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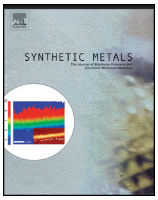

The effect of reaction medium on the conductivity and morphology of polyaniline doped with camphorsulfonic acid

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ABSTRACT

Since commercial airliners are struck by lightning quite often during their operation, there is a need to elaborate new materials for lightning strike protection combining high conductivities with light weight. Conducting polymers are thought to be one of the most promising compounds that can be used for this application. From a variety of commercially available conducting polymers, polyaniline, PANI, fits criteria of chemical stability, appropriate conductivity and density the best. The aim of this study is to find the optimal conditions of the process of polyaniline doping with camphor sulphonic acid, CSA, to obtain the material that can be used as a conducting filler for lightning strike protection coatings. We present the comparison of physicochemical properties of polyaniline films doped in the presence of m-cresol, N-methyl-2-pyrolidone and dimethylsulfoxide, respectively. The morphology of obtained PANI/CSA films is characterized by means of scanning electron microscopy equipped with 3D roughness reconstruction software. The applicability of two methods of conductivity measurements, i.e. four point probe and bipotentiostatic techniques, is evaluated in respect to PANI/CSA films of various morphology.

1. Introduction

It is estimated that every commercial airliner is struck by lightning once per year [1]. Since the average current of a lightning is between 30 kA and 50 kA, with a maximum of 200 kA [2], lightning strike can have severe consequences to the aircraft, including vaporization of metal control cables and/or other critical aircraft parts [3]. The conventional solution to the lightning strike problem is the use of aluminum aircraft frames [4]. Nevertheless, the possibility of weight reduction and fuel saving as well as simplifying manufacturing processes of elements of exterior fuselage of aircraft has encouraged aerospace companies to switch their attention from metal to composite structures [5]. Intrinsically conducting polymers, CPs, are thought to be among the most promising compounds that can be used for the development of lightning strike protection coatings.

Conducting polymers, such as polyaniline, polypyrrole and polythiophenes, are unique class of organic materials able to conduct electrical current. CPs have already found applications in a wide range of areas including electrochemistry, optoelectronics, electro-mechanics, thermoelectricity, photovoltaics, materials science, etc [6–8]. Due to the ease of synthesis, novel properties and potential applications, polyaniline (PANI) is one of the most extensively studied conducting organic compounds [9]. Low mechanical stability, however, makes it difficult to use PANI as a stand-alone material. This limitation is overcome by the development of composite materials with PANI particles used as a conducting filler [10].

The conductivity of PANI is strongly dependent on its redox state as well as the presence and chemical structure of doping ions. As the result of the doping process, the conductivity of PANI can increase of ten orders of magnitude or more [11]. With the use of acid solution processing routes discovered by Cao et al. [12] it is possible to dope PANI with camphor sulphonic acid (CSA) and obtain homogeneous material with conductivity up to 300 S/cm [13]. PANI/CSA was shown to possess metallic-like behavior [14] and was used as a filler in poly(methylmethacrylate) composites to produce highly conductive electrospun nanofibers [15]. The most popular solvent used for solution processing route of PANI is m-cresol [16–19]. mainly because it promotes the transfer of delocalized polarons by increasing the aromaticity of the chain [20]. On the other hand, since PANI equilibration is electrochemically driven, it is not dependent on the presence of m-cresol. This makes it reasonable to verify how the physicochemical properties of PANI will change if the process of doping will be performed in

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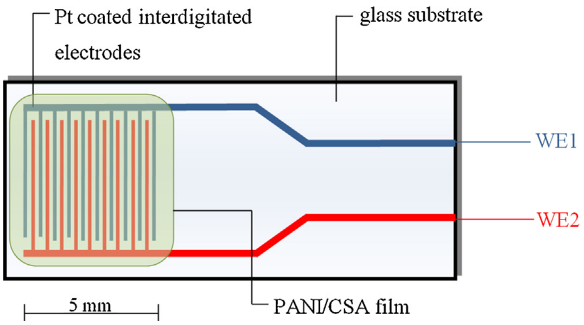

Fig. 1. The schematic representation of the interdigitated electrode.

other solvents, e.g. *N*-methyl-2-pyrolidone and dimethylsulfoxide, which are less toxic than m-cresol.

In this study, we present the comparison of morphology and conductivity of PANI/CSA films doped in the presence of m-cresol, *N*-methyl-2-pyrolidone and dimethylsulfoxide, respectively. The morphology of obtained PANI/CSA films is characterized by means of scanning electron microscopy equipped with 3D roughness reconstruction software. The conductivity of PANI/CSA films is measured by means of four point probe technique and with the use of a dual mode bipotentiostat. This allows to explain the effect of reaction medium on the physicochemical properties of PANI/CSA as well as gives us the basics needed for the optimization of the synthesis conditions of PANI/CSA to obtain material suitable for the production of lightning strike protection coatings.

