

Preparation of Conducting Polyaniline/Nylon 6 Blend Fibre by Wet Spinning Technique

Abdolreza Mirmohseni^{1*}, Dariush Salari², and Reza Nabavi²

(1) Polymer Research Technology Laboratory; (2) Petroleum Research Technology Laboratory, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz-5166616471, I.R. Iran

Received 20 October 2005; accepted 21 February 2006

ABSTRACT

Conducting polymers have been widely investigated for both academic and industrial purposes over two decades. Polyaniline (PANI), a member of the intrinsically conducting polymer family was blended with Nylon 6 in concentrated formic acid. Conducting fibres were spun from the blend solution by wet spinning method. In this process the solvent is replaced by non-solvent and consequently the polymer is precipitated. Qualitative studies were carried out on the effect of coagulation bath. Coagulation bath containing 7.5% w/w Li_2SO_4 has improved mechanical properties of the fibres. The electrical resistance of fibres containing 5-25% w/w of PANI, varies between 0.665 to 0.015 $\text{M}\Omega\cdot\text{cm}^{-1}$. It was found that the electrical resistance of fibres depends on their moisture content. Cyclic voltammetric studies were carried out in -350 to 1000 mV vs. Ag/AgCl. These studies showed that PANI/nylon 6 fibres were electroactive. Further more fibre containing 25% w/w of PANI has high electroactivity stability.

Key Words:

polyaniline;
Nylon-6;
conducting fibres;
blend fibre;
wet spinning.

INTRODUCTION

Conducting polymers have been the subject of much interest, not only from fundamental scientific interest [1-2] but also from practical applications such as anticorrosive properties [3], gas sensors [4] and membrane separation [5]. Among the many

potentials applications of these polymers, there is a growing interest in developing conducting fibres, artificial muscles and actuators.

PANI, because of its low cost and environmental stability has attracted much research interests for

(*)To whom correspondence to be addressed.
E-mail: mirmohseni@tabrizu.ac.ir

various applications including conducting fibres [6-8]. PANI can be dissolved in solvents such as *N*-methyl-2-pyrrolidone (NMP), *m*-cresol and concentrated sulphuric acid thus it could be spun into conducting fibres [9-12]. Grafting and coating of the conducting polymers on insulating fibres such as polyethylene terephthalate [13-14], and nylon [15], have been also reported. The conducting fibres were also prepared by blending PANI with polypropylene [16], polyamide-11 [17], polyethylene oxide [18], and polyacrylonitrile-co-poly-methylacrylate [19]. Wet spinning process is a common method for production of conducting fibres [17,20]. A polymer solution is extruded as a filament into a coagulation bath through which it is pulled by a take up roll.

PANI is soluble in formic acid. Similarly nylon 6 can be dissolved in formic acid. A blend of PANI with nylon 6 can be therefore prepared by solution processing method. The prepared blend can be used to prepare PANI/nylon 6 fibres using wet spinning method. The results would introduce new electronic fibres. Effect of coagulation bath on mechanical properties of fibre is aimed to investigate. The characterization of the blend fibre is also investigated by a four-probe technique and cyclic voltammetry.

EXPERIMENTAL

Reagent and Materials

Analytical reagent grade chemicals were used throughout, unless otherwise stated. Ammonium persulphate, aniline, hydrochloric acid, concentrated sulphuric acid 98% w/w, concentrated formic acid (98% w/w), para-toluene sulphonic acid and lithium sulphate were all purchased from Merck Chemicals. Nylon 6 ($M_w = 1.86 \times 10^4$ g/mol) was purchased from Aliaf Co. (Tehran-Iran).

Instrumentation

A galvanostate/potentiostat model Wenking TG97 from Bank (Germany) was used for electrical resistance measurements. Cyclic voltammetric studies were carried out by a cyclic voltammeter at Sahand Pardazan, Iran.

Synthesis of Emeraldine Base Form of PANI

PANI Powder in Emeraldine base form was prepared by chemical oxidative polymerization method as previously described [21].

