

High-Strength-High-Modulus Polyimide Fibers II. Spinning and Properties of Fibers

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Synopsis

The polyimides based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) described in Part I of this series were dissolved in *p*-chlorophenol and spun into fibers using a coagulating bath of ethanol. The fibers as spun had in general low tenacities and low moduli, but a heat treatment at 300–500°C under tension produced a remarkable increase in strength and modulus, and fibers with a tensile strength of 26 g/den (3.1 GPa) and an initial modulus higher than 1,000 g/den (120 GPa) could be obtained. Thus, the annealed fibers of polyimides are comparable to aramid fibers in mechanical properties. To heating in air and in the saturated steam, the polyimide fibers showed higher resistance than the aramid fibers. The polyimide fibers surpassed the aramid fibers in resistance to acid treatment and ultraviolet (UV) irradiation, but were inferior in resistance to alkali treatment. The annealed fibers of polyimides displayed distinct X-ray diffraction patterns. The chain repeat distance of 20.5 Å determined on the fibers of polyimide prepared from BPDA and *o*-tolidine, and 20.6 Å determined on the fibers of polyimide derived from BPDA and 3,4'-diaminodiphenyl ether are reasonable when the dimensions of monomeric units and the shapes of the molecular chains are considered. The X-ray reflections of both polyimide fibers were indexed satisfactorily on the basis of postulated unit cells.

INTRODUCTION

One of the important reasons for the high strength and high modulus of aramid fibers is explained in terms of stiff molecular chains of aromatic polyamides. In this regard, the polyimides in which aromatic rings are joined by rigid imide rings to form the stiff backbones favor the formation of strong and stiff fibers. Contrary to expectation, however, the study on polyimide fibers is rather scanty. This may be due to the difficulty in finding powerful solvents for high-molecular weight polyimides. In the technique now in use, the difficulty is overcome by the invention of two-step method. In the first step, fibers are spun from the solution of polyamic acid which is soluble in usual organic solvents. In the second step, the polyamic acid fibers are converted *in situ* to polyimide fibers by heat treatment at a high temperature. Irwin et al.^{1,2} prepared the polypyromellitimide fibers in this manner. The fibers showed excellent high temperature performance, but the tenacity and initial modulus were limited to small values. In a patent application,³ it is reported that the fibers of polyimide made from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and benzidine by the two-step

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method showed a strength of 10 g/den and a modulus of 8,000 kg/mm². Most recently, Jinta et al.⁴ studied the preparation of a variety of polyimide fibers by the two-step method and reported that the fiber of copolyimide having a tensile strength of 19.7 g/den and a modulus of 1,310 g/den could be produced.

Although the products of polyimides are mostly manufactured by the two-step technique described above, it is desirable to prepare high-molecular aromatic polyimides in a single step. An attempt is made in a patent⁵ to produce fibers from the copolyimides which were prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and stoichiometric amount of the mixture of aromatic diisocyanates with the evolution of carbon dioxide. In spite of a complicated operation scheme including spinning, drawing, and heat treatment, the highest tenacity and modulus reported in the patent are no more than 2.65 g/den and 70 g/den, respectively.

As reported in Part I of this series, a number of aromatic polyimides and copolyimides with high molecular weights could be prepared in a single step from BPDA and various aromatic diamines. Our preliminary experiments⁶ showed that these polyimides could be converted to fibers with higher strengths than those reported in the literature. This induced us to make a series of systematic experiments of fiber spinning using the polyimides described in the previous paper. As expected, some of the heat-treated fibers of polyimides showed strengths higher than 20 g/den and moduli higher than 1,000 g/den. The polyimide fibers showed excellent thermal properties surpassing the aramid fibers in resistance to heating in air and in the saturated steam. To the UV irradiation also, the polyimide fibers were much more stable than the aramid fibers. The polyimide fibers were considerably stable in the acid medium, but were highly susceptible to the hydrolytic degradation in the alkaline medium, contrary to the chemical properties of the aramid fibers.

SPINNING

Spinning Liquids (Dopes)

p-Chlorophenol was used as a solvent. Some important properties of spinning dopes will be stated in connection with practice. The 9 wt% solution of BPDA/PMDA(7/3)-OTOL with an η_{inh} of 2.34 dissolved in *p*-chlorophenol shows at 65°, 80°, and 101°C the Newtonian flow in the region of low shear rates, but the viscosity tends to decline at higher shear rates, as illustrated in Figure 1. This is the property common to all well-dissolved, homogeneous polymer solutions. Phenol also has a strong solvent action on polyimides, as described in the previous paper, but the solution in phenol does not exhibit the Newtonian behavior even at very small shear rates. The viscosity of phenol solution increases steeply with decreasing shear rate. Such a rapid change in viscosity in the region of low shear rates may be associated with a particular structure produced by the aggregation of polymer molecules in the solution. Therefore, *p*-chlorophenol which provides the solutions with the normal viscosity behavior is regarded as preferable to phenol as a solvent of spinning dopes. In fact, the dopes made with *p*-chlorophenol were spun more favorably than the dopes made with phenol.

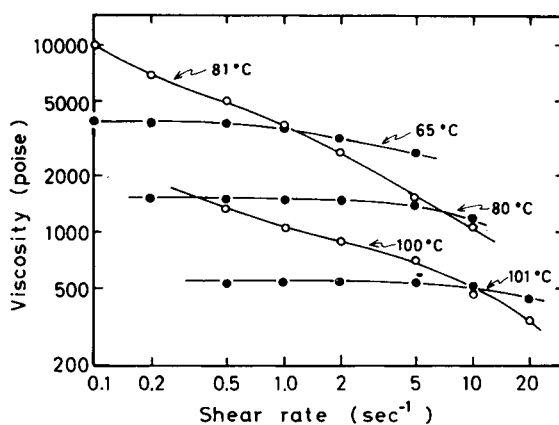


Fig. 1. Logarithmic plots of viscosity of 9 wt% solution of BPDA/PMDA(7/3)-OTOL against shear rate at various temperatures. Solid circles: In *p*-chlorophenol. Open circles: In phenol.

Temperature and concentration are the important factors for the preparation and treatment of spinning dope. The notable effect of temperature on the viscosity is seen in Figure 1. In Figure 2, the logarithms of low-shear rate-limiting values of viscosities of various solutions of BPDA/PMDA(7/3)-OTOL in *p*-chlorophenol are plotted against $1/T$. All of the plots give the straight lines in agreement with the expression of viscosity, $\eta = A \cdot \exp(E/RT)$, where E is the activation energy. The values of E calculated for each sample based on the data of Figure 2 are plotted against concentration in Figure 3. Although the solutions are made up of polyimides with different inherent viscosities, E vs. c plot gives a straight line. From the slope of the line, it can be calculated that the viscosity of dope increases 3.3 times larger at every 1 wt% increase in concentration at 100°C. On account of this behavior, the concentration of spinning dope was limited to a maximum of 10 wt%.

