Fabrication of Polyaniline/PolyimideComposite Fibers with Electrically Conductive Properties

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ABSTRACT: A series of polyaniline/polyimide (PANi/PI) composite fibers was prepared via dry-jet wet spinning followed by in situ polymerization growth. Current–voltage curves indicated the transformation from electric insulation to electrical conductivity along the fiber axial direction. The composite fibers exhibited a sensitive response to immersion in solutions with different pH values. This work provides a simple approach to fabricate PANi/PI composite fibers that could be applied in the antistatic textile and military industries.

Introduction

Polyaniline (PANi) is a typical conductive polymer with conjugated π–electron systems; this polymer has attracted considerable attention because of its relatively high conductivity, redox reversibility, and environmental stability [1]. PANi materials have been prepared using different approaches, including chemical polymerization [2], template synthesis polymerization [3], and electrochemical polymerization [4]. With the development of nanotechnology, PANimaterials with nanostructures such as nanofibers, nanotubes, nanosheets, and nanospheres have been synthesized and applied. Much effort has been directed toward incorporating PANi with conventional polymers to fabricate composite materials, such as films, hydrogels microspheres, and fibers. These composite materials demonstrate advantages during processing because they combine the mechanical properties of conventional polymers and the functional properties of PANi. Polyimide (PI) fibers are regarded as high-performance organic fibers because of their good thermal stability and mechanical properties, low thermal expansion coefficient and creep, inertness to chemical solvents, and resistance to radiation. The fibers have been widely used in high-technology areas, such as high-temperature dust removal, flame retardation, radiation resistance, electrical insulation, and composite reinforcement. To date, various PI fibers with different chemical structures have been prepared via one-step or two-step spinning techniques. However, with the development of high-technology fields, pure PI fibers with basic properties have become insufficient for applications that require electrical conductivity. Therefore, the fabrication of PI fibers with electrical conductive properties comparable with those of their high-performance counterparts is highly significant. Chatzidaki[5] prepared a PANi/PI hollow fiber membrane through the dry/wet spinning method and significantly improved the perm-selectivity ratios for specific gases such as CH_4/CO_2 and N_2/CO_2. Liu [6] synthesized PANi/PI composite membranes with good thermal, mechanical, and electromagnetic interference properties through the in situ polymerization of aniline in the presence of aligned PI nanofiber membranes. However, composite

fibers comprising a conductive polymer and conventional PI fibers have yet to be conducted. The demand for PI fibers with electrically conductive properties has recently increased. To meet this demand, dry-jet wet spinning followed by in situ polymerization growth was adopted in the present study to fabricate a series of PANi/PI composite fibers. The mechanical, thermal, and electrically conductive properties of these fibers were systemically investigated.

Experimental

As a PI precursor, a PAA solution was prepared from the condensation reaction of PMDA/BPDA and ODA with an equivalent molar ratio in DMAc at 0 °C [7]. After polymerization, a PAA solution with a solid content of 15 wt% and an intrinsic viscosity ($[\eta]$) of ~2.2 dL g-1 was obtained. The viscous PAA solution was filtered and degassed under vacuum at 50 °C before fiber spinning.

The procedure of PI fiber preparation is illustrated in Scheme 1. PAA fibers were prepared via dry-jet wet spinning. To ensure the good fluidity of the precursor solution, the PAA spinning dope was kept at a constant temperature of 50 °C with a recirculating heater. The spinning dope was extruded through a spinneret plate with 100 holes of 0.12 mm in diameter, passed through air, and then immersed in a coagulation bath filled with deionized water–ethanol (v/v = 1/1). The driving pressure was set at 150 psi, and the proportioning pump was used with a flow rate of 0.2 mL min^{-1}. PAA fibers were obtained after solvent release and the subsequent solidification. Thermal treatments were adopted to complete the imidization of PAA fibers; the thermal program proceeded by heating at a rate of 5 °C min^{-1} to 100 °C, 200 °C, and 300 °C. Finally, the as-prepared PI fibers were subjected to a stretching process in a heating furnace at 400 °C to improve further their mechanical properties.

The PI fibers were placed in a H_2SO_4/H_2O_2 solution (v/v = 3/1) for 30 s and then rinsed with deionized water. PANi/PI composite fibers were then prepared via the in situ polymerization of aniline on the surface of the treated fibers. In brief, the treated PI fibers were immersed in a mixture of aniline and HCl at 0 °C before an HClsolution of $FeCl_3$ with an equal molar ratio as aniline was added dropwise with stirring. Polymerization was conducted for 2, 4, 6, 12, and 24 h. Finally, the composite PANi/PI fibers were thoroughly washed with diluted HCl solution and deionized water before drying at 50 °C overnight in a vacuum oven.

