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Electrospun PANI-PMMA and PANI-PMMA-AgNO$_3$ Composite Nanofibers

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ABSTRACT: In this paper we report upon the preparation and characterization of electrospun nanofibers of doped polyaniline (PANI)/poly(methyl methacrylate) PANI-PMMA/AgNO$_3$ by electrospinning technique. At first, Doped polyaniline (PANI) was obtained by the polymerization of aniline using chemical oxidative polymerization in the presence of ammonium peroxydisulfate (APS). The doped PANI was dedoped by ammonia solution. Then, the electrospinning method was applied on the solutions involving PANI-PMMA, PANI-PMMA-AgNO$_3$. The as-prepared PANI-PMMA and PANI-PMMA-AgNO$_3$ composite nanofibers were investigated for structural characterizations by means of SEM, FTIR and UV-VIS. SEM technique was used to investigate the morphology of the accumulated fibers or particles on the Al surface collector. SEM revealed the nanofibers with the diameter Micro to nanofibers formed a non-woven material with highly porous and agglomerated structure. The presence of Ag in the case of Ag containing composite nanofibers was confirmed by EDAX.

Keywords: *Composites, Electrospinning, Nanofiber, Polyaniline, Poly(methyl methacrylate), SEM*

INTRODUCTION

Electrospinning is an interesting process for producing non-woven fibers with the average diameters in the range of micro-to nanometers while traditional melts spun fibers range in a diameter of about 5 to 200 μm [1,2]. Electrospinning is a unique, simple, low-cost and effective approach not only for the preparation of polymer nanofibers [3] but also for the ceramic oxide materials [4] and the composite nanofibers involving metals and metal oxides [5-12]. In this process, continuous filaments drown from a polymer solution or a melt through a spinneret by high electrostatic forces to deposit it on a grounded-metal collective screen [13]. Electrospinning of a variety of synthetic as well as natural polymer fibers for different applications have also been reported in the literature [14]. A search in the literature indicated that different polymers such as chitosan, dextral, polyacrylonitrile, polyvinyl alcohol, poly(methyl methacrylate), polystyrene, polycaprolactone, poly(vinyl pyrrolidone), biodegradable poly(L-lactide), nylon 6 and cellulose acetate [2-12] do elec-

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trospinning as well as different conducting polymers.

Polyaniline (PANI) is one of the most conductive polymers that have been used in many electronic, optical and electrochemical applications, due to its low cost, good environmental stability, redox reversibility, and electrical conductivity [15,16]. However, processing PANI into nanofibers by using the electrospinning is a challenge, mainly due to its rigid backbone that is related to its high degree of aromaticity making the elastic properties of the solution insufficient for electrospinning [17,18]. In this regard, non-conductive hosting polymers such as poly(methyl methacrylate) (PMMA), is blended to assist polyaniline to form composite fibers [19,20]. Consequently, the nanofibers of PANI have garnered much interest because of their properties as candidates for chemical sensors [21], light-emitting and electronic devices [22]. Yet, some disadvantages such as poor mechanical properties do exist, although combining PANI with carbon materials reinforces its stability and enhances some of its properties, such as capacitance [23,24]. A literature survey indicates that limited research studies on the preparation of PANI and PANI composite fibers have been reported [25]. The objectives of this study were to identify and detail the primary materials and process factors necessary to produce PMMA-PANI and PMMA-PANI-$AgNO_3$ composite nanofibers using the electrospinning process. In this work, we have chosen PMMA as a known soluble polymer in the preparation of electrospun fibers to prepare PANI containing fibers. Accordingly, we wish to describe the preparation of PMMA-PANI and PMMA-PANI-$AgNO_3$ composite nanofibers via electrospinning method. Electrospinning has attracted a lot of interest as a technique that is very simple and inexpensive in the production of micro to nanofibers. It provides a potential way to fabricate infinite, continuous nanofibers.

EXPERIMENTAL

Materials

1-metyl-2-pyrrolidinone, NMP (99%), chloroform 99%, dimethyl sulfoxide 99%, silver nitrate, poly metyl metacrylate (PMMA) with an average molecular weight (Mw) of about 50000-80000 g/mol were purchased from Merck.

Instrumentation

IR and UV-Vis spectra were recorded on Perkin Elmer Gx and UV (KON) model BIO-TEK 922, respectively. To characterize the morphology of the electrospun nanofibers and nanoparticles, the samples were sputter coated with gold and examined at different accelerating voltages and Scanning Electron Microscope (SEM) images were obtained by a Philips XL-30.