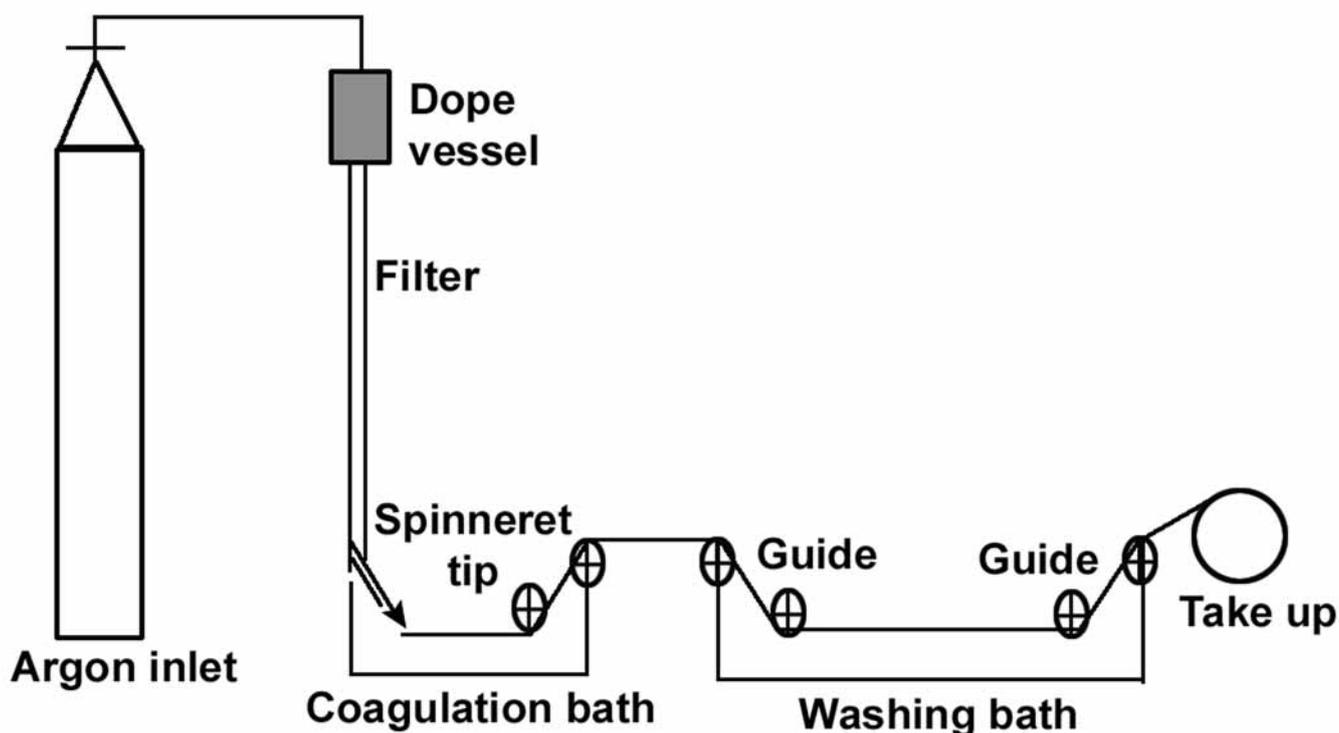


Figure 1. Schematic diagram for spinning fibres.

Preparation of Conductive PANI/Nylon 6 Blend Fibres

For the preparation of spinning dopes, PANI was dissolved in both concentrated sulphuric and formic acids while stirring at room temperature in a flask until a homogeneous solution was produced.

Nylon 6 was dissolved in both concentrated sulphuric and formic acid. Spinning dopes were then prepared by mixing the solutions with a vigorous stirring at room temperature for 24 h. Fibre spinning was conducted on a wet spinning machine as designed (Figure 1). The pressure of argon gas was varied to control the spinning rate.

The spinning dopes were spun into coagulation bath at room temperature (23°C). The as-spun fibres were passed through washing bath to remove residual solvent and then were taken up.

Characterization of Blended Fibres

To measure electrical resistance of the fibres, the polymer fibres were dipped into aqueous (0.5 M) paratoluene sulphonic acid for 24 h and taken out to wash by distillation water. It was then dried at room temperature. The electrical resistance was measured by using the four-probe technique ASTM (D-4496-87) (Figure 2). In this technique, in the first stage, a sample fibre (length 8 cm, thickness about 0.1 mm) was placed between outer electrodes, and the second part of cell was then placed on fibre sample to complete conduction. In the second stage, galvanostat was set on 0.1 microampere and the electrical resistance measurement was carried out by ohmmeter, (Figure 2). All cyclic

