

Electroconductive Polymer Composite: Fibrous Carrier–Polypyrrole

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SYNOPSIS

Obtaining a "hybrid" electroconductive polymer composite material on the basis of a fibrous carrier and polypyrrole (pPy) was studied. As fibrous carriers, polyacrylonitrile (PAN) and chemically modified polyacrylonitrile possessing ion-exchange properties were used. FeCl_3 , chosen as an initiator for oxidative polymerization of pyrrole (Py), was introduced in the fibrous matrix by sorption from an aqueous or diethylether solution. The polypyrrole film was deposited onto/in a matrix prepared in this way by polymerization of pyrrole in a vapor phase, from the vacuum, or from a solution of Py in toluene. In some cases, an additional doping of the obtained (electroconductive) pPy film, with iodine vapors in the vacuum, was also applied. An electroconductive composite material, with volume resistivity of about $10 \Omega \text{ cm}$, was obtained. The results, related to the different nature of the fibrous carrier and different procedures for the oxidizer introduction or pPy deposition, were discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Although polymers, whose backbones (or pendant groups) are responsible for the generation and propagation of charge carriers, are considered to be more scientifically interesting as electrically conductive materials, formidable problems (poor mechanical properties, poor processability, environmental instability, etc.) must be solved before they can be widely used. A new synthetic way of obtaining new electroconductive polymer material, e.g., to so-called hybrid systems,¹ is considered as a way of overcoming the above-mentioned undesirable features. It means a use of electrically conductive polymer as a "filler" in nonconductive polymer matrix, but with low cost, light weight, mechanical durability, environmental stability, and ease of processability. With such a filler one can include variable conductivity by controlling the extent of oxidation or reduction, the ability to dictate the nature of the majority car-

riers, and facile cycling between conductive and insulating states.

The aim of this work is obtaining a "hybrid" electroconductive polymer composite material on the base of fibrous carrier and polypyrrole which can be used as such or as a filler for producing electrostatic discharge (ESD) and electromagnetic interference–radiofrequency interference (EMI–RFI) shield materials.²

The fibrous carrier is chosen because of a high specific surface area, good mechanical features, and ease of shaping. As fibrous carriers, polyacrylonitrile (PAN) and chemically modified polyacrylonitrile, possessing ion-exchange properties [with amidoximes groups (type I³) or carboxylic groups (type II⁴)] have been used. A chemical modification has been undertaken in order to increase the ability of the substrate to absorb Fe(III) —ions (from FeCl_3)—initiator for oxidation polymerization of pyrrole (Py).

The polypyrrole (pPy) film has been deposited onto a previously prepared fiber carrier by polymerization of Py in a vapor phase, from the vacuum, or from a solution of Py in toluene. In some cases, an additional doping of the obtained (electrocon-

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ductive) pPy film, with iodine vapors in vacuum was also applied.

The choice of the fibrous cationit as a carrier is made on the basis of data in Ref. 5, where Sata used the ferric ion form cation exchange membrane as a matrix to produce a conductive composite by immersing such a membrane in an aqueous pyrrole solution. Polypyrrole was formed on the membrane surface, as well as into the membrane matrix, and ferric ions in the membrane were reduced to ferrous ions.

Data for a use of fibers for mentioned purpose has not been found in the literature. There are data, however, about a preparation of polyacrylonitrile, or polyvinyl alcohol-polypyrrole composite films.^{6,7} Polymer films with various percentages of FeCl_3 as an oxidizing agent have been made by casting techniques, while the conductive composites have been prepared by exposing these films to pyrrole vapors in vacuum.

As far as the utilization of textile materials is concerned, there are the data of obtaining composite with electromagnetic shielding characteristics by electrochemical deposition of Ni and pPy onto nonwoven polyester fabrics impregnated by graphite⁸ or obtaining the superparamagnetic-conductive textile composites by a two-step solution deposition process. First, colloidal magnetite particles are adsorbed spontaneously onto the textile fibers (polyester, nylon, cotton, etc.) from an aqueous dispersion utilizing a simple dipcoat procedure. Then these treated fibers are further coated with a conducting polymer overlayer (polypyrrole).⁹

EXPERIMENTAL

In this work the fibers utilized were polyacrylonitrile (PAN) (Malon, "OHIS"—Skopje; 2.2 and 3.3 dtex) and cation exchange fibers obtained by chemical modification of PAN fiber in the procedures described in Refs. 3 and 4. The cationit with amidoxime groups³ (type I) has a static ion-exchange capacity (SIC) of 3 to 7.6 mmol/g, and the cationit with carboxylic groups (type II)⁴ has $\text{SIC}_{\text{H}(\text{Na})}$ (in respect to proton or sodium cation) between 3 and 7.5 mmol/g.

