Preparation of Electrically Conductive and High Performance Polyimide/Silver Composite Fibers via in-situ Single Stage Self-metallization Technique

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ABSTRACT

Surface silvered polyimide (PI) composite fibers with high electrical conductivity were prepared by an in-situ single stage self-metallization technique[1] using pyromellitic dianhydride/4,4'-oxydianiline(PMDA/ODA) based polyamic acid (PAA) as the precursor fibers and ammonia silver solution as the silver source. Silver polyamate were formed when immersing the PAA fibers into ammonia silver solution via an ion exchange reaction. After thermal treatment in several heating tubes with different temperature, the PI/Ag composite fibers were obtained. The surface morphology, electrical conductivity, thermal stability and mechanical properties of the composite fibers in relating ion exchange and thermal treatment conditions were investigated. SEM observation showed that continuous silver layer could be formed on PI fiber surface and the surface resistances of the conductive composite fibers were in the range of $10^3 \sim 10^4$ Ω/cm. The tensile strength and initial modulus of the composite fiber can be reached 288.45 MPa and 4.08 GPa, respectively.

Key words: polyimide composite fibers, ammonia silver solution, conductive

INTRODUCTION

Aromatic polyimides have been known for their chemical and radiation resistance, excellent mechanical and electrical properties, and outstanding thermal stability. It can withstand 500°C high temperature in a short time and can be at 300°C for long-term use. So far, it has had more than 50 years history of development. Since it owns good performance and outstanding features, as well as in structural materials and functional materials and other fields of great prospect, PI materials have been considered Problem Solver[2].

This excellent material, people are struggling to expand its applications in recent years. With the improving in synthesis and processing technologies, PI fiber researches have been paid increasingly attention. The ordinary PI fibers during use is prone to producing static electricity, it would seriously limit its scope of application, such as precision instrument workshop, large computer rooms, etc., because the role of electrostatic field will cause interference and damage to instruments. So on the antistatic modification of PI fibers is an urgent task. Our lab has been doing metallized polyimide research[3], therefore PI fibers for antistatic modification has some advantages. In-situ single stage self-metallization technique is used for antistatic modification of PI fibers. Polyamide acid precursor fibers is prepared first, then the original fibers through the solution containing silver ions to silver ions exchange. After that the heating conditions can make acid amide fibers into PI fibers, while silver ions reduced to metal silver.

EXPERIMENTAL

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Materials

PMDA and 4,4'-ODA were obtained from Shanghai Research Institute of Synthetic Resins. They were purified prior to use. Dimethylacetamide (DMAc) (analytical pure, water content 0.01%) was provided by Tianjin Fu Chen Chemicals Reagent Factory and used without further purification. $AgNO_3$ (99.5%) and Ammonia solution (25%) were purchased from Beijing Beihua Chemicals Company and used as received. All other reagents were of analytical quality and used without further purification as received.

Preparation of PMDA/4,4'-ODA metallized polyimide fibers

The following procedures were used to prepare (PMDA/ODA)-based metallized fibers.

PAA(20wt%) synthesis was performed by first dissolving the 4,4'-ODA(9.017g) in DMAC(80ml) and then adding the PMDA(9.823g) in 1h. After that the mixture had been stirred at 0°C for 2h. The inherent viscosity of PAA was 2.08dl/g.

The PAA solution had been eliminated air bubbles in a vacuum for 4 hours. Then the metallized fibers preparation process was shown in Figure 1. We changed the temperature of the first heating tube to get silvered fibers of different performance. The temperature of the first heating tube were 150°C，180°C，210°C，240°C and 270°C respectively. A following heating tube with the temperature of 320°C was employed before taking up.

