# Annealing effect on electromechanical behaviour of polyanilines organic acids-doped

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## ARTICLE INFO

## ABSTRACT

This work presents an extensive experimental qualification of an innovative polyaniline synthesized by a more sustainable approach as sensing element. The electromechanical properties of polyanilines prepared by two different approaches (PANI1 from a traditional method and PANI2 from a more environmentally friendly route) are investigated in order to verify the applicability of these materials for the development of force and pressure transducers. The two PANI were chemically characterised and investigated through several mechanical tests. The variation of their resistance was continuously monitored during loading/unloading cycles up to 40 kN after heat treatment in order to evaluate the modification of the electromechanical properties at different temperatures.

It was observed that both the polyanilines exhibit a strong change of their resistance value as function of the compression load acting on the samples. Moreover, PANI2 shows a high resistance which is a good property for insert the element into any measurement circuit avoiding problems of impedance losses due to cables or other circuit elements. The results will also show that both PANIs have steady behaviour at high temperatures up to 85°–100 °C.

## 1. Introduction

Stress/strain sensors have become popular in numerous areas ranging from the monitoring of the mechanical stability of civil structures [1] to medical applications in therapy, health control and rehabilitation [2]. These sensors are characterized by the ability to convert a stress or strain effect in another kind of signal (electrical resistance change) that can be easily measured and processed. Therefore, more in detail for these devices the electrical resistance change is a function of the applied mechanical strain/stress. Although numerous materials have been investigated for this application, intrinsically conducting polymers (ICPs) have gained wide consents. Among them, blends of polypyrrole (PPY) and polyaniline (PANI) and their composites have been particularly investigated for their piezoresistive behavior [3] and conflicting results have been obtained. Therefore, to data PANI-based materials are far to be really applied owing to numerous limitations (typically low sol-

ubility, oxidation level and doping control, toxic byproducts) that need to be overcome [4]. In this regard, we have recently started to investigate the dependence of the gauge factor (GF) on the kind of dopant and preparation method [5].

Herein, we report a comparison on the variation of resistance as a function of the applied load (or compression) between pellets of polyanilines prepared by a traditional [6] and a more sustainable [5] way and doped with different organic acids.

In particular, the present paper the effect of different heat treatments on the materials performances is investigated.

## 2. Materials and methods

### 2.1. Reagents and instruments

All chemicals were purchased from Sigma Aldrich and used as received without further purification.

FT-IR spectra of KBr dispersed samples were recorded on a JASCO FT/IR-410 spectrophotometer in the 500–4000 $cm^{-1}$ range. X-ray powder diffraction (XRPD) analyses were performed using a Rigaku D IIIMAX horizontal-scan powder diffractometer with Cu Kα radia-

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tion. Uniaxial compression tests were carried out by means of a MTS alliance RT/100 universal mechanical test machine and resistance measurements were collected by an Agilent 34401A multimeter.

The molecular weight distribution of the sample fractions soluble in dimethylformamide (DMF) was evaluated by size exclusion chromatography (SEC) using a Shimadzu LC10ADVP HPLC equipped with a refractive index (RI) as detector. The SEC column was a Phenomenex phenogel 5u 55A (300 × 4.6 mm) molecular weight distribution analyses were carried out at room temperature using ultrapure dimethylformamide (DMF) as the eluent. The flow rate was set at 0.3 mL/min and the injection volume was 20 μL. Polystyrene standards were used to calibrate the column.

## 2.2. Samples preparation

Two different types of polyaniline (PANI1 and PANI2) were prepared by two different protocols. Both the polymers were dedoped by a $NH_4OH$ aqueous solution and then redoped by two different organic acid dopants: dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA).

### 2.2.1. PANI1 preparation

PANI1 was prepared in agreement with a method reported in the literature [6]. 5.0 g (53.8 mmol) of aniline and 22.0 g (96.5 mmol) of $(NH_4)_2S_2O_8$ were separately solubilized in 50 mL of HCl 10 M and 80 mL of deionized water respectively and cooled at 4 °C. When the oxidant aqueous solution was added dropwise to the solution containing aniline chloride the polymerization reaction took place immediately. After 6 h the reaction mixture was quenched by the addition of acetone and a dark green solid was collected by filtration, washed several times by water and acetone and dried under air. A 65% polymerization yield was calculated. The product was spectroscopically characterized and identified as emeraldine salt (ES) [5].

