

Synthesis of polyaniline in electrospun microfibers via in-situ polymerization and the formation of self-assemble polyaniline particles

Haiying Cui, Hui Zhou, Xuejing Zhang, Chengting Zhao

School of Food & Biological Engineering, Jiangsu University, Zhenjiang 212013, China

1049708440@qq.com

Keywords: Conductive microfibers; Electrospinning; In-situ polymerization; Polyaniline; Nanoparticles

Abstract. This study reports on the synthesis of the polyaniline (PANi) in electrospun poly(vinylchloride-acrylonitrile) (PVC-AN) via in-situ oxidative polymerization of aniline using ammonium peroxydisulfate (APS) as the oxidant. Self-assemble polyaniline nano-particles were obtained from dissolving the conductive microfibers in dimethylformamide (DMF). The formation of PANi in microfibers can be explained by electrons transformation process, in which the electrons are abstracted from the aniline molecules in the microfibers and transferred through a conducting PANi membrane to APS in the external solution. Thus the aniline was oxidized without physically contact with oxidant molecules. The average diameter of conductive fibers was about 1.0 μm ; and the particles had average diameters around 350 nm and inclined to aggregate to become much larger particles with the diameter up to 2.0 μm based on the scanning electron microscope (SEM) images. The differences in the details of molecular structure between PVC-AN fibers, PANi and PVC-AN-PANi fibers were discussed on the basis of FTIR spectra. Results from Differential scanning calorimetry analysis (DSC) and X-ray diffraction (XRD) indicated the PVC-AN-PANi microfibers form an interpenetrating polymer network (IPN) structured complex with certain molecular interactions.

Introduction

Conductive polymer composites are attractive various applications due to their low cost, corrosion resistance, electrochemical behavior in served as bio-function materials, and ease of processing [1, 2]. Polyaniline (PANi) is one of the most important conductive polymers, due to its easy synthesis, outstanding electrochemical properties, thermal and environmental stability. Unlike other conjugated polymers, PANi has a simple and reversible acid/base doping/de-doping chemistry enabling control over properties such as free-volume, solubility, electrical conductivity and optical activity [3-7].

In recent years, to prepare conductive polymer in nano/micro-scale have created a new field of polymer science. In various fabricating techniques, electrospinning is being used to an increasing extent to produce ultra thin nano/microfibers from a wide range of polymer materials [8-11]. Electrospun polymer fibers possess many extraordinary properties including small diameters and the large specific surface areas, and the high degree of structural perfection. Unlike nanorods, nanotubes, and nanowires that are produced mostly by synthetic, bottom-up methods, electrospun nanofibers are produced through a top-down nano-manufacturing process, which results in continuous and low-cost nanofibers that are also relatively easy to be aligned, assembled and processed into applications. Furthermore, electrospinning is highly versatile and allows the processing not only of many different polymers into polymeric microfibers but also the co-processing of polymers and low molecular weight non-volatile materials, simply by using ternary solutions of the components for electrospinning to form a combination of fibrous functionalities [12-14]. Small molecules like drugs or monomers could be incorporated into electrospun fibrous carriers, which provide the possibility to synthesize functional polymers in the carriers.

In this work, PANi was in-situ polymerized in poly (vinylchloride-acrylonitrile) (PVC-AN) microfibers which obtained from electrospinning. Aniline-contained PVC-AN microfibers were

firstly prepared through electrospinning, followed by in-situ polymerizing aniline in PVC-AN microfibers using ammonium peroxydisulfate as the oxidation. The conductive microfibers were then fabricated by PANi particles were also obtained by dissolving the conductive microfibers in dimethylformamide (DMF). The morphology of conductive microfibers and PANi nanoparticles were observed using optical and electron microscopy. The structure of the fibers and particles were characterized by X-ray diffraction (XRD) as well as Fourier-transform infrared (FTIR) spectra, UV-Vis spectroscopy and differential scanning calorimetry (DSC) analysis. The electronic properties were tested using four-point probe conductivity measurements and cyclic voltammetry.

Experimental

Materials. The monomer of aniline, copolymer of PVC-AN, DMF and ammonium peroxydisulfate were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used without any further purification.