The introduction of oxidizing agent (FeCl_3) in the fiber carrier was done by absorption from solvents with different surface tensions [0.3 g (fiber) ionit in 100 mL 0.1 M FeCl_3 or in conc. aqueous solution, 0.4 M, or in 30 mL saturated solution of FeCl_3 in diethyl-ether¹⁰], which enable a different surface wetting.

A pPy film was deposited, onto a previously prepared fiber carrier, by polymerization of Py in a vapor phase, from the vacuum (2×10^4 Pa), or from a solution of Py (2 M) in toluene. In some cases an additional doping of the obtained (electroconductive) pPy film, with iodine vapors in vacuum was also done.

All the chemicals were from Merck, analytical grade, and they were used as received.

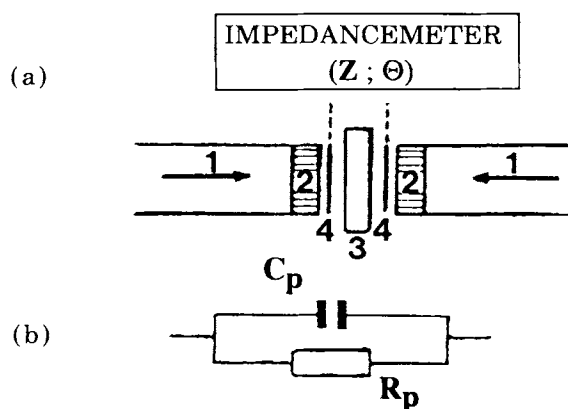
The obtained composite material, as well as the fiber carrier itself, were characterized by the impedance spectroscopy (IS) (Impedancemeter HP, model 4800 A).

Scanning electron microscopy (SEM) micrographs were done by means of a Cambridge Stereoscan S 90, in a ceramic matrix.

Impedance measurements were made in the range of frequencies from 10 Hz to 500 kHz, by placing the sample (0.3 g) between two metallic (Ni) square (quadratic) contacts, with a surface area of 3 cm² (Scheme 1). In all cases the thickness of the fiber layer between contacts (L) was about 0.85 mm.

RESULTS AND DISCUSSION

As mentioned, the effects of treatments providing electroconductive features were followed by IS spectroscopy. Impedance spectroscopy spectra were also done for all intermediates resulting from some kind of modification. All these spectra were compared with frequency dependencies of the impedance Z and the phase angle θ for the nonmodified PAN fiber (3.3 dtex). See Figure 1 (curves 1 and 1').



Scheme 1 (a) Schematic presentation of the unit of measurement; (b) equivalent electric circuit for *ex situ* (atmospheric) conditions: (1) metallic clamps, (2) insulator (Teflon), (3) fiber (0.3 g), and (4) Ni contacts.

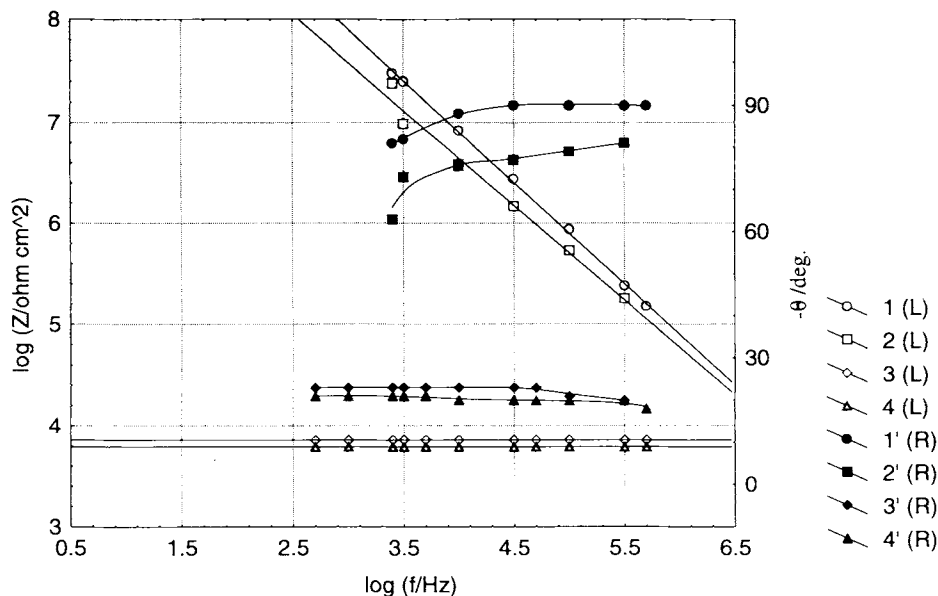


Figure 1 Bode diagrams for (1, 1') nonmodified PAN fiber, (2, 2') following the treatment of 30 min in 0.1M aqueous solution of FeCl₃, and samples treated (3, 3') dry or (4, 4') wet after the FeCl₃ sorbtion in vacuum and vapor of Py.