Electrospinnig

The electrospinning set-up consisted of a 20 mL syringe and an 18-gauge stainless steel needle that were positioned horizontally on a clamp. The metal electrode and the collector were made of copper and aluminum, respectively. Generally, viscose solutions were prepared by heating and stirring the appropriate amount of dried dedoped PANI and additives, if needed, in solvents. The solutions were transferred into hypodermic syringes. Then, appropriate voltages were applied between two electrodes, and the webs of fibers accumulated on the surface of the aluminum foil, which was used as the collector.

Preparation of PMMA fibers coated with PANI

Initially, Doped polyaniline (PANI) was obtained by the polymerization of aniline using chemical oxidative polymerization in the presence of ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$. The doped PANI was dedoped by ammonia solution that described in the literature [14]. Then, 0.50 g PMMA was dissolved in 2 ml chloroform with stirring for 1 h at 50 °C. Then, the viscose solution was transferred to a syringe and the electrospinning was performed at 14 kV with 11 cm distance between two electrodes. In the last step, some of PMMA fibers were placed in dedoped PANI solution in DMSO. After a few minute they were brought out and dried. Putting PMMA fibers in PANI solution and bringing them out were performed several times.

Preparation of PANI-PMMA fibers

A: 0.50 g PMMA was dissolved in 2 ml chloroform with stirring at 50 °C until viscose solution was achieved. In another container, 0.01 g dedoped PANI was dissolved in 1 ml NMP with stirring at 50 °C until thoroughly was dissolved. Then PMMA solution was added to the PANI solution. The obtained mixture was continuously stirred until a homogenous solution was obtained. The resulting viscose solution was transferred to a syringe and the electrospinning was performed at 16-17 kV with 11 cm distance between two electrodes.

B: 0.50 g PMMA was dissolved in 1ml NMP with stirring at 50 °C until viscose solution was achieved. In another container, 0.01 g dedoped PANI was dissolved in 1ml NMP with stirring at 50 °C until thoroughly was dissolved. Then PMMA solution was added to the PANI solution. The obtained mixture was continuously stirred for 10 min until a homogenous solution was obtained. The resulting viscose solution was transferred to a syringe and the electrospinning was performed at 16-17 kV with 11 cm distance between two electrodes.

Preparation of PANI-PMMA-AgNO$_3$ fibers

Initially, 0.0132 g silver nitrate was dissolved in 2 ml NMP with stirring until completely dissolved. In another container, 0.60 g PMMA was dissolved in 2 ml NMP with stirring at 50 °C until thoroughly dissolved. Then, 0.2 ml of the former solution was added to the later and stirred to get a viscose solution containing silver nitrate and PMMA. First, the obtained mixture was colorless but after adding silver nitrate solution the color was become orange. The last step, 0.01 g dedoped PANI was dissolved in 1 ml NMP with stirring for 1 h at 50 °C and was added to the previous solution. The mixture was stirred until a homogenous grey solution was achieved. The resulting viscose solution was transferred to a syringe and the electrospinning was performed at 18 kV with a 12 cm distance between two electrodes.

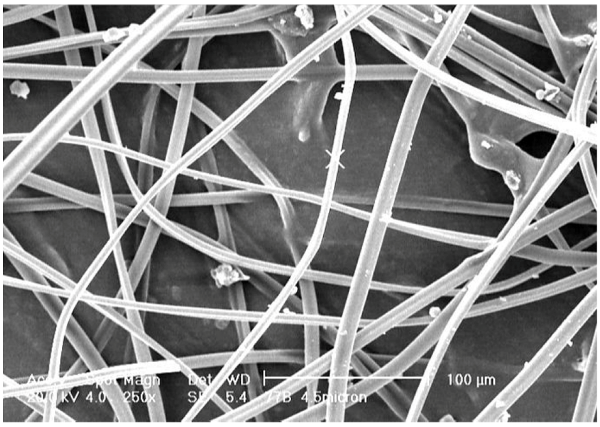


Fig. 1. SEM image of electrospun PMMA fibers in chloroform solution (The scale bar is 100 µm).

RESULTS AND DISCUSION

PMMA fibers coated with PANI

First, the electrospinning of solution containing PMMA in chloroform solvent was followed. A large diameter fiber was formed that was easily visible. Fig. (1) shows the SEM image of PMMA fibers. These fibers are elongated and without knots and their diameter size distribution is in the range of 4.5 to 18 mµ.

