

Associated Polymers, Solvents and Doping Agents to Make Polyaniline Electrospinnable

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Abstract. Polyaniline (PANI) is a conductive polymer that has both metal (electrical, electronic, optical and magnetic properties) and polymer characteristics (low density, low-cost and resistance to chemicals). Polyaniline becomes a conductor by treatment with a dopant that acts by extracting electrons (oxidation) or by inserting electrons (reduction). The reduced solubility of PANI in all common solvents restricts its capacity to be electrospun into uniform fibers. The present paper reviews the methods to increase the solubility of PANI by blending it with other polymers and doping it with organic acids, highlighting the best polymer/solvent couples and doping agents.

1. Introduction

Conducting polymers, which have been discovered in 1976 [1], have many useful properties such as mechanical flexibility, ease of processing and, above all, adjustable electrical conductivity [2]. Amongst these polymers, polyaniline (PANI) has been studied for many applications [3] such as chemical sensing [4-6], logic circuit components [7], electromagnetic shielding [8], and anticorrosion coating [9] due to its uncomplicated synthesis, room temperature process, high conductivity and relative environment stability [10]. Polyaniline has the general polymeric structure shown in fig. 1. Polyaniline contrasts from the other inherently conducting polymers, such as polypyrroles and polythiophenes, in that it has three readily accessible oxidation states, which range from the fully reduced leucoemeraldine state ($y = 1$) to the half oxidized emeraldine ($y = 0.5$) form to the fully oxidized pernigraniline state ($y = 0$) (fig. 1). Polyaniline shows the highest conductivity in the emeraldine state [11].

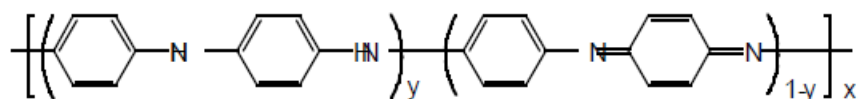


Figure 1. $y = 1$ (leucoemeraldine) 0.5 (emeraldine) and 0 (pernigraniline).

The electrical properties of polyaniline can be easily adjusted from insulating to conducting range by a doping/de-doping procedure, when the electrical properties are changed by the partial oxidation or reduction of the polymer chain [12]. The electrical conductivity can be increased by many orders of magnitude from 10^{-10} – 10^{-5} to 10^2 – 10^5 S \times cm⁻¹ upon doping, which covers the whole insulator-semiconductor-metal range [13].

2. Alternatives to obtain the electrospinning solution/dispersion (associated polymers and solvents)

Despite the great potential of PANI, its processing remains a difficult problem to handle, due to its insolubility in ordinary organic solvents. Because of this, PANI is hardly processed alone by electrospinning, and various other polymers are mixed with PANI in the spinning solution [14-18]. Approximately 1% solubility was observed in N-methyl, 2-pyrrolidone (NMP), which also acts as a plasticizer [19-23]. It was also found that 2-hydroxyethyl ammonium formate is a versatile solvent as reaction medium in preparing organo-soluble polyaniline with reasonable molecular weights by oxidative coupling polymerization. Low viscosity and superficial tension of PANI.HCSA (polyaniline doped with camphorsulfonic acid) in a chloroform solution prevents electrospinning, which becomes possible only by the addition of another polymer such as poly (ethylene oxide) (PEO) or poly (methyl methacrylate) (PMMA) to the chloroform solution [24-27]. The use of PEO leads to superior uniformity of the spinning solution, while when using PMMA phase separation phenomena occur. In addition, PANI / PEO nanofibers are more conductive [28]. Mixtures of polyaniline with polyethylene oxide (PEO - Mw 6000,000) and polymethyl methacrylate (PMMA - Mw 996,000) [8, 28] were also tested. Chloroform was used as solvent [29], and the undissolved part has been removed by filtration. The used solutions were 1% wt% PANI.HCSA / 1 wt% PEO or 1% wt% PANI.HCSA / 5 wt% PMMA, both solutions lacking phase separation tendency. At these concentrations the electrospinning polymer jet was uniform and stable. A study on the use of the electrospinning technique for PANI-poly (styrene sulfonic acid) (SPS), poly (vinyl butinol) (PVB) and polyethylene oxide (PEO) blends shows that the introduction of polyethylene oxide into the electrospinning solution alters the hydrophilicity of the obtained nanofibers, enhancing the response to humidity, improves the sensitivity and decreases hysteresis. All nanofiber sensors obtained this way show an impedance variation of about three orders of magnitude in the 20-90% RH range with high sensitivity. For example, the nanofiber response from PANI-SPAS / PEO / PVB (mass ratio 20/3/14) shows a rapid response, with a response time of $t_{90\%}$ for adsorption and desorption processes of 8 s and 6 s respectively [30]. Nanofibers from mixtures of PANI with poly (styrene sulfonic acid) solved in N, N-dimethyl formamide exhibited a highly porous structure, and their impedance varied rapidly and reversibly in an exponential fashion with the amount of adsorbed water [31]. Poly (3-hydroxybutyrate) (PHB) - PANI mixtures were electrospun using chloroform and 2,2,2-trifluoroethanol (TFE) as solvents. In the case of chloroform, the nanofibers produced were resistant but had a heterogeneous surface, with a wide scattering of diameters and spongy surface structure; the use of TFE leads to a significant improvement in the properties of nanofibers, which became smooth, uniform and thin, but with a lesser mechanical strength. An interesting effect is the improvement of PANI conformation, from the coil-like shape to a shape much closer to linearity, resulting both from the use of TFE and from the interaction between PHB and PANI. Changing the solvent also leads to increased fiber hydrophilicity as well as improved thermal resistance [32]. A polylactic acid (PLA) and PANI mixture with low polylactic acid content (about 1%) demonstrated solubility in chloroform and was electrospun to give nanofibers with diameters in the range of 10 nm - 300 nm [33].

