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Application of Polyaniline for the Modification of Polylactide Fibres

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Abstract

Polyaniline was deposited on a polylactide nonwoven by the in situ method in the form of emeraldine salt (Green Protonated Emeraldine), i.e. by oxidative polymerisation on the fibre surface. The nonwoven was also padded with a solution of Blue Emeraldine Base. Depending on the type of polyaniline (PANI) deposited, the resulting samples showed different conductance values. Changes in electrical resistance were assessed versus the procedure of final treatment. Thermogravimetric measurements showed an increase in the temperature of decomposition of about 50 °C compared to that of an unmodified sample. The nonwoven with the deposited layer of PANI was overlaid with a layer of complexing polymers by the layer-by-layer method. The effect of such a modification on the electro-conductive (resistance) and sorption properties of nonwovens was examined.

Key words: polylactide fibres, modification, polyaniline, polylactide nonwoven, layer-by-layer method, electrical resistance.

regeneration of tissue, implantable electrodes for neuron recording or stimulating, especially in the brain, among others. From among conductive polymers, the most frequently used include polyacetylene (PA), polypyrrole (PPy), polythiophene (PT) and polyaniline (PANI), being the most popular electro-conductive polymer. The latter is usually prepared by the oxidative polymerisation of aniline initiated with ammonium persulfate [2, 3]. According to [4], PANI occurs in three basic forms: leucoemeraldine, emeraldine and pernigraniline. One can obtain PANI with different degrees of oxidation, which is presented in **Figure 1** (see page 120).

Beside these chemical forms of PANI, the nanostructures of polyaniline have aroused growing scholarly interest, as shown by paper [4], containing about 600 references. Some of the papers suggest the possibility of producing fibers from PANI [5, 6]. Fibers were spun using polyaniline (emeraldine base) and 2-acrylamido-2-methyl-1-propan sulfonic acid in various solvents [5]. Fibers spun from a 14% by wt. solution in dimethylpropylene urea (DMPU) showed good strength. However, the instability of the spinning process impeded its implementation on a technological scale. Recently nanofibers have been obtained from the mixture of PLA and PANI or poly(aniline-co-benzoic) copolymer [6].

Interestingly, layers of PANI can be deposited on flat surfaces or microsphere surfaces, e.g. as reported in papers [2, 3], which describe the deposition of PPy and PANI layers on sulfonated polystyrene rubber. The polymerisation of aniline was performed by its oxidative polymerisation with the use of ammonium

persulfate at a temperature of 0°C and 25°C. The electric conductance of PANI layers deposited on polystyrene does not depend on temperature; and the thicker the PANI layer, the better (0.8 nm to 27.3 nm).

Fibers overlaid with PANI layers were also obtained. The *in situ* deposition of a PANI layer on a fiber surface is reported in paper [8], in which fibers were immersed in a solution containing aniline and a doping substance, and then the oxidative polymerisation of aniline was carried out. After removing oligomers and non-reacted aniline from the fibers, an electro-conductive layer of PANI remained on their surface.

Polyamide fibers coated with PANI were obtained by Chandran and Narayanankutty [7] using two methods of aniline polymerisation: two-bath and single-bath treatments. In the first method, polyamide 6 fibers were immersed in previously distilled aniline or aniline hydrochloride at a temperature of 40°C for an appropriate length of time to ensure its diffusion. Then, after removing excess aniline, the fibers were immersed in a mixture of an oxidiser and doping agent. In the second method, fibers were immersed in a solution of aniline hydrochloride for a specified time and polymerisation was gradually initiated by adding a solution of oxidiser and doping agent so as to gradually change the aniline to an oxidiser ratio.