As it can be seen, in the condition of measuring (contact area of 3 cm²) and technical characteristics of the instrument, the data for $f < 2.5$ kHz (or $Z > 10 M\Omega$) cannot be achieved.

Within the measured range of frequency, however, a relatively good linear dependence, $\log Z - \log f$ with the slope of -1 , has been achieved, as well as relatively constant values of the phase angle θ (from -85° to -90°) indicating a dominant influence of the capacity component within the measured value of the impedance resistance. Namely, the impedance related with the material with good dielectric features is usually expressed by a parallel equivalent electric circuit (EEC) [Scheme 1(b)], which includes capacitance C and ohmic resistance R . Consequently, we can calculate the value of C , as well as the dielectric constant of Malon fiber (for certain layer thickness), from the obtained fre-

quency dependence of Z , and the value of the phase angle:

$$C_{10 \text{ kHz}} = \frac{\sin \theta}{2\pi f |Z|} = \frac{\sin 88}{2 \times 3.14 \times 10^4 \times 8.25 \times 10^6} = 1.93 \times 10^{-12} \text{ Fcm}^{-2}$$

$$\epsilon = 11.3 \times C \times L = 11.3 \times 1.93 \times 0.085 = 1.85$$

The R component and the electric resistivity of the fiber may be approximately calculated as follows:

$$R = \frac{|Z|}{\cos \theta} = \frac{3 \times 10^7}{\cos 81} = 1.92 \times 10^8 \Omega \text{cm}^2$$

$$\rho = \frac{R}{L} = \frac{1.92 \times 10^8}{0.085} = 2.26 \times 10^9 \Omega \text{cm}$$

Table I Impedance Characteristics of Composite Material: Ionit I/PPy in Accordance with SIC

dtex	SIC (mmol/g)	Z (Ωcm^2)	$-\theta$ (deg)	ρ (Ωcm)
3.3	7.60	2.28×10^3	2	2.68×10^4
2.2	5.46	6.60×10^2	12.5	7.76×10^3
2.2	3.00	4.50×10^2	20	5.29×10^3

$f = 10$ Hz to 100 kHz; duration of vaporing with Py 24 h.

Table II Impedance Characteristics of Composite Material: Ionit II-pPy Depending on the Ionite Type, H or Na, SIC, and Duration of the Polymerization Process

SIC (mmol/g)	Ionite Type	τ_{pPy} (h)	Z (Ωcm)	$-\theta$ (deg)	ρ (Ωcm)
3	H	12	126	7	1.48×10^3
3	Na	12	135	5	1.59×10^3
3	Na	24	147	6	1.73×10^3
7.5	Na	24	210	21	2.47×10^3

0.3 g fiber (3.3 dtex); surface of electrodes contacts 3 cm^2 ; $f = 10 \text{ Hz}$ to 100 kHz .

The value of ρ is lower than the theoretical one ($\sim 10^{14}$) which probably results from the inability to determine Z at lower frequencies.

After the treatment of this sample with FeCl_3 solution, the dependencies presented with curves 2 and 2' in the same figure (Fig. 1) have been obtained. As seen, the capacity character of the dependence $\log Z - \log f$ is expressed again, while the measured values of Z , within the entire range of frequencies, are slightly lower. The values of C and ϵ are as follows:

$$C_{10 \text{ kHz}} = \frac{\sin 76}{2 \times 3.14 \times 10^4 \times 3.69 \times 10^6}$$

$$= 4.18 \times 10^{-12} \text{ Fcm}^{-2}$$

$$\epsilon = 11.3 \times 4.18 \times 0.085 = 4.02$$

The increased value of ϵ results from the higher percentage of moisture, as well as of the free ions in the sample. According to Ref. 11 the percentage of moisture in such cases may be calculated as follows:

$$x_w = 100 \frac{\log(C_{it}/C_{to})}{\log 80} = 100 \frac{\log(4.18/1.93)}{\log 80} = 17.6$$

Table III Impedance Characteristics of Composite Material: Ionit II-pPy Depending on Duration of Vaporing (Polymerization)

τ_{pPy} (days)	Z (Ωcm^2)	$-\theta$ (deg)	ρ (Ωcm)
1	159	5	1.87×10^3
3	115.5	6.5	1.36×10^3
5	471	17	5.54×10^3
7	519	17	6.10×10^3

0.3 g fiber (3.3 dtex, SIC = 5.9 mmol Na/g); surface of electrodes contacts 3 cm^2 ; $f = 10 \text{ Hz}$ to 100 kHz .

where C_{it} is the capacity component of impedance Z for the nonmodified Malon fiber treated with FeCl_3 , C_{to} is the capacity component of impedance Z for the nonmodified Malon fiber, while 80 is a relative dielectric constant of the water (at room temperature).

