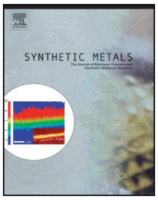
Synthetic Metals 222 (2016) 170–179

Contents lists available at ScienceDirect

Synthetic Metals

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



Tailoring of polypyrrole backbone by optimizing synthesis parameters for efficient EMI shielding properties in X-band (8.2–12.4 GHz)

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ARTICLE INFO

Article history:
Received 2 July 2016
Received in revised form 8 September 2016
Accepted 17 October 2016
Available online 24 October 2016

Keywords:
Polypyrrole
Oxidant
Dopant
Conductivity
EMI shielding effectiveness

ABSTRACT

This paper describe the effect of reaction conditions i.e. oxidant concentration (ferric chloride), dopant concentration and nature of dopant (sodium lauryl sulphate [SLS], sodium dodecyl benzene sulphonate [SDBS], lithiosulphoisophthalic acid [LiSiPA] and naphthalene disulphonic acid [NDSA]) on the conductivity and electromagnetic shielding properties of polypyrrole (PPy). PPy was synthesized using one mole of dopant [SLS] and varying concentrations of oxidant (2, 3, 4 and 5 mol per mole of pyrrole). The conductivity and shielding effectiveness of PPy obtained was found to be dependent on the concentration of oxidant and it was highest when the molar ratio of pyrrole: oxidant: dopant was 1:2:1. In the second set of experiments, dopant concentration [0.6, 1, 1.4 and 1.8 mol per mole of pyrrole] was varied keeping the concentration of pyrrole: oxidant as 1:2 to determine the optimum concentration of dopant. The polymer prepared using pyrrole: oxidant: dopant ratio as 1:2:1 showed the highest conductivity as well as the shielding effectiveness. Using these optimized conditions polypyrrole was synthesized using different dopants [i.e. SLS, SDBS, LiSiPA and NDSA]. Polypyrrole synthesized using optimized conditions and SLS as dopant had highest conductivity (42 S/cm) and electromagnetic shielding effectiveness of −126 dB in the X-band [8.2-12.4 GHz] which is the highest value ever reported for the PPy synthesized by chemical oxidative polymerization. The shielding properties discussed in the present paper are very close to the conventional metals with an additional advantage that the primary mechanism of shielding is absorption dominant.

1. Introduction

Electromagnetic interference (EMI) is a form of pollution which affect the overall performance of any electronic gadget. The common examples of EMI are the interference of mobile signals with laptop and radio speakers resulting into a buzzing sound. In some cases end results may be frightful as in the form of loss of energy, revenue and sometimes even the loss of precious human life. So, now a days microwave shielding materials have received considerable interest in commercial applications. Hence more economical electromagnetic wave (EM) shields with wide bandwidth, uniformity, low sample thickness and light weight has become the focus of current studies. There are two main mechanism of EMI shielding, one is reflection and second is absorption of the EM wave by shield. So shielding effectiveness (SE) can be attributed as: SE = A + R + M where A, R and M represents the absorbed, reflected and multiple internally reflected wave loss. Leading mechanism of EMI shielding by metals is typically reflection. For reflection by the shield, the shield must have mobile charge carriers (electrons in metals and electrons and holes in semiconductors) which interact with the electromagnetic radiation. That's why electrical conductivity is basically the most important requirement for EMI shielding. Metals, although easily available, but not preferred for EMI shielding as they are highly susceptible to corrosion and are also heavy and in some fields like stealth technology, absorption of EM wave is preferred over reflection. So the preferred material should be one which can withstand corrosive environment and also make a light weight protective shield and it should protect material by absorption mechanism. Conducting polymers offers a solution for problems of heavy weight and corrosive nature as well. The EMI shielding and microwave absorbing properties of these polymers can be explained in terms of electrical conductivity and presence of bound/localized charges leading to strong polarization and relaxation effects. Conducting polymers are capable of electrical charge transfer to the same extent as an electrical conductor or a semiconductor [1,2]. It is important to note that the electrical

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http://dx.doi.org/10.1016/j.synthmet.2016.10.016

conduction, thermal stability and solubility of conducting polymers can be tailored according to the desired applications in microelectronics, information industry, batteries, super capacitors and sensors, bio- medicines, microwave shielding and corrosion protection [1,3–7]. There are many conducting polymers such as polyaniline (PANI), polythiophene (PTP), poly(phenylacetylene) (PPA), polypyrrole (PPy) etc. which are capable of suppressing EMI [1,8–12]. Among all, PPy is the most promising material for the EMI shielding purpose because of its captivating electrical property, environmental stability and relative ease of synthesis which makes it one of the most studied conducting polymer [13–16], Its electrical conduction, thermal stability can be tailored easily by restraining the use of oxidant and dopant and hence makes it a real advantage for mentioned applications [17–19]. Earlier many researchers have reported synthesis of highly conductive polypyrrole via electrochemical process [20–22] that has a disadvantage of low yield of polymer, but by chemical oxidative polymerization route comparatively high yield is obtained and can be synthesized in bulk [16,23–25].