In this regard, the aromatic polyimides under discussion are radically different from the aromatic polyamides from which aramid fibers are produced. The solutions of the latter change into optically anisotropic liquids which are often referred to as "liquid crystals" when the concentration

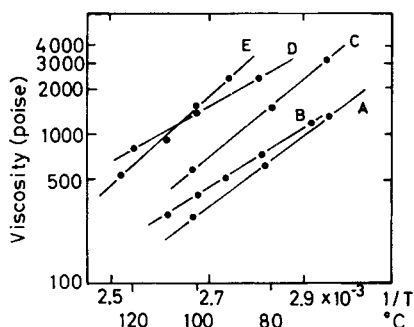


Fig. 2. Logarithm of low-shear rate-limiting value of viscosity vs. $1/T$ plots of solutions of BPDA/PMDA(7/3)-OTOL. Concentrations of solutions and inherent viscosities of polyimides are: A (8 wt%, 2.80 dl/g), B (6 wt%, 4.56 dl/g), C (9 wt%, 2.34 dl/g), D (5 wt%, 4.95 dl/g), E (11 wt%, 2.34 dl/g).

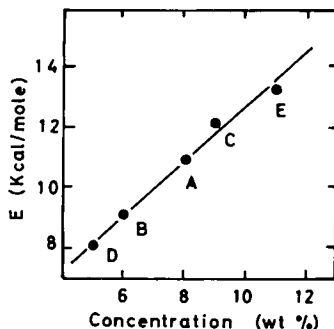


Fig. 3. Plot of activation energy of viscosity (E) against concentration of solution.

passes over a certain limit. As soon as this state is reached, the viscosity falls down suddenly to a very low level. Therefore, the solutions of aromatic polyamides with concentrations higher than 20 wt% can be treated easily in practice. On the contrary, the solution of polyimides in the scope of this study remain optically isotropic until they finally turn into intractable gels at a concentration of about 10 wt%. This difference between aromatic polyamides and polyimides in solution state gives rise to the different structures and properties of spun fibers, as will be described later.

For the preparation of spinning dope, the polyimide was dissolved in *p*-chlorophenol with stirring at 90°C in an atmosphere of nitrogen using a flask equipped with a powerful stirrer until a homogeneous viscous solution was produced. The quantity of polyimide to be dissolved was adjusted to the concentration of dope desired ranging from 8 to 10 wt%. The dope was deaerated under a reduced pressure of 80 mmHg and filtered through a stainless steel mat (Brunswick's Dynalloy $\times 7$, mean filter rating 14 μm).

As-Spun Fibers

The dope kept at 100°C in a reservoir under nitrogen was extruded from a single-holed spinneret of gold-platinum alloy by a pressure source of nitrogen. The diameter and depth of spinneret hole were 150 μm . The dope extruded from the spinneret fell down vertically upon the coagulating bath of ethanol passing an air gap of 20 mm. The temperature of the bath liquor was kept at 10°C. The thread introduced into the bath was wound around a pair of equal-sized rollers 55 mm in diameter which were installed on the same level being dipped in the bath liquor and rotated by the frictional force caused by the running thread. The thread ran horizontally back and forth between the rollers four times and emerged from the bath to be collected on a rotating spool. The total distance of travel of the thread in the bath liquor was about 5 m. The circumferential speed of collecting roll was 18.9 m/min. The degree of stretching expressed by the ratio of the speed of collection to the speed of extrusion was very small, ranging from 1.3 to 2.9. The higher stretching caused the interruption of spinning by the fracture of fiber. The conditions of spinning and the mechanical properties of the spun fibers are tabulated in Tables I, II, and III, which give the data of fibers made from the polyimides of Series I, II, and III, respectively.

The symbol, S-I, n , in Table I denotes the spun fiber derived from the polyimide, P-I, n , of Table I of the previous paper. Similarly, the symbol, S-

TABLE I
Conditions of Spinning and Properties of As-Spun Fibers of Polyimides Made From BPDA/PMDA-OTOL (see Table I of the Previous Paper)

As-spun fiber	Dope			Spinning		Fiber properties				
	Concentration (wt%)	Temperature (°C)	Back pressure (bar)	Speed (m/min)	Strength (g/den)	Elongation (%)	Modulus (g/den)	Modulus (GPa)	Denier	
S-I,1	10	100	4.1	18.9	5.30	33.1	148	19	10.0	
S-I,2	8	80	3.3	18.9	6.44	18.7	211	27	5.5	
S-I,3	8	80	3.3	18.9	5.80	17.0	199	26	6.3	
S-I,4	9	90	2.7	18.9	4.85	16.4	193	25	8.8	
S-I,5	8	80	2.9	18.9	3.38	26.5	105	13	6.4	
S-I,6	8	100	3.5	18.9	4.27	31.5	113	15	5.4	

TABLE II
 Conditions of Spinning and Properties of As-Spun Fibers of Polyimides Made From BPDA/PMDA-DADE (See Table IV of the Previous Paper)

As-spun fiber	Dope		Spinning			Fiber properties				
	Concentration (wt%)	Temperature (°C)	Back pressure (bar)	Speed (m/min)	Strength (g/den)	Elongation (%)	Modulus (g/den)	Modulus (GPa)	Denier	
S-II,1	8	90	3.3	18.9	1.69	50.0	40	5.2	10.3	
S-II,2	8	100	2.4	18.9	2.04	45.8	44	5.7	7.9	
S-II,3	9	90	3.1	18.9	2.20	106.0	41	5.3	12.1	

TABLE III
 Conditions of Spinning and Properties of As-Spun Fibers of Polyimides Made From BPDA-DADE/DABZ (See Table V of the Previous Paper)

As-spun fiber	Dope			Spinning			Fiber properties			
	Concentration (wt%)	Temperature (°C)	Back pressure (bar)	Speed (m/min)	Strength (g/den)	Elongation (%)	Modulus (g/den)	Modulus (GPa)	Denier	
S-III,1	8	120	2.9	18.9	2.14	41.6	53	6.8	6.9	
S-III,2	8	90	2.2	18.9	2.16	41.1	60	7.7	6.9	
S-III,3	8	100	2.9	18.9	2.21	58.8	61	7.9	8.4	
S-III,4	8	120	3.1	18.9	2.63	79.0	59	7.6	10.3	
S-III,5	8	90	3.1	18.9	2.48	99.6	49	6.3	11.5	
S-III,6	8	90	2.9	18.9	1.91	62.7	49	6.3	11.8	

II, n , of Table II denotes the fiber made from the polyimide, P-II, n , shown in Table IV of the previous paper. The spun fiber made from P-III, n , shown in Table V of the previous paper is denoted in Table III by S-III, n , in similar manner as in the foregoing cases.

