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POLYANILINE DOPED WITH ACIDS. METHODS OF SYNTHESIS AND MODIFICATION

ABSTRACT *The research was aimed at the development of the composition and technology of semiconducting materials based on polyaniline. Such materials, which have simple methods of production, are lightweight and have high thermal resistance, may be used in electrotechnical, electronic, and automotive devices, such as power generators and cooling or heat recovery elements.*

The technology for the production of semiconductive materials based on polyaniline-modified hydrochloric or camphorsulfonic acid is presented. The influence of the acid type on the electrical conductivity of the polymer was determined. Thermal analysis was performed for the obtained materials.

Keywords: polyaniline, conducting polymers, chemical modification, conductivity
DOI: 10.5604/01.3001.0009.4413

1. INTRODUCTION

Intrinsically conducting polymers (ICPs) have been a subject of great interest for material engineering since the 1960s. These polymers may be applied in the electric, electronic, thermoelectric, electrochemical, electromagnetic, electromechanical, electroluminescent, electrorheological and chemical multidisciplinary areas, as materials for membranes and sensors [1-6].

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Intrinsically conducting polymers may differ in their charge transport properties. They can thus be classified into three groups:

- conjugated polymers: in a similar way to metals, conduction bands are formed due to the delocalization of electrons in chemical bonds. These polymers exhibit conjugated π -bond systems. Other polymers, which don't contain multiple bonds, exhibit a different mechanism. Their conductivity results from the interaction of empty d-orbitals along their backbone;
- redox polymers: polymers containing electroactive groups, which can carry the charge;
- ion-conducting polymers: charged ions are transported through the polymer chains.

One polymer may exhibit more than one mechanism of charge transport. This phenomenon is often used in the modification for conduction improvement, since the practical use of intrinsically conductive polymers is limited due to their much lower electrical conductivity compared to metal. In such cases, the conducting composites are compounded, with the polymer matrix being filled with a conducting additive (e.g. metals, carbons or other ICPs).

The following polymers can be taken as examples of intrinsically conductive structures: polyacetylene (PA), polypyrrole (PPY), polythiophene (PT), polyaniline (PANI), poly(p-phenylene vinylene) (PPV) and poly(p-phenylene) (PPP), and their derivatives. The structural formulas of these ICPs are shown in Figure 1.

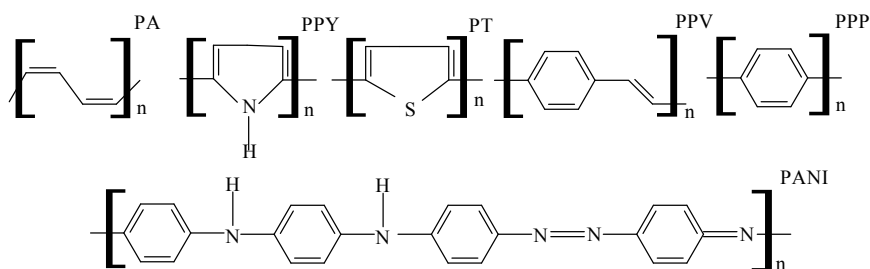


Fig. 1. The chemical structure of intrinsically conducting polymers

Polyaniline (PANI) is one of the most common conducting polymers. This material is relatively inexpensive, its synthesis and processing technologies are simple, and a variety of modification methods is available. Polyaniline is a p-type semiconductor with a delocalized π -bond system. The electrical conductivity of PANI is determined mainly by molar mass, degree of crystallinity and oxidation (Fig. 2), the particle arrangement and the amount or type of additives [1-6].

Polyaniline may occur in three basic forms of different colour and oxidation state:

- pernigraniline ($n = 0$): the oxidized form, purple-blue in colour;
- leucoemeraldine ($n = 1$): the reduced form, white or yellow in colour, with electrical conductivity in the range of 1 S/cm
- emeraldine ($n = 0.5$): the intermediate and most popular form, easy to synthesise and environmentally stable, blue-green in colour. The unmodified structure is an electric insulator with conductivity in the range of 10^{-10} S/cm. Emeraldine doped by, for example, HCl is characterized by metallic conductivity of 10^5 S/cm.

The differences in the chemical structure of various forms of PANI are presented in Figure 2.