The impedance features of this sample, treated, dry, or wet after the FeCl_3 sorption, in vacuum and vapor of Py are also presented in Figure 1, curves 3 and 3' and 4 and 4', respectively. As it may be seen, the value of Z within the broad area of frequency (10 Hz to 500 kHz) is practically constant and equal to 7.2×10^3 or $6.15 \times 10^3 \Omega\text{cm}^2$, while the phase angle θ is also constant and equal to -18° to -23° . These data indicate the dominant influence of the ohmic component R and formation of an electroconductive film at the fiber's surface.

The increased mass of the PAN fiber, after the process of polymerization of Py in a vapor phase, in the vacuum, is equal to 0.0355 g, i.e., 11%, for the dry sample, or 0.0386 g (11.95%), for the wet one. As is well known, for this type of a composite ($\rho_{PAN} \gg \rho_{pPy}$) the value of ρ_{comp} is determined by the content of the electroactive component in the composite. Thus, for a rubber with $\rho \sim 10^{14} \Omega\text{cm}$ containing 15 wt % carbon black, ρ decreases to approx. 10^4

Table IV Impedance Characteristics of Composite Material: Ionit II-pPy Depending on Duration of Vaporing (Polymerization) in the Presence of Iodine Vapor

τ_{pPy} (days)	Z (Ωcm^2)	$-\theta$ (deg)	ρ (Ωcm)
1	15.60	3	183.5
3	14.45	2.5	170
5	43.50	20	512

0.3 g fiber (3.3 dtex, SIC = 5.9 mmol Na/g); surface of electrode contacts 3 cm^2 ; $f = 10 \text{ Hz}$ to 100 kHz .

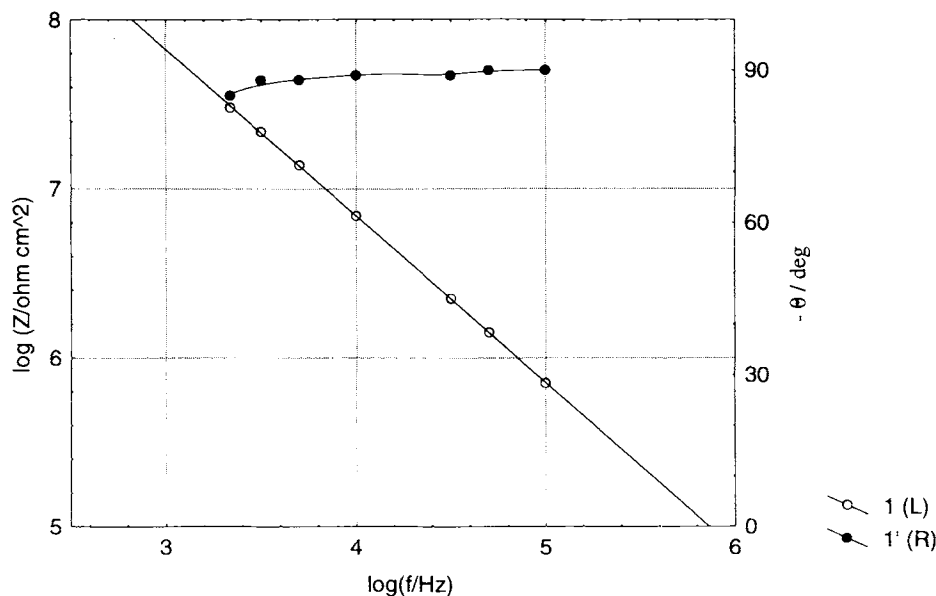


Figure 2 Bode diagram of composite based on ionit II ($\text{SIC}_{\text{Na}} = 5.9 \text{ mmol/g}$), washed after the treatment with FeCl_3 , and pPy (time of vaporing with Py, 24 h).

Ωcm , and for 60 wt % to only $10 \Omega\text{cm}^2$. In our case for the PAN fiber-pPy composite (with 11–12 wt % pPy) the calculated value of ρ ($\rho = 7.2 \times 10^3 / 0.085 \approx 8.5 \times 10^4 \Omega\text{cm}$) is for about five orders of magnitude lower, while comparing with the literature data ($\rho_{\text{PAN}} \sim 10^{14} \Omega\text{cm}$) even for nine ones.

Further on, the previously modified Malon fiber, i.e., ionit type I, has been treated in the same way. The impedance results related with this ionit, with different SIC: 3, 5.46, and 7.5 mmol/g, following different degrees of modification, are presented in Table I.

