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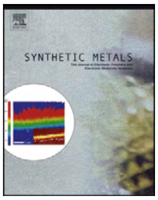

Electrospinning PVDF/PPy/MWCNTs conducting composites

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ABSTRACT

Conducting PVDF/PPy composites (PPy composites) were prepared by using the highly porous electrospun (e-spun) nonwoven web as a host polymer. E-spun nonwoven web was made by electrospinning a solution of PVDF and $CuCl_2{\cdot}2H_2O$ in solvent of *N*,*N*-dimethylacetamide (DMAc). The PPy composites were fabricated by exposing a nonwoven web containing oxidant to pyrrole vapors. Field-emission scanning electron microscopy (FE-SEM) analysis was conducted to show the microstructure of the nonwoven webs and the uniform coating of PPy on the e-spun fiber surfaces of the PPy composite. The information of PPy on the e-spun fibers surface was confirmed by attenuated Fourier-transform infrared spectrometer (ATR FT-IR) and X-ray photoelectron spectroscope (XPS). The thermal property of PPy composites was also investigated by differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). The electrical conductivity of the PPy composites was affected by the fabrication method and oxidant content in the nonwoven web. The electrical conductivity and mechanical strength of the PPy composites were improved when surface-modified multi-walled carbon nanotubes (MWCNTs) were added to the e-spun fibers. Energy-filtered transmission electron microscopy (EF-TEM) results confirmed that the MWCNTs were well arranged and embedded in the e-spun fibers. The observed conductivity of the conducting PPy-MWCNTs composite was 10^{-1} S/cm.

1. Introduction

Electrospinning is a process for fabricating continuous nanoscale fibers with diameters in the sub-micrometer to nanometer range, using a high-voltage power supply [1]. The nonwoven webs that are manufactured from these electrospun (e-spun) fibers have attracted considerable attention because of the outstanding characteristics of these e-spun fibers, such as high porosity, small diameter, excellent pore interconnectivity and high surface-to-volume ratio [2]. Electrospinning is less expensive and simpler than the conventional spinning process. Owing to the useful properties of e-spun fibers, many synthetic and natural polymers, including single and blended polymers, have been electrospun into fibers that can be employed in a variety of applications such as filtration, membrane separation, and thermal insulation and in the manufacture of protective clothing, sensors, conducting devices, wound dressings, and scaffolds for tissue engineering [2,3].

Polypyrrole (PPy) is one of the most extensively studied conducting polymers because it has good environmental stability, low toxicity, and higher conductivity than other conducting polymers; further, it can be synthesized via a facile route [4]. Because of its poor mechanical properties, it is difficult to fabricate PPy into the desirable form [5], but because of the simplicity of the chemically oxidative polymerization of PPy, this shortcoming can be overcome by manufacturing composites of PPy using a host polymer that is mechanically strong. Such a host polymer includes hydrophilic and hydrophobic polymers such as polyethylene oxide (PEO) [6], polyacrylonitrile (PAN) [7], polyamide 6 (PA 6) [8], styrene–ethylene–butylene–styrene (SEBS) [9], polymethyl methacrylate (PMMA) and polystyrene (PS) [10]. PPy fibers can also be fabricated using the melt electrospinning and coaxial electrospinning technique [11,12]. Since pyrrole has high vapor pressure at room temperature, vapor-phase polymerization can be employed to produce PPy. The host polymer is initially treated with an oxidizing agent and then exposed to pyrrole vapors; this results in the formation of a conducting PPy film on the surface of the host polymer [6,8,10,11]. PPy-based composites have been extensively investigated in a variety of applications such as membranes, drug delivery, rechargeable batteries, super-capacitors, sensors, and electromagnetic interference shielding where the performance of the composites is governed by the high surface area and high average pore diameter of the porous host polymer [4].

Carbon nanotubes (CNTs) such as single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multi-walled CNTs (MWCNTs) have attracted considerable attention in recent years because of their excellent electrical and mechanical properties [13]. SWCNTs, DWCNTs, and MWCNTs have been used in the preparation of e-spun polystyrene (PS) fibers [14]. MWCNTs

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are the best dispersed in dimethyl formamide (DMF) compared with other CNTs. Non-beaded e-spun PS fibers were formed by increasing the amount of the MWCNTs. The electrical conductivity of the composite increased with increasing amount of MWCNTs in the e-spun fibers and attained an electrical percolation threshold of around 4% of the MWCNTs in the composite. The mechanical properties of the composite could be enhanced by increasing the amount of MWCNTs [14].

In the present study, conducting PPy composites were fabricated by using a nonwoven web of polyvinylidene fluoride (PVDF) as the host polymer and copper (II) chloride ($CuCl_2{\cdot}2H_2O$) as the oxidant. PVDF was chosen because of its useful properties such as high piezoelectricity, high chemical resistance, good mechanical properties, biocompatibility, and easy electrospinnability. $CuCl_2{\cdot}2H_2O$ was used as an oxidizing agent and also for doping PPy. To obtain a more uniform microstructure of the conducting composite, the oxidant was introduced in the polymer solution, and the resulting mixture was electrospun into a highly porous oxidant-containing nonwoven web. This nonwoven web was then reacted with the pyrrole monomer in a closed vessel. The conducting composite was fabricated via in situ vapor-phase chemical oxidative polymerization. Surface-modified MWCNTs were introduced in the polymer solution to enhance the mechanical properties and electrical conductivity of the composite. The morphology of all the samples was characterized using a field-emission scanning electron microscope (FE-SEM) and energy-filtered transmission electron microscope (EF-TEM). The chemical structure of the surface of e-spun fibers was analyzed by X-ray photoelectron spectroscope (XPS). The electrical conductivity was measured by a four-point method. The mechanical properties and thermal stability were determined by using a tensile tester and a thermal analyzer, respectively.

