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Adsorption and polymerization of aniline on a carboxylic group-modified fibrous substrate

Jing Wang[a,b,*], Kaka Zhang[c], Liang Zhao[a,b], Wei Ma[a], Tieliang Liu[a]

[a] *Institute of Chemistry, Henan Academy of Sciences, Zhengzhou 450002, PR China*
[b] *High & New Technology Research Center, Henan Academy of Sciences, Zhengzhou 450002, PR China*
[c] *School of Material Science and Engineering, Zhengzhou University, Zhengzhou 450001, PR China*

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ABSTRACT

A carboxylic group-modified poly(acrylonitrile) fiber (CPAN) was prepared and used as a substrate for aniline adsorption and polyaniline (PANI) deposition in this study. Results from batch adsorption tests showed that grafting of carboxylic group could substantially improve the adsorption capacity of CPAN for aniline monomer at optimal pH 3.0–6.0; however, in strong acidic solutions, both the raw poly(acrylonitrile) fiber (PAN) and the as-synthesized CPAN had no obvious adsorption for aniline. Results from in-situ polymerization tests showed that both PAN and CPAN could obviously accelerate the polymerization of aniline, as indicated from evolution of solution temperature and UV–vis spectra. However, as shown by SEM photographs, the deposited PANI was more uniform on CPAN as compared with PAN. Besides, the produced PANI/CPAN composite showed higher PANI content and conductivity than the PANI/PAN composite. The proposed mechanism was that the intermediate products of aniline polymerization were apt to adsorb on both the PAN and CPAN surfaces, and thus substantially accelerated the polymerization rates. Due to the relatively strong site-to-site electrostatic interaction and hydrogen bonding, higher content of PANI was deposited on the CPAN surface and the distribution was more uniform as compared with PAN.

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1. Introduction

The conducting polymer viz. polyaniline (PANI) has been widely studied in sensors, battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and pollutant adsorbents, etc. [1,2]. However, its difficult processibility and poor mechanical property are demonstrated to be serious obstacles to its applications. One of the methods to solve these problems is to prepare its composite with a suitable substrate that provides the desired mechanical properties. Extensive substrates have been studied for PANI deposition including carbon-structured materials [3–6], inorganic materials [7–11], and organic polymers [12–17]. Among them, organic polymers have been paid increasing attention due to their unique properties such as light weight, flexibility, good environmental stability, low cost, and multiple application forms [15,18].

At present, in-situ chemical oxidation polymerization (or surface polymerization) is the mostly used method for preparation of the PANI/organic polymer composites because it is easy for scale-up and has a high yield of PANI [2,19]. Unfortunately, the direct and uniform deposition of PANI on the organic polymer substrates is often difficult because of the inertness of surfaces [15] and the poor adhesion between PANI and substrate [7,13]. Considering that the physical–chemical interactions (e.g. hydrogen bonding, chemical bonding) between PANI and the host polymer has significant impacts on properties and applications of the composite materials [14], many modification methods have been developed to introduce active groups on the substrate surface. For example, Wu and Chen [7] used a silane-bearing aniline compound to modify the substrate and found that the PANI films grown on this modified surface had better adhesion compared to that grown on unmodified substrate. Kang et al. [13] concluded that there existed an improved adhesion between the PANI base and the surface functionalized polymers (i.e. $-$COOH and $-SO_3H$) as compared with the pristine polymers. Zhong et al. [15] modified the polypropylene (PP) film through poly(acrylic acid) (PAA) grafting and found that the nanostructured PANIs could be strongly bonded with the substrate because the PAA brushes not only acted as templates for the PANI structures but also as dopants. Wu et al. [20] pretreated the wool textiles by a molecular template, i.e. poly(2-methoxyaniline-5-sulfonic acid) (PMAS), and found that introduction of sulfonate groups into the fabrics could result in the formation of an adherent, uniform and stable PANI layer.

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[*] Corresponding author at: No. 56 Hongzhuan Road, Zhengzhou 450002, PR China. Tel.: +86 371 65511153; fax: +86 371 65511153.
E-mail address: wangj12@163.com (J. Wang).

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Poly(acrylonitrile) (PAN) fiber, a popular engineering polymer, exhibits extensive applications in textile and water purification [18,21–23]. Because of its good mechanical and thermal properties, the PAN fiber is expected to be a good substrate for PANI deposition. For example, Toptaş et al. [22] and Xia and Lu [23] prepared PANI/PAN composites using pristine PAN fiber as the starting material. However, the conducting PANI layer on the PAN fiber was nonuniform [23], probably due to the aforementioned inertness of the substrate surface. Therefore, a surface functionalized PAN fiber is essential to be developed for uniform deposition of PANI and the formation mechanism of PANI on this fiber should also be investigated.

In this paper, a novel carboxylic group-modified poly(acrylonitrile) fiber (CPAN) was prepared and used as the substrate for PANI deposition. Considering that adsorption of aniline or its oligomer on the substrate surface is deemed as the first step during the aniline polymerization process [9,24], the adsorption properties of aniline monomer by CPAN were studied with variation of pH values of aqueous solutions. Then PANI was deposited on CPAN using the in-situ chemical oxidation polymerization method. The polymerization course was monitored by recording the solution temperature, color and ultraviolet–visible (UV–vis) spectra. The formation of PANI was confirmed by PANI content, Fourier Transform Infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) analyses. The composite fibers were further characterized by thermal gravimetric analysis (TGA) and conductivity. Based on the adsorption and characterization results, an illustration scheme was proposed at the end of this paper to elucidate the PANI deposition mechanism on the fibrous substrate.