The initial fibers are with different finess, i.e., a different specific surface area, while the different ion-exchange capacities have been obtained by chemical treatment, in accordance with Ref. 3. The impedance characteristics of ionit in all three cases, before and following the treatment with FeCl_3 , are

actually very similar to those of the nonmodified sample of the PAN fiber. What concerns the impedance characteristics of the obtained composite PAN-pPy, following the application of the vacuum vaporing with Py, the following may be considered:

1. The obtained composites within the entire investigated range of frequency of 10 Hz to 500 kHz, are characterized with constant values of Z and θ , meaning "ohmic behavior."
2. The constant values of Z and θ depend on SIC of the samples; it is obvious that in all cases the value of Z is actually and exclusively determined by the formed pPy film over the ionit and that even at insufficiently homogeneous films, the measuring signal is transmitted through pPy.
3. Values of ρ of the obtained composites (con-

Table V Changes in the PAN Fiber Mass During Absorption of FeCl_3 from Aqueous or Etheric Solution (Previously Swollen for 24 h in Dimethyl Formamide–Water Solution)

Sample No.	Solution	Time of Treatment (h)	Sorbition of FeCl_3 (wt %)	ρ_{PAN} (Ωcm)
1	0.1M FeCl_3 in water	0.5	7.70	2.8×10^8
2	0.4M FeCl_3 in water	0.5	11.10	2.5×10^8
3		60	29.20	7.1×10^7
4	sat. FeCl_3 in ether	0.5	18.40	3.5×10^7
5		60	37.20	2.8×10^6

Table VI Mass of the Deposited pPy Film and Impedance Characteristics of the PAN-pPy: Composite Material

Pretreatment	Deposited pPy/mg and (wt %)				ρ_{comp} (Ωcm)			
	Polym. in Vacuum		Polym. in Solution		Vacuum		Solution	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
0.4M FeCl ₃ in water (60 h)	47 (12.1)	92 (23.7)	62 (16.0)	77 (19.8)	$\sim 1.2 \times 10^4$	261	1.2×10^5	6×10^4
Sat. FeCl ₃ in ether (60 h)	122 (29.6)	168 (40.8)	107 (26.0)	117 (28.4)	~ 70	~ 12	$\sim 10^3$	~ 200

All values are the average ones from three independent experiments.

sidering the total thickness of the composite material, for 0.3 g, about 0.085 cm), range between $5.3 \times 10^3 \Omega\text{cm}$ for the ionit with SIC 3 to $2.7 \times 10^4 \Omega\text{cm}$ for SIC 7.6, while the value of θ is decreased, i.e., $\theta \rightarrow 0$, by increasing SIC, indicating a more expressed ohmic character of the impedance.

The same procedure was applied to ionit II. The impedance of the composite material obtained by ionit II, following the treatment with the FeCl₃ solution and Py vapors in the vacuum, are presented, in Table II depending on the type of the ionit, H or Na, SIC, and the polymerization duration.

The ionit itself, regardless of the form, H or Na, expresses dielectric features comparable with a nonmodified PAN fiber, both prior and following the treatment with the FeCl₃ solution.

What concerns the composite material ionit II/pPy, in all cases, the contribution of pPy to conductivity is significant. Dependence of impedance characteristics of the ionit form, H or Na, has not been noticed; in both cases ρ is about $1.5 \times 10^3 \Omega\text{cm}$, while certain dependence of Z and θ from SIC of the ionite, as well as from the duration of vapping, has been observed.

Considering that the conductivity depends mostly on the duration of the vapping with pyrrole, the following experiment has been performed: cationit in Na form (0.3 g) with SIC 5.9, treated 30 min in FeCl₃ solution (0.1 M) vaped with pyrrole in vacuum, 1, 3, 5, and 7 days, in phases (each 2 days), spraying with FeCl₃ solution.

The impedance characteristics are presented in Table III.

As seen in all samples, the ohmic component of the impedance resistance is dominant, while the electric resistivity ranges from $1.87 \times 10^3 \Omega\text{cm}$, first

day, $1.36 \times 10^3 \Omega\text{cm}$ the third, and $5.54 \times 10^3 \Omega\text{cm}$ the fifth day; i.e., a slight increase of the impedance resistance, after the third day has been registered.

The assumption, in all cases so far discussed, is that the doping of the pPy film, i.e., its electroneutrality is provided by the chloride anion. In order to provide an additional doping, the same experiment was repeated, using the vapping by pyrrole in the presence of iodine (I₂) vapor. The results of the impedance characteristics of the obtained composite materials are presented in the Table IV.

As seen, the electric resistivity has been additionally decreased for another order of magnitude, again retaining the tendency for increasing the impedance Z after the third day of polymerization.

An attempt has been made to convert the composite material into tablets under a pressure of 50 kPa; high compressibility has been noticed, much higher than the one for the nonmodified fiber, indicating an adhesive role of the pPy film. The impedance characteristics of the tableted samples are analogous with those of the nontableted ones.

