Synthesis and Properties of Phosphorus-containing Polyimide Fibers

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ABSTRACT

A series of polyamic acid copolymers (co-PAAs) containing phosphorous groups in the main chain were synthesized via various ratios of two diamines, i.e., bis(3-aminophenyl)methyl phosphine oxide (DAMPO) and 4,4′-oxydianiline (ODA), with 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) by polycondensation in N,N′-dimethyl acetamide (DMAc) and the co-PAA solutions were spun into fibers by a dry-jet wet spinning process, and then polyimide copolymer (co-PI) fibers were obtained by thermal imidization. The as-prepared PI fibers have smooth and dense surface as well as uniform diameter. Compared with the blank PI-0,the T_gs of co-PI fibers increased considerably with DAMPO content. TGA results indicated that the co-PI fibers possessed a good thermal stability up to 510 °C and a residual char yield of up to 61% at 850 °C. All co-PI fibers exhibited excellent elongation, and their tensile strength and modulus can reach 0.9 GPa and 14.97 GPa when the molar ratio of DAMPO/ODA was 6/4 and the draw ratio was 3.0.

INTRODUCTION

Among high-performance fibers, aromatic polyimide (PI) fibers are known for their excellent resistance to heat, thermal stability, chemical and solvent resistance, and radiation stability. Owing to these outstanding properties, aromatic PI fibers are widely used in manufacturing, microelectronic, engineering, and aerospace industries. Since the earliest work on PI fibers was reported by Irwin[1], a few decades later, the preparation of high-performance PI fibers was mainly carried out by Japanese[2-5]and Soviet researchers[6, 7].

Two methods are usually employed for thePI fibers fabrication. First, PI solution is directly used to spin PI fibers into a coagulation bath. The PI fibers produced by a one-step method usually possess a high tensile strength and initial modulus. However, the solubility of PI solutions and the toxicity of solvents hinder the large-scale production for the one-step method. Second, a typical two-step technique is primarily adopted in the preparation of PI fibers. A precursor polymer solution, such as polyamic acid (PAA) or poly (amic ester) (PAE), is spun and followed by thermal or chemical imidization. Using the two-step method to fabricate PI fibers can overcome the solubility problem of PI solutions. Recently, Liu[8] and Wu[9] reported that controlling the aromatic rigid units (AAQ monomer), hydrogen bonding[10, 11] (between AAQ and cyclic imide units),and draw ratios can enhance the tensile strength and modulus to as high as 2.8 GP and 115 GPa, respectively.

PI fibers are commonly applied in high-temperature resistant filters and fireproof materials. However, in some special applications, such as spaceships, space suits, and satellite ropes, commercial PI fibers cannot meet the needs of high-flame retardancy and super high-temperature resistance. Meanwhile, phosphorus materials exhibit the good flame retardancy and thermal stability. Here, phosphorous-containing monomer, i.e., bis(m-aminophenyl)methyl phosphine oxide (DAMPO), was synthesized and a series of co-PI fibers were prepared by adjusting the percentage of DAMPO conten

tthrough a two-step approach. The high-temperature resistance and mechanical properties of as-prepared PI fibers were discussed.

EXPERIMENTAL

Chemicals and Materials

4,4′-Oxydianiline (4,4′-ODA, >99.5%) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) were purchased from Shanghai Research Institute of Synthetic Resins, and s-BPDA was dried in vacuum at 260 °C overnight prior to use. Triphenyl phosphine,N,N′-dimethyacetamide (DMAc, analytical purity of ≥99.5%) was purchased from Tianjin Fine Chemical Co.,Ltd. and used as received.All other chemicals were obtained and without further purification. Bis(*m*-aminophenyl) methyl phosphine oxide (DAMPO)was synthesized according to a modified method[12].

Characterization

T_g was determined by DSC with TA Q100 at a heating rate of 5 °C/min. The measurement of mechanical properties was carried out on XQ-1 instrument with ASTM standard (D3379-75, edition 1987) at a cross-head speed of 20 mm/min. More than 10 monofilaments for one sample were tested and the average data were used to characterize the mechanical property of the sample. TA-Q50 instrument was employed to analyze the thermal stability of the fibers at a heating rate of 10 °C/min under nitrogen atmosphere. The surface morphology of PI fibers was determined by XL-30 and scanning electron microscope (SEM).