As can be seen in the tables, the fibers as spun have generally small strengths and moduli. Among them, however, the fibers made from the polyimides of Series I (Table I) have larger strengths and moduli compared with fibers made from the polyimides of Series II and III (Tables II and III). All of the fibers have abnormally large elongations. This suggests that the fibers are not sufficiently oriented molecularly. Therefore, the possibility is foreseen that both strength and modulus can be improved by the accomplishment of high molecular orientation. This is evidenced by a series of experiments of heat treatment.

HEAT TREATMENT

A horizontal electric furnace with a heating zone of 20 cm was used for the heat treatment. A quartz tube 30 cm in length and 1.4 cm in inner diameter was inserted in the furnace. A filament as spun was drawn out from a feed roll, admitted through the quartz tube, and wound up at a speed of 1.74 m/min on a reel placed behind the outlet of the furnace. The time of heating of fiber in the furnace is estimated at several seconds. A weight was hung on the filament before the entrance of furnace by a device of rollers to effect a tension on the filament, which ranged from 0.01 to 1.25 g/den. A very small tension was sufficient to cause a considerable elongation of fiber being heated at high temperature. In the experiments, a maximum tension to which the fiber could resist was applied to each sample. The draw ratio is expressed by the ratio of denier before treatment to the denier after treatment, and the ratio at the maximum tension is referred to as the maximum draw ratio. The oxidative degradation of fiber was minimized by the flow of nitrogen which was admitted into the quartz tube to stream in parallel with fiber at a rate of 300 mL/min while the fiber was being heated. The average linear velocity of nitrogen in the tube is calculated at 1.95 m/min. The increase of flow rate up to 1 L/min brought about no distinguishable change in the properties of heat-treated fibers.

The temperature of treatment is an important factor for the increase in tenacity and modulus. For the spun fibers made from the polyimides of Series I, the optimum was found between 400°C and 500°C, while the temperatures of 350–400°C were optimum for the treatment of fibers made from the polyimides of Series II and III. The as-spun fibers of polyimides of Series II and III could not be processed at temperatures higher than 400°C because the fibers were broken in the furnace. In this connection, reference must be made to the DSC curves of the polyimides of Series II and III which exhibit a distinct endothermic peak at a temperature around 400°C, although the solid state of sample is retained. It can be assumed that the effect of "pseudo-melting" would have caused the fracture of fibers at temperatures higher than 400°C. It is to be noticed, however, that the lower temperature of heat treatment does not result in the lower thermal resistance of heat-treated fibers. As will be described later, the fibers of polyimides of Series II and III heat treated at lower temperatures exhibit

higher thermal resistances than the fibers of polyimides of Series I heat treated at higher temperatures.

The conditions and results of heat treatment are listed in Tables IV, V, and VI. The symbols, H-I,*n*, H-II,*n*, and H-III,*n*, denote the fibers obtained by the heat treatment of S-I,*n*, S-II,*n*, and S-III,*n*, respectively.

The results summarized in the tables reveal an amazing effect of heat treatment on the mechanical properties of polyimide fibers. Particularly attracting is the effect on the fibers of polyimides of Series I. As can be seen in Table IV, the highest strength of 26.1 g/den (3.1 GPa) is manifested by the fiber, H-I,4, heat treated at 500°C, and the highest modulus of 1,280 g/den (151 GPa) is recorded by the same fiber heat treated at 450°C. The strength and modulus before the heat treatment were only 4.85 g/den (0.62 GPa) and 193 g/den (25 GPa), respectively (see Table I.) The comparison between heat-treated fibers and untreated fibers demonstrates how powerful is the effect of heat treatment on the polyimide fibers. The mechanical properties of H-I,4 are favorably comparable with those of high-strength and high-modulus aramid fibers.

The heat-treated fibers of polyimides of Series II and III, shown in Tables V and VI, respectively, are lower in strength and modulus than the fibers of polyimides of Series I, but yet the strength of 20 g/den or thereabouts are seen in the tables. A weak point of these fibers lies rather in the low moduli which are generally smaller than 700 g/den.

The mechanical properties of heat-treated fibers of each series depend largely on the chemical compositions of polyimides. For the polyimides of Series I, the highest strength and modulus of fiber are obtained when the BPDA/PMDA molar ratio is 7/3, as illustrated in Figure 4. It is important to notice that the largest draw ratio is achieved on the fiber with this chemical composition. Contrary to the strength and modulus, the highest elongation is displayed by the fiber of homopolyimide with no PMDA.

For the polyimides of Series II also, the highest strength, modulus, and draw ratio are exhibited by the fiber with the BPDA/PMDA molar ratio of 7/3, as Figure 5 shows. The polyimides of Series II with the BPDA/PMDA molar ratios smaller than 7/3 could not be spun into fibers, as described before.

The polyimide of Series III with the DADZ/DABZ molar ratio of 7/3 provides the fiber with the highest strength and modulus, as Figure 6 shows. The largest draw ratio is achieved on the fiber with this molar ratio. As in the case of the fibers of polyimides of Series I, the fiber of the homopolyimide shows the highest elongation.

X-RAY DIFFRACTION PATTERNS

Evidence on the high degree of molecular orientation and crystallization of the heat-treated fibers of polyimides is provided by the measurements of X-ray diffraction patterns. As was the case with the mechanical properties, the X-ray diffraction patterns of fibers are changed drastically by the heat treatment. The polyimides of Series I which yield fibers with higher strengths and moduli exhibit the most qualified diffraction patterns for crystallographic analysis. Figures 7 and 8 show the X-ray diffraction patterns of S-I,1 (as spun) and H-I,1 (heat treated at 500°C), respectively. The

TABLE IV
Conditions of Heat Treatment and Properties of Heat-Treated Fibers Made From BPDA/PMDA-OTOL

Heat-treated fiber	Conditions of heat-treatment			Properties of heat-treated fibers				
	Temperature (°C)	Tension (g/den)	Draw ratio	Strength (g/den)	Elongation (%)	Modulus (g/den)	Modulus (GPa)	Denier
H-I,1	450	1.25	1.7	14.4	1.7	617	73	6.0
	500	0.9	1.6	14.6	1.7	587	69	6.1
H-I,2	550	0.45	1.5	12.7	1.5	584	69	6.8
	450	1.21	1.9	17.5	2.1	768	91	2.9
H-I,3	500	0.75	1.7	15.8	1.9	795	94	3.2
	550	0.22	1.7	18.9	2.2	827	98	3.2
H-I,4	450	0.76	3.3	23.7	2.8	1060	125	1.9
	500	0.37	3.2	23.8	2.8	1026	121	2.0
H-I,5	550	0.1	3.5	23.4	2.8	1067	126	1.8
	450	0.43	4.6	22.3	2.6	1280	151	1.9
H-I,6	500	0.07	3.8	26.1	3.1	1086	128	2.3
	450	0.09	3.8	19.0	2.2	916	108	1.7
H-I,6	500	0.06	4.9	20.5	2.4	938	111	1.3
	450	0.18	3.9	14.6	1.7	997	118	1.4

TABLE V
Conditions of Heat Treatment and Properties of Heat-Treated Fibers Made From BPDA/PMDA-DADE