It has to be pointed out that when comparing the conductivity of the composite materials, obtained under equal conditions (the quantity of FeCl₃, duration of vapping with pyrrole) significant changes have not been noticed, neither the ionit nor the nonmodified Malon fiber is the carrier. The only difference is the more homogenous distribution of the pPy in the case of ionit. This might mean that only physically, not chemically, bounded FeCl₃ initiates the polymerization of pyrrole. This is in connection with the conclusions stated in Ref. 12, where poly(4-vinylpyridin) with FeCl₃ or CuCl₂ were used as a matrix. It has been stated that only the free Fe³⁺ and Cu²⁺ ions are initiating polymerization of the pyrrole. The same has been stated in Ref. 7, and proved by the results obtained from our measure-

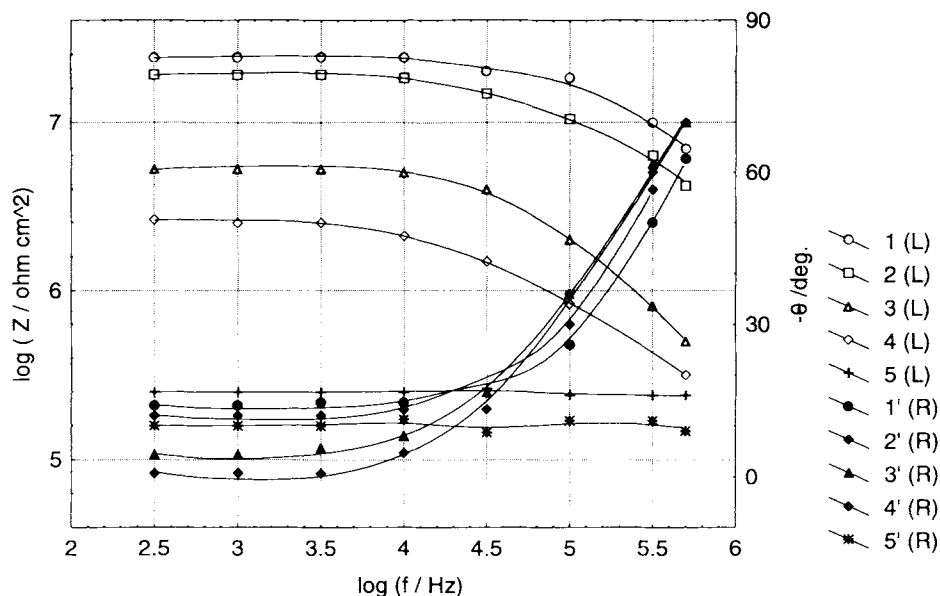


Figure 3 Bode diagrams for PAN fibers treated in FeCl_3 solutions (sample numbers and treatment conditions are given in Table V).

ments. For all ionits, after the treatment with FeCl_3 the increase in mass is approximately equal to the sum of the absorbed quantity of FeCl_3 for the non-modified fiber and that corresponding to the ionic capacity, while the conductivity is not considerably and correspondingly higher in comparison with the nonmodified fiber.

In order to prove the initiation only with free Fe^{3+} ions, the following experiment was carried out (Fig. 2). Actually, the ionit, well washed with water after the treatment with FeCl_3 was vaporized. As seen in Figure 2, the impedance spectrum is characteristic for the dielectric, which means that polymerization of pyrrole has not been initiated.

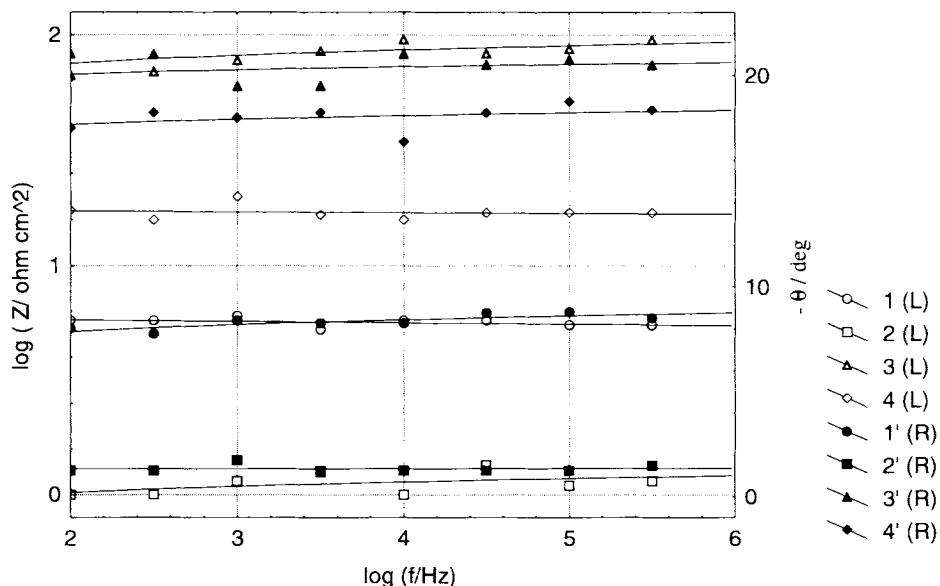


Figure 4 Bode diagrams for PAN-pPy: composites obtained by pPy deposition in vacuum onto dry or wet PAN samples previously treated in FeCl_3 solutions for 60 hs. (1, 1') dry sample/etheric sol. FeCl_3 , (2, 2') wet sample/etheric sol. FeCl_3 , (3, 3') dry sample/aq. sol. FeCl_3 , and (4, 4') wet sample/aq. sol. FeCl_3 (Table VI).