Preparation of co-PI fibers

Series of PAAs solutions with different phosphorus contents were successfully synthesized by adjusting molar ratios of DAMPO/ODA. The co-PAA solutions were spun viathedry-jet wet spinning method to form co-PAA fibers and then the as-prepared co-PAA fibers were subjected to thermal imidization to produce co-PI fibers.

RESULTS AND DISCUSSION

Glass transition temperatures of PI fibers

The T_g of PI fiber was measured by DSC. The DSC curves were shown in **Figure 1**. Their T_gs were 261, 265, 273, 279, 290, 295 and 297 °C, which corresponded to molar ratios of DAMPO/ODA 1/10, 1/9, 2/8, 3/7, 4/6, 5/5, and 6/4, respectively. Definitely, the T_gs of co-PI fibers were higher than the blank one and increasing DAMPO content lead to an obvious increasing of T_gs. It was considered that higher T_g of co-PI fibers was related to the rigid structure of DAMPO than ODA, thereby requiring more energy to move the chain segments. The monomer, DAMPO, contains more rigid structure than ODA. Hence, increasing of DAMPO content will result in higher T_gs. Furthermore, the T_gs of PI fibers (DAMPO/ODA 6/4) with different draw ratios (1.6, 2.0, and 3.0) were also studied in **Figure 1** (b). The results indicated that increasing the draw ratio has no influence on glass transition temperature.

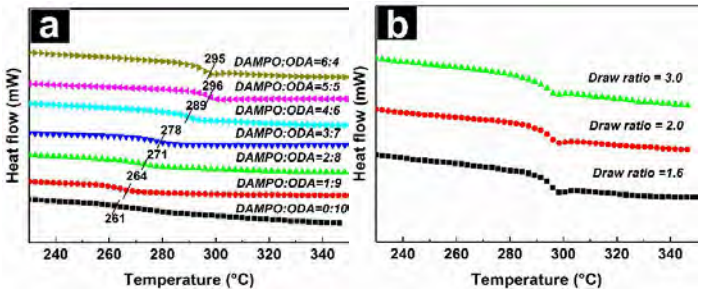

Figure 1. DSC spectraof PI fibers with DAMPO ratios (a) and draw ratios (b).

Thermal stability of PI fibers

The thermal stability ofthe PI fibers was characterized by TGA, and their TGA and derivative curves were shown in **Figure 2**.Nearly no weight loss was observed from room temperature to 500 °C. In **Figure 2** (b), PI-0 fiber only exhibited the highest decomposition rate at 600 °C. However, theco-PI fibers showed two quicker decomposition rates: the first one at 522 °C was associated with the decomposition of P-C bond, whereas the second one at 600 ° was related to the decomposition of PI backbone. With increasing DAMPO content, the decomposition started earlier because of easier degradation of P-C bond. However, the phosphorous element had a positive effect on the flame retardant. The temperatures of 5% and 10% weight loss ($T_{5\%}$and $T_{10\%}$, respectively) were listed in **TABLE 1**. The $T_{5\%}$s decreased from 559 °C to 514 °C, and $T_{10\%}$s also decreased from 583 °C to 523 °Calong with DAMPO content.The residues at 850 °Cwere58.9, 64.4, 66.7, 63.0, 62.0, 61.3, and 61.9% corresponding to DAMPO from 0 % to 60%, which indicated that introduction of DAMPO facilitated more char yield, i.e., better flame retardancy.

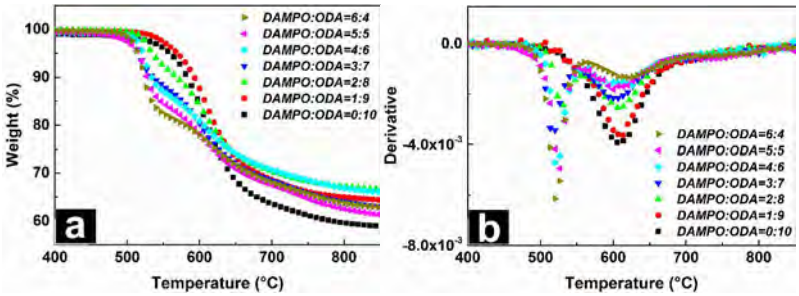

Figure 2. TGA and their derivativecurves of co-PI fibers.

