

Electrospun Nanofibers of Conductive Polymer Composites

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ABSTRACT

Multi-functional micro and nano structures of polypyrroles have received great attention. Polypyrrole has advantages i.e. easy polymerization, high conductivity and good thermal stability; but disadvantages of brittleness and hard processibility can be overcome by the production of their nanocomposites. Conjugated polymer composites with different dielectric properties can be widely used in electronics industry, sensors, batteries, smart windows and to reduce electromagnetic interference.

In this study monodispersed polypyrrole composite nanospheres were synthesized by the presence of surfactants. Pyrrole (Py) was adsorbed onto copolymer particle core dispersions. Surfactants were introducing the electronegative sites onto the surfaces of particles, which the pyrrole cationic ions can be adsorbed via static forces to surfaces, and Py can be oxidatively polymerized to encapsulate the matrix.

Keywords: Nanofiber, electrospinning, polypyrrole

1 INTRODUCTION

In electrospinning process, the solution must gain sufficient charges such that the repulsive forces within the solution are able to overcome the surface tension of the solution. Subsequent stretching or drawing of the electrospinning jet also depends on the ability of the solution to carry charges, in other words the conductivity of solution. Electrospinning technique to produce conductive composites from polypyrrole by in situ polymerized in AN-VAc copolymer matrix was realized recently in our group. The nanofiber diameters and surface morphology show changes according to conductivity of polymeric material [1]. In our previous study, the effect of vinyl acetate content of AN-VAc copolymers on nanofiber diameters has been investigated. Increasing VAc content of copolymers resulted in decreasing nanofiber diameter which is related to low intrinsic viscosity [2].

2 RESULTS AND DISCUSSIONS

2.1 Preparation of Nanoparticles

Polypyrrole/Acrylonitrile-co-Methylacrylate latexes are obtained by emulsion polymerization. Emulsion polymerization of Acrylonitrile (AN) and Methylacrylate (MA) or Vinylacetate (VAc) was performed in aqueous medium with the presence of surfactant Dodecyl Benzen Sulfonic Acid (DBSA) and initiator Potassium Persulfate (KPS) or Ammonium persulfate (APS). After copolymerization, different amounts of pyrrole are added into emulsion latexes and reaction continued with the present initiator. At the end of the polymerization of polypyrrole on the polymer matrix latexes, nanoparticles of PPy/ polymeric matrix are separated and the morphology is followed by Scanning Electron Microscopy (SEM). Nanoparticle size is determined by Particle Size Analyzer (light scattering) and measured by SEM images as well. Nanoparticles were successfully obtained as 80-100 nm diameter depending on the different initial concentration of pyrrole. Then the polypyrrole containing and non-containing nanoparticle latexes are precipitated with methanol and dried in oven.

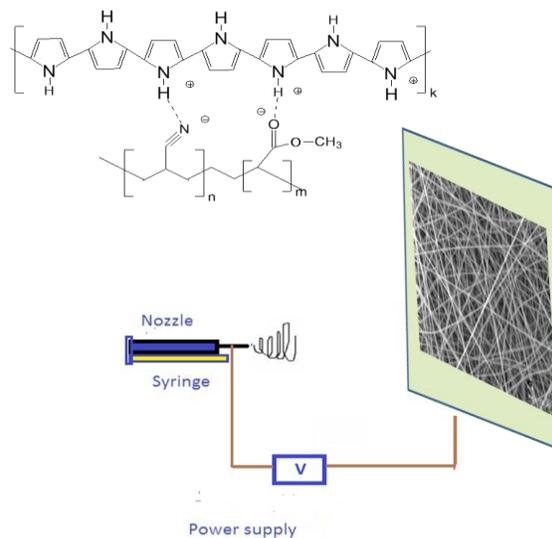


Fig. 1 Scheme of electrospinning details and polymer matrices

Dried composites were dissolved in Dimethyl Formamide (DMF) and electrospun which consist of a power supplier, pump, syringe and metal collector(Fig 1).

The distance between collector and syringe, percentage of solid by weight, applied voltage was not changed by trials. At the end of the electrospinning, nanofibers were obtained in the range of 200-700 nm diameter. Nanofibers are characterized by SEM and Dynamic Mechanic Analyzer. Particles are characterized by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) (Fig 2), NMR, UV-Visible Spectroscopy and Differential Scanning Calorimetry (DSC). UV-Visible Spectroscopy results are correlated with particle sizes and it was observed that the UV-Visible absorption proportional with the particle size of nanoparticles. DSC analysis showed that the glass transition temperature is increased by the increasing pyrrole addition. The thin films were characterized by Dynamic-Mechanic Analyzer (DMA) as obtaining stress-strain curves, and it was seen that the Young's Modulus of films are increased by increasing amounts of pyrrole added.