Electrospinning. The PVC-AN powder was dissolved into the DMF with a small amount of aniline (5 v/v%) by magnetically stirring overnight at room temperature. The polymer solution with aniline was then filed into a glass syringe terminate by a stainless steel needle (inner diameter about 0.6 mm). The electrospinning process was carried out at ambient conditions of room temperature with relative humidity of $45 \pm 5\%$. A fixed electrical potential of 15 kV was applied across a distance of 12 cm between the tip and the collector. The feed rate of solutions was controlled at 20 $\mu\text{l}/\text{min}$ by means of a single syringe pump (New era pump systems, Inc., USA). The pure PVC-AN fibers were also prepared for comparison.

In-situ polymerization and the formation of PANi particles. After electrospinning, the obtained microfibers were immediately place into saturated ammonium peroxydisulfate solution for in-situ polymerization of aniline. The reaction was operated at room temperature for 2 h. After polymerization, the microfibers were taken out from the solution and soaked in acetone for 30 min to remove redundant aniline. They were then dried at room temperature for 2 h. The self-assemble PANi particles were obtained by dissolving conductive microfibers into DMF with vigorous magnetic stirring; and then the nanoparticles were centrifuged and dried in vacuum over night. As the comparison, PANi was prepared by directly adding aniline into ammonium peroxydisulfate solution.

Characterization. The surface morphology of electrospun fibers and self-assemble PANi particles was observed using ZOOM645 optical microscope (Maidisen Trument Co., Ltd. Nanjing, China). The surface morphology of the nanofibers was assessed using a JSM-5900 scanning electron microscope (Japan Electron Optics Laboratory Co. Ltd.). Fourier-transform infrared (FTIR) spectroscopy were obtained on a Spectrum Two IR Spectrometers (PerkinElmer, USA). The scanning range was $650 - 4000\text{ cm}^{-1}$ and the resolution was 1 cm^{-1} . X-ray diffraction (XRD) patterns were acquired in the 2θ rang of $5-50^\circ\text{C}$ using a Bruker AXS D8 Discover diffractometer with $\text{CuK}\alpha$ radiation source ($\lambda=1.54\text{ \AA}$). Differential scanning calorimetry (DSC) analysis were carried out using Q200 differential scanning calorimeter (TA Instruments CO., USA). Sealed samples were heated at $10^\circ\text{C min}^{-1}$ from 20 to 200°C . The nitrogen gas flow rate was 40 ml min^{-1} .

Results and Discussion

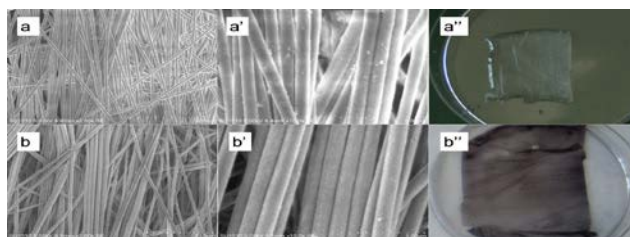


Fig. 1: SEM microimages of electrospun nanofibrous precursors from DMF solutions of 0.2 g/ml PVC-AN as the carrier (a $\times 2000$ and a' $\times 10000$), conductive microfibers of PVC-AN-PANi

synthesizing from the precursors with ANi contents of 5 wt% ($b \times 2000$ and $b' \times 10000$); photograph of the microfibers precursors (a'') and conductive microfibers mats.

As shown in Figure 1, the diameter of PVC-AN and PVC-AN-PANi fibers were similar, that in the range of 0.8 to 1.3 μm . The precursor microfibers mat treated of ammonium persulfate solution and the conductive microfibers mat (with PANi polymerized in the fibers by oxidation of ammonium persulfate) were immersed in distilled water for obtaining their photographs, as shown in Figure 1 a'' and b'' . It can be easily to find that the precursor microfibers mat was colorless and transparent, while the conductive microfibers mat was non-uniform dust blue.

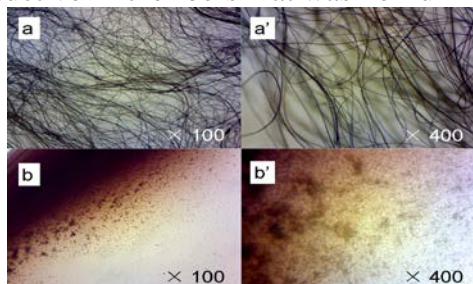


Fig. 2: Optical photographs of (a) PVA-AN-PANi microfibers and (b) self-assemble PANi particles. Magnification 10×10 and 10×40 .

