

Fabrication and gas sensing behavior of poly(3,4-ethylenedioxythiophene) coated polypropylene fiber with engineered interface



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ABSTRACT

Conductive composite fibers were successfully fabricated by coating poly(3,4-ethylenedioxythiophene) (PEDOT) layers on the surface of polypropylene-graft-poly(acrylic acid) (PP-g-PAA) fibers through *in situ* chemical oxidative polymerization. It was found that the adhesion between the conductive PEDOT layers and the modified PP fiber substrates was significantly enhanced due to the electrostatic attractions between PEDOT chains and carboxylic groups of grafted PAA. In this study, we investigated the influence of the 3,4-ethylenedioxythiophene (EDOT) concentration and the oxidant species on the electrical conductivity of the composite fibers, and the result show that the maximum conductivities of PP-g-PAA/PEDOT composite fibers prepared with FeCl₃ and iron(III) p-toluenesulfonate (FepTS) as oxidants reached 0.069 S/cm and 10.09 S/cm, respectively. The composite fibers were applied as a sensor for HCl and NH₃ gas detection and exhibited a rapid and reversible response. The influence of the oxidant species on the sensing properties for HCl and NH₃ gas detection is further discussed, and some features such as fast response time (less than 2 s) and high relative resistance changes (63% for HCl and 110% for NH₃ gas) were achieved.

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1. Introduction

Smart materials like piezoelectric materials [1], shape-memory materials [2], self-healing materials [3], sensors [4], etc., have flourished rapidly in this decade. Commercial smart materials are based on ceramics or metal alloys which require high temperature and robust processing conditions and machineries. To achieve a degree of commercial success facile conditions and process to prepare smart materials which could be integrated with continuous mass production is indispensable. Smart textiles are those materials where the smart component is backed up by the textile which bestows flexibility, easy fabricability, mass productivity and integrability.

Intrinsically conducting polymers (ICPs) are primarily used for supercapacitors [5], electrochromic devices [6], photovoltaic devices [7], and sensors [8–12]. However, the applications of these ICPs have been limited by their complex production process and the poor mechanical flexibility resulting from their rigid conjugated backbone

structure. Almost in all applications, conducting polymers are backed up by a substrate either plastic or ceramic owing to its poor mechanical strength [13]. To address these drawbacks, ICPs were also used to form electrically conductive composite fibers with various insulating fibers by *in situ* polymerization [14,15]. Owing to the advantages of the excellent flexibility of the substrate and the electrical conductivity, the electrically conductive composite fibers as flexible smart materials are used in various fields such as heat generators [16], electromagnetic interference shielding [17], strain sensors [18] and flexible or stretchable conductors [19]. In this work, we take the advantage of its reversible redox ability to fabricate and characterize smart textile sensor. ICPs coated fabric is a promising medium for chemical sensing of analytes that are electronically active when encountering the conducting polymers at room temperature, which can cause changes in resistance of the sensing materials [20]. Recently, polyaniline coated fabrics [21–23] and polypyrrole coated fabrics [24] have been utilized as sensing materials to detect pH and various hazardous gas such as ammonia, nitrogen dioxide, carbon monoxide, and propane. Among a wide variety of ICPs, PEDOT is now regarded as one of the most promising conducting polymers for practical applications on account of its high conductivity, good processability, excellent thermal and chemical stability [25].

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However, fabrication of conductive composite fibers based on ICPs suffer from the limitation of the poor adhesion between the conductive coating and the synthetic fiber substrates due to the low surface energy of most conventional polymeric materials. To overcome these problems, effective strategies are required to improve the adhesion between the ICPs and the polymeric substrates. Although *in situ* polymerization or oxidative chemical vapor deposition of PEDOT on nylon 6, PET fabric, and viscose fabric are recently reported [26,27], little research has been explored to improve the adhesion between the PEDOT coating and the polymeric substrates and to develop sensors based on PEDOT coated fabrics.

Herein, we fabricated a flexible composite fiber based on PEDOT as sensor for HCl and NH₃ gas. Electrically conducting layers of PEDOT were tightly coated onto the surface of PP-g-PAA fiber substrate *via in situ* polymerization (illustrated in Scheme 1). Moreover, the performance of the as-prepared PP-g-PAA/PEDOT composite fibers as chemical sensors for detecting HCl and NH₃ gas was evaluated and the sensing mechanism was discussed.

2. Experimental

2.1. Materials

Commercial multifilament PP fibers (monofilament with a diameter of 33 μm) were extracted by acetone for about 24 h to remove additives before use. Acrylic acid (AA), benzophenone (BP), acetone, ethanol, and FeCl₃ were obtained from Sinopharm Chemical Reagent Co. Ltd., China. EDOT monomer and FepTS were purchased from Energy-Chemical Co. Ltd., China. All reagents were of analytical grade and used without any further purification.

2.2. Preparation of PP-g-PAA/PEDOT composite fibers

2.2.1. Photo-induced graft polymerization of AA from PP fiber surfaces

Ma et al. [28] developed a sequential two-step photo-induced living graft polymerization process to decrease unwanted homo-polymerization and graft surface-confined polymer layers, where radical sites were first formed under UV irradiation with a photo-initiator molecule, and then monomers polymerize from these reactive sites. A similar procedure was followed to obtain PP-g-PAA fibers reported here.