Results and discussion

The surface of the PI fibers changed from smooth to rough after treatment with H_2SO_4/H_2O_2 (Figs. 1a and 1b). The PANi nanoparticles were obviously visible by SEM (Fig. 1c) when the polymerization time was prolonged to 2 h. When the polymerization time was prolonged from 2 h to 24 h, more PANinanoparticleswere deposited on the PI fibers (Fig. 2).

PANi is unique among conductive polymers because of its high conductivity, goodenvironmental stability, reversible doping–dedoping process, and controllable physical and electrochemical properties via oxidation and protonation. When the PANi nanostructure is covered or are introduced into the fibers, their electroactivenature can be strengthened[1]. Fig. 3 shows the I−V curves of the PANi/PI composite fibers with different polymerization times along the fiber axial direction. The pristine PI fibers were electrically insulative, and no electrical signals were detected. When the polymerization time of PANi was increased to 2 h, the composite fibers became electrically conductive with a current of 2.6 μA at 10 V. When the polymerization time was prolonged to 4 h, the current increased to 15.6 μA at 10 V. When the polymerization time was continuously prolonged to 6 h, the current of the composite fibers clearly increased to 36 μA at 10 V. When the polymerization time was further

prolonged to 12 h, the current increased to 82 µA at 10 V. When the polymerization time was prolonged from 12 h to 24 h, the current increased from 82 µA to 100 µA at 10 V. The results indicate that the electrical conductivity of the composite fibers strengthened after prolonging the polymerization time from 2 h to24 h.

In general, the polymerization time is initially short, and a few PANinanoparticlesare produced on the PI fibers. The surface of PI fibers was not completely coated, which resulted in a low electrical conductivity (Fig. 1c). As the polymerization time was prolonged, more PANinanoparticles were deposited on the surface of the PI fibers and the PANi layers became denser. Electron transfer, which readily occurs on the surface of PANi/PI composite fibers, increases electrical conductivity. Favorable electroactivity, as well as mechanical and thermal stabilities, enables the conductive fibers to be useful in various fields, such as electrical devices and sensors. Moreover, compared with metal fibers, PANi/PI fibers are better candidates as lightweight conductive materials in aircraft and spacecraft because of their lower densities.

Among various conductive polymers, PANi has been the most extensively studied because of its various states with different degrees of oxidation and protonation. Thetransformations in oxidation state and the protonation of the imine nitrogen atoms cause significant changes in electrical and optical properties [6, 8]. Fig. 7 shows images of the PANi/PI composite fibers in 0.1 M HCl, deionized water, and 0.1 M NaOH solution. The composite fibers immersed in 0.1 M HCl appeared light green. In general, the protonated emeraldine salt is formed in an acidic environment. Meanwhile, the composite fibers immersed in deionized water turned dark green. When the solution was changed to 0.1 M NaOH, the composite fibers appeared black. In an alkaline environment, deprotonation occurs and the emeraldine base is generated, which is black and provides electrical insulation. The emeraldine salts and emeraldine base could be effectively reversed by quickly protonating anddeprotonating the composite fibers, which exhibit a responsive behavior to different pH environments. Given their pH sensitivity and repeatability, the PANi/PI composite fibers could be applied in various areas, such as real-time pH detection.

Conclusions

To summarize, PANi/PI composite fibers were fabricated through the in situ polymerization of aniline in the presence of PI fibers, which were prepared by dry-jet wet spinning. The composite fibers, which display the advantages of both PI and PANi, exhibited good electrical conductivity. When the polymerization time was prolonged from 0 h to 24 h, the electrical conductivity along the direction of the fiber axis obviously increased. Furthermore, the reversibility of quick protonation and deprotonation makes the PANi/PI composite fibers respond to different pH environments. When the solution changed from acid to base, the color of the composite fibers shifted from light green to black. This work proposes a simple method of fabricating conductive fibers without the need for external doping to enhance the conductivity of composite fibers. It is crucial for the fabrication and application of functional fibers as lightweight conductive materials in the sensor, antistatic textile, and military industries.

Acknowledgments

References

[1] H. Ding, M. Wan, Y. Wei, Adv. Mater. 19 (2007) 465-469.

[2] X. Zhang, S.K. Manohar, Chem. Commun. (2004) 2360-2361.

[3] H. Qiu, M. Wan, B. Matthews, L. Dai, Macromolecules. 34 (2001) 675-677.

[4] J. Ye, S. Zhai, Z. Gu, N. Wang, H. Wang, Q. Shen, Mater. Lett. 132 (2014) 377-379.

[5] L.M. Santos, J. Ghilane, C. Fave, P.C. Lacaze, H. Randriamahazaka, L.M.Abrantes, J. Phys. Chem.C. 112 (2008) 16103-16109.