2. Experimental

2.1. Materials and solution preparation

PVDF (Kynar® 761) was obtained from Arkema Ltd. (Korea). Copper (II) chloride dihydrate (97.5%), ethanol, and *N*,*N*-dimethylacetamide (DMAc) were purchased from Samshun Pure Chemical Co. Ltd. (Korea). Extra-pure pyrrole (99%) was purchased from Aldrich Sigma (USA). Surface-treated MWCNTs were obtained from Nanohub Ltd. (Korea). MWCNTs with a concentration of 1 wt% (mass of CNTs/mass of polymer) were dispersed in DMAc by using an ultrasonifier for 30 min, and then, PVDF was completely dissolved in the CNT solution at 40–50 °C to obtain a polymer concentration of 19 wt%. A known weight of $CuCl_2{\cdot}2H_2O$ (20, 40, or 60%) (mass of oxidant/mass of polymer) was added to the polymer solution. The mixture was stirred for 6 h at 50 °C to obtain a homogeneous solution.

2.2. Electrospinning process

The electrospinning setup consisted of a plastic syringe (5 ml) and a steel needle (i.d. = 0.5 mm). The needle was connected to a high-voltage power supply (Chungpa EMT Co., Korea). The e-spun fibers were deposited on Al sheet covered on a rotating drum. The solvent for the PVDF was DMAc with a concentration 19 wt%. Electrospinning was conducted at a distance of 10 cm between the needle tip to the collector; the flow rate of 0.1 ml/h was controlled by a syringe pump (Kd Scientific series 100, USA); and the high-voltage power supply was 15 kV. All the experiments were carried out at 25 °C and at a relative humidity of 30–50%.

2.3. Vapor-phase polymerization

The nonwoven webs containing the oxidant were cut into samples of dimensions 2 cm × 2 cm and placed into a tightly sealed small chamber filled with pyrrole vapors. The polymerization reaction was carried out at 25 °C for 10 min. The composite samples were washed with copious amounts of ethanol to remove the pyrrole residues from the samples, and then, the samples were dried in vacuum overnight. The PPy content of the composites was weighed using a balance of 4 digits.

2.4. Characterization

The solution viscosity was measured using a viscometer (Brookfield LVDVII, USA). The solution was placed in the viscometer chamber, and the viscometer was immersed in a water jacket. Viscosity measurements were conducted using a cylindrical spindle with a spindle number of 18 in an ambient atmosphere. The solution conductivity was determined in ambient atmosphere by using a conductivity meter (Hanna instruments, HI 2300, Korea).

The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, JSM-T300, JEOL, Japan). Before the observations, the samples were coated with gold by sputter coating. The microstructures of the electrospun nanofibers were determined by an energy-filtered transmission electron microscope (EM912Ω, Carl Zeiss Inc., Switzerland) equipped with a Köhler illumination system.

The chemical compositions of the nonwoven webs were analyzed using an attenuated Fourier-transform infrared spectrometer (ATR FT-IR, JASCO 6100, Japan). The samples were placed on the top of the ATR set and scanned in the range of 400–650 cm^{-1}. A total of 20 scans were collected for signal averaging.

Analysis of the surface of the nonwoven webs was conducted using a MultiLab 2000 XPS (Thermo VG Co., USA).

The thermal properties were analyzed using a differential scanning calorimeter (DSC 2010, TA Instrument, USA). The samples were sealed in Al cassettes under dry conditions. DSC scans were obtained after heating the samples from 25 to 220 °C at a rate of 10 °C/min. All the DSC experiments were conducted under nitrogen environment. Thermal stability measurements were carried out under nitrogen flow by using a thermogravimetric analyzer (TGA, TA Instruments, USA) in the temperature range of 25–700 °C at a heating rate of 20 °C/min.

Tensile tests were performed at a constant humidity (40%) and temperature (25 °C) by using a tensile tester (LR 5K, LLOYD instruments, UK) equipped with a 100-N load cell. The crosshead speed was maintained at 5 mm/min. The sheet resistivity of the samples was measured using the four-point probe method (ATI, CMT-SR1000N, Korea) at room temperature. The electrical conductivity (σ) was calculated by the use of the method suggested by the manufacturer.

3. Results and discussion

PVDF was dissolved in DMAc, and various concentrations of the oxidant were then added. $CuCl_2{\cdot}2H_2O$ was as the oxidizing agent and also as the doping agent. Nonwoven PVDF webs containing various concentrations of the oxidant (0, 20, 40, and 60%) were fabricated under the following processing conditions: 10-cm traveling distance, and 0.1 ml/h volume feed rate; a 15-kV high-voltage power supply was used. PVDF was electrospun from a polymer solution of 19 wt% concentration in DMAc. Nonwoven PVDF webs have beaded e-spun fibers, whose average diameter is 76 nm, shown in Fig. 1(a). Nonwoven webs containing the oxidant have non-beaded e-spun fibers and their average fiber diameter are 86, 156 and 229 nm, respectively, as shown in Fig. 1(b), (c), and (d). The fibers diameters of e-spun PVDF containing oxidants are bigger than these of e-spun PVDF fibers. Moreover, the fiber diameter increases with increasing oxidant content in the