A total number of 20 PP fibers were fixed onto a 12 × 1 cm rectangular copper frame using stainless steel clips, and then dip-coated in a 5 vol.% solution of BP in ethanol for 10 min. The specimen was removed from the solution and dried at room temperature for 30 min to evaporate the ethanol. The specimen was then carefully transferred into a quartz test tube and purged with nitrogen. UV irradiation of the fibers was performed for 10 min by a LED-UV processor (UVATA-UPA100 series; UVATA Precision Optoelectronics CO., LTD). The processor has a wavelength of 365 ± 5 nm and an intensity of 450 mW/cm² when the

distance between UV lamp and fiber surface was 50 mm. After irradiation, the substrate was taken out of the quartz test tube, sonicated in ethanol for 10 min to remove any unreacted BP, and then dried at room temperature.

The BP grafted PP fibers were then immersed into 40 mL AA/water solution with different concentrations, the dissolved oxygen in the reaction solution was removed by bubbling nitrogen for 60 min at flow rate of 5 L/min, and then exposed to the UV irradiation (450 mW/cm² at 365 nm) for a specified time. After irradiation, the substrate was sonicated in water for 30 min to remove any unreacted acrylic acid. The non-grafted PAA was removed by soaking the fibers in deionized water for 2 h at 100 °C. Finally, the fibers were dried under vacuum for 24 h for further use.

2.2.2. *In situ* polymerization of PEDOT onto the PP-g-PAA fiber surfaces

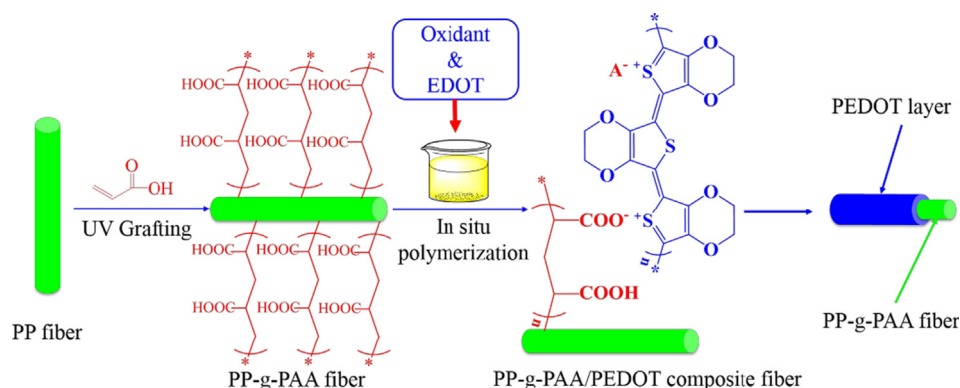
According to literature [29], the oxidative *in situ* polymerization is best carried out with ionic oxidants in a suitable higher oxidation state like iron-III. Normally, to obtain the PEDOT with the high conductivity, the optimum mole ratio of iron-III and EDOT monomer is 2.3:1. Therefore, this mole ratio was also used in this work. The PP-g-PAA fibers were immersed in 5 mL ethanol solution of EDOT and oxidant with varying concentration for 30 min. During this period, the solution was maintained at about 0–5 °C for inhibiting the polymerization during immersion. After that, the PP-g-PAA fibers were removed from the reaction solution and dried under atmospheric conditions (25 °C, relative humidity 60%) for 24 h. EDOT on the surface of the PP-g-PAA fibers polymerized to PEDOT during this drying process. A control specimen was prepared following the same procedure using the neat PP fibers as substrate. The as-prepared PP-g-PAA/PEDOT composite fibers were subsequently rinsed with deionized water and ethanol under ultrasonic treatment for up to 1 h to remove the residual reactants and oligomer, and then dried in vacuum at 40 °C for 24 h.

In this paper, EDOT were polymerized on the surface of PP-g-PAA fibers either with FepTS or FeCl₃, thus the composite fibers were denoted as PP-g-PAA/PEDOT-FepTS and PP-g-PAA/PEDOT-FeCl₃, respectively.

2.3. Characterization

The surface morphologies of pristine PP fibers and as-prepared composite fibers were observed using a JEOL JSM-5600LV.

The chemical structures of pristine PP fibers and as-prepared composite fibers were characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) Spectroscopy. ATR-FTIR spectra were recorded on Nicolet 6700 with variable angle horizontal ATR accessory, on which a 45° rectangle ZnSe crystal was used. The intensities of characteristic peak at wavenumber 1705 cm⁻¹, corresponding to the —C=O stretches in the carboxylic acid groups of PAA, and the peak at wavenumber 1376 cm⁻¹, corresponding to the CH₂ and CH₃ groups of PP were used for analysis. Results are presented as peak area ratio



Scheme 1. Illustration of the fabrication mechanism of the PP-g-PAA/PEDOT composite fibers (where A⁻ is the dopant anion: chloride or p-toluenesulfonate).

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