Synthetic Metals 202 (2015) 49–62

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

In-situ deposition of polyaniline and polypyrrole electroconductive layers on textile surfaces by the reactive ink-jet printing technique

Z. Stempien [a,*], T. Rybicki [b], E. Rybicki [c], M. Kozanecki [c], M.I. Szynkowska [d]

[a] Institute of Textile Architecture, Lodz University of Technology, 116 Zeromskiego Street, 90-924 Lodz, Poland
[b] Institute of Automatic Control, Lodz University of Technology, 18/22 Stefanowskiego Street, 90-924 Lodz, Poland
[c] Department of Molecular Physics, Lodz University of Technology, 116 Zeromskiego Street, 90-924 Lodz, Poland
[d] Institute of General and Ecological Chemistry, Lodz University of Technology, 116 Zeromskiego Street, 90-924 Lodz, Poland

ARTICLE INFO

Article history:
Received 10 September 2014
Received in revised form 17 January 2015
Accepted 23 January 2015
Available online 6 February 2015

Keywords:
Polyaniline (PANI)
Polypyrrole (PPy)
Textiles
Reactive ink-jet printing
Electroconductive layers
EMI shielding

ABSTRACT

A facile and original method of deposition of polyaniline (PANI) and polypyrrole (PPy) by reactive ink-jet printing on different textile fabrics is proposed. Polyaniline- and polypyrrole-coated conducting fabrics were obtained by chemical oxidation of aniline hydrochloride or pyrrole by ammonium peroxydisulfate on polyacrylonitrile (PAN), cotton, poly(ethylene terephthalate) (PET), cotton/PET, wool, and cotton/wool fabrics. The conducting fabrics were characterized chemically by means of Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and energy-dispersive spectroscopy (EDS). The morphology of the coatings was observed by optical microscopy and scanning electron microscopy (SEM). The conducting properties (surface resistance) of the fabrics were measured by means of the four-probe method. The optimal conditions of the PANI and PPy deposition on textiles by reactive ink-jet printing were established. The obtained results prove that the proposed method is very simple, practically could be carried out on the basis of water-containing inks, giving a very good adhesion of the *in-situ* formed conductive polymer to the substrate and ensuring a very low surface resistance. The variation of the surface resistance *vs*. concentration of aniline hydrochloride or pyrrole for different textile fabrics was obtained. The mechanism of the PANI and PPy deposition and adhesion on textiles based on the electrokinetic phenomena is proposed and proved by the changes in relative resistance of PANI/PAN and PPy/PAN composites during the multi-cyclic flexing, washing and dry-cleaning processes, and re-doping with HCl. An application of PANI and PPy conductive textiles in electromagnetic interference (EMI) shielding is proposed. The results showed that PANI/PAN and PPy/PAN composites achieved very good and moderate EMI shielding effectiveness, respectively.

1. Introduction

Polyaniline (PANI) is one of the most promising conducting polymers because of its unique properties, *i.e.*, excellent environmental stability [1] and partial solubility in various solvents. It is the most versatile polymer because of simple and inexpensive preparation, and also because of its desirable properties, such as thermal and chemical stability, low specific mass, controllability, and high conductivity at microwave frequencies [2].

A new approach to highly conductive textile materials is the use of intrinsically conductive organic polymers [3]. Another common route is to apply dispersions or powders of fully prepared conductive polymers as coatings. These approaches usually result in relatively low-conducting materials. An interesting alternative is to create the conductive polymers by *in-situ* polymerization of monomers on the textiles. Basically, the oxidative polymerization on a fabric may follow three procedures: application of the oxidant to the textile followed by addition of monomer, application of monomer followed by oxidizing agent, and application of a polymerizable mixture of monomer and oxidant [4,5]. Among the different methods of PANI deposition, the ink-jet printing technique is very attractive as it allows not only patterns of high resolution and high repeatability to be obtained, but also repeatable layer-by-layer structures. Ink-jet printing is a versatile method for controlled deposition of functional materials with suitable geometry on various substrates [6]. It does not require any contact between the deposition system and the substrate. The only constraint of this technique is the requirement of fluids (inks) with suitable viscosity and surface tension. This technique has already been successfully applied to produce polymeric sensor devices,

* Corresponding author. Tel.: +48 42 631 33 11.
E-mail address: zbigniew.stempien@p.lodz.pl (Z. Stempien).

http://dx.doi.org/10.1016/j.synthmet.2015.01.027
0379-6779/

and PANI nanodispersions were used as ink-jet printable inks [7–9]. These experiments opened up possibilities of novel, facile, and economic polymer-printed electronic applications in areas of sensing, energy storage, displays, organic light-emitting diodes, and others. It allows the large-scale production of devices such as sensors for a variety of applications [10,11]. Hohnholz and coworkers have developed a quite simple and inexpressibly method to obtain custom patterns from conductivity polymer using a standard laser printer [12]. Considering this development, a straightforward and low-cost method to produce conducting polymer (PANI or PPy) patterns using a conventional DeskJet printer was presented [13]. Recent advances in polyaniline research comprising the polymerization mechanism, structural aspects, properties and applications are reviewed [14].