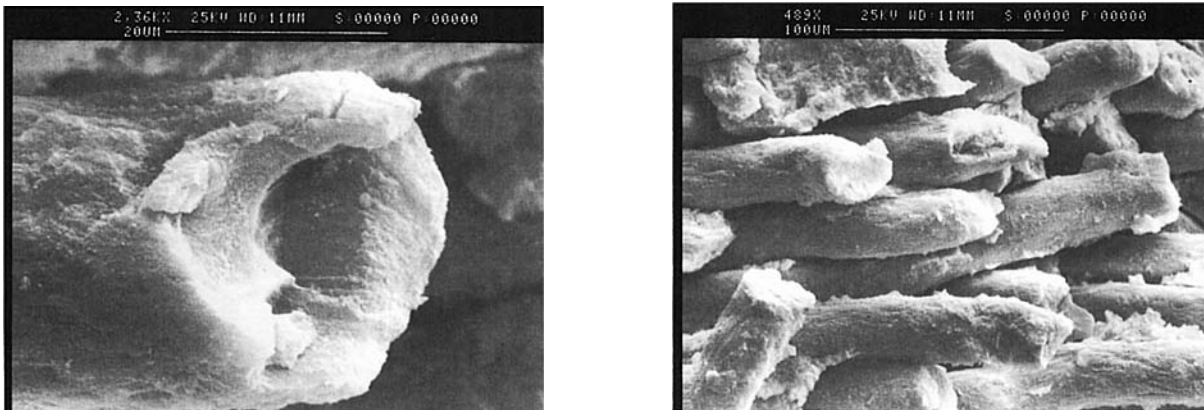


Figure 5 SEM micrographs for the best sample (Table VI).

The more homogenous distribution of pPy in the obtained composite material, when the ionit as the carrier has been applied, probably results from the better wetting of the ionit in the FeCl_3 solution. It means that similar effect may be expected by mild hydrofilization of the fiber, to a certain extent. However, the final result, i.e., the conductivity of the composite material, with partially hydrolyzed Malon fiber as a carrier and the pPy film, has not been significantly improved.

Instead of chemical modification of the polyacrylonitril fiber, other possible approaches in achieving the projected results are as follows:

1. To increase the time of absorption of FeCl_3 , since 30 min are enough only for saturation of the ionic capacity, i.e., for chemical absorption.
2. To achieve partial, so-called opening of the PAN fiber structure, i.e., certain swelling.
3. To replace the water in FeCl_3 solution with another solvent, providing better wetting of the fiber, for example diethylether.¹⁰
4. To generate the pPy film over the fiber, in pyrrole solution, in some suitable solvent which will dissolve only the pyrrole and will not dissolve FeCl_3 and polypyrrole (e.g., toluene).¹⁰

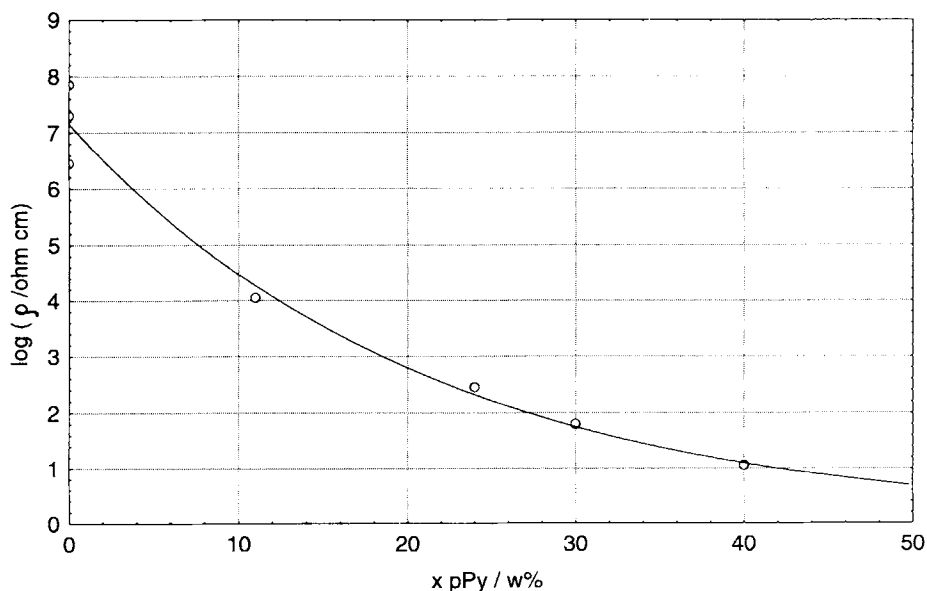


Figure 6 Dependence of the volume resistivity of PAN-pPy composite (pPy deposited in vacuum) on the pPy content (wt %) in the composite (Table VI).