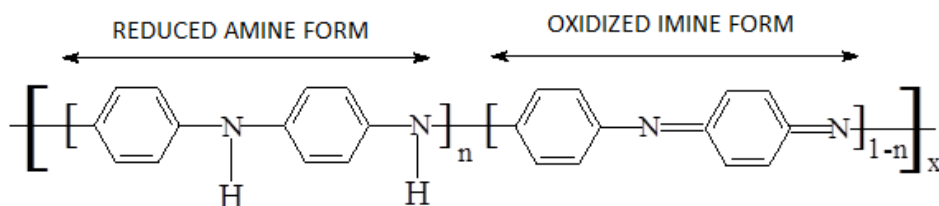


Fig. 2. The chemical structure of polyaniline

The conducting polyaniline can be used as a conductive adhesive, a conductive ink or paint, and an anti-static or electrostatic-discharge-sensitive material. It may also be used in the manufacture of intelligent fibres used for thermoregulatory textiles (in the fields of sport, the military and medical diagnostics) and cooling coatings (involving direct cooling without fans or refrigerants). Other important applications of polyaniline are heat recovery, cathodic corrosion protection (for steel, copper and iron), data collecting and telecommunication.

Polyaniline can be synthesized by chemical, electrochemical, enzymatic, plasma, and photolytic methods, and by the use of a template. Most often PANI is produced by oxidative polymerization in an aqueous solution or in the presence of an acid to achieve the salt product. The average particle size of PANI varies from a few dozen to a few hundred nm. The shape of the particles can be very diverse: spherical, granular, globular, cylindrical or dendritic-branched.

2. MATERIALS

Aniline (Reagent Plus 99%, Sigma-Aldrich), Ammonium persulfate (ACS Reagent $\geq 98\%$, Sigma-Aldrich), Camphor-10-sulfonic acid (β) (98%, Aldrich), Hydrochloric acid 35-38% (a.p., CHEMPUR), 2-Acrylamido-2-methyl-1-propanesulfonic acid (99%, Aldrich), Dichloroacetic acid (ReagentPlus®, $\geq 99\%$ Sigma-Aldrich).

3. SYNTHESIS

The polyaniline was prepared via oxidative polymerization, in an aqueous medium in the presence of ammonium persulfate as the oxidizing agent. During the polymerization, the temperature was set at 0 – 5°C. The polyaniline obtained was marked PANI and was treated as a reference sample. The protonation process was carried out with several types of acids which were either used singly, in the case of organic camphorsulfonic acid and inorganic hydrochloric acid, or in a system with two organic acids, solid 2-acrylamido-2-methylpropane sulfonic acid and liquid

dichloroacetic acid. Samples were marked PANI-CSA for modification by camphorsulfonic acid, PANI-HCl for modification by hydrochloric acid and PANI-AMPSA/DCA for the two acids. Protonation by single acids was first performed *in situ* during the polymerization by adding the acid (in an equal amount to the monomer) to the aqueous solution. The samples were marked PANI-CSA(S) and PANI-HCl(S). The protonation was also performed as a modification of emeraldine. These samples were marked as PANI-CSA(M) and PANI-HCl(M) and were prepared via the post-synthetic dissolution of the polymer in toluene with the addition of the chosen acid (in an equal amount to the polymer). The composite PANI-AMPSA/DCA was produced in a two-step process. First, the polyaniline and AMPSA (as the protonating– agent/counterion) were ground and mixed in a mortar, then a dispersion in DCA (an acidic solvent) was prepared, filtered off and dried. The protonating agent AMPSA was added to the polyaniline in a weight ratio of PANI:AMPSA 1:0.6.

4. MEASUREMENT METHODS

All the materials produced were tested by thermal analysis. This method combines the temperature characteristics of the mass changes (TG) and the thermal effects (DSC) occurring in the material at a set temperature regime. This is a quick method of determining the purity of the material, its quantitative composition and its temperatures of operating, processing and degradation. Thermal analysis can be useful in estimating the risk involved during usage of the material, thanks to the possibility it provides of determining the energy released or absorbed during the material's thermal degradation.

Thermal analysis was performed in air on a TGA/DSC Star System from METTLER TOLEDO. In all cases, the temperature rise and range were 10°C/min and 25-1000°C, respectively.

Measurements of resistivity were also made for all polyaniline-based materials.

For good reproducibility of the results, the measurements were carried out in a special cell with a cross-section of 1 cm². The cell, filled with the tested material, was closed and loaded with a 0.65 kg punch. 60 seconds after the load application, the resistance of the sample was measured using a Keithley 65117 electrometer at 20 V DC [7, 10]. The values of resistivity were calculated from the equation (1):