Heat-treated fiber	Conditions of heat treatment			Properties of heat-treated fibers					
	Temperature (°C)	Tension (g/den)	Draw ratio	Strength (g/den)	Strength (GPa)	Elongation (%)	Modulus (g/den)	Modulus (GPa)	Denier
H-II,1	390	0.19	1.7	11.6	1.5	8.3	303	38	5.3
	400	0.19	1.4	6.4	0.8	23.9	127	16	7.3
H-II,2	350	0.15	5.0	14.5	1.8	5.1	401	50	1.6
	360	0.05	3.8	13.3	1.7	7.4	297	37	2.1
H-II,3	300	0.02	3.6	13.7	1.7	7.2	363	45	3.3
	330	0.12	9.2	18.9	2.4	4.4	502	63	1.3

TABLE VI
Conditions of Heat Treatment and Properties of Heat-Treated Fibers Made From BPDA-DADE/DABZ

Heat-treated fibers	Conditions of heat treatment			Properties of heat-treated fibers					
	Temperature (°C)	Tension (g/den)	Draw ratio	Strength (g/den)	Strength (GPa)	Elongation (%)	Modulus (g/den)	Modulus (GPa)	Denier
H-III,1	390	0.29	3.0	11.4	1.4	6.7	289	37	2.4
	400	0.06	1.7	7.6	1.0	16.7	169	21	4.1
H-III,2	380	0.47	3.8	14.2	1.8	4.7	414	52	1.8
	390	0.12	2.9	12.3	1.6	7.7	326	41	2.4
H-III,3	360	0.05	8.4	18.9	2.4	4.4	569	72	1.0
H-III,4	350	0.46	6.1	17.6	2.2	2.7	689	87	1.7
	360	0.08	8.1	21.0	2.7	3.9	617	78	1.3
	370	0.01	3.8	17.1	2.2	4.9	522	66	2.7
H-III,5	340	0.21	7.3	16.6	2.1	3.1	606	77	1.6
	350	0.05	8.3	17.1	2.2	3.6	576	73	1.4
H-III,6	360	0.08	7.9	18.7	2.4	4.0	568	72	1.5
	370	0.03	10.4	17.8	2.3	4.0	511	65	1.1

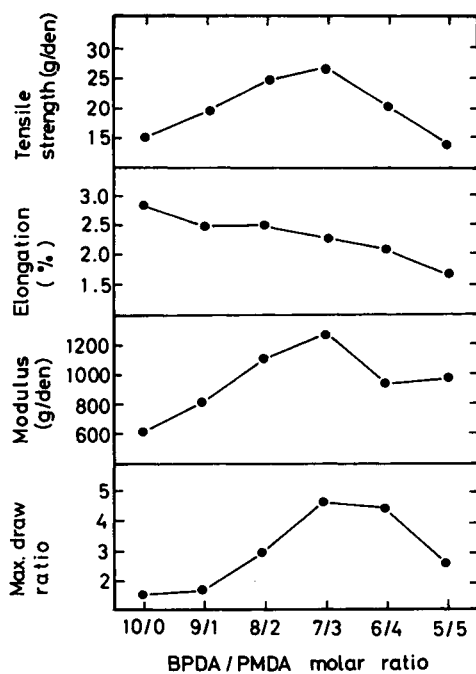


Fig. 4. Tensile strength, elongation at break, initial modulus, and maximum draw ratio of fiber of BPDA/PMDA-OTOL as a function of BPDA/PMDA molar ratio.

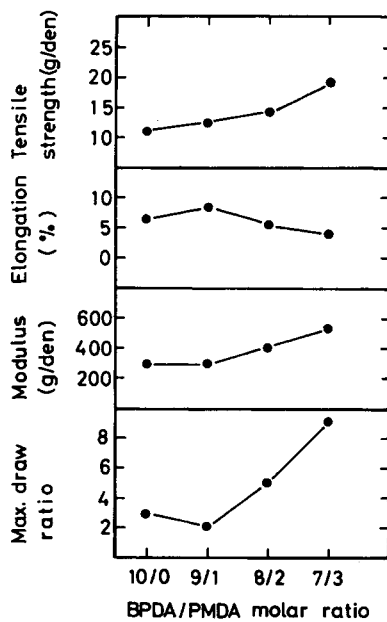


Fig. 5. Tensile strength, elongation at break, initial modulus, and maximum draw ratio of fiber of BPDA/PMDA-DADE as a function of BPDA/PMDA molar ratio.

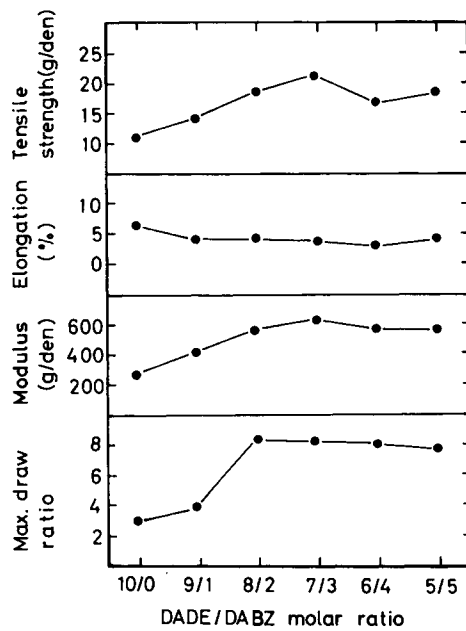


Fig. 6. Tensile strength, elongation at break, initial modulus, and maximum draw ratio of fiber of BPDA-DADE/DABZ as a function of DADE/DABZ molar ratio.

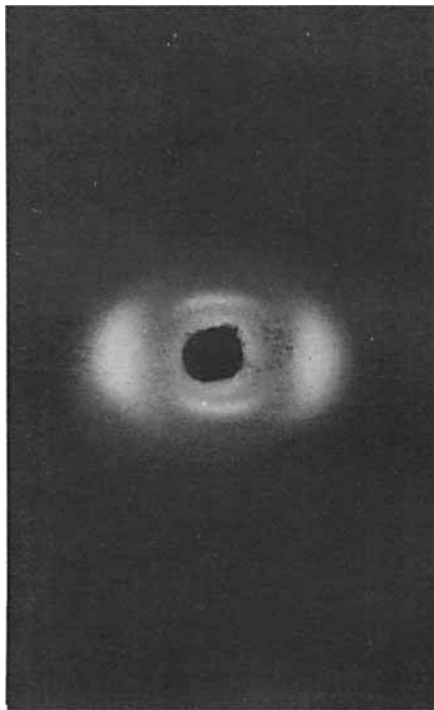


Fig. 7. X-ray diffraction pattern of as-spun fiber, S-I,1, photographed on a flat film.