TABLE 1. TGA data of PI fibers.

Sample	Ratio of diamine DAMPO/ODA	$T_{5\%}$[a] (°C)	$T_{10\%}$[b] (°C)	Residue at 850 °C (wt %)
PI-0	0 / 10	559	583	58.9
PI-1	1 / 9	569	592	64.4
PI-2	2 / 8	534	568	66.7
PI-3	3 / 7	515	535	63.0
PI-4	4 / 6	521	533	62.0
PI-5	5 / 5	515	527	61.3
PI-6	6 / 4	514	523	61.9

***[a] Corresponding temperature at 5%weight loss, [b] Corresponding temperatureat10%weight loss.**

Surface morphology of PI fibers

The surface morphology of PI fibers (a–g)was observed by SEM, as shown in **Figure 3**. All the fibers exhibited smooth surfaces, and the diameters were uniform. The average diameter was about 14 μm. The dense surfaces of all fibers came from the quick dual-diffusion process in the coagulation bath and the uniform diameters with process controlling.

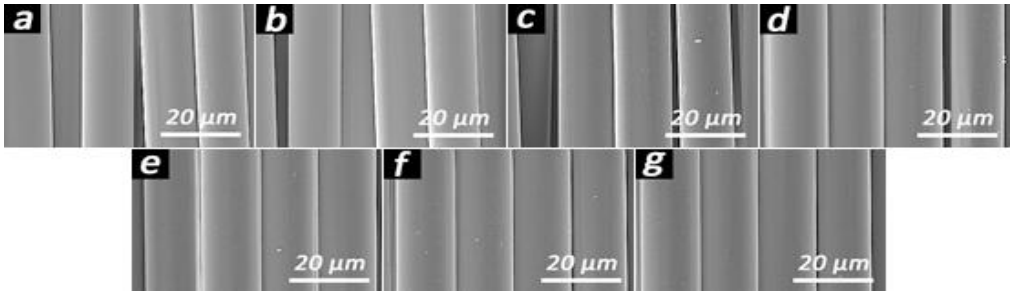

Figure 3. Surface morphologies of fibers (a-g corresponding to PI-0 to PI-6).

Mechanicalproperties of PI fibers

For polymeric fibers, the mechanical propertyis considered to be a significant parameter, particularly in engineering applications. **Figure 4** and **Figure 5** showed the variation of mechanical properties with DAMPO content and draw ratio.Both strength and modulus decreased with DAMPO content. The abovementioned results indicated that introduction of DAMPO efficiently improvedthe elongation of co-PI fibers. In particular, the elongation of PI-6 wasnearly five times higher than that of PI-0. However, the draw ratio also influencedthe mechanical property. In **Figure 5**, PI-6' and PI-6'' had higher draw ratios of 2.0 and 3.0 comparing with PI-6 (draw ratio=1.6). Fibers with higher draw ratio exhibited higher strength, modulus, and lower elongation. The abovementioned results showed that 60% DAMPO co-PI fiber can also achieve adequate mechanical property like PI-0 fiber merely by increasing the draw ratio.

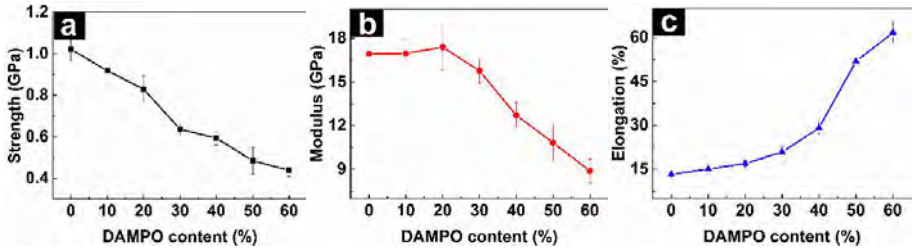

Figure 4. Variation of mechanical properties with DAMPO content for PI fibers.