Polyamide 6 fibers were pretreated with a 0.012 N chromic acid, washed with water and immersed in aniline for 24 h. The polymerisation of aniline was performed for 4 h with the use of ammonium persulfate. It was found that the fiber overlaid with a layer of PANI, regardless of the

■ Introduction

Electro-conductive polymers find widespread technical application in electronics, optoelectronics and biomedical engineering. The beneficial properties of conductive polymers compared with those of metallic plastics, such as higher flexibility, ease of processing, biocompatibility, and red-ox stability make it possible to use them in numerous practical applications. Many applications of electro-conductive polymers in biomedical engineering have been reported by Guimard *et al.* [1]. From among the biomedical applications, the authors mention biocompatible and biodegradable scaffolds for the

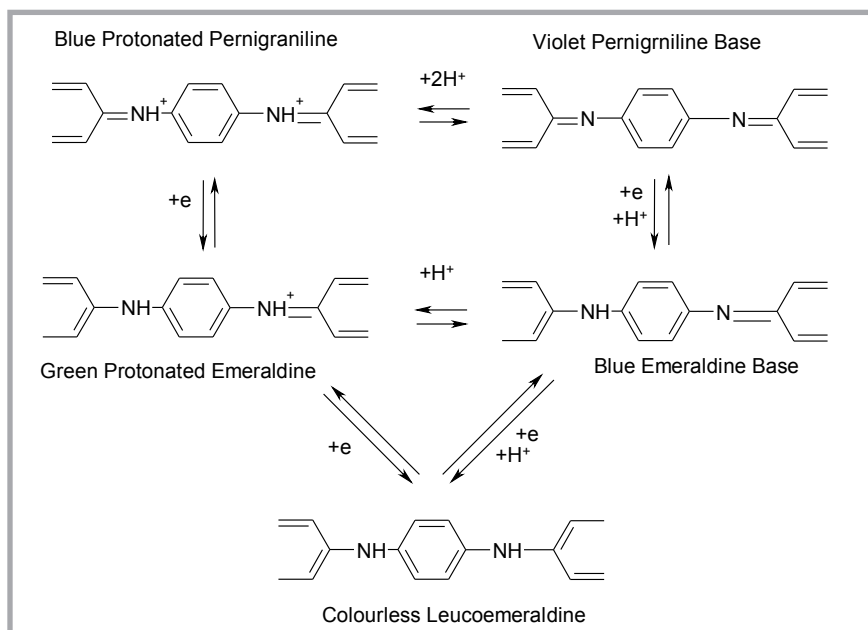


Figure 1. PANI with different degrees of oxidation.

method used, changed its electric conductance in cycles when its medium was altered from basic to acidic.

A similar method of forming a PANI surface layer on polyester and polyamide fibers was the subject of several patents by Kuhn and Kimbrell [10]. PANI layers were also deposited on polyester fibers from PANI solution in organic solvents containing dodecylbenzenesulfonic acid to impart antistatic properties to these fibers [11].

Fibers or films modified with PANI were used to make polymeric composites. One of the methods of making composites consisted in depositing PANI layers by the layer-by-layer method (LbL) [12], in which PANI layers were deposited on various products such as glass, plastic, and metal or silicones [12].

The aim of the present study was to prepare polylactide nonwoven overlaid with PANI and to examine the electro-conductive, sorption and thermogravimetric properties of such nonwovens.

Additionally, it was decided to assess the possibilities of further modification by successive depositions of polymer layers and the effect of such a modification on the properties of PLA nonwovens. Such a modification would make it possible to use the resultant nonwovens for making sensory systems and electro-active scaffolds in accordance with the suggestions included in [7].

Materials and methods

The following nonwovens were used in the study: nonwoven WA_4 with a surface weight of 81.37 g/m² made by the stitching method from commercial PLA 62/01 fibers, nonwoven WA_5 with a surface weight of 103 g/m² made by the stitching method from commercial PLA Ingeo fibers, type SLN-2660D-SOLID from FET Taiwan. Analar aniline Champur was freshly distilled under a vacuum. Polyaniline (emeraldine base), $M_w = 5000$ g/mol, poly(acrylic acid), $M_w = 450\,000$ g/mol, poly(ethylene oxide), $M_v = 1\,000\,000$ g/mole, and polyvinylpyrrolidone, $M_w = 25\,000$ g/mole, were provided by Aldrich. Poly(dimethylaminoethyl methacrylate), $M_w = 63\,000$ g/mole, was prepared according to [12].