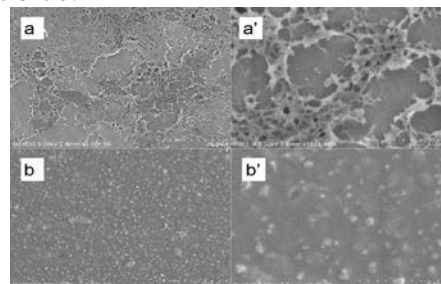


Fig. 3: SEM images of (a) PVC-AN-PANi aggregation obtained from dissolving PVC-AN-PANi fibers into DMF and then dried in vacuum oven and (b) PANi particles. Magnification of $\times 2000$ and $\times 10000$.

More details about the surface topographies of the PVA-AN-PANi fibers and the self-assemble particles of PANi observed under optical microscope are shown in Figure 2. Clearly, the PVC-AN-PANi fibers were not very uniform with some of the fibers inter-twisted into clumps.

This study also provided a new method for the synthesis of PANi nanoparticles. The self-assemble process occurred when PVC-AN-PANi microfibers was placed into DMF. Since DMF is the good solvent to dissolve PVC-AN, the PANi molecules were release from PVC-AN matrix, and then form the particles by the intermolecular force. The optical microscope images of PANi particles were shown in Figure 2 b and b' with different magnification of $\times 100$ and $\times 400$.

Unlike conventionally prepared PANi that shows a coarse granular structure, the self-assemble PANi particles are solid and spherical in shape with the diameter range from 200 nm to almost 2.0 μm . It is found from the SEM image of Figure 3 b and b' that the PANi particles are aggregated with each other to form larger particles. The products of PVC-AN/PANi composite were also obtained by dissolving PVC-AN-PANi microfibers in DMF, but without centrifuging. As shown in Figure 3 a and a' , PANi particles adhere with each other as well as embedded in the matrix of PVC-AN.

As shown in Figure 4 a, all the typical characteristic peaks of the PANi are displayed in the range of 1700-6500 cm^{-1} . The main characteristic peaks of PANi at 1500 and 1580 cm^{-1} indicated the C=N and C=C stretching modes for the benzene rings. The bands at 1380 and 696 cm^{-1} can be assigned to C-N stretching of the secondary aromatic amine and aromatic C-H out-of plane bending vibrations, respectively. The band at 1140 and 823 cm^{-1} due to the aromatic C-H in-plane bending and the out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring. The spectra of PVC-AN fibers shows most significant characteristic peak at 1440 cm^{-1} (-CH₂- deformation).

All DSC thermograms are shown in Figure 4 b. the DSC curve of PVC-AN microfibers exhibited a wide endothermic response corresponding to the softening temperature of PVC at 56.7 $^{\circ}\text{C}$ and a small endothermic response at 98.7 $^{\circ}\text{C}$ which indicated the glass transition temperature of PAN. As an amorphous polymer, PANi shows only a broad endotherm might be caused by dehydration and lies from 70 $^{\circ}\text{C}$ to 110 $^{\circ}\text{C}$. DSC thermogram of PVC-AN-PANi fibers shows a broad endotherm range from 40 to 90 $^{\circ}\text{C}$ with the peak at 69.4 $^{\circ}\text{C}$. Furthermore, the glass transition temperature of PAN was shift to about 99.2 $^{\circ}\text{C}$. These indicated that the structure of PVC-AN molecular chains was impacted significantly by the formation of PANi.

The XRD pattern of PVC-AN microfibers shows two obvious peaks centered at $2\theta=17.3^\circ$ and 31.8° (Figure 4 c). The PVC-AN-PANi microfibers shows one big peak around $2\theta=14.0^\circ$. The different diffraction peaks between the PVC-AN and PVC-AN-PANi microfibers indicated that the formation of PANi in microfibers significantly affected the molecular structure of PVC-AN. Therefore, we believe there was an interpenetration network formed in the PVC-AN-PANi microfibers.

