadiazole fiber prepared by the present method corresponds to that prepared by Frazer et al.^{3,4} in high temperature properties, and is superior to du Pont's Nomex nylon.

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