Deposition of a Green Protonated Emeraldine (GPE) layer on PLA nonwoven by the *in situ* method

PLA nonwovens: WA_4 and WA_5 were immersed in a solution containing 0.1 mole (9.2 g) of aniline and 0.1 mole of HCl (100 ml of 1M solution), additionally acidified with 1 M HCl to pH = 1. Then a solution of oxidiser containing 0.125 mole (2.85 g) of (NH₄)₂S₂O₈ in 100 ml of water was added. Immediately a green colour appeared, followed by precipitation. The system was left at room temperature for 2 h and then rinsed several times with distilled water. After the deposition of a PANI layer, the nonwoven was rinsed with 1.2 M HCl to remove non-reacted aniline and oligomers.

The nonwoven with deposited Green Protonated Emeraldine (GPE) was green.

Deposition of a PANI layer in the form of Blue Emeraldine Base (BEB)

A solution of emeraldine base was prepared by dissolving 4.185 g of polyaniline in 150 ml of dimethylacetamide. The resultant PANI solution was then diluted with water in a proportion of 1:8 to obtain a suspension containing 0.1 M of BEB. This intensively blue solution was used to deposit a BEB layer on WA_5 nonwoven, which was then dried in air. The nonwoven sample was blue.

Deposition of polyelectrolyte layers

The nonwovens with a deposited GPE layer were overlaid with polymer layers forming polycomplexes with PANI or an appropriated top layer according to the LbL procedure [14]. Samples were immersed in a diluted solution (10⁻² M) with an appropriate polymeric component such as poly(acrylic acid), poly(dimethylaminoethyl methacrylate), poly(ethylene oxide) or polyvinylpyrrolidone. After the deposition of each layer, the samples were repeatedly rinsed in distilled water to remove the non-reacted reagent.

Testing electric resistance

The electric resistance of the samples tested was measured by means of an ALDA AVG meter using the two-electrode method. Samples in the form of 10 mm strips were installed in a holder with a 5 mm slot (active length measured: 5 mm). Measurements were carried out during which the pressure was increased until the resistance of the sample was constant; 12 measurements were performed for each sample. Extreme values were rejected, and the average value was calculated from 10 measurements. The standard deviation was also calculated.

Thermogravimetric analysis

Thermogravimetric analysis was carried out by means of a TGA 7 thermoanalyser (Perkin Elmer) with a Pyris program. Measurements were performed in an atmosphere of synthetic air (80 % nitrogen and 20% oxygen) at a heating rate of 15°C/min. The gas flow rate was 20 cm³/min.

Spectrometric analysis

The IR spectra of the PANI-coated and initial nonwovens were recorded by means of an FTIR Perkin Elmer spec-

trometer, model 2000, with a Spectrum v3.02 program and ATR accessory – the MIR version equipped with a KRS5 crystal providing an angle of incidence of 45°. A sample of emeraldine (BEB) was prepared in the form of a KBr tablet, and the spectrum was obtained by the transmission method.

The UV-VIS spectra of the PANI-coated nonwovens were recorded by means of a UV-VIS-NIR spectrometer, type V-670, from Jasco, in the reemission mode. The values of reemission were recalculated into values of Kubelka-Munk's function.

Determination of moisture absorption

The moisture absorption of the PLA nonwovens was performed according to PN-80-P-04635.

Results and discussion

Two types of PANI layers were deposited on PLA nonwovens by two methods.

