Note

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HIGH-STRENGTH AND HIGH-MODULUS COPOLY(*p*-PHENYLENEPYROMELLITIMIDE/ BIPHENYLTETRACARBOXIMIDE) FIBERS

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ABSTRACT: In order to obtain high-strength, high-modulus and thermo-stable fibers, copolyimide fibers were prepared from *p*-phenylenediamine/pyromellitic dianhydride (PMDA)/3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) copolymers by chemical imidization and subsequent hot-drawing. Drawability and tenacity increased with increasing content of BPDA in the copolymers, and PMDA/BPDA (mole ratio 30/70) copolyimide fiber showed tenacity 21.6 g/d and initial modulus 1130 g/d. Heat durabilities of these copolyimide fibers were much superior to those of para-aramid fibers such as Kevlar® and Technora®.

1. INTRODUCTION

Polyimides prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and rigid aromatic diamines such as *p*-phenylenediamine (P) are pseudo-rigid polymers having chain extending bonds which are parallel and oppositely directed, if a proper conformation is chosen, and give comparatively high-strength and high-modulus fibers. For example, Koton et al. [1] have obtained a fiber with a tenacity 10 g/d and an initial modulus 590 g/d from benzidine and BPDA by wet spinning of the precursor poly (amic-acid) solution and thermal imidization. More recently, Kaneda et al. [2] reported that high-strength and high-modulus fibers could be produced from BPDA polyimides which were soluble in *p*-chlorophenol, by dry-jet wet spinning of the solutions and hot drawing. For example, *o*-tolidine/pyromellitic dianhydride (PMDA)/BPDA (mole ratio 100/30/70) copolymer yielded a fiber having a tenacity 26 g/d and an initial modulus 1100 g/d. However, naturally, polyimides such as P-BPDA homopolymer which are insoluble in *p*-chlorophenol can not be spun. Moreover, the existence of methyl substituent on the aromatic ring is unfavorable from a point of view of thermal stability. In the past, we studied the preparation of high-strength and high-modulus fibers from wholly aromatic rigid polyimides and found that low crystalline polymers

obtained by the chlorine substitution on the aromatic ring or by the random copolymerization had better drawability and gave higher strength fibers than highly crystalline polymers [3,4]. In this study, in order to obtain high-strength, high-modulus and thermo-stable fibers, the author prepared copolyimide fibers from P/PMDA/BPDA copolymers by wet spinning of the precursor solutions, chemical imidizing and hot drawing finally, because the chemical imidization method is superior to the thermal method to produce high-strength fibers as previously reported [3,4], and evaluated their tensile properties and heat durabilities.

2. EXPERIMENTAL

2.1 Materials

BPDA purchased from Mitsubishi Kasei Ltd. was recrystallized from 1,2,4,5-tetrachlorobenzene. Reagent grade *p*-phenylenediamine (P) and PMDA purchased from Daicel Ltd. were used without further purification. *N*-methylpyrrolidone (NMP) purchased from Mitsubishi Kasei Ltd. was dried over molecular sieves 5A.

2.2 Preparation of the Spinning Dopes

By a conventional method, P was reacted with PMDA/BPDA (mixture of powders) in NMP to form the poly (amic-acid) solutions. Then, acetic anhydride and pyridine (0.25 equivalent based on amic-acid u-

Table 1 Hot-drawing Conditions and Tensile Properties of P/PMDA/BPDA Copolyimide Fibers

PMDA/BPDA (mole ratio)	η_{inh} of poly- ^{a)} (amic-acid)	Conditions of hot-drawing		Denier	T (g/d)	E (%)	Mi ^{b)} (g/d)
		Temp. (°C)	Draw ratio				
100/0	3.58	575	1.1	46	6.1	0.8	850
80/20	1.90	575	1.8	52	10.3	1.3	860
70/30	1.63	600	2.3	48	12.3	1.7	890
60/40	2.54	575	2.5	30	19.4	1.9	1120
40/60	3.82	575	4.0	22	19.6	2.4	980
30/70	2.11	525	6.0 ^{c)}	24	21.6	2.1	1130
		550	1.0				
		475	3.7 ^{c)}	26	16.2	2.1	880
0/100	2.03	575	1.0				

a) η_{inh} was measured in NMP at a polymer concentration 0.5 g/100 mL at 25 °C

b) T: Teacity, E: elongation, Mi: initial modulus.

c) The fiber was drawn and then heat-treated.