### 2.2.2. PANI2 preparation

PANI2 was prepared following our previous synthetic procedure reported in the literature [6]. 2.0 g (10.9 mmol) of N-(4-aminophenyl) aniline (i.e. aniline dimer, AD) was solubilized in 55 mL of HCl 0.2 M at room temperature. Then, 5.6 mL of $H_2O_2$ 30% w/w were quickly added to the previous solution, followed by 2.9 mg of $FeCl_3·6H_2O$. After 24 h the reaction mixture was quenched by acetone addition and an insoluble dark green product, spectroscopically characterized and identified as ES [6], was collected by filtration, abundantly washed by water and acetone and dried under air. The product was obtained with a 79% yield.

### 2.2.3. PANI/DBSA and PANI/CSA pellets preparation

1 g of PANI1 and PANI2 was separately dedoped (deprotonated) by 40 mL of $NH_4OH$ 1 M (40 mmol). After 24 h the corresponding emeraldine bases (EB1 and EB2) were filtered, washed several times with water until the mother liquors became neutral and dried under air. Each polymeric base was split in two portions. Each portion was dispersed in 20 mL of $CHCl_3$ and redoped by the addition of dodecylbenzenesulfonic acid (DBSA, 1.8 g, aniline/DBSA = 2) or camphorsulfonic acid (CSA, 1.2 g, aniline/CSA = 2). Each mixture was stirred for 24 h at room temperature. Then, PANI1/DBSA, PANI1/CSA, PANI2/DBSA and PANI2/CSA samples were collected by filtration, washed by acetonitrile and dried under air.

PANI/dopant pellets having diameter of 13 mm and thickness of 1 mm were prepared by pressing 200 mg of each material for 30 min at 100 kN using an Atlas Manual Hydraulic Press.

## 2.3. PANI/dopant heat treatment

Before any heat treatment, all pellets underwent a set of four loading/unloading electromechanical investigations sequence (see Section 2.4). Then, all the samples were subjected to subsequent thermal treatments and tested again.

The heat treatments consist on warming up quickly each sample in an oven, holding it at the desired temperature for 1 h under nitrogen atmosphere (to avoid oxidation phenomena) and finally cooling the sample at room temperature. More in detail, all samples were subjected to three subsequent heating steps at 85 °C, 100 °C and 150 °C respectively.

The maximum temperatures to which samples were exposed were lower than the melting/boiling point of organic acids: 204.5 °C for DBSA and 203 °C for CSA. After each annealing treatment all pellets were reground, recompressed and their electromechanical response was again investigated.

## 2.4. Electromechanical characterization

In order to find out the electromechanical properties of the two types of PANI, a proper measurement setup was arranged. Each powdered sample was placed inside the cylindrical cavity of the cubic polycarbonate container shown in Fig. 1 and underwent consecutive loading-unloading cycles while its resistance value was continuously measured. A steel disk was inserted at the base of the cavity and the pellet was formed in contact with it by the gradual compression of a cylindrical steel piston inserted in the cavity. This solution had the advantages of insulating the pellet but also of allowing the resistance measurement keeping the compressed pellet on the steel base during the tests. Indeed, the steel base and the piston allowed both the mechanical compression and the resistance estimation since they were used as two test leads for the multimeter.

The MTSalliance RT/100 universal mechanical test machine used for all uniaxial compression testsprovides a maximum load of 100 kN both for tensile and compression and a maximum velocity of 508 mm/min. The tests can be controlled in force or displacements by the MTS Testworks 4 control software, which allows customizable loads or displacement laws. To test the electromechanical properties of PANI, the MTS system was operated in force control. The axial loads were measured by a load cell MTS 4501058, with ±100 kN measurement range and 0.1 V/kN sensitivity, whereas the axial displacement was measured by a deflectometer MTS model632.06H-30 with ±12.5 mm measurement range. A software was developed with LabVIEW to automatically read the value of the electrical resistance at a sampling frequency of 1 Hz and store the acquired values in the host PC.

For each PANI sample four continuous loading/unloading cycles from 0 kN to a maximum of 40 kN were performed. The first cycle was performed only on the container components (Figs. 1 and 2), in the absence of any PANI pellet, in order to estimate the deformation of these parts under the same loading conditions of the full PANIs tests. Then, the second loading/unloading cycle was necessary to geometrically stabilize the samples and put them in complete contact with the loading plates. Finally, the other two cycles were done in order to verify the measurement repeatability. This test procedure was performed on pellets in atmosphere conditions, but also after three different heat treatments at 85 °C, 100 °C and 150 °C as it will be explained in the next section.

Note that, for each loading/unloading cycle, all the measurements had a starting point at the time when the load reached the conventional level of 500N. This assumption was made to ensure that the reference resistance R0 was measured when the initial friction and possible air gaps were eliminated.