The focus of the paper is to optimize parameters required for the synthesis of PPy to achieve high EMI shielding and thermal stability. For this purpose each parameter viz. oxidant concentration, dopant concentration and nature of dopant was systematically varied to investigate the effect of these parameters on the structural, morphological, electrical conductivity, thermal stability and EMI shielding properties. The EMI shielding properties were measured in terms of total shielding effectiveness (SE_T) which can be defined as the mitigation of propagating electromagnetic wave, in the frequency range of 8.2–12.4 GHz (X-Band).

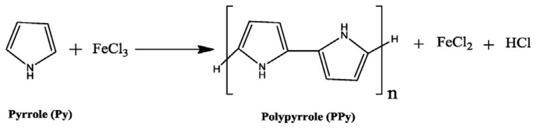
2. Experimental

2.1. Materials

Pyrrole (Across, India) was purified by distillation under reduced pressure and stored in refrigerator at 4 °C. Ferric chloride (Fisher scientific), sodium lauryl sulphate [SLS] (Fisher scientific), sodium dodecyl benzene sulphonate [SDBS] (TCI chemicals), naphthalene disulphonic acid [NDSA] (Sigma Aldrich) and lithiosulphoisophthalic acid [LiSiPA] (Sigma Aldrich) were used as received.

2.2. Preparation of polypyrrole [PPy]

The polymerization of pyrrole monomer was carried out in the presence of different dopants by chemical oxidation using $FeCl_3$ as oxidant according to the following reaction scheme:



Several polymer samples were prepared by varying the reaction parameters i.e. oxidant concentration (0.1, 0.15, 0.2 and 0.25 mol per 0.05 mol of pyrrole), dopant concentration (0.03, 0.05, 0.07 and 0.09 mol per 0.05 mol of pyrrole) and nature of dopant. A typical procedure used for polymerization is given below:

2.3. Polymerization procedure

In a typical polymerization, required amount of pyrrole monomer was mixed with the aqueous solution of dopant and stirred till we get a homogenous solution. Required amount of $FeCl_3$ (dissolved in water) was added drop wise and the reaction mixture was stirred continuously for 6 h. The precipitate so obtained after polymerization was separated and washed continuously with distilled water until the pH of the filtrate became neutral. The precipitate was then finally washed with methanol to remove oligomers and kept for drying under vacuum till constant weight. The dried mass was then crushed to obtain powder of polymer. Schematic representation of synthesis procedure is given in Fig. 1.

Several samples of PPy were prepared by varying moles of ferric chloride keeping the pyrrole and dopant concentration constant i.e. pyrrole: dopant as 1:1. The samples have been designated as PO 1, PO 2, PO 3 and PO 4. Similarly at an optimized concentration of oxidant, samples were prepared using varying concentrations of SLS and the samples have been designated as PD 1, PD 2, PD 3 and PD 4. In order to investigate the effect of nature of dopant (SLS, NDSA, SDBS and LiSiPA), PPy was synthesized using optimized conditions (pyrrole: oxidant: dopant as 1:2:1) and the samples have been designated as P-SLS, P-SDBS, P-LiSiPA and P-NDSA. The details of sample preparation along with designation are given in Table 1.

3. Characterization

3.1. FT-IR

Structural characterization of PPy was done by recording FT-IR spectrum using Thermoscientific Nicolet 6700 FT-IR. For recording FT-IR spectra, circular pellets of PPy mixed with KBr were used.

3.2. Thermogravimetric analysis (TGA)

Investigation of thermal stability of PPy was carried out by recording thermogravimetric (TG)/derivative thermogravimetric (DTG) traces (TA instrument Q-50 TG) in nitrogen atmosphere at a flow rate of 60 cm^3/min). In each experiment 5 ± 2 mg of sample was heated at a heating rate of 10 °C/min.

3.3. X-ray diffraction analysis

The wide angle X-ray measurement was performed on polymeric powder samples. The measurements were performed on Rigaku Ultima IV type-II automatic high resolution modulator type X-ray diffractometer system (20–60 kV, 2–60 mA) at a radial scattering range of 2–60° using Cu Kα.

3.4. Morphological characterization

Morphology of polypyrrole was investigated using field emission scanning electron microscopy (FE-SEM) EVO-50 operated at accelerating voltage of 20 kV. For scanning polymeric powder was spread over carbon tape on the stub and a gold coating was applied on the powder.

3.5. Electrical conductivity

The electrical conductivity of polypyrrole was measured by four probe method using low resistivity meter from Keithley 2420 Source Meter and Keithley 2182A Nanovoltmeter. The four point's setup consists of four equally spaced tungsten metal tips with finite radius. Each tip is sustained by spring on the end to minimize sample damage during probing. These inner probes draw no current because of high input impedance. It is supposed that the metal tip is infinitesimal and sample is semi-infinite in the lateral dimensions. For bulk samples where sample thickness (w) is much higher than probe spacing (s) i.e., w > >s, we assume projection of current stemming from the outer probe tips. The resistivity is