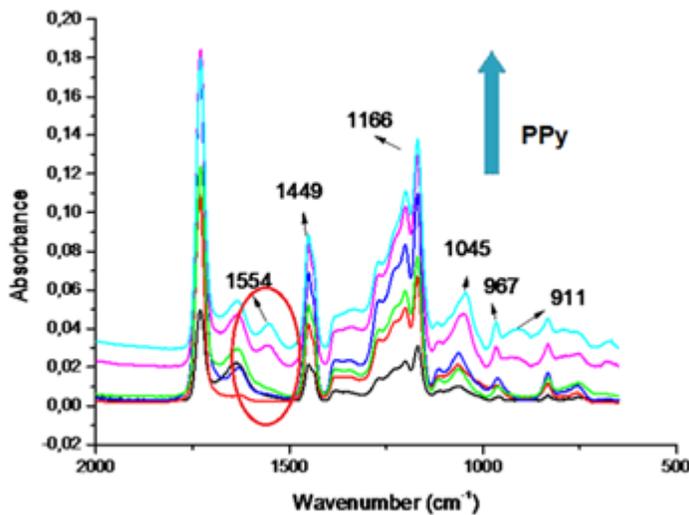
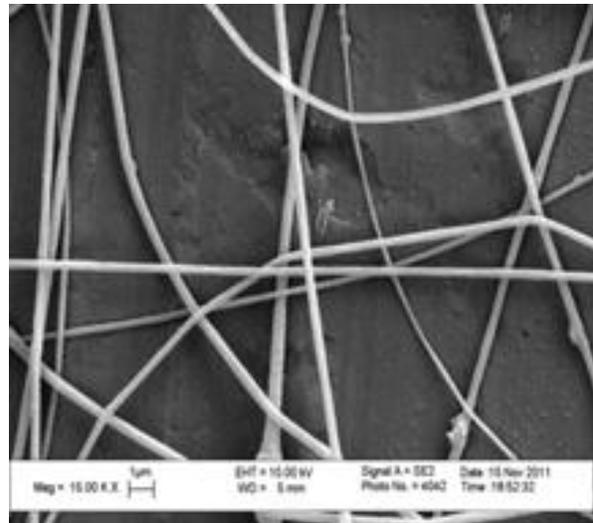


Fig. 2 FTIR-ATR Spectrophotometric results of PPy/Poly(AN-co-MA) with different initial Py content

In-situ oxidative polymerization of monomer of conjugated polymer in solution favored the formation of well defined nanoparticles of nanocomposites with a controlled diameter. Nanofibers of composites were obtained by electrospinning have shown narrow diameter distribution and were characterized in terms of electrical properties by using Electrochemical Impedance Spectroscopic (EIS) measurements.

a



b

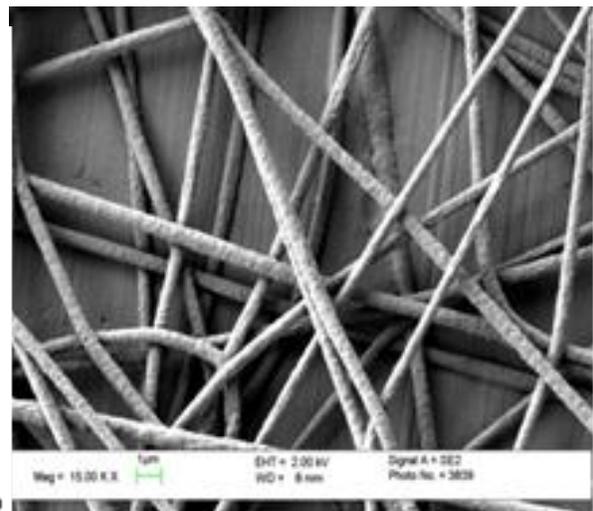


Fig 2 The SEM images of a) 0 µl, b) 100 µl pyrrole added samples for Poly(AN-co-MA)

The relationship between conjugated polymer content, viscosity and fiber diameter were examined and increase in PPy content caused decrease in nanofiber diameter, determined by scanning electron microscopy (SEM) and atomic force spectroscopy (AFM) and increase in AC conductivities were followed by Electrochemical Impedance Study.

Effect of fiber diameter on electrical conductivity of nanofibers indicated that significant increase in conductivity is observed as the fiber diameter decreases. Due to intrinsic fiber conductivity or packing density effect, the fiber diameter reduction was observed.

2.2 Electrospinning of Composites

Each solutions were stirred at room temperature with 400 rpm speed for 2 hours. The electrospinning device contains a syringe pump (NE-500 model, New Era Pump Systems, Inc., USA) and DC power supplier (ES50 model, Gamma High Voltage Inc., USA). The solutions were taken into a 2.5 ml syringe and pumped at a 0.5 ml/h feed rate. Applied voltage was 15 kV. Figure 1 demonstrates the scheme of the setup of electrospinning.

2.3 FTIR-ATR Analysis of nanofibers

The characteristic peaks can be easily seen as well by the FTIR-ATR spectrums of nanoparticle powders in Figure 2 . The peak at 1554 cm^{-1} shows the PPy ring vibration and also peak at 1449 cm^{-1} shows the PPy ring vibration (C=C stretching) too. At the 1166 cm^{-1} C-H in-plane deformation is observed. 1045 cm^{-1} peak refers to N-H in-plane deformation . Peaks at 967 and 911 cm^{-1} are the =C-H out of plane vibration . Figure 2 also indicates that the 1554 cm^{-1} peak is appearing and increasing by the increase of initial pyrrole amount up to $300\text{ }\mu\text{l}$.

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