2. Experimental

2.1. Materials and methods

Polyaniline base, PANI (MW = 50 000 g/mol, Sigma-Aldrich), ±10-camphor sulfonic acid, CSA (98%, TCI Chemicals), m-cresol (98%, TCI Chemicals), *N*-methyl-2-pyrolidone, NMP (99%, TCI Chemicals) and dimethylsulfoxide, DMSO (99.9%, Sigma Aldrich) were used as received.

PANI was doped with CSA according to the literature report [21]. 0.067 g of PANI base, 0.088 g of CSA and 2 ml of solvent (m-cresol, NMP or DMSO, respectively) mixture was homogenized by placing it in the ultrasonic bath for 30 min. The mixture was then heated in a water bath up to 70 °C and continuously stirred for 60 min. PANI/CSA-cresol turned into black-dark green suspension of high viscosity, both PANI/CSA-NMP and PANI/CSA-DMSO were suspensions of a small viscosity of black (PANI/CSA-NMP) and black-green (PANI/CSA-DMSO) color. Few drops of each PANI/CSA suspension were placed on glass slides (5 mm x 25 mm) or interdigitated electrodes (Fig. 1.) and dried in the oven at 65 °C for 72 h.

2.2. Characterization

The morphology, roughness, thickness and surface profiles of PANI/CSA films were measured by means of scanning electron microscope Phenom ProX equipped with 3D Roughness Reconstruction software. The conductivity of PANI/CSA films deposited on the glass slides was measured by means of four point probe (Digital Multimeter Prema 5017) and calculated by dividing length of the specimen by its resistivity and cross-section area [22]. The dual mode bipotentiostat Autolab PGSTAT302N + BA was used to measure the conductivity of PANI/CSA films deposited on interdigitated electrode during chronoamperometric measurements involving the application of −0.5 V for 60 s. Because of the small value of the offset potential (10 mV), the conductivity was calculated by dividing the difference between currents recorded for two working electrodes, WE1 and WE2 (see scheme on Fig. 1) by the offset potential multiplied by two and the thickness of polymer layer [23].

3. Results and discussion

3.1. Morphology of PANI/CSA films

Since the nanostructure and morphology of conducting polymers is essential for the determination of their properties and potential applications [24], scanning electron microscope has been used to evaluate the surface properties of PANI/CSA films. SEM images (Fig. 2.) show great variability among PANI/CSA films doped in the presence of different solvents. PANI/CSA film doped in m-cresol is the most uniform and smooth among all polymer films. It forms the continuous polymer layer covered uniformly with needle-type PANI structures of the length between 10 and 15 μm and the diameter of around 600 nm. This type of PANI structures has been previously described by Leng et al. [25]. who synthesized “needle” aniline oligomer assemblies in an aqueous medium using sodium dodecylsulfate as a surfactant. It was found that such fibrillar microstructures present better conductivities compared to irregular structures [26] and have potential applications, such as molecular wires, actuators, chemical sensors and biosensors [27].

The morphology of PANI/CSA doped in the presence of NMP is much different than for the same polymer doped in m-cresol. In this type of polymer film, PANI/CSA particles form large aggregates covering the substrate in the coral reef-like structure. Also here, PANI fibrils can be found among polymer aggregates, but now they

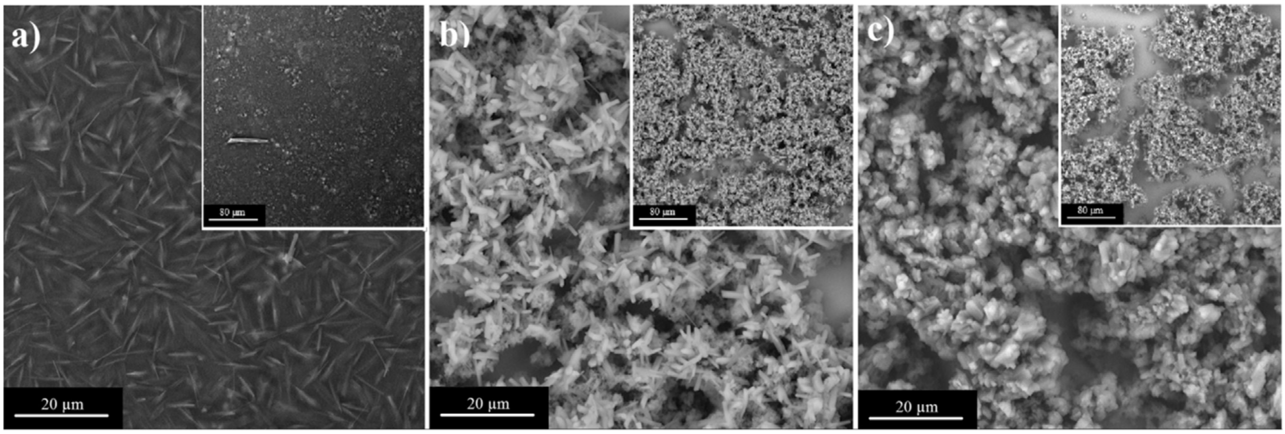

Fig. 2. SEM images of PANI/CSA films doped in the presence of m-cresol (a), NMP (b) and DMSO (c); the scale bar is 20 μm, in inset the scale bar is 80 μm.