3. Doping agents

Doping and returning to the de-doped form plays a key role in the sensing mechanism of conductive polymers [34]. By controlling the pH of the dopant acid solution, the doping agents can be added in any desired amount until all imine nitrogen atoms (half of the total) are doped. Moreover, dopants can be removed by the interaction of the emeraldine salt form with common bases, such as ammonium hydroxide. The ability to switch between conductive and insulating forms makes PANI a polymer sensitive to acidic / basic and reducing / oxidizing compounds such as ammonia (NH₃), nitrogen dioxide (NO₂), hydrogen (H₂), some volatile organic compounds [35-38]. Relatively numerous doping agents have been tested in the production of polyaniline with applications in the field of sensors. A study of the potential of some of the most common mineral acids as polyaniline doping agents has

highlighted the fact that perchloric acid has the highest effectiveness, followed by sulfuric acid, nitric acid, hydrochloric acid and hydroiodic acid, as it can be seen in fig. 2 [39].

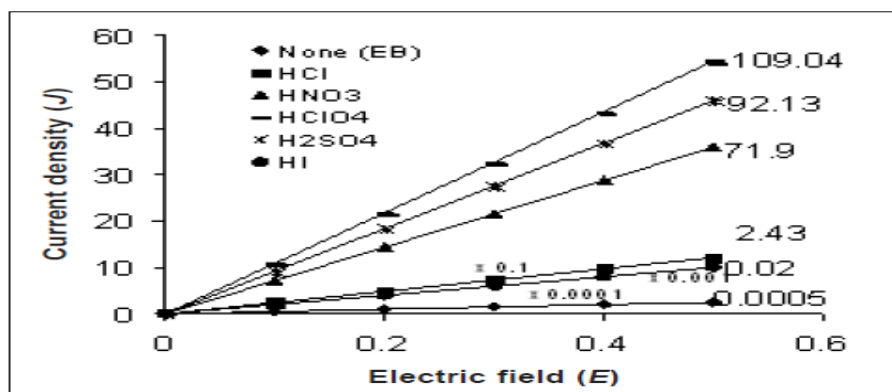


Figure 2. Scaled plots of current density versus electric field for emeraldine salt with different dopants showing the slopes as the conductivity in S/cm.

A relatively frequently used doping agent is 10-camphor sulfonic acid (HCSA), an organic acid that confers a certain solubility and high conductivity to polyaniline [8, 11, 28, 38, 40]. The doping procedure involves grinding 1 g of PANI base, 1.32 g of HCSA and 30 mL of m-cresol in a homogenizer and shaking at an initial temperature of 50 °C for about 45 minutes followed by drying for 24 hours to obtain a fine powder [38-40]. In another procedure, camphorsulfonic acid is first fully dissolved in chloroform, and then an adequate amount of polyaniline base is dispersed in the solution. This is sonicated for 5 min, kept under magnet stirring for 6 to 8 hours and filtered before mixing with polyethylene oxide [41]. A schematic representation of HCSA-doped polyaniline is shown in fig. 3 [42].

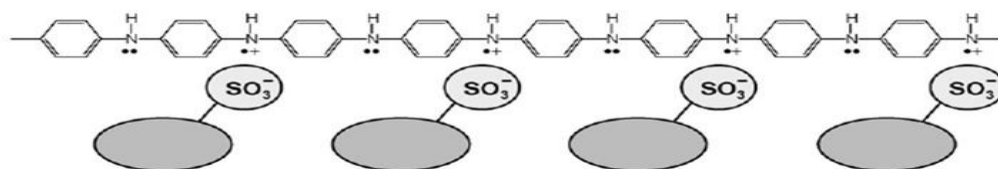


Figure 3. HCSA doped polyaniline.