[6] D. Chen, Y.E. Miao, T. Liu, ACS Appl. Mater. Inter. 5 (2013)1206-1212.

[7] C. Zhang, Q. Zhang, Y. Xue, G. Li, F. Liu, X. Qiu, Chem. Res.Chin. Univ. 30 (2014) 163-167.

[8] B. Ding, Y. Si, X. Wang, J. Yu, L. Feng, G. Sun, J. Mater. Chem. 21 (2011) 13345-13353.
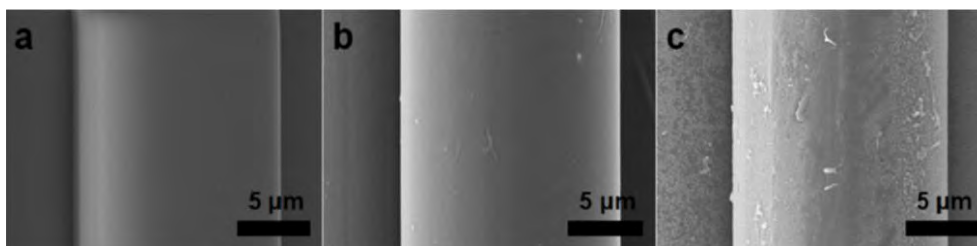
Fig. 1. SEM images of (a) PI fiber, (b) surface treated PI fiber, and (c) PANi deposited on the PI fiber prepared by FeCl3oxidization polymerization for 2 h.
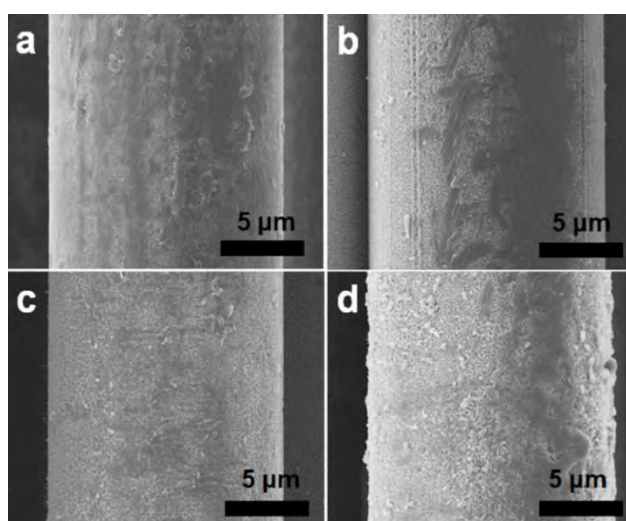

Fig.2. SEM images of PI fiber coated with PANinanoparticles with different deposition time of (a) 4 h, (b) 6 h, (c) 12 h, and (d) 24 h.
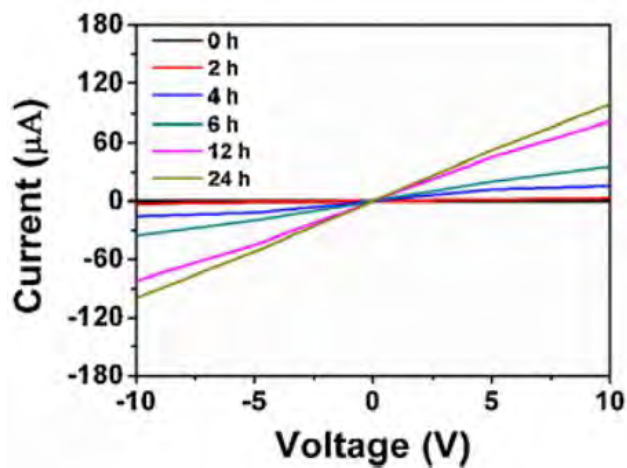
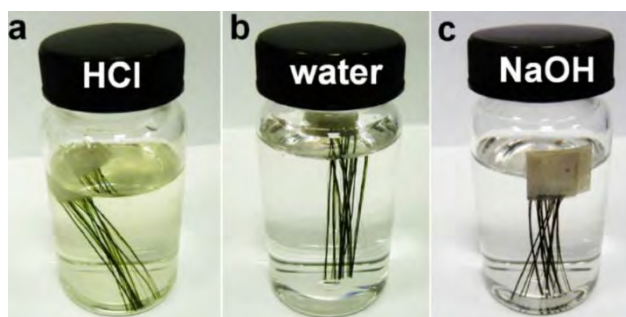Fig. 3. Current–voltage plots of PANi/PI fibers prepared at different deposition time.

Fig. 4. Effect of pH on color of PANi/PI composite fibers when immerged in (a) 0.1 M HClsolution, (b) deionized water, and (c) 0.1 M NaOH solution