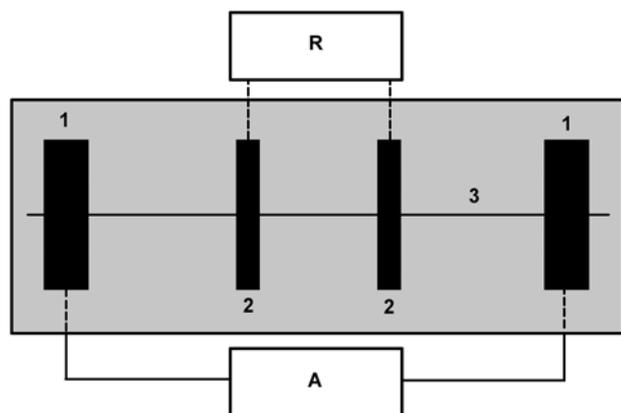


Figure 2. Schematic diagram for four-probe cell. (1) outer electrodes, (2) inner electrodes, (3) fibre sample, (A), galvanostat and (R) ohmmeter.

voltametric studies were performed in a single compartment, three electrodes cell under N_2 atmosphere. Fibre of 2 cm length was placed into platinum mesh, and it was bended to ensure the complete contact of fibre to electrode. This electrode was used as a working electrode. Counter electrode was a platinum mesh and the reference electrode was an Ag/AgCl electrode.

RESULTS AND DISCUSSION

Qualitative studies were carried out on the spinnability of spinning dopes with both concentrated sulphuric and formic acid solvents by pulling filaments from the solution and observing their stability. At the same concentrations, the spinning dopes, which were made by concentrated sulphuric acid, were viscous and the coagulation rate of filament was slower than the spinning dopes, made by concentrated formic acid. The concentrated formic acid was, therefore, nominated for preparation of spinning dopes.

It was found that using distilled water as coagulation bath; fibres with weak mechanical properties were formed. Coagulation bath containing 7.5% w/w of Li_2SO_4 is usually used for wet spinning of nylon 6 [22]. Using the same idea, the coagulation bath was used for spinning of blended fibres. The fibres could be spun continuously and the mechanical properties of the

Table 1. The electrical resistance ($M\Omega \cdot cm^{-1}$) of fibres containing various content PANI as function of time at room temperature. All the measurements were carried out using 0.1 microampere current.

PANI (%) \ Time (h)	5	11.5	14.2	20	25
2	0.665	0.412	0.353	0.053	0.015
4	1.09	0.712	0.493	0.076	0.048
14	1.32	1.07	0.715	0.105	0.064
24	2.26	1.34	0.825	0.124	0.111
36	N.D	2.11	0.865	0.188	0.127
48	N.D	2.41	0.915	0.247	0.213
72	N.D	N.D	1.48	0.310	0.255
180	N.D	N.D	N.D	0.570	0.372

N.D: Not determined.

fibres were improved. It is probably due to the diffusion of lithium ions in nylon 6 structure and interaction with peptide groups that prevents the formation of hydrogen bonding [22]. Fibres containing further than 25% w/w of PANI could not be prepared because of poor mechanical properties.

The electrical resistances of fibres containing various concentrations of PANI were measured (Figure 3). Increasing the PANI concentration in the blend, the electrical resistance of fibre was decreased. The changes of electrical resistances of the fibres containing various concentrations of PANI were measured as a function of time (Table 1). It was found that the electrical resistance increased as a function of time. It is probably due to moisture loss. Because it is known that residual moisture can increase the emeraldine salt conductivity significantly [23-24].

Cyclic voltammogram of the fibre containing 25% w/w of PANI was recorded (Figure 4). It is well known that polyaniline undergoes two separate oxidation and reduction processes. The well defined oxidation-reduction responses indicate that the fibre is electroactive. The first response (A and A') is due to oxidation-reduction of leucoemeraldine to emeraldine and vice-versa. The second response (B, B') is due to oxidation of emeraldine to pernigraniline (fully oxidized form) and vice-versa [25]. The fibre has high electroactivity stability, in which the conformity of peaks was saved even after fifty-five scans (Figure 5). PANI will be oriented