2. Experimental

2.1. Materials

The carboxylic group-modified poly(acrylonitrile) fiber (CPAN) was prepared following the procedure in our previous report [25] using commercial poly(acrylonitrile) (PAN) fiber (a copolymer of acrylonitrile ($\geq$90% by weight) with other monomers, Shanghai Petrochemical Co. Ltd., China) as the starting material. Analyses from FTIR and acid–base titration demonstrated that nearly all nitrile groups in the starting PAN were converted to carboxylic groups and 7.1 mmol/g of carboxylic groups were successfully grafted onto the CPAN.

Aniline (analytical grade) was distilled under reduced pressure prior to use. The aniline solution was prepared by dissolving an appropriate amount of aniline with ultrapure water (18.2 MΩ cm, Millipore, USA) for adsorption tests. The pH was adjusted to the desired values using diluted HCl and NaOH solutions. $(NH_4)_2S_2O_8$ (analytical grade) was used as the oxidant for aniline polymerization as received. All other reagents were analytical grade and used without further purification.

2.2. Adsorption of aniline on CPAN

Batch adsorption tests were conducted to investigate aniline adsorption on the fibrous substrate as a function of pH values of aqueous solutions (2–10). To start the test, 0.04 g of CPAN were mixed with 40 mL of aniline solution on a shaking table (25 °C, 150 rpm). After equilibration for 20 h, the mixture was filtered (0.45 μm), and the filtrate was analyzed for the aniline concentration by a UV–vis spectrophotometer (UV1800, Shimadzu, Japan) at 280 nm. Adsorption capacity (Q_e, mg/g) of CPAN (or PAN) for aniline was calculated using the equation

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \tag{1}$$

where C_0 and C_e (mg/L) are initial and equilibrium concentrations of aniline, respectively, V (L) is volume of aniline solution, and M (g) is dry mass of CPAN (or PAN).

2.3. Polymerization of aniline on CPAN

In a typical test, 0.50 g of CPAN fiber were dispersed in 25 mL of 1 mol/L HCl aqueous solution containing 0.2 mol/L aniline monomer. Then 25 mL of 1 mol/L HCl aqueous solution containing 0.2 mol/L $(NH_4)_2S_2O_8$ were added in one portion. The mixture was reacted under ultrasonication for 30 min (KQ-200VDE, Kunshan, China), and then allowed to stand still overnight. The temperature of the water bath was kept at 5–10 °C throughout the reaction. Finally, the product (PANI/CPAN composite) was separated, washed by copious amounts of distilled water and dried at 60 °C. The neat PANI and PANI/PAN composite were also prepared for comparison according to the same aforementioned procedure, except that the substrate was absent or changed to PAN fiber. The content of PANI deposited on CPAN and PAN was calculated using the following formula:

$$\%PANI = \frac{W - W_0}{W_0} \times 100 \tag{2}$$

where W_0 is the initial weight of bare PAN or CPAN fibers, and W is the weight of PANI/PAN or PANI/CPAN composite fibers after PANI deposition.

The progress of aniline polymerization was monitored by recording temperature, color and UV–vis spectra of the reaction mixture. Typically, 0.1 mL of sample was withdrawn every 3 min during the aniline polymerization process and placed in a 1 cm cell of the spectrophotometer after dilution to 4 mL with deionized water. Then the UV–vis spectra were recorded with a UV1800 spectrophotometer (Shimadzu, Japan) to interpret evolution of the reactants.

2.4. Sample characterization

The as-synthesized CPAN and PANI/CPAN composites were characterized by FTIR, SEM, TGA and conductivity. For FTIR analyses, the samples were thoroughly ground with KBr in an agate mortar. After being compressed in a powder sheeter (FW-4A, Tianjin Tuopu Instrument, Tianjin, China), the infrared spectra were collected in 400–4000 cm^{-1} range at a spectral resolution of 2 cm^{-1} using a Thermo Nicolet IR 200 instrument (Thermo Electron Corp., USA). Surface morphologies of the PANI/fiber composites were examined by SEM (JSM-6390LV, Japan) to elucidate the distribution of PANI on CPAN and PAN substrates. Thermal behavior of the samples was monitored with the Netzsch STA 449C thermal analyzer (Germany) under N_2 atmosphere at a heating rate of 10 °C/min. Conductivity of the PANI/fiber composites was measured by a digital multimeter (VC9807A+, Victor, China) at room temperature using the formula

$$\kappa = \frac{L}{\pi r^2 R} \tag{3}$$

where κ, R, r and L were conductivity (S/cm), resistivity (Ω), radius (cm) and length (cm) of a single fiber, respectively. Here, the radii of PAN and CPAN were 17.2 μm and 20.8 μm respectively, as could be seen from SEM, and the distance between the two probes was 1 cm. The reported conductivity value was an average of 10 different measurements.

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