$$\rho = R \cdot s/l \text{ [}\Omega\cdot\text{cm]} \quad (1)$$

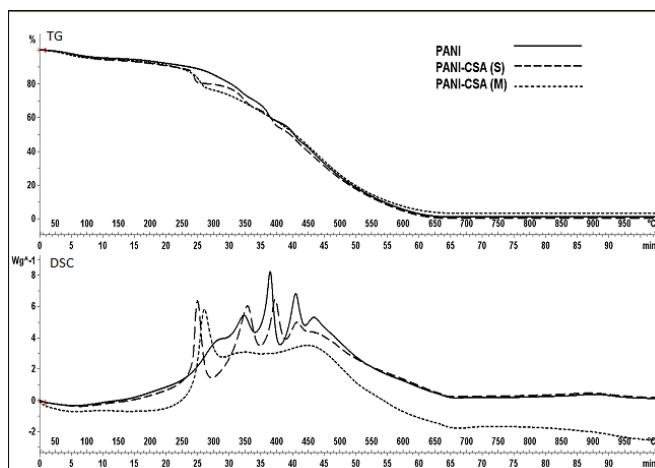
where

$s = g \cdot 1$ because $l = 1 \text{ cm}$,

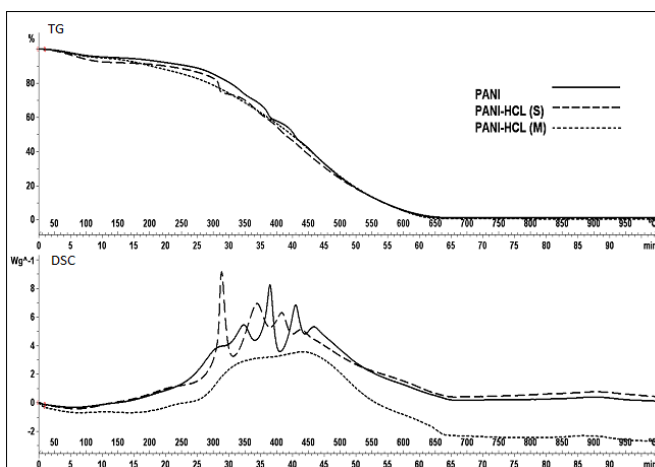
g – the height of the tested material in the cell [cm].

5. RESULTS AND ANALYSIS

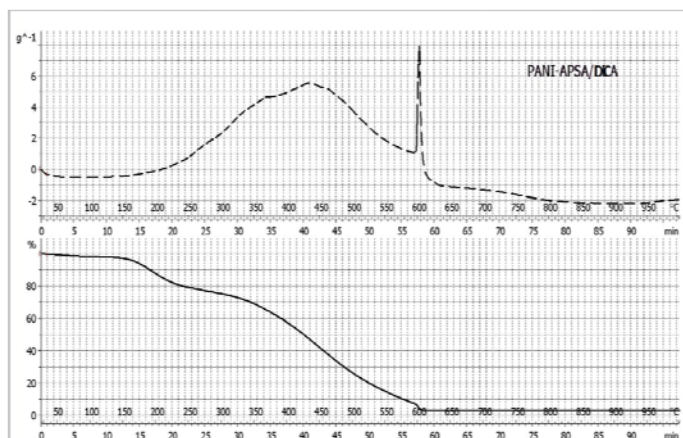
All the materials were obtained as powders and tested in this form. The DSC / TG thermograms created for all materials are shown in Figures 3 – 5.



Rys. 3. The thermogram of PANI protonated by CSA *in situ* during the polymerization (S) and post-synthetic protonation(M)



Rys. 4. The thermogram of PANI protonated by HCL *in situ* during the polymerization (S) and post-synthetic (M) protonation



Rys. 5. The thermogram of PANI modified by the AMPSA and DCA two acid system

The single (HCl, CSA) acidic modifiers do not affect the thermal resistivity of polyaniline. Regardless of the modifying method, the materials degrade at a temperature above 250°C, just like unmodified polyaniline. The modification does not influence the thermal degradation of polyaniline or its accompanying effects. Modification by the two organic acids in tandem of the tandem organic acids significantly lowers the thermal stability of polyaniline (to 150°C).

None of the prepared materials were contaminated during the synthesis or modification. The DSC and TG curves do not reveal signals (peaks) from foreign compounds.

The content of the CSA introduced to the PANI matrix *in situ* during the polymerization is two times lower than in the case of post-synthetic modification and reaches 10% by weight.

The content of the HCl in the polyaniline introduced *in situ* reaches 20 wt%. The post-synthetic modification results in no bonding between the HCl and PANI, as the TG curves corresponding to the PANI-HCl (M) and unmodified PANI are similar.

In the case of both the HCl and CSA, the maximum amount that chemically bonds to the polymer matrix is 20 wt% of the acid.

The two-step modification results in the total acidic modifier content amounting to 20 wt% in the case of PANI-AMPSA/DCA. The results of the resistivity measurements are shown in Table 1.