The last step, in order to create fibers with polyaniline coating, electrospun PMMA fibers were placed in solution containing PANI. Fig. (2) shows the SEM image of PMMA fibers with PANI coating. The di-

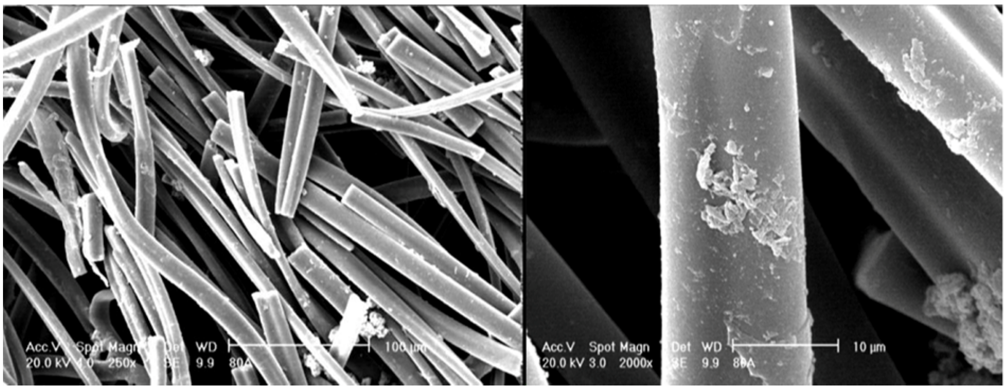
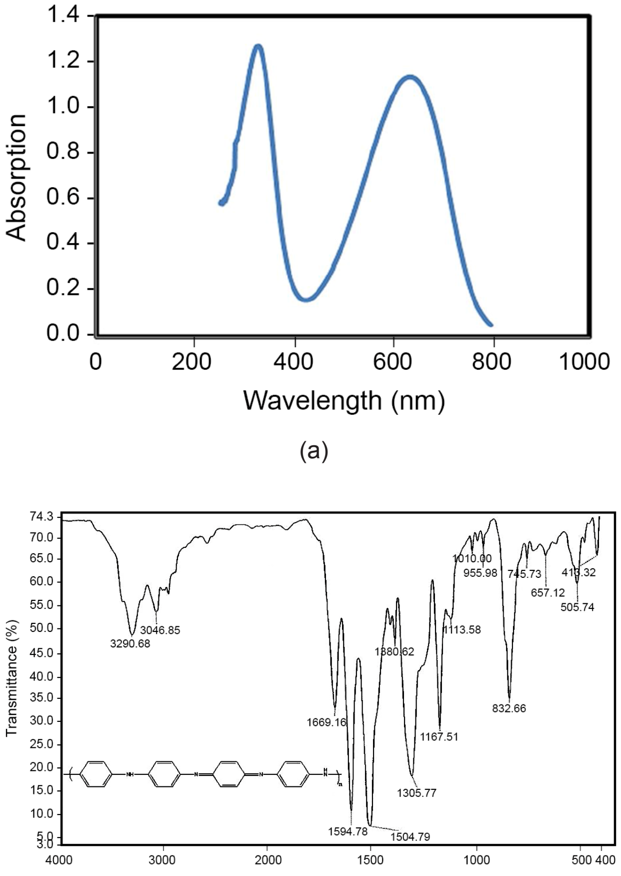


Fig. 2. SEM image of electrospun PMMA fibers with PANI layer (The scale bar is 100 µm).

ameter of the fibers is estimated in the same range as the diameter of the uncoated fibers and it can be seen that the PMMA fibers are broken and reduced to shorter fibers by being placed in a polyaniline solution in DMSO. The surface of the fibers contains particles that can indicate polyaniline

Electrospun PANI-PMMA

Aniline was polymerized using chemical oxidative polymerization in the presence of ammonium peroxydisulfate [$(NH_4)_2S_2O_8$]. Then, doped PANI was dedoped by ammonia solution. The FT-IR spectrum of dedoped PANI is show in Fig. 3 the characteristic peak around 3290 cm^{-1} arise due to the stretching vibrations of N-H, the peaks as about 1594 and 1504 cm^{-1} are absorption of quinone and benzene rings of PANI. The peak at 1305 cm^{-1} is related to the CN stretching modes, the peak at 832 cm^{-1} is attributable to the out-of-plane bending of C-H [12-14]. UV-Vis spectrum of dedoped PANI solution in NMP is shows two absorption peaks at 320 and 620 nm, which are due to the π–π* transition of benzoid rings and the excitation absorption of quinoid rings, respectively (Fig. 3) [6].



(a)

(b)

Fig. 3. UV-Vis (a) and FT-IR (b) spectra of dedoped PANI solution in NMP.