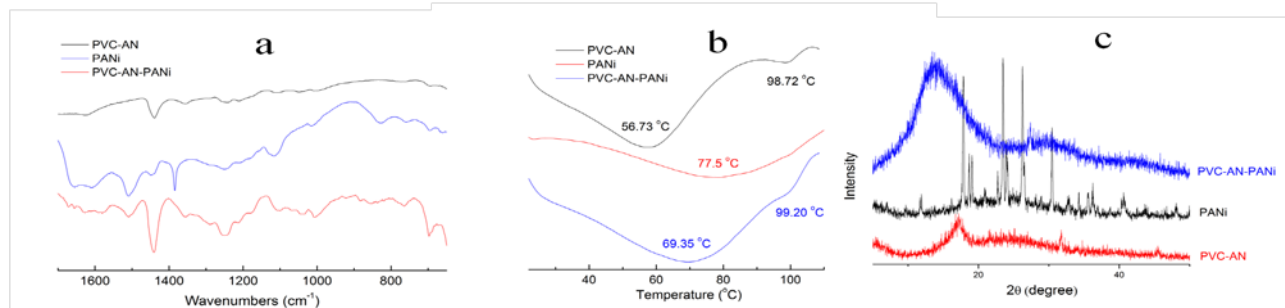


Fig. 4 (a) FTIR spectrum of the PVC-AN microfibers, PANi particles and the conductive microfibers of PVC-AN-PANi;

(b) DSC curves of PVC-AN, PANi nanoparticles and the conductive microfibers of PVC-AN-PANi;

(c) XRD patterns for PVC-AN microfibers, PVC-PAN-PANi microfibers and PANi particles.

Summary

The synthesis of PANi in electrospun PVC-AN microfibers has been successfully achieved through a in-situ polymerization of ANi using ammonium peroxydisulfate (APS) as the oxidant. The PANi particles with diameters ranged from 350 nm to 2.0 μm were also obtained in this work by dissolving the polymeric microfibers in DMF solution. The in-situ polymerization of PANi in electrospun microfibers provided a novel method for obtaining conductive microfibers for various applications in the fields of microelectronic devices and biosensors.

References

- [1] A.Laforge, L.Robitaille: *Macromolecules*. Vol. 43 (2010), p. 4194-4200.
- [2] J.Ge, E.Neofytou, T.J.Cahill III, R.E.Beygui, R.N.Zare: *ACS Nano*. Vol. 6 (2012), p. 227-233.
- [3] Q.W.Tang, J.H.Wu, H.Sun, J.M.Lin, S.J.Fang, D.Hu: *Carbonhydr. Polym.* Vol. 74 (2008), p. 215-219.
- [4] M.Ayad, G.El-Hefnawy, S.Zaghlol: *Chem. Eng. J.* Vol. 217 (2013), p. 460-465.
- [5] Y.F.Huang, C.W.Lin: *Polymer*. Vol. 53 (2012), p. 2574.
- [6] X.N.Wu, X.R.Qian, X.H.An: *Carbonhyd. Polym.* Vol. 92 (2013), p. 435-440.
- [7] J.H. Zhu, H.B.Gu, Z.P.Luo: *Langmuir*. Vol. 28 (2012), p. 10246-10255.
- [8] E.D.Boland, T.A.Telemeco, D.G.Simpson, G.E.Wnek, G.L.Bowlin: *J. Biomed. Mater. Res. B*. Vol. 71B (2004), p. 144.
- [9] J.M.Corey, C.C.Gertz, B.S.Wang, L.K.Birrell, S.L.Johnson, D.C.Martin, E.L.Feldman: *Acta. Biomater.* Vol. 4 (2008), p. 863-875. ,
- [10] N.Bolgen, I.Vargel, P.Korkusuz, Y.Z.Menceloglu, E.Piskin: *J. Biomed. Mater. Res. Part B Appl. Biomater.* Vol. 81B (2007), p. 530-543.
- [11] J.P.Chen, G.Y.Chang, J.K.Chen: *Colloids. Surf. A*. Vol. 313 (2008), p. 18-188.
- [12] X.Q.Li, Y.Su, S.P.Liu, L.J.Tan, X.M.Mo, S.Ramakrishna: *Colloids. Surf. B*. Vol. 75 (2010), p. 418-424.
- [13] X.Q.Li, L.Lin, Y.A.Zhu, W.W.Lin, T.S.Yu, M.Q.Ge: *Polym. Compos.* Vol. 34 (2013), p. 282-287.
- [14] D.G.Yu, X.X.Shen, C. B.White, K.White, L.M.Zhu, S.W.A.Bligh: *Nanotechnology*, Vol. 20 (2009), p. 055104(9pp).