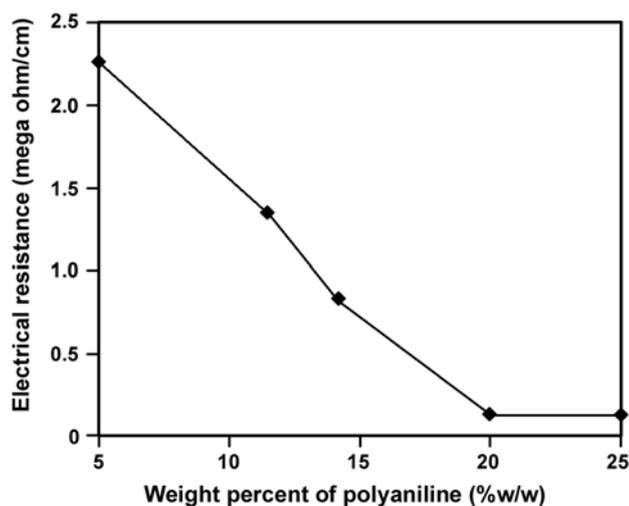


Figure 3. Variation of electrical resistance with increasing of PANI contents in blend. Data was plotted for fibres, which was placed 24 h at room temperature.

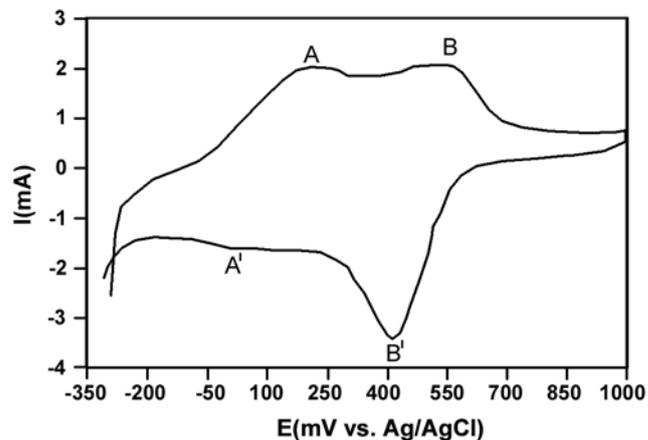


Figure 4. Cyclic voltammogram of fibre containing 25 % w/w of PANI. Scan rate 50 mV/s, electrolyte 0.1 M HCl.

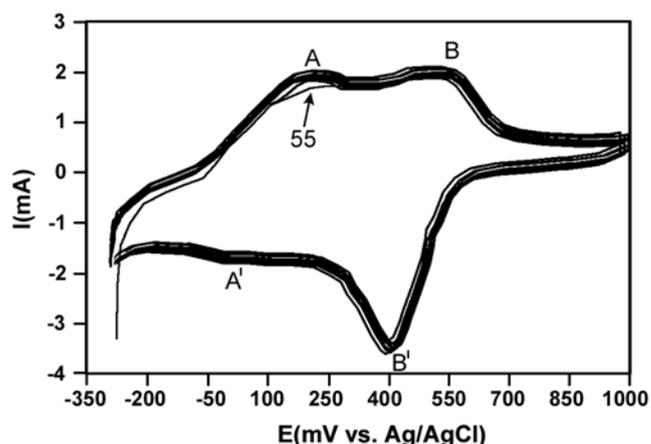


Figure 5. Cyclic voltammograms of fibres containing 25% w/w of PANI in various scans: 1, 5, 10, 15, 20, 30, 40, 50, 55. Scan rates 50 mV/s, electrolyte 0.1 M HCl.

probably along fibre-axial in the wet spinning process.

CONCLUSION

Conducting fibres of PANI/nylon 6 blend was prepared by wet spinning technique from concentrated formic acid. It was found that coagulation rate of filament in formic acid was faster than concentrated sulphuric acid. Coagulation bath with 7.5% w/w of Li_2SO_4 provided a good precipitation conditions with an improved mechanical properties of the fibres. The electrical resistance of the fibres decreased from insulating state to the conducting state when the PANI contents of blends increased.

The moisture content of fibres influences the electrical resistance and it is increased by losing the moisture. Cyclic voltammetric studies revealed that the fibres have a good electro-activity and the PANI chains in the fibres have obtained regular arranging by wet spinning method.

ACKNOWLEDGEMENTS

We are most grateful the continuing financial support of this research project by Tabriz University.