The electrospinning system was first operated on a 1% dedoped PANI solution in NMP solvent at room temperature. Electrospray took place, resulting in the spraying of droplets. As the jet accelerated towards the cathode and the solvent evaporated, PANI particles were deposited on the collector cathode. The morphology of the PANI particles covered on the Al foil is presented in the SEM image (Fig. 4). As shown, some micro to nano particles in accompany with very limited number of nanofibers. Further efforts by modification of parameters such as needle- Al foil distance, voltage and concentration failed to result in the preparation of fibers. This might be due to the solubility limitation of PANI in NMP and low viscosity of the prepared solution. To remove the problem and improve the processability of PANI, an auxiliary soluble polymer was considered to be added to improve the viscosity. A literature survey as well as our experience on the preparation of PMMA electrospun nanofiber directed us to choose PMMA as the second component. So, electrospinning was tried on a solution of a mixture of PANI and PMMA.

A: To prepare such solution, PMMA and PANI polymers were separately dissolved in choloroform and NMP solvents and then mixed together. The electrospinning process was applied and fine electrospun fibers were successfully collected on the Al foil. The morphology of PMMA-PANI composite nonofibers

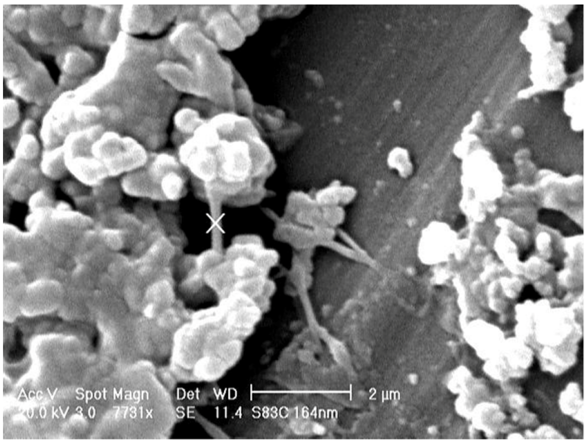


Fig. 4. SEM image of PANI particles coated on the Al foil (The scale bar is 2 μm).

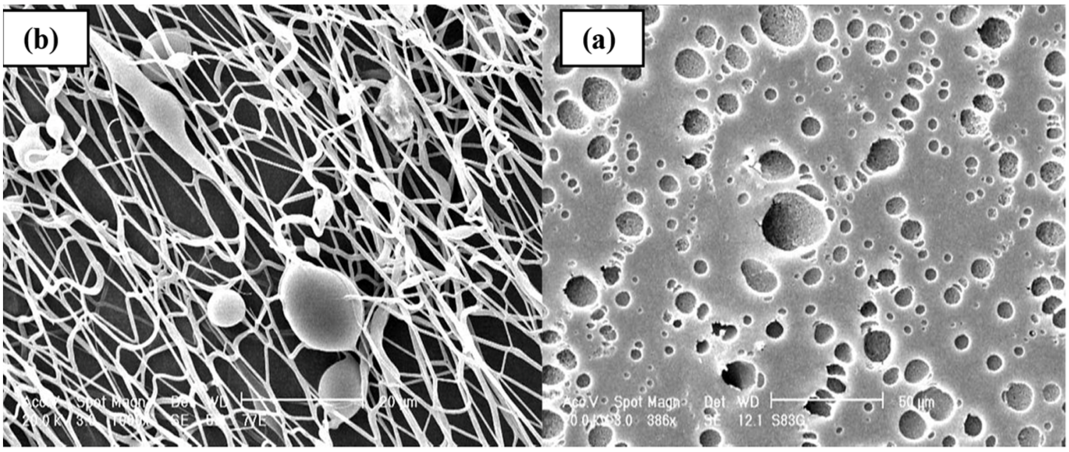


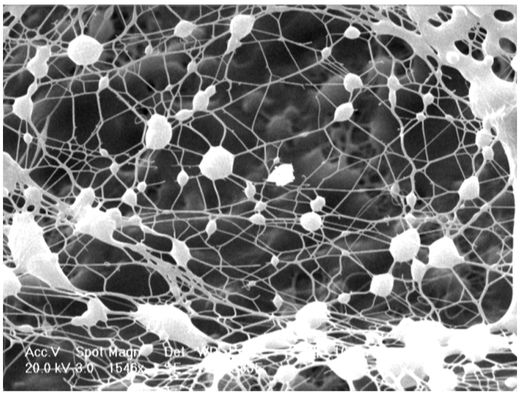
Figure 5. SEM image of PMMA-PANI composite nanofibers in $CHCl_3/H_2O$ solvent (a) and in NMP solvent (b).

was investigated by SEM. The SEM image shown in Fig. 5 presents smooth nanofibers with several millimeters length and average diameter in the range of about 300-400 nm. The fibers contain some large size beads, indicating the resistance of the jet to extensional flow.