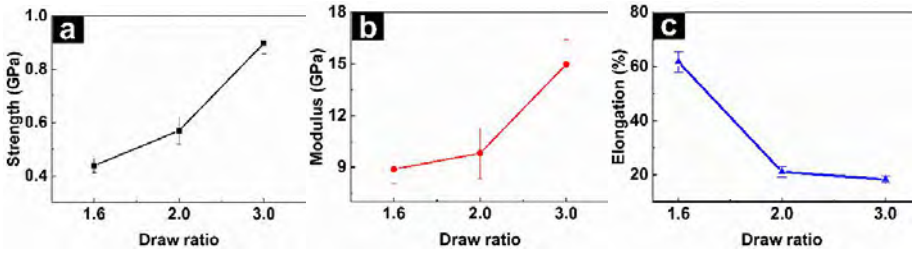

Figure 5. Variation of mechanical properties with draw ratio of co-PI fibers.

CONCLUSIONS

A series of PAAcopolymer solutions containing phosphorous groupsin main chain weresynthesized and then spun into PAA fibers via thedry-jet wet spinning processing. The PI fibers wereobtained by thermal imidization of PAA fibers. The main resultsare summarized as follows.(i) The $T_g$sof PI fibers increase from 268 °C to 295 °C with increasing phosphorous monomer (DAMPO). (ii) TGA results indicate a good thermal stabilityof up to 510 °C. The residual char amounts at 850 °C arein the range of 61 %-67% for all co-PI fibers, and these amounts are higher than that of PI fiber without phosphorous moieties. (iii) The co-PI fiber with DAMPO/ODA =6/4 and draw ratio of 3.0 exhibitsa tensile strength and an initial modulus of 0.90 GPa and 14.97 GPa, respectively, which means the co-PI fibers can also reach adequate mechanical property like PI-0 fiber only by increasing

the draw ratio. In summary, the co-PI fibers exhibit good thermal stability and mechanical properties with the incorporation of phosphorous monomer in the main chain.

REFERENCES

[1] IRWIN R. S., NEWARK, CHARLES E. S. Formation of polypyromellitimide filaments: US, 3415782 [P]. **1968**-

[2] HARA S., YAMADA T., YOSHIDA T. Novel polyamideimide precursors and hardenable compositions containing the same: US, 3,829,399 [P]. **1974**-

[3] MUNEYOSHI M M. T. Method of preparing a soluble high molecular weight aromatic polyamide imide composition: US, 3,860,559 [P]. **1975**-

[4] PATTERSON P. T. System and method for authenticating an electronically transmitted document US, 4,064,389 [P]. **1977**-

[5] MAKINO H K. Y., HARADA T. Process for producing aromatic polyimide filaments US, 4,370,290 [P]. **1983**-

[6] Method for Obtaining Polyimide Fibres GB, 2,025,311 [P]. **1980**-

[7] MITTAL K. Polyimides: Synthesis, characterization, and applications. Volumes 1 & 2 [M]. 1984.

[8] GAO G., DONG L., LIU X., et al. Structure and properties of novel PMDA/ODA/PABZ polyimide fibers [J]. Polymer Engineering & Science, **2008**, 48(5): 912-917.

[9] NIU H., QI S., HAN E., et al. Fabrication of high-performance copolyimide fibers from 3,3',4,4'-biphenyltetracarboxylic dianhydride, p-phenylenediamine and 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone [J]. Materials Letters, **2012**, 89(63-65.

[10] LIU X., GAO G., DONG L., et al. Correlation between hydrogen-bonding interaction and mechanical properties of polyimide fibers [J]. POLYMERS FOR ADVANCED TECHNOLOGIES, **2009**, 20(4): 362-366.

[11] NIU H., HUANG M., QI S., et al. High-performance copolyimide fibers containing quinazolinone moiety: Preparation, structure and properties [J]. Polymer, **2013**, 54(6): 1700-1708.

[12] ZHAO Y., FENG T., LI G., et al. Synthesis and properties of novel polyimide fibers containing phosphorus groups in the main chain [J]. RSC advances, **2016**, 6(48): 42482-42494.