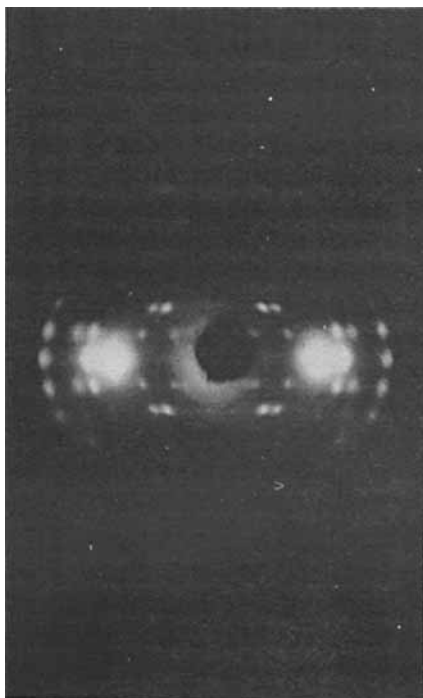


Fig. 8. X-ray diffraction pattern of heat-treated fiber, H-I,1, photographed on a flat film.

material forming these fibers is the homopolyimide (P-I,1) prepared from BPDA and OTOL.

A remarkable difference in diffraction pattern is seen between undrawn and drawn fibers. While the as-spun fiber, S-I,1, shows a very diffuse diffraction pattern, the heat-treated fiber, H-I,1, manifests a distinct fiber diagram consisting of many discrete interference spots. In this regard, the aromatic polyimides are very different from the aromatic polyamides. The latter produce highly oriented as-spun fibers from optically anisotropic spinning liquids.⁷ On the contrary, the polyimides under discussion are similar to the random-coiled, conventional polymers in that unoriented fibers are spun out from optically isotropic liquids, and the molecular orientation and crystallization are generated by the subsequent process of stretching.

From the distinct layer line streaks of the diffraction pattern of H-I,1, the identity period in the direction of molecular chain (chain repeat distance), can be derived. The mean value of identity period is determined to 20.5 Å, as Table VII shows.

Oda⁸ studied the X-ray diffraction pattern of the fiber of polyimide prepared from BPDA and *p*-phenylenediamine (DABZ). His crystallographic analysis resulted in the monoclinic cell with the *c* axis (fiber axis) of 16.0 Å. If the molecule takes the planar form with *cis* configuration, as Figure 9(a) shows, the chain-repeat distance is calculated at 15.2 Å. If the molecule is the planar *trans* chain, as Figure 9(b) shows, the repeat distance is calculated at 16.2 Å. Because of the steric interferences between the hydrogen atoms standing face to face on the opposite benzene rings of BPDA, the

TABLE VII
Identity Period of Polyimide Fiber, BPDA-OTOL

Layer line	$\sin\psi$	Spacing Å	Identity period Å
I	0.0756	20.37	20.4
II	0.1499	10.27	20.5
III	0.2265	6.80	20.4
IV	0.2982	5.16	20.6
V	0.3769	4.08	20.4
VI	0.4490	3.43	20.6
VII	0.5249	2.93	20.5
VIII	0.5965	2.58	20.6

Mean 20.5

planar chain conformation is unlikely to occur, and the rings connected by a single bond must twist away from the planar position to minimize the internal conformation energy. According to the study of Oda, the dimension of c axis results in 16.0 Å when a ring of BPDA twists by an angle of 60° with respect to another.

Sidorovich et al.⁹ have found that the dimensions of c axes determined on the fibers of polypyromellitimides prepared with p -phenylenediamine, benzidine, and 1,4''-diamino- p -terphenyl increase by 4.3 Å per benzene ring of the diamine component. According to Ginzberg et al.,¹⁰ the c axis of the unit cell of crystal of polyimide made from 3,3',4,4'-diphenylethertetracarboxylic dianhydride and benzidine is larger by 4.4 Å than that of the polyimide made from the same dianhydride and p -phenylenediamine.

On the basis of the data of Oda and those given above, the dimension of c axis of BPDA-OTOL fiber is calculated at 20.3–20.4 Å, which is the value very near the identity period observed. In the calculation, the effect of methyl groups of o -tolidine is ignored. It is assumed that the benzene rings of o -tolidine are not in the same plane, but the twisting of benzene rings of o -tolidine around the connecting single bond has no effect on the dimension of c axis.

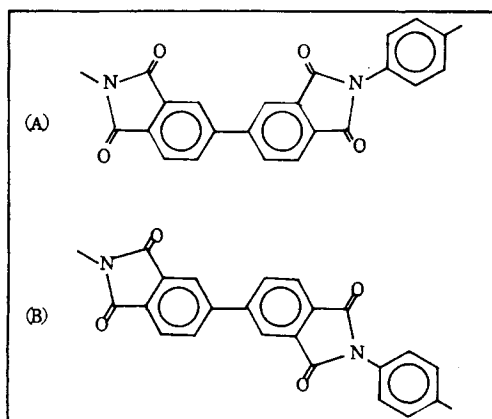


Fig. 9. Configurations of polyimide chain consisting of BPDA and DABZ. (a) Planar *cis* configuration (b) Planar *trans* configuration

Although the analysis has not been carried out as far as the determination of the accurate positions of atoms, the diffraction spots of H-I,1, can be interpreted satisfactorily in terms of an orthorhombic unit cell with

$$\alpha = 16.7 \text{ \AA}, b = 13.0 \text{ \AA}, c = 20.5 \text{ \AA} \text{ (fiber axis)}$$
$$V = 4,450.55 \text{ \AA}^3$$

If the number of chemical repeat units ($C_{30}H_{18}N_2O_4 = 470.34$) in a cell is 8, the density is calculated at 1.40. The density observed is 1.33.

In Table VIII are shown the spacings observed (d) and the spacings calculated (d_c) based on the postulated indices for every diffraction spots measured.

It is interesting to compare the diffraction pattern of S-I,4 (as spun) with that of H-I,4 (heat treated at 500°C), because the latter shows the highest strength among all of the polyimide fibers in the scope of this study. The fibers are composed of the copolyimide, P-I,4, having the composition of BPDA/PMDA(7/3)-OTOL. The diffraction pattern changes remarkably by the heat treatment, as can be seen in Figures 10 and 11, but two points are particularly noticeable.

First, the diffraction pattern of H-I,4 made from the copolyimide is not so distinct as that of H-I,1 made up of the homopolyimide. From a viewpoint of X-ray diffraction pattern, H-I,4 having the largest strength and modulus is assumed to have a lower degree of crystallinity than H-I,1. It is shown, therefore, that the strength and modulus of fiber are not determined solely by the degree of crystallinity, although this is an important factor. The lower crystallinity of H-I,4 results from the presence of the units of PMDA which are randomly scattered in the molecular chains, but these intervening units facilitate the stretching of fiber in return. For the production of H-I,4, the spun fiber (S-I,4) could be stretched 380–460% of the original length by heat treatment, but for the production of H-I,1 from S-I,1, a stretch of only 150–170% was permitted. In the present case of polyimide fibers, the higher capacity for stretching seems to form a dominant factor in producing higher mechanical properties.