Table 2 Heat Aging of P/PMDA/BPDA Copolyimide Fibers^{a)}

PMDA/BPDA (mole ratio)	Tensile properties taken as reference			% Retained				
	T (g/d)	E (%)	Mi (g/d)	after 1 h at 400 °C			after 90 h at 290 °C	
				T	E	Mi	T	E
60/40	18.8	1.8	1150	70	71	99	—	—
40/60	19.6	2.4	980	98	85	112	83	74
30/70	21.6	2.1	1130	87	98	97	87	98
0/100	15.8	2.2	870	92	86	97	80	86
cf.								
Kevlar [®]	23.2	3.5	530	38	38	115	36	35
Technora [®]	26.6	4.2	640	24	47	62	21	24

a) T: teacity, E: elongation, Mi: initial modulus.

nits) were added, in order to obtain voidless and transparent coagulated fibers, as previously reported [3].

2.3 Preparation of the Copolyimide Fibers

The dopes obtained in 2.2 were wet-spun into the coagulant bath consisting of NMP/water (volume ratio 25/75) at room temperature. The coagulated fibers were drawn 1.3–1.5 times in water (room temperature) and then immersed in a mixture of acetic anhydride/pyridine (volume ratio 30/70) overnight at room temperature for chemical imidization. The dried fibers were hot-drawn under nitrogen for a contact time of 2–5 s. The details of wet-spinning, chemical imidization and hot-drawing were described in the previous paper [3]. Denier described later in Table 1 was that of 20 filaments yarn.

2.4 Measurements

Inherent viscosities (η_{inh}) of poly (amic-acids) and tensile properties of fibers were measured as previously reported [3].

3. RESULTS AND DISCUSSION

3.1 Tensile Properties of P/PMDA/BPDA Copolyimide Fibers

P/PMDA/BPDA copolyimide fibers were prepared by the method described in 2.3. Table 1 shows hot-drawing conditions and tensile properties of the resultant fibers. The hot-drawing condition shown in Table 1 was that under which the highest strength fiber was obtained for each copolymer. Drawability and tenacity increased with increasing content of

BPDA in the copolymers, as was expected. The fibers obtained from P-PMDA homopolymer and copolymers containing P-PMDA as a main component could not be drawn by one step process above 525 °C, since these fibers were easy to fuse during hot-drawing, probably because they were difficult to crystallize thermally. Therefore, these fibers were drawn at a comparatively lower temperature and then annealed at a higher temperature at constant length. PMDA/BPDA (mole ratio 30/70) copolymer gave the fiber with the highest tenacity (21.6 g/d), similarly as *o*-tolidine copolyimide fibers reported by Kaneda et al [2]. Maximum initial moduli reached about 1100 g/d for the copolymers containing BPDA 40 - 70 mole%.

3.2 Heat Aging of P/PMDA/BPDA Copolyimide Fibers

Heat aging of P/PMDA/BPDA copolyimide fibers was carried out in air under two different conditions. One was at 400 °C for 1 h and the other was at 290 °C for 90 h. For comparison, high-strength and high-modulus aramid fibers, i.e. Kevlar® [poly (*p*-phenyleneterephthalamide)] and Technora® [poly (*p*-phenylene/3,4'-oxydiphenylene (mole ratio 50/50) terephthalamide)] were treated under the same conditions. The results were shown in Table 2. In general, heat durabilities of the copolyimide fibers under the two different conditions were overwhelmingly superior to the aramid fibers, as was expected. Generally, heat aging causes both the chemical and physical deteriorations, but it is difficult to distinguish them. Retention of tensile properties of PMDA/BPDA (60/40) copolyimide fiber was rather inferior to those of the other copolyimide fibers. It is considered that the reason for the above results is the physical deterioration of the fiber, i.e. the growth of crystallites which was accompanied by the increase of size of defects during the heat aging test. Hindeleh and Abdo [5] carried out heat aging of Kevlar-49 in air at 150 °C and measured the change of crystallinity, micropara-

crystallite lateral size (mPC size) and tensile properties. Until 28 days of the heat aging, decrease of tenacity of the fiber occurred in parallel with the increase of mPC size, although they did not mention it. It is reasonable to consider that the fiber does not deteriorate at 150 °C by chemical degradation due to the stable chemical structure of the fiber. It is also considered that the decrease of tenacity of the fiber is caused by the physical deterioration described above, and similarly, copolyimides containing P-PMDA as a main component are easy to deteriorate physically. Furthermore, the initial moduli of Kevlar and PMDA/BPDA (40/60) copolyimide fiber increased more than 10% after heat treatment at 400 °C for 1 h. This result is probably caused by the growth of crystallites and the increase of orientation of the fibers, because Kevlar is a fiber of the as-spun type and it was not heat-treated, and PMDA/BPDA (40/60) copolyimide fiber was not sufficiently heat-treated at the drawing condition, owing to the short treatment time. The reason for the decrease of initial modulus of Technora after the same heat aging is possibly the relaxation of orientation because of its lower crystallinity.

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