TABLE 1
The resistivity of the polyaniline-based materials

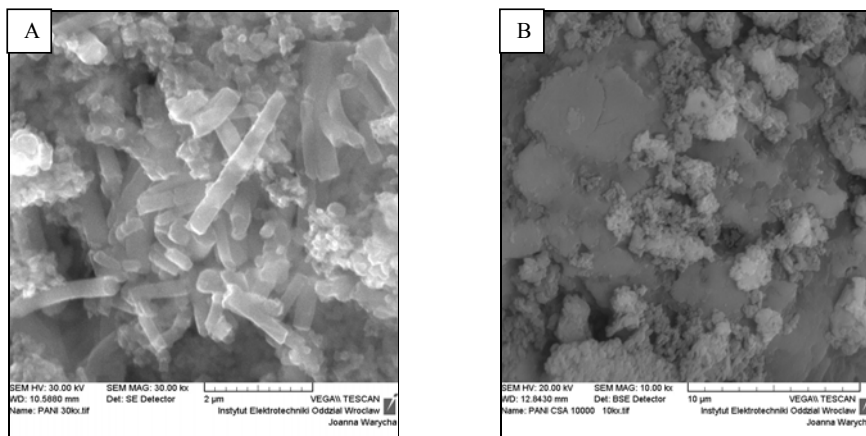
SAMPLE	RESISTIVITY [$\Omega \cdot \text{cm}$]
PANI	$5 \cdot 10^{12}$
PANI-HCl (S)	$1,8 \cdot 10^3$
PANI-HCl (M)	$1,45 \cdot 10^{10}$
PANI-CSA (S)	$4,8 \cdot 10^{11}$
PANI-CSA (M)	$3,85 \cdot 10^7$
PANI-AMPSA/DCA	$4,8 \cdot 10^5$

Each modification by acids decreases the resistivity of the polymer. However, some significant differences are visible. The inorganic acid is more effective *in situ*. PANI-HCl(S) reaches values of electrical conductivity typical for semiconductors, and of about seven orders of magnitude higher than the PANI-HCl(M) prepared via post-synthetic modification. In the case of organic acid, the results are the opposite. The resistivity decreases by an order of magnitude after protonation *in situ* (PANI-CSA(S)) and the post-synthetic protonation results in a decrease of four orders of magnitude (PANI-CSA(M)).

Comparing the resistivity values for both acids, the inorganic HCl is clearly more effective as a modifier. According to [5, 8-9], however, the organic CSA may also act as a plasticizer. This is advantageous for processing and, in some cases, might be more important than high electrical conductivity.

The two-step modification of polyaniline decreases the resistivity by 7 orders of magnitude (PANI-AMPSA/DCA).

For chosen samples, microscopic observations were done with the use of a VEGA II scanning electron microscope from TESCAN. The SEM images showed that the addition of hydrochloric acid as the synthesis solution forces a cylindrical shape of the PANI particles (Fig. 6). In other cases, the polyaniline formed globular particles.



Rys. 6. SEM pictures of polyaniline protonated (A) by inorganic hydrochloric acid (PANI-HCl) at a magnification of 30 000x and (B) by organic camphorsulfonic acid (PANI-CSA) at a magnification of 10 000x

6. SUMMARY

Among the materials modified by acids, the greatest improvement in electrical conductivity, without the thermal stability of the obtained material being negatively affected, was observed for the PANI-HCl (S), which is polyaniline modified by hydrochloric acid *in situ* during the polymerization. Microscopic observation showed that it is also the material with the best structure, since the elongated polymer structure has a great

impact on the conducting path. However, the hydrochloric acid, due to its own chemical structure, does not have plasticizing groups, as in the case of large organic counterions in CSA and AMPSA. Thus, it doesn't facilitate the processing of the polymer.

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POLIANILINA PROTONOWANA KWASAMI. METODY SYNTEZY I MODYFIKACJI

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STRESZCZENIE *Prowadzone badania miały na celu opracowanie składu surowcowego i technologii wytwarzania półprzewodzących materiałów na bazie polianiliny. Takie tworzywa o prostych metodach wytwarzania, dodatkowo lekkie i wytrzymałe termicznie można stosować w elektrotechnice, elektronice, czy przemyśle motoryzacyjnym, jako generatory prądu, elementy chłodzące bądź do odzysku ciepła.*

Przedstawiono technologię wytwarzania materiałów półprzewodzących na bazie polianiliny modyfikowanej pojedynczym kwasem solnym lub kamforosulfonowym oraz układem dwóch kwasów organicznych. Określono wpływ rodzaju zastosowanego kwasu na przewodność elektryczną polimeru. Wykonano analizę termiczną dla otrzymanych materiałów.

Słowa kluczowe: *polianilina, polimery przewodzące, modyfikacja chemiczna, przewodność elektryczna*

Ewa KOLASIŃSKA, Ph.D., Eng. – in 2007 graduated from Wrocław University of Science and Technology, from the Faculty of Chemistry, with a specialization in the Chemistry and Technology of Polymers. Since 2007 she has been employed in the Electrotechnical Institute, Division of Electrotechnology and Materials Science, in Wrocław. Her main areas of professional interest are nanotechnology, polymer nanocomposites and thermal analysis.



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