Second, the X-ray diffraction pattern of H-I,4 has only the characteristics of BPDA-OTOL crystals, as can be seen from the comparison between Figure 8 and 11. The diffraction spots due to the crystalline region of PMDA-OTOL are not found at all. This means that only the major dianhydride component, BPDA, takes part in crystallization, being disturbed by the minor component, PMDA, scattered randomly in the molecular chains.

The fibers made from the polyimides of Series II and III show generally diffuse diffraction patterns, except H-III,1, heat treated at 390°C. H-III,1 is made up of the homopolyimide, P-III,1, whose composition is BPDA-DADE. The X-ray diffraction pattern of H-III,1 is shown in Figure 12. This fiber, like H-I,1, exhibits an excellent fiber diagram. The identity period in the direction of fiber axis determined from the layer line streaks is 20.6 Å, as shown in Table IX.

It is interesting to see that BPDA-DADE fiber has almost the same chain-repeat distance as that of BPDA-OTOL fiber described above. This is likely to occur because the dimension of DADE unit is assumed to be similar to

TABLE VIII
 Spacings Observed (d), Calculated (d_c), Postulated Indices and Intensities of Diffraction
 Spots of Heat-Treated Fiber, H-I,1

Spot	d Å	d_c Å	Index (hkl)	Intensity
A ₁	10.24	10.26	(110)	w
A ₂	5.13	5.13	(220)	vs
A ₃	4.17	4.17	(400)	s
A ₄	3.25	3.25	(040)	s
I ₁	13.00	13.00	(101)	m
I ₂	10.96	10.98	(011)	m
I ₃	6.72	6.65	(211)	m
I ₄	4.27	4.24	(031)	m
I ₅	3.88	3.90	(411)	m
I ₆	3.30	3.30	(501)	s
		3.37	(331)	
II ₁	7.30	7.25	(112)	s
II ₂	6.48	6.47	(202)	s
II ₃	5.46	5.49	(022)	w
II ₄	4.60	4.59	(222)	m
II ₅	3.86	3.87	(402)	m
II ₆	3.33	3.32	(422)	s
II ₇	2.94	2.90	(242)	w
III ₁	4.32	4.32	(303)	w
III ₂	3.65	3.66	(033)	m
III ₃	3.36	3.35	(233)	m
IV ₀	5.16	5.13	(004)	m
IV ₁	4.58	4.58	(114)	m
IV ₂	3.63	3.62	(224)	m
IV ₃	3.28	3.24	(404)	m
IV ₄	2.76	2.74	(044)	w
V ₁	3.90	3.91	(015)	m
V ₂	3.53	3.54	(215)	w
V ₃	2.90	2.93	(405)	vw
VI ₁	3.18	3.16	(206)	s
VI ₂	3.04	3.02	(026)	w
VI ₃	2.84	2.84	(226)	w
VI ₄	2.64	2.64	(406)	w
VII ₁	2.69	2.67	(027)	w
VII ₂	2.59	2.59	(307)	vw
		2.54	(227)	
VII ₃	2.42	2.42	(037)	w
		2.39	(407)	
VIII ₀	2.58	2.56	(008)	w
VIII ₁	2.31	2.29	(228)	w
VIII ₂	2.22	2.21	(038)	w
		2.18	(408)	

A: Spots on the equator.

I-VIII: Spots on the layer lines.

s: strong, m: medium, w: weak, v: very.

that of OTOL unit. The analysis of the diffraction pattern of H-III,1 shows that the X-ray reflections can be indexed satisfactorily on the basis of a monoclinic unit cell with

$$a = 14.8 \text{ \AA}, b = 8.20 \text{ \AA}, c = 20.6 \text{ \AA} \text{ (fiber axis)}, \gamma = 56^\circ$$

$$V = 2,072.61 \text{ \AA}^3$$

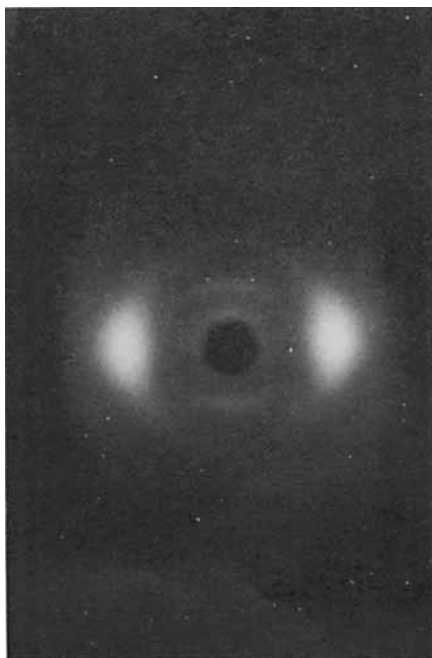


Fig. 10. X-ray diffraction pattern of as-spun fiber, S-I,4, photographed on a flat film.

If the number of chemical units ($C_{28}H_{14}O_5N_2 = 458.43$) involved in a cell is 4, the density is calculated at 1.47. The density observed is 1.42. The spacings of diffraction spots observed (d) and the spacings calculated (d_c) by the quadratic equation for monoclinic crystals on the basis of postulated

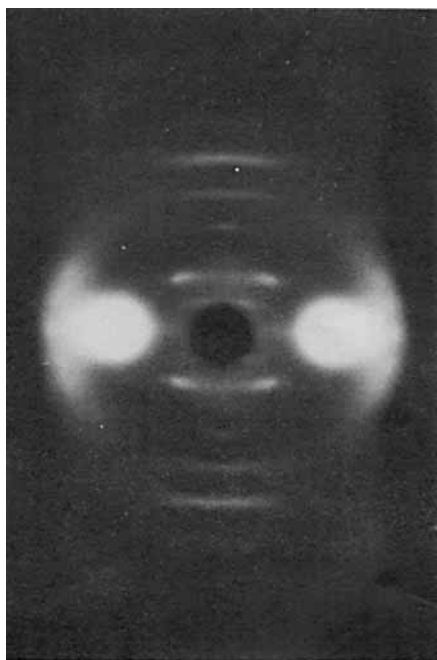


Fig. 11. X-ray diffraction pattern of heat-treated fiber, H-I,4, photographed on a flat film.