The way HCSA doping affects the conductive characteristics of polyaniline is illustrated in 4. Also HCSA was used to dope polyaniline that was mixed with poly (ethylene oxide) in the proportions of 1/10 to 1/2, observing an increase in the conductivity when the PANI content was increasing [43]. Polyaniline doped with HCSA was dissolved in a mixture of chloroform / ethanol (9: 1 by volume) and the resulting solution was mixed with poly (vinyl pyrrolidone) (PVP) (1.5 PVP / PANI) and polyethylene oxide (PEO) (0.62 PEO / PANI), the two polymer solutions being then electrospun to obtain sensors. It was found that PANI-PEO was the most porous layer with good electrical performance and high sensitivity to ammonia, but fragile when subjected to environmental stress such as high humidity and temperature, while PANI-PVP proved to be a very good sensor for NO₂, but it was strongly influenced by humidity even at low values [44].

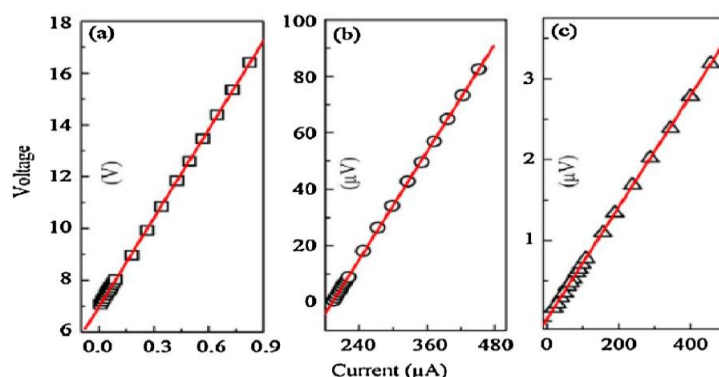


Figure 4. Current–voltage characteristics of (a) PANI base, (b) PANI (HCl doped) and (c) PANI (HCSA doped) [5].

Dodecylbenzene sulfonic acid (DBSA) appeared as a promising dopant and surfactant and is frequently applied in various protocols for soluble PANI synthesis [45]. A few examples are polymerization in solution [46] emulsification / reverse emulsion polymerization [47] and re-doping of emeraldine base (EB-PANI) [48]. The solubility of PANI doped with dodecylbenzene sulfonic acid (DBSA) or camphor sulfonic acid in chloroform and xylene, has been reported. The long chain of DBSA is supposed to confer solubility to the synthesized polymer in ordinary organic solvents [47]. To study the role of DBSA as dopant, blends of vinylidene polyfluoride (PVDF) / emeraldine base (EB) and PVDF / PANI doped with DBSA, respectively, were electrospun. It has been noted that both emeraldine base and emeraldine salt affect the solution properties and have a significant influence on the process, the morphology and diameter of the fiber. Electrospinning of the solution containing doped PANI is easier to perform compared to a solution containing PANI salt because both the viscosity and the ionic conductivity of the solution are significantly modified by the addition of doped PANI. In order to obtain uniform fibers, the applied tension should be adjusted when PANI salt is used to obtain small diameter nanofibers [49]. A comparative study of three dopants: hydrochloric acid, sulfuric acid and formic acid highlighted the superior efficacy of the latter, providing the highest conductivity [50]. Doped polyaniline was obtained by aniline oxidation polymerization using ammonium peroxide sulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) as dopant and the obtained polymer was electrospun after mixing with polyvinyl alcohol and polyvinyl alcohol - AgNO_3 . The electrospinning of 0.036 M PANI solution in N-methyl-2-pyrrolidone resulted in the formation of micro to nanoparticles, while electrospinning a PANI / PVA solution altered the electrospinning behavior and resulted in the formation of fine composite electrospun fibers. When the composition is further modified by the addition of AgNO_3 , three-component electrospun composite fibers are obtained [51]. Enzymes, such as urease, were also used as dopants for PANI [52-58]. The urease is fixed in the PANI-PVP matrix, which results in an increase in the sensitivity of the nanofibers to ammonia.

4. Conclusions

The paper summarizes the types of polymer that are currently associated with PANI to improve its processability, the concept of doping and the types of dopants that are most frequently used. Various organic/inorganic acids are analyzed as effective dopants to improve the conducting properties of polyaniline, proving that the electronic and optical properties of polyaniline can be simply controlled and tailored by the oxidizing/reducing agents and acid/base doping added during the polymerization process. The nature of the solvent used to make PANI spinnable depends decisively by the nature of the dopant and that of the associated polymer that are used, and some of the most efficient solvents are m-cresol and xylene which solve PANI doped with dodecylbenzene sulfonic acid or camphor sulfonic acid.

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