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PAN fibers with nanoprecipitated Ag and Au for use in textronics*

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Silver and gold nanoparticles have been linked with the structure of polyacrylonitrile (PAN) fibers as a result of a synthesis. The nanoparticles were formed in the dimethylformamide (DMF) solution, which is uncommon for their synthesis, but is a typical solvent for polyacrylonitrile. The examination of metallic nanoparticles doped fibers showed the presence of these particles in the samples. Analysis of Energy Dispersive X-ray Spectrometry (EDX) results showed that silver content in the fibers was the same as in the precursors of metal ions. The amount of silver in the fibers was significantly greater than the amount of gold in the corresponding sample. The Dynamic Light Scattering Method (DLS) and Visible and Ultraviolet Spectroscopy (UV-Vis) analyses indicated a difference between the sizes of metallic nanoparticles. The obtained composite polyacrylonitrile fibers doped with silver and gold nanoparticles were characterized by high flexibility and reduced electromagnetic radiation. The authors are convinced that the results obtained during the research will considerably contribute to the development of textronics discipline.

Keywords: *nanoparticles; PAN fibers; textronics*

1. Introduction

Research on fibers with metallic nanoparticles, Ag and Au is of great significance for the development of a new textronics discipline. It is an interdisciplinary field which is a synergetic combination of textile industry, electronics, information technology, using the knowledge of automatics and metrology [1, 2]. The main tasks of textronics include designing, manufacturing, functionalizing and characterizing electronic elements and systems made of fibrous materials. In modern textronics applications, textile products can be used not only as protective (for instance from electromagnetic fields) or carrier materials, but also as components of electronic devices. Currently, there are no commercially available textronics products on the market but extensive research has been carried out as shown in the literature reports on new textronics products [3, 4].

The properties of fibers depend on the method of their formation and parameters such as temperature, spinning rate, composition of solidification bath or the type of fiber-forming polymer and additives. Therefore, it is very difficult to make a fiber with optimal parameters and it requires not only the knowledge of chemistry and physics but also considerable experience.

Polyacrylonitrile (PAN) is a well-known polymer with a good thermal stability and mechanical properties. Pure PAN and its copolymers have been widely studied for almost a century and various technological applications have been found for them [5]. Studies on nanomaterials are also connected with the development of textronics and e-textiles. A new generation of PAN fibers was elaborated (e.g. fibers with ceramic nanoparticles, such as silica, hydroxyapatite, montmorillonite or carbon nanotubes) [6–11].

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The basic condition to achieve expected results of using functional nanoparticles is the assurance of their regular dispersion in the fiber being created. Agglomerates of nanoparticles that can occur, cause negative effects, for instance deterioration of strength and the need of using large amounts of such additives (exceeding even 30 % in relation to polymeric matrix) [10]. Only regular dispersion of additives in the fiber being formed determines efficient use of the nanoparticles properties, which also has crucial technological and economical aspects.

In the Department of Man-Made Fibers Technical University of Lodz, composite fibers with silver nanoparticles [8], magnetic or luminescent particles [9, 10] or montmorillonite [11] have been obtained by introducing suitable additives into the bulk (by adding to spinning dope).

PAN fibers forming by wet method comprises extruding a spinning solution through nozzles into