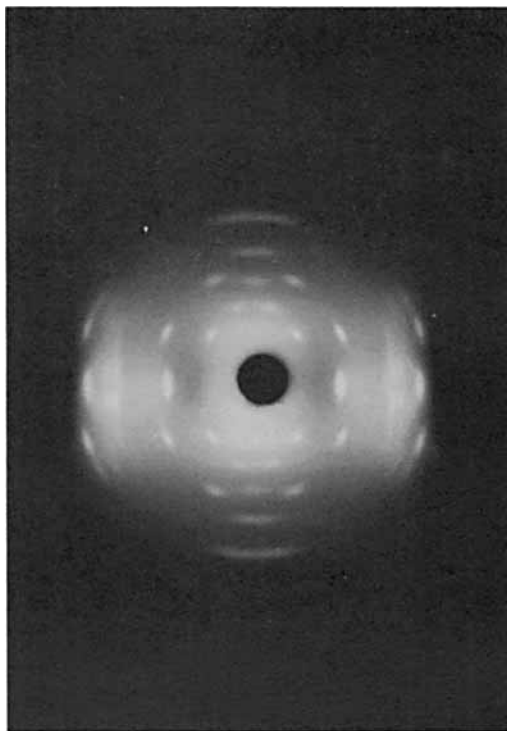


Fig. 12. X-ray diffraction pattern of heat-treated fiber, H-III,1, photographed on a flat film.

indices are listed in Table X together with the intensities of reflections. It is to be noticed that the heat-treated fibers of homopolyimides based on BPDA display distinct X-ray diffraction patterns that can be submitted to crystallographic analysis.

THERMAL PROPERTIES

The intrinsic merit of aromatic polyimides consists in the excellent temperature stability. The TG curves of several samples picked out of the polyimides of Series I, II, and III are shown in Figure 13. For comparison, poly(*p*-phenylene terephthalamide) (PPDT) which provides high-strength aramid fibers was tested in addition. All the samples were submitted to the thermogravimetry in the form of powder in air. In general, the polyimide

TABLE IX
Identity Period of Polyimide Fiber, BPDA-DADE

Layer line	$\sin\psi$	Spacing Å	Identity period Å
II	0.1493	10.3	20.6
III	0.2250	6.84	20.5
IV	0.2977	5.17	20.7
V	0.3710	4.15	20.7
VI	0.4494	3.43	20.6

Mean 20.6

TABLE X
 Spacings Observed (d), Calculated (d_c), Postulated Indices and Intensities of Diffraction
 Spots of Heat-Treated Fiber, H-III,1

Spot	d	d_c	Index (hkl)	Intensity
A ₁	6.12	6.12	(200)	vs
A ₂	4.11	4.10	(220)	s
A ₃	3.40	3.40	(020)	vs
A ₄	2.46	2.45	(2 $\bar{2}$ 0)	m
I ₁	4.01	4.02	(221)	s
I ₂	3.79	3.81	(121)	s
II ₁	7.87	7.88	(102)	s
II ₂	5.28	5.26	(202)	s
II ₃	3.83	3.81	(222)	w
II ₄	3.24	3.23	(022)	s
II ₅	2.86	2.93	(402)	w
		2.78	(122)	
III ₁	6.59	5.99	(103)	m
III ₂	3.48	3.51	(303)	m
		3.52	(223)	
III ₃	3.24	3.24	(333)	m
IV ₀	5.17	5.15	(004)	m
IV ₁	4.78	4.75	(104)	w
V ₀	4.15	4.12	(005)	m
V ₁	3.70	3.68	(115)	w
V ₂	2.89	2.89	(225)	w
V ₃	2.75	2.82	(125)	w
VI ₁	3.32	3.32	(106)	m
VI ₂	2.68	2.63	(226)	w
VII ₀	2.93	2.94	(007)	w

A: Spots on the equator. I-VII: Spots on the layer lines.

s: strong, m: medium, w: weak, v: very.

samples show higher resistances to heat than PPDT, as can be seen from Figure 13. Particularly, the homopolyimides such as P-I,1 and P-III,1 show the prominent high-temperature performance. The temperature at which 10% of the original weight has been lost is 532°C for PPDA, 560°C for P-I,1, and 573°C for P-III,1.

Although the homopolyimides exhibit very high thermal performance, the resistance to heat is reduced by copolyimidization, as can be seen from TG curves of P-I,4 and P-III,4. It is to be regretted that P-I,4, which provides the fiber with the highest strength and modulus, exhibits only a low level of thermogravimetric property. P-II,3, a copolyimide of Series II, shows a good thermal resistance. However, it is to be noticed that the thermogravimetric measurements provide only a cursory survey of the heat resistance.

From a practical point of view, the thermal properties were measured on the fibers of polyimides. H-I,4 with the highest strength (26.1 g/den) and H-III,4 also with a high strength (21.0 g/den) were heated under a small tension of 0.34 g/den at 300°C in an oven in air, and at 200°C in an autoclave in the saturated steam under pressure, for various periods of time and the retention of strength was measured. For reference, Kevlar 49 with an initial strength of 26.0 g/den was tested in the same manner. The results of heating

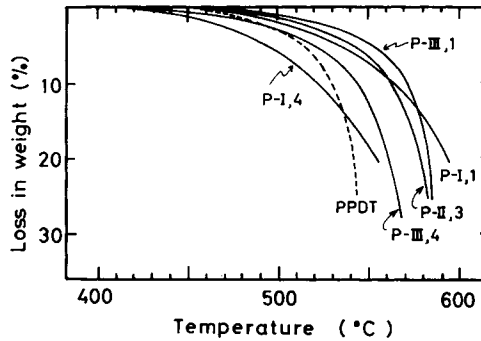


Fig. 13. TG curves of polyimides of Series I, II, and III, and poly(*p*-phenylene terephthalamide) (PPDT).

in air are shown in Figure 14, and the results of heating in the saturated steam are shown in Figure 15. In either case of heating, H-III,4 stands at the top of three fibers in stability. H-I,4 ranks second, but has only a little advantage over Kevlar 49 ranking lowest in stability.

CHEMICAL PROPERTIES

Polyimide fibers, H-I,4 and H-III,4, and polyamide fiber, Kevlar 49, were treated with 40 wt% acetic acid, 40 wt% sulfuric acid, 10 wt% sodium hydroxide solution, and 50 wt% calcium chloride solution in water at 85°C for various periods of time, and the retention of tensile strength was measured.

All of the fiber samples were stable to the prolonged heating in 50 wt% aqueous solution of calcium chloride, but they were susceptible to the hydrolytic action of acetic acid, sulfuric acid, and sodium hydroxide. A striking contrast was seen between the polyimide fibers and Kevlar 49 with respect to their resistances to the acid and alkaline reagents. Figure 16 shows that the polyimide fibers are highly resistant to heating in 40 wt% sulfuric acid, while Kevlar 49 loses strength rapidly. Similar effect can be seen in the case of heating in 40 wt% acetic acid. On the other hand, as Figure 17

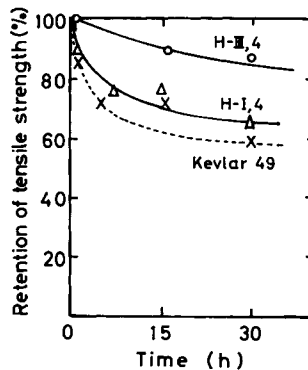


Fig. 14. Retention of tensile strength of polyimide fibers, H-I,4 and H-III,4, and Kevlar 49 as a function of time of heating at 300°C in air.