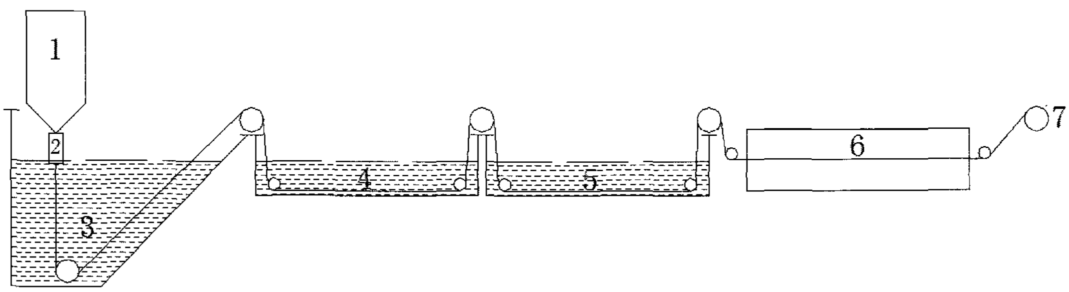

Figure 1 Flow process diagram of spinning metallized polyimide fibers. (1) PAA solution with 0.6 MPa Nitrogen gas; (2) spinning spinneret with 100 holes; (3) coagulation bath by using water; (4) ammonia silver solution(0.02M); (5) washing bath, water; (6) heating tube with different temperature; (7) taking up.

Characterization

Inherent viscosity was determined using an Ubbelohde viscometer (JULABO Technology(Beijing) Co.,Ltd) and the PAA solution containing 0.5% solid (w/w) in DMAc at 35°C.

Surface morphology of the fibers were determined by scanning electron microscope (SEM)(HITACHI S-4700 SEM instrument).

Surface conductivities were measured with an SDY-4 four point probe made by GuangZhou Semiconductor Material Academe.

Thermal gravimetric analysis (TGA) was performed on a TA Q50 instrument which the heating rate was 10K/min.

The tensile mechanical properties of the monofilament fiber was measured using YG001A-1 monofilament strength meter(Taicang Hongda Fangyuan Electric Co., Ltd.).

RESULTS AND DISCUSSION

The tensile mechanical properties and surface conductivities

Silvered PMDA/4,4'-ODA polyimide composite fibers were prepared via in-situ single stage self-metallization technique while the concentration of ammonia silver solution was 0.02M, first heating tube temperature were 150°C, 180°C, 210°C, 240°C and 270°C respectively, and further heated at 320°C in another heating tube before taking up. The tensile mechanical properties and surface conductivities of the fibers are showed in table 1.

Table 1 The tensile mechanical properties and surface conductivities of the fibers

Samples	150°C PI/Ag	180°C PI/Ag	210°C PI/Ag	240°C PI/Ag	270°C PI/Ag	PAA	PI
Tensile strength/MPa	147.77	166.26	179.78	288.45	230.30	296.13	457.24
Modulus/GPa	2.93	4.02	2.83	4.08	2.99	4.53	5.65
Elongation at break/%	5.18	5.37	8.73	12.56	14.02	14.13	11.92
Resistivity /$\Omega \cdot cm^{-1}$	5.7×10^3	4.5×10^3	6.3×10^3	8.6×10^3	7.0×10^3	NC	NC

NC-not conductive

As can be seen from Table 1, with the temperature, the PI/Ag fiber strength properties showed increasing trend, while the conductivity is decreased. Because the higher the temperature, the higher the degree of imidization. The maximum tensile strength is 288.45MPa which decreased 36.9% compared to PI fiber at 240°C. The minimum resistivity which is $4.5\times10^3 \Omega \cdot cm^{-1}$ obtained at 180 °C.

Surface morphology

Compared with the PAA and PI fibers, through in-situ single stage self-metallization technique prepared PI/Ag fibers, surface marked with a layer of silver. As can be seen from Figure 2, PAA and PI fibers have smooth surface. After through silver ammonia solution and then heated in 180°C and 320 °C heating tubes, the surface of PI/Ag fibers have a layer of silver nanoparticles which make the composite fibers with conductivity.