REFERENCES

- Zotti G., Cattarin S., Comisso N., Cyclic potential sweep electropolymerization of aniline: The role of anions in the polymerization mechanism, *J. Electroanal. Chem.*, **239**, 387-396, 1988.
- Dalmolin C., Canobre S.C., Biaggio S.R., Rocha-Filho R.C., Bocchi N., Electropolymerization of polyaniline on high surface area carbon substrates, *J. Electroanal. Chem.*, **578**, 9-15, 2005.
- Mirmohseni A., Oladegaragoze A., Anti-corrosive properties of polyaniline coating on iron, *Synth. Met.*, **114**, 105-108, 2000.
- Mirmohseni A., Oladegaragoze A., Determination of chlorinated aliphatic hydrocarbons in air using a polymer coated quartz crystal microbalance sensor, *Sens. Actuators, B, Chem.*, **102**, 261-270, 2004.
- Mirmohseni A., Price E., Electrochemically controlled transport of small charged organic molecules across conducting polymer membrans, *J. Member. Sci.*, **100**, 239-248, 1995.
- Hsu C.H., Electrically conductive fibres, *US Patent No. 5788897*, 1998.
- Hsu C.H., Method for preparing a high strength, high modulus electrically conductive fibre, *US Patent No. 5882566*, 1999.
- Nouri M., Haghighatkish H., Entezami A.A., Edrisi E., Conductivity of textile fibres treated with Aniline, *Iran. Polym. J.*, **9**, 49-58, 2000.
- Wang H.L., Romero R.J., Mattes B.R., Zhu Y., Winokur M.J., Effect of processing conditions on the properties of high molecular weight conductive polyaniline fibre, *J. Polym. Sci. Part B: Polym. Phys.*, **38**, 194-204, 2000.
- Monkman A.P., Adas P., Structural characterization of polyaniline free standing films, *Synth. Met.*, **41**, 891-896, 1991.
- Yang C.Y., Coa Y., Smith P., Heeger A.J., Morphology of conductive, solution-processed blends of polyaniline and poly(methyl methacrylate), *Synth. Met.*, **53**, 293-301, 1993.
- De Paoli Maro-A., Duek E.R., Rodrigues M.A., Poly(aniline)/cellulose acetate composites: Conductivity and electrochromic properties, *Synth. Met.*, **41**, 973-978, 1992.
- Kim M.S., Kim H.K., Byun S.W., Jeong S.H., Hong Y.K., Joo J.S., Song K.T., Kim J.K., Lee C.J., Lee J.Y., PET Fabric/polypyrrole composite with high electrical conductivity for EMI shielding, *Synth. Met.*, **126**, 233-239, 2002.
- Anbarasan R., Vasudevan T., Gopalan A., Chemical grafting of poly(aniline) and poly(*o*-toluidine) onto PET fibre-A comparative study, *Eur. Polym. J.*, **36**, 1725-1733, 2000.
- Trivedi D.C., Dahawan S.K., Shielding of electromagnetic interference using polyaniline, *Synth. Met.*, **59**, 267-272, 1993.
- Passainiemi P., Laakso J., Osterholm H., Pohl M., TEM and WAXS characterization of polyaniline/PP fibres, *Synth. Met.*, **84**, 775-776, 1997.
- Zhang Q., Jin H., Wang X., Jing X., Morphology of conductive blend fibres of polyaniline and polyamide-11, *Synth. Met.*, **123**, 481-485, 2001.
- Norris I.D., Shaker M.M., Ko F.K., Macdiarmid A.G., Electrostatic fabrication of ultrafine conducting fibres: polyaniline/polyethylene oxide blends, *Synth. Met.*, **114**, 109-114, 2000.
- Jianming J., Wei P., Shenglin Y., Guang L., Electrically conductive PANI-DBSA/co-PAN composite fibres prepared by wet spinning, *Synth. Met.*, **149**, 181-186, 2005.
- Pomfret S.J., Adams P.N., Comfort N.P., Monkman A.P., Electrical and mechanical properties of polyaniline fibres produced by a one-step wet spinning process, *Polymer*, **41**, 2265-2269, 2000.
- Boara G., Sparpaglione M., Synthesis of polyaniline with high electrical conductivity, *Synth. Met.*, **72**, 135-140, 1995.
- Karimi M., Haghighatkish M., Some properties of polyamide-6 fibres produced by wet spinning, *J. Polym. Sci & Tech (Persian)*, **2**, 81-93, 2002.
- Angelopoulos M., Ray A., Macdiarmid A.G., Polyaniline: Processability from aqueous solutions and effect of water vapor on conductivity, *Synth. Met.*, **21**, 21-30, 1987.
- Javadi H.H.S., Angelopoulos M., Macdiarmid A.G., Con-

duction mechanism of polyaniline: Effect of moisture, *Synth. Met.*, **26**, 1-8, 1988.

25. Mirmohseni A., Wallace G.G., Preparation and characterization of processable electroactive polyaniline-polyvinyl alcohol composite, *Polymer*, **44**, 3523-3528, 2003.