Polypyrrole, also frequently studied conducting polymer, exhibits high electrical conductivity and moderate environmental stability, and is suitable for multifunctional applications. Chemical or electrochemical oxidative polymerization methods are widely used which yield polymer in its doped state, which is very important from the technological perspective. Chemical polymerization methods produce a fine insoluble black PPy powder with an electrical conductivity depending on the specific preparation conditions, such as type of oxidant, solvent, monomer concentration, oxidant to monomer ratio, reaction temperature, and co-dopant or surfactant concentration [15]. The PPy produced by the electrochemical methods shows higher conductivity, good mechanical properties and environmental stability. The disadvantage of electrochemical preparation is that the amount of polymer deposited is dependent on the working electrode surface and the amount of charge consumed. The most common printing methods such as screen, rotary, and ink-jet printing used to manufacture conducting polymers including PPy have been reviewed in detail by Weng et al. [10]. Ink-jet printed films of conductive PPy have already been successfully used for vapor sensing at room temperature [16] or for flexible substrates [17].

Ink-jet printing techniques are regarded as the most promising mechanisms for producing plastic electronics and textronics systems. They need inks which provide adherent, compact features with appropriate resolution and conductivity. In the case of polymer deposition, ink should contain dissolved or finely dispersible nanoparticles of conducting polymer. The disadvantages of these techniques are that clogging of the nozzles of the printing head is sometime observed and the relatively low conductivity of the prints obtained.

In this paper, a facile and original method of deposition of polyaniline and polypyrrole by the reactive ink-jet printing technique on different textile fabrics is proposed. Polyaniline- and polypyrrole-printed conductive layers on fabrics were obtained by chemical oxidation of aniline hydrochloride or pyrrole by ammonium peroxydisulfate on polyacrylonitrile (PAN), cotton, poly(ethylene terephthalate) (PET), cotton/PET, wool, and cotton/wool fabrics. The conducting fabrics were characterized chemically by means of Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and energy-dispersive X-ray spectroscopy (EDS). The morphology of the coatings was observed by optical microscopy and scanning electron microscopy (SEM). The conducting properties (surface resistance) of the fabrics were measured by means of the four-probe method. The optimal conditions of the PANI and PPy deposition on textiles by reactive ink-jet printing were established.

The proposed reactive ink-jet printing method makes it possible to produce flexible, conductive, lightweight and practical smart textiles, especially for textronic systems and in EMI shielding.

2. Experimental

2.1. Reagents and materials

Aniline hydrochloride 97% was obtained from Aldrich, and used as received. Pyrrole, a product of SAFC, China, ≥98%, was supplied by Sigma–Aldrich and used as received. Ammonium peroxydisulfate was from Chempur, Poland; analytical grade was used without purification. As substrates, six different commercial undyed textile fabrics were employed in the experiments. Table 1 shows the fundamental characteristics of the textile substrates used.

Polyaniline hydrochloride (PANI salt) and polypyrrole (PPy) as reference powders for FTIR and Raman measurements were synthesized separately. The synthesis of PANI salt was based on mixing aqueous solutions of 0.2 M aniline hydrochloride and 0.24 M ammonium peroxydisulfate at room temperature (oxidant/monomer molar ratio: 1.2), followed by separation of PANI hydrochloride precipitate by filtration and drying. More precisely, 1.296 g of aniline hydrochloride was dissolved in double-distilled water in a volumetric flask to 50 mL. Next, 2.738 g of ammonium peroxydisulfate was dissolved in water to 50 mL. Both solutions were kept at room temperature, then mixed in a beaker, briefly stirred, and left at rest to polymerize for 24 h. The next day, the resulting dark–green PANI precipitate was collected on a filter, washed under low pressure with methanol, followed by washing with water, and finally with acetone.

In the similar manner, the synthesis of PPy reference powder was based on mixing aqueous solutions of pyrrole 0.3 M and ammonium peroxydisulfate 0.3 M at room temperature (oxidant/monomer molar ratio–1:1), followed by the separation of PPy precipitate by filtration and drying. More precisely, 1.05 mL (1.016 g) of pyrrole was dissolved in double-distilled water in a volumetric flask to 50 mL. Next, 3.42 g of ammonium peroxydisulfate was dissolved in water, also to 50 mL. Both solutions were kept at room temperature, then mixed in a beaker, briefly stirred, and left at rest to polymerize for 24 h. Next day, the resulting black PPy precipitate was collected on a filter and washed under low pressure with methanol, followed by washing with water and finally with acetone. PANI hydrochloride and PPy powders were dried in air and then in vacuum at 60 °C.

2.2. Deposition of PANI and PPy layers on textiles

The formation of PANI or PPy conductive layers was achieved by the oxidative ink-jet printing of aniline hydrochloride or pyrrole

Table 1
Characteristics of textile substrates used.

Fabric material	Weave type	Surface weight, g/m^2	Warp density, yarns/cm	Weft density, yarns/cm
PAN	Twill 2/1	220	24	17
Cotton	Plain 1/1	120	34	25
Wool	Plain 1/1	150	16	16
PET	Plain 1/1	100	32	38
Cotton/PET (50/50)	Twill 3/1	250	48	24
Cotton/wool (25/75)	Plain 1/1	180	44	28