1. The first method consisted in padding WA_5 nonwoven with BEB solution according to paper [15, 16]. The presence of a PANI layer was confirmed by IR spectra. **Figure 2** shows the IR spectra of WA_5 nonwoven padded with emeraldine base, unmodified nonwoven and emeraldine base. The latter is dominated by two bands ascribed to the stretching vibration of quinone ring (1596 cm⁻¹) and benzene ring (1498 cm⁻¹). The spectrum of unmodified PLA nonwoven shows no band within this range, while in the spectrum of the nonwoven padded with emeraldine base, one can observe additional small bands in a position consistent with that of the bands of emeraldine base. To

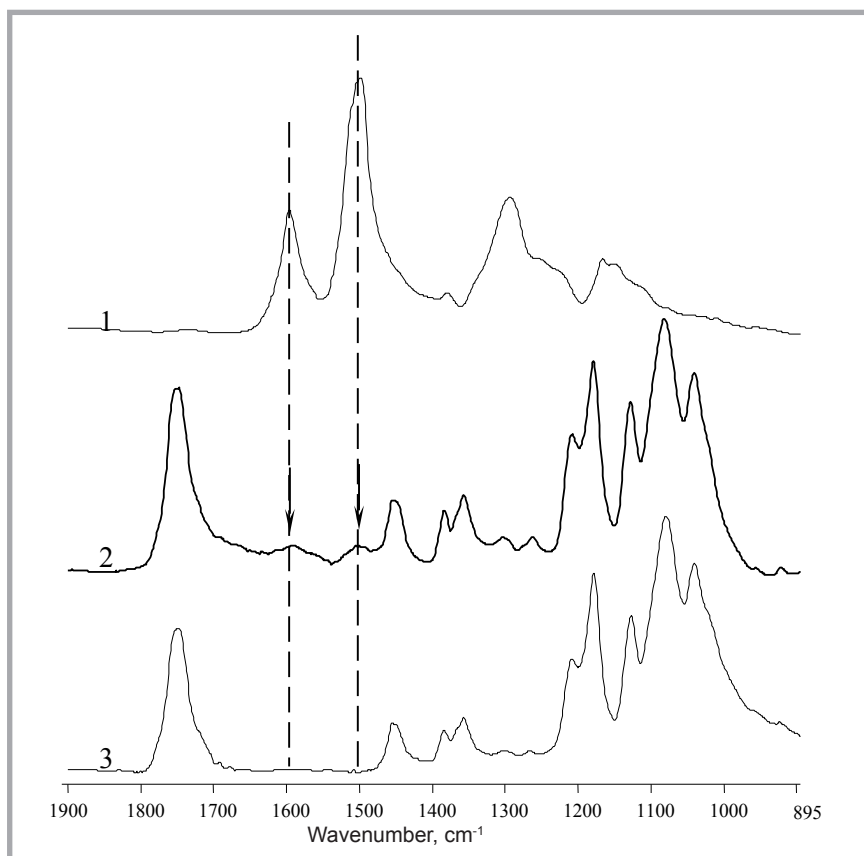


Figure 2. Standardised IR spectra: 1 – emeraldine base, 2 – nonwoven padded with emeraldine base solution, 3 – unmodified nonwoven.

convert emeraldine base into a conductive salt form, the nonwoven was doped with 1M HCL. The nonwoven changed its colour to green but did not show any electric conductance.

The UV-VIS spectra of the non-doped and 1 M HCl-doped nonwovens are shown in **Figure 3**, which also shows the spectrum of the nonwoven modified with emeraldine salt using the *in situ* method.

In the spectrum of the sample padded with BEB solution (spectrum 1), one can observe two bands at 328 nm and 602 nm, corresponding to excited π electrons in the benzene and quinone rings, respectively [17, 18]. The spectrum of the sample modified by the *in situ* method (spectrum 3) shows two bands at 405nm and 770 nm that are characteristic of the protonated form of PANI. The UV-VIS spectrum of the sample padded with em-

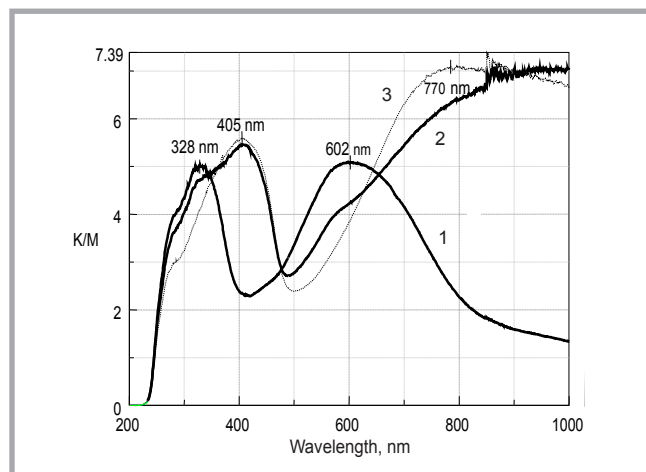


Figure 3. UV-VIS spectra: 1 – WA_5 nonwoven padded with emeraldine base solution, 2 – nonwoven doped with HCl, 3 – nonwoven modified in situ.

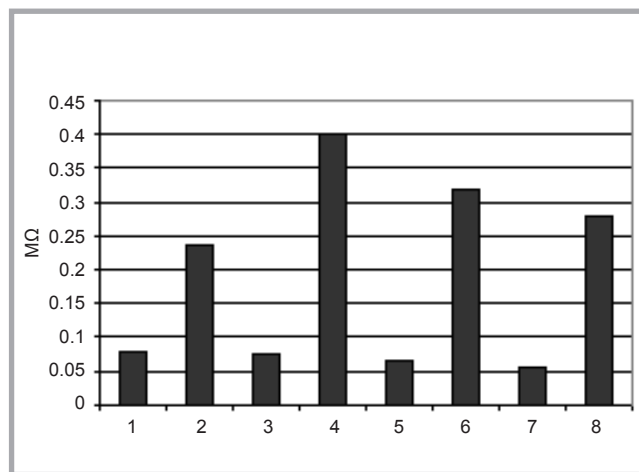


Figure 4. Electrical resistance of nonwovens modified in situ and rinsed in HCl solution (odd numbers) and NaOH solution (even numbers).

Table 1. Maxima of Kubelka-Munk's function in the UV-VIS spectra of WA_4 nonwovens with a PANI layer deposited *in situ* after acid and base treatments.

Type of bath	Position of Kubelka-Munk's function's maximum in UV-VIS spectrum, nm	
–	380	730
NaOH	564	
HCl	380	750
NaOH	544	
HCl	360	760

Table 2. Moisture absorption by PLA nonwovens at 100% RH.

Type of nonwoven	Deposited layers	Moisture content in percent at 100% RH
WA_5		0.33
WA_4		0.10
WA_5	PANI	2.73
WA_4	PANI	0.82
WA_4	PANI+PEO	1.65
WA_4	PANI+PVPy	0.95
WA_5	PANI+ PEO	3.37
WA_5	PANI+PVPy	2.58
WA_4	PANI+ PEO +PKA	4.98
WA_4	PANI+PVPy+PKA	1.39
WA_5	PANI+ PEO +PKA	0.89
WA_5	PANI+PVPy+PKA	1.82

eraldine base (BEB) and then doped with HCl (spectrum 2) consists of absorption bands corresponding to the base and protonated forms. One can assume that the protonation was insufficient to impart electro-conductive properties to this nonwoven sample.

2. In the second method, a layer of PANI was directly deposited on the nonwoven surface in the form of emeraldine salt by the *in situ* oxidative polymerisation of aniline. The nonwovens modified by the *in situ* method were subjected to UV-VIS analysis. The UV-VIS spectrum of the WA_4 nonwoven with a PANI layer deposited by the *in situ* method show

the presence of two absorption bands at about 380 nm and 750 nm, characteristic of the conductive form of PANI. Then the WA_4 nonwoven with the deposited PANI layer was immersed successively in 0.1 M NaOH and 0.1 M HCl solutions. After each bath, the sample was dried and its UV-VIS spectrum recorded. The sample treated with the base changed its colour from green to blue, while its UV-VIS spectrum showed no bands at 380 nm and 750 nm; however, there was the appearance of a band at 560 nm, which corresponds to the conversion of emeraldine into its base form. These changes were of a reversible character and were repeated in cycles. The positions of

Kubelka-Munk's function in particular spectra are listed in **Table 1**.

The resistance measurements of the samples with a PANI layer deposited by the *in situ* method confirm a considerable decrease in the resistance of the modified samples compared with that of the initial samples, showing no conductance. In the case of WA_4 nonwoven, its electric resistance ranged from 7.5 kΩ to 17.6 kΩ and that of WA_5 nonwoven varied from 40.4 to 50.2 kΩ. However, some scatter of the results was observed. A high scatter can be due to the non-uniformity of the deposition. Hence the values measured should be treated as estimated (approximate) values.

The WA_5 nonwoven sample with deposited PANI was successively immersed in 0.1N HCl and 0.1N NaOH and then rinsed in water each time after carrying over, followed by measurement of its resistance. Changes in the resistance are illustrated in Figure 4. It was found that the resistance of the samples tested reproducibly and reversibly depended on the type of electrolyte used. These observations correlate with the above-mentioned changes in UV-VIS spectra caused by alternate rinsing in NaOH and HCl solutions.

3. The nonwoven with a deposited PANI layer was overlaid with successive layers of two types of polycomplexes, one of which (polycomplexes of type I) constituted complexes of polyelectrolytes, such as PAA and PDAMA, formed as a result of electrostatic interactions. The second type (polycomplexes of type II) consisted of polycomplexes stabilised with hydrogen bonds, formed with the contribution of poly(ethylene glycol) or polyvinylpyrrolidone. The arrangement of the succes-

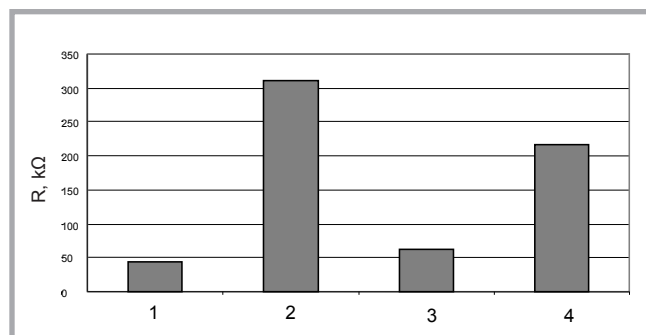


Figure 5. Electrical resistance of WA_4 nonwoven modified with type I polycomplexes versus the number of layers and type of this final layer: 1 – PANI+PKA+PDAMA; 2 – PANI+PKA+PDAMA+PKA; 3 – PANI+PKA+PDAMA+PKA+PDAMA; 4 – PANI+PKA+PDAMA+PKA+PDAMA+PKA.

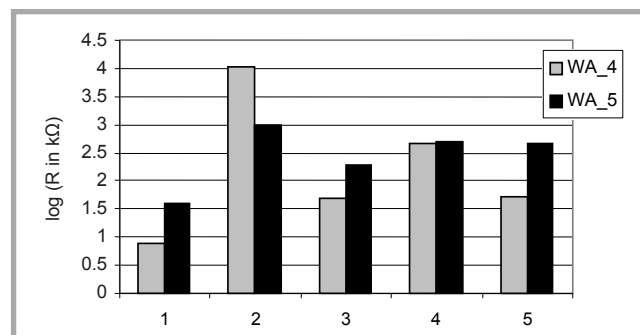


Figure 6. Electrical resistance of nonwovens modified with type II polycomplexes versus the number of layers and type of final layer (R in kΩ): 1 – PANI; 2 – PANI+PGE; 3 – PANI+ PVPy; 4 – PANI+PGE+PKA; 5 – PANI+PVPy+PKA.

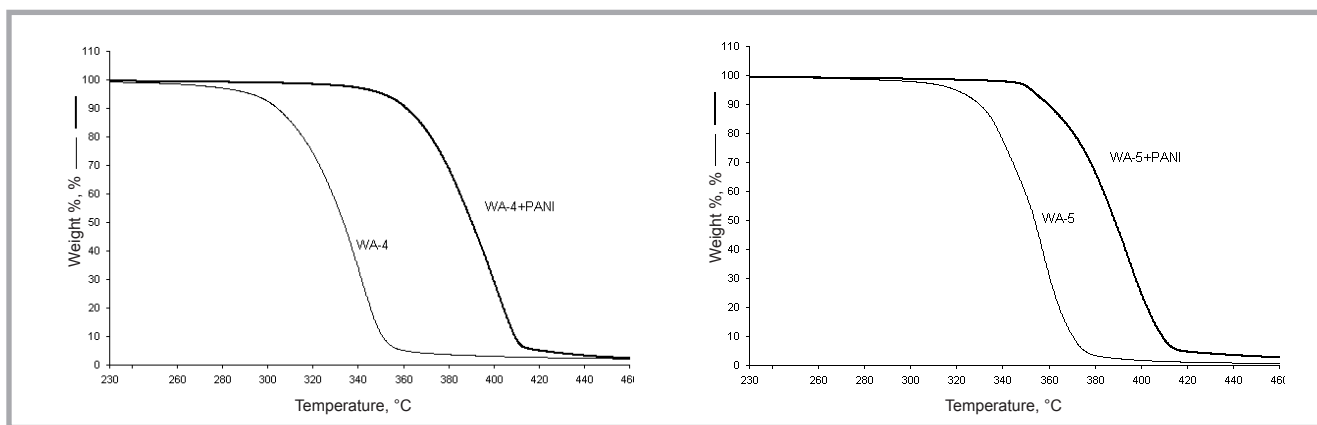


Figure 7. Thermograms of unmodified nonwoven samples and those modified by *in situ* deposition of a PANI layer.

sively deposited polymer layers of type I complexes and the results of resistance measurements are shown in **Figure 5**. The results obtained seem to indicate a shielding effect caused by the deposition of polymeric polycomplex layers on the surface overlaid with PANI. This effect, i.e. the increase in resistance, is particularly visible when the top layer contains acidic groups derived from PAA. **Figure 6** shows changes in the resistance of nonwovens with deposited layers of type II polycomplexes. Considering the very great differences in resistance found in this case, a logarithmic axis of ordinates was used. As is seen from the results presented, the deposition of non-polar polymer such as poly(ethylene oxide) brings about an even more distinct shielding effect, reflected by the resistance, which is increased by several orders of magnitude.

The results of measuring the moisture absorption of the nonwovens modified by the *in situ* deposition of PANI layers (GPE), as well as after the deposition of successive layers of polycomplexes (LbL method) are listed in **Table 2**. From **Table 2**, it follows that the deposition of PANI on PLA nonwoven increases its hydrophilicity. Further layer deposition does not increase the nonwoven's ability to absorb moisture. In some cases, the sorption is even slightly decreased due to screening access to the PANI layer (GPE).

The nonwoven samples modified with PANI by the *in situ* method (GPE) were also subjected to thermogravimetric analysis. A comparison of the thermograms of PANI-modified and unmodified samples is illustrated in **Figure 7**. The half-decomposition temperature of samples with deposited PANI is higher by 40–60°C than that of unmodified samples, which seems to be due to the pres-

ence of PANI, forming a protective layer impeding the access of air oxygen to the sample tested.

Conclusions

Based on the results presented, it can be concluded that the modification of PLA nonwoven by the *in situ* deposition of PANI layers imparts electro-conductive properties that can be effectively changed by means of a base or acid.

It was found that the presence of PANI on the surface of PLA nonwoven increases its moisture absorption.

The presence of PANI on the modified surface of PLA causes a significant change in its thermogravimetric properties. The thermal decomposition of PLA nonwovens modified with PANI takes place within a temperature range 40–60°C higher than that of an unmodified sample. It seems that the presence of PANI on the fiber surface can impede the access of oxygen, which otherwise contributes to the destruction of “unshielded” fiber.

A shielding effect was observed in the case of depositing successive polymeric complex layers on the PLA nonwoven modified with PANI. This effect manifested itself in a decrease in both electric resistance and hydrophilicity. These results, however, require additional examinations to confirm this thesis, which will be dealt with during further studies.

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