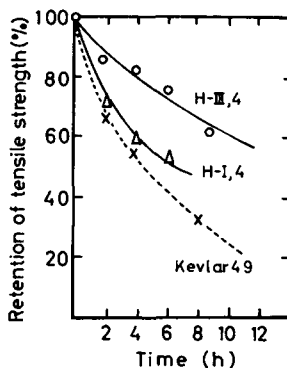


Fig. 15. Retention of tensile strength of polyimide fibers, H-I,4 and H-III,4, and Kevlar 49 as a function of time of heating at 200°C in saturated steam under pressure.

indicates, Kevlar 49 is less susceptible to 10 wt% aqueous sodium hydroxide than the polyimide fibers.

The polyimide fibers are less hydrophilic than Kevlar 49 which, like other nylon fibers, shows a high moisture content. The equilibrium moisture regain of Kevlar 49 at an atmosphere at 20°C and 80% relative humidity (RH) is 4.56%, while the regain measured on H-I,4 at the same atmosphere is 0.65% on the bone-dry base.

RESISTANCE TO UV IRRADIATION

H-I,4, H-III,4 and Kevlar 49 were irradiated by Xe arc light at 80-100°C in a weatherometer, and the retention of tensile strength was measured. The results are graphically illustrated in Figure 18. It can be seen that the polyimide fibers are much more resistant to irradiation than Kevlar 49. Particularly, H-III,4 exhibits a strong resistance to irradiation. It is interesting to see that the fibers of polyimides of Series III, as represented by H-III,4, possess the highest stability to the thermal, chemical, and photochemical processings.

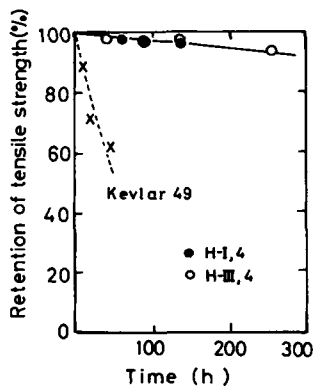


Fig. 16. Retention of tensile strength of polyimide fibers, H-I,4 and H-III,4, and Kevlar 49 as a function of time of dipping in 40 wt% H_2SO_4 at 85°C.

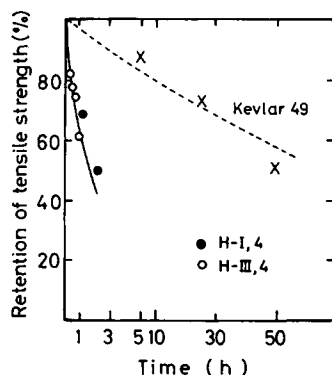


Fig. 17. Retention of tensile strength of polyimide fibers, H-I,4 and H-III,4, and Kevlar 49 as a function of time of dipping in 10 wt% aq. NaOH at 85°C.

EXPERIMENTAL

Viscosity

A coaxial cylindrical rheometer of Tokyo Seiko Co. was used. The sample liquid was loaded in the space between coaxial cylinders. The outer cylinder was rotated at a constant angular velocity and the torque produced on the surface of inner cylinder was measured by a transducer. The viscosity was computed from the torque and the angular velocity with consideration of the form factor of the rheometer.

Tensile Strength, Elongation at Break, Fiber Denier, and Initial Modulus

The weight and elongation at break of fiber were measured by the officially standardized method [JIS L 1013 (1981)], using a tensile tester (TOM-5 of Shinko Tsūshin Co.), which permitted the automatic registration of stress-strain curve of fiber on a chart. The spun length was 20 mm and

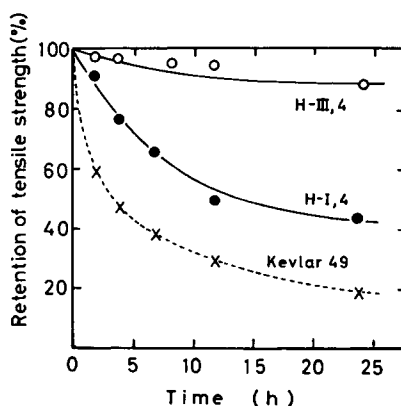


Fig. 18. Retention of tensile strength of polyimide fibers, H-I,4 and H-III,4, and Kevlar 49 as a function of time of UV irradiation at 80-100°C in weatherometer.

the rate of elongation was 10 mm/min. The fiber denier was determined by the vibration method using a well-designed vibroscope, Denicom of Kyokko Seikō Co. The tensile strength in grams per denier (g/den) was calculated from the load at break in grams and the denier of the same fiber. The result is reported by the average value of ten sample fibers. The elongation at break also was estimated from the stress-strain curve. The elongation given in percent represents the mean value for ten sample fibers used for the measurement of strength. The initial modulus was calculated from the initial slope of stress-strain curve and the denier of fiber. The result is reported by the mean for ten sample fibers in grams per denier. The conventional unit, g/den, was converted to SI unit by $1 \text{ g/den} = 8.83 \times 10^{-2} \times \rho \text{ GPa}$ where ρ is the density of fiber.

Thermogravimetry

The measurements were done with 10 mg of powder samples in air at a rate of temperature rise of 5°C/min. The du Pont Instrument, 951-Thermogravimetric Analyser, was used.

Density

A density gradient liquid column was formed in a graduated glass tube using *n*-hexane-carbon tetrachloride mixture at 25°C. Fragments of fibers were thrown gently in the tube and graduation of tube at which the fragments suspended was read after 3 days.

UV Irradiation

Weatherometer-MHQ-1 of Toyo Seiki Co. with a 6,000 W Xe lamp as a light source was employed. The lamp was enclosed with an aluminum cylinder 20 mm in inner diameter. The position was so adjusted that the lamp was situated at the center of cylinder. The sample fibers, 15 cm in length, were hung on the inner surface of cylinder so that they could be exposed uniformly to the radiation. The Kevlar fibers were washed thoroughly before irradiation to remove oiling agents. The sample fibers were heated up to 80-100°C by the radiation from the lamp during irradiation. The sample fibers were taken out after a certain period of time and the strengths were measured. The retention of strength was expressed in percent to the original strength. The result is reported by the mean for ten sample fibers.

X-Ray Diffraction

The WAXS was photographed on a flat film using a Laue camera with the incident beam perpendicular to the fiber axis. The sample-to-film distance was calibrated by taking the diffraction pattern of an aluminum foil whose well-known spacing of (111) planes was used as a standard. Monochromatic CuK_α rays generated at 40-50 kV and 100-200 mA, filtered by a nickel foil, were used. The time of irradiation was varied from 10 to 100 min to obtain a desired density of photograph.

Moisture Regain

About 20 g of fiber sample was dried in an oven kept at 100°C to the constant weight. The sample was then placed in a desiccator over a saturated aqueous solution of ammonium sulfate at 20°C. The relative humidity of atmosphere in the desiccator was 80%. The sample was allowed to stand in the desiccator until the constant weight was reached. The moisture regain is reported in percent on the basis of bone-dry weight.

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