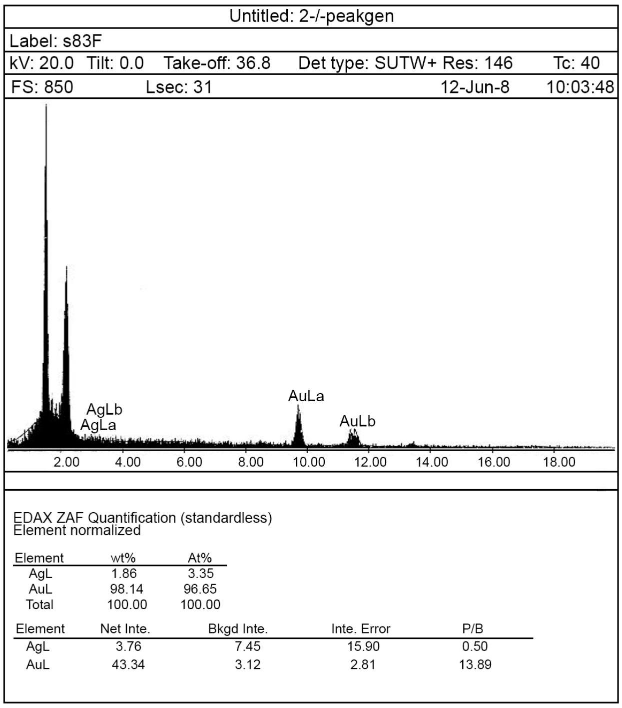
B: Electrospinning was performed on a solution of PMMA and PANI in NMP. The corresponding SEM image is presented in Fig. 6. The SEM image showed the PANI-PMMA composite coating on the aluminum collector plate, which is seen as particles with holes of 1 to 3 µm. Nanometer pores were also seen inside these cavities.

Electrospun PVA-PANI-AgNO$_3$

Addition of $AgNO_3$ salt to the mixture of PMMA-PANI was performed to investigate the effect of silver salt on the electrospinning process and the quality and morphology of the collected composite on the Al foil. To prepare PMMA-PANI-$AgNO_3$ solution, PMMA polymer and PANI/$AgNO_3$ mixture were separately dissolved in chloroform and NMP solvents and then mixed together. The electrospinning of solution containing PMMA-PANI-$AgNO_3$ was followed. SEM image of PVA-PANI-$AgNO_3$ composite fibers, shown in Fig. 6 (a), the fibers are in the form of a spider's nest and have large knots that are connected and networked through these knots. The fiber diameter is estimated in the range of 30 to 60 nm and the fiber diameter distribution is low. EDAX analysis of PMMA-PANI-$AgNO_3$ composite nanofibers shown in Fig. 6 (b) demonstrates the presents of Ag in the fibers.



(a)



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EDAX ZAF Quantification (standardless)
Element normalized

Element	wt%	At%
AgL	1.86	3.35
AuL	98.14	96.65
Total	100.00	100.00

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
AgL	3.76	7.45	15.90	0.50
AuL	43.34	3.12	2.81	13.89

(b)

Fig. 6. SEM image (a) and EDAX (b) of the PMMA-PANI-$AgNO_3$ composite nanofibers (The scale bar is 20 µm).

Quantitative analysis reported by EDAX is in agreement with the original Ag weight used in the preparation of composite.

CONCLUSIONS

Electrospinning of 0.036 M solution of PANI in NMP under the experienced conditions results in the formation of micro to nano particles on the Al collector foil. This method might be used to the production of PANI film on the surface of some targets using a rotating collector. Modification of the PANI solution composition by the addition of PMMA as an auxiliary polymer altered the electrospinning behavior and resulted in the formation of fine composite electrospun fibers. When the composition is further modified by the addition of $AgNO_3$, three-component electrospun composite fibers is achieved. Modification of parameters such as solvent, auxiliary polymer, weight ratio of three components and electrospinning conditions are under investigation to increase the contributions of PANI and silver in the composite nanofibers because of the fact that the main goal is the preparation of composite nanofibers that could potentially be doped to increase the conductivity. Also, the possible role of Ag+ as doping agent and its influence on the conductivity of the final composite fibers are the issues of interest that are being followed and will be reported.

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