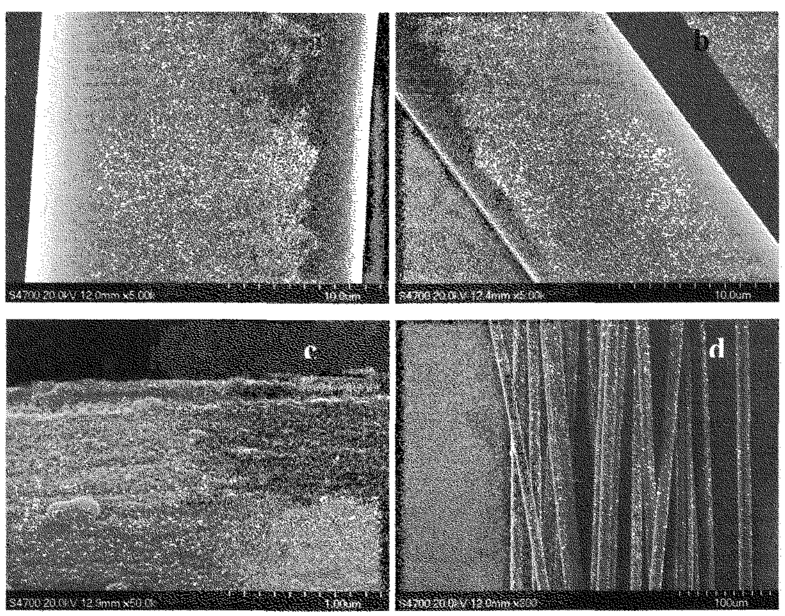

Figure 2 Surface morphology of fibers (a) PAA fiber; (b) PI fiber; (c) PI/Ag fiber heated under 180°C; (d) PI/Ag fiber heated under 180°C.

Thermal stability

Figure 3 illustrates the PI/Ag composite fibers with high heat resistance, 5% weight loss temperature is

396.15°C. Compared with the PAA and PI fibers, PI/Ag fibers had been completely imidization. In air, PI/Ag fibers in the fiber decomposition temperature is lower than the PI fibers' about 130 °C, because the silver particles on the fiber has the function of catalytic degradation.

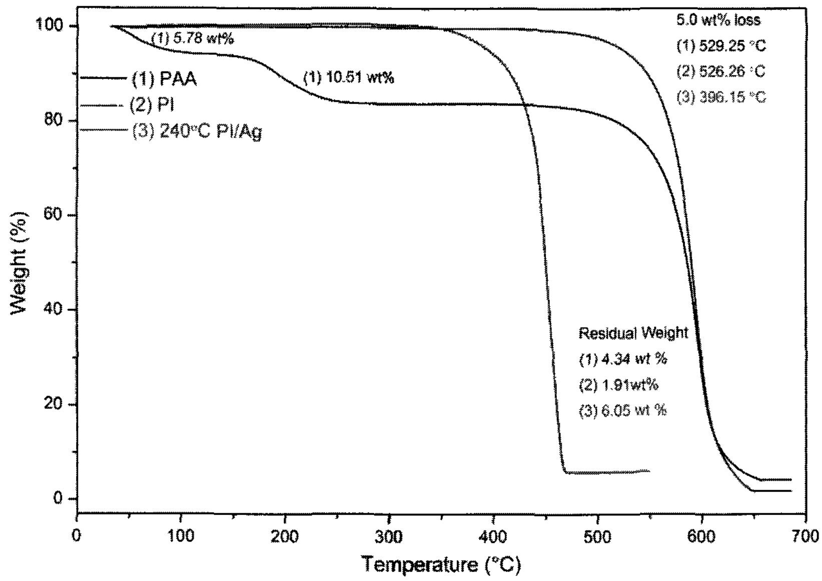

Figure 3 Thermal gravimetric analysis (TGA) of PAA, PI and PI/Ag fibers

SUMMARY

PI/Ag composite fibers were prepared by in-situ single stage self-metallization technique. When the first heating tube temperature was 240°C, the tensile strength and initial modulus of the composite fiber can be reached 288.45 MPa and 4.08 GPa, respectively. The minimum resistivity which is $4.5\times10^3\Omega\cdot cm^{-1}$ obtained at 180°C. Fiber surface form a layer of metallic silver nanoparticles after through silver ammonia solution and then heated in heating tubes. The composite fibers with high thermal stability, and 5% weight loss temperature is 396.15°C.

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