The results obtained from these experiments are presented in the Tables V and VI, and Figures 3 and 4.

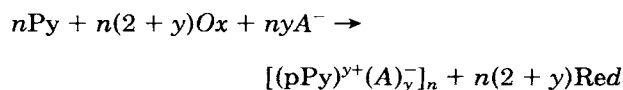
A PAN fiber, previously swollen for 24 h in dimethyl formamide–water = 40 : 10, module 1 : 50, has been subjected to the process of sorption. Here-with, the diameter of the fiber was changed for about 20%, but it was concluded that such preparation does not significantly influence the final effect; so it can be excluded.

The results presented in Figure 3 and Table V indicate that for the absorption of a higher quantity of FeCl_3 , and formation of more homogenous and thicker pPy films, the most important thing is a good wetting of the fiber, which can be achieved in an etheric solution of FeCl_3 instead of in the aqueous one. The duration of the absorption process is also very crucial.

The data presented in Table VI show that the best results have been obtained by a sample where FeCl_3 is introduced by etheric solution, which is later on placed wet in pyrrole vapors under vacuum. The obtained material shows pure ohmic reaction ($\theta \cong 0$) while the value of Z ranges from 1 to $2 \Omega\text{cm}^2$. The pPy is relatively homogeneously distributed, which may be seen from the SEM micrographs presented by Figure 5.

The calculated values of the inside (PAN fiber) and outside diameters (PAN–pPy) range between 12–14 and 24–26 μm , respectively. On the other hand the calculated average thickness of the pPy film (for $\Delta m = 0.168 \text{ g}$ and specific area of PAN fiber of $0.26 \text{ m}^2/\text{g}$) is approx. 1.5 μm .

As seen from Table VI, in all cases the mass of the obtained pPy is higher than the expected quantity, calculated in accordance with the basic equation for the process (taking into consideration the absorbed quantity of FeCl_3 and the value of y which frequently ranges about 0, 25):



where Ox is Fe^{3+} ; A^- is Cl^- and Red is Fe^{2+} .

At the moment, considering the widely accepted mechanism of pPy synthesis by recombination of cation radicals,¹³ we cannot explain this phenomenon. However, besides a good fit between absorbed oxidizer and the obtained pPy, e.g., in Ref. 10, the data comparable with ours^{6,7,14} can also be found.

Similar or a little worse characteristics are shown by the material obtained by immersing the wet or dry fiber, after the absorption in etheric or aqueous solution of FeCl_3 , in the solution of pyrrole in toluene.

Samples which have been used dry (after the absorption) in the polymerization phase, are more inhomogeneous, resulting in worse impedance characteristics. Probably, at the wet samples, the water or the ether solvent supports the homogenous distribution of the oxidizer and the pyrrole, while the dry ones, due to inadequate wetting, especially by aqueous solutions, localize the oxidizer in higher concentrations in certain places.

In general, actually at all samples, through all tests, inhomogeneities in relation to the generated pPy film have been observed where the degree of inhomogeneity varies, probably as a result of the operating laboratory conditions, as well as of the heterogeneousness of the fiber itself. Significant improvement may be achieved by using a bundle or a strip from mutually parallel fibers, and with an equal bundle density.

In Figure 6 a regular decrease of the resistivity of the PAN–pPy composite with increasing participation of the electroconductive pPy in the composite is presented. The experimental results are related to a deposition of pPy in the vacuum onto pretreated samples of PAN fibers in saturated aqueous and/or etheric solutions with FeCl_3 for 60 h.

CONCLUSIONS

On the basis of the obtained experimental results it can be concluded as follows:

1. Electroconductive composite fibrous carrier PAN–pPy with volume resistivity of approx. $10 \Omega\text{cm}$ is obtained.
2. No significant difference is observed using a modified or a nonmodified PAN fiber as a carrier, which implies that only physically bonded Fe^{3+} ions (added as FeCl_3) initiated the polymerization process of pyrrole at the fiber surface.
3. Deposition of pPy onto fibrous carriers from the vacuum is more effective compared with that of polymerization in solution (with simultaneous formation of a certain amount of homopolymer in the solution). The volume resistivities of the obtained composites in the

vacuum are lower due to the higher content of pPy.

4. Wet samples of the PAN fibers (after the treatment in the FeCl₃ solution) used in the phase of polymerization (in vacuum or solution) have shown more homogeneous distribution of pPy over the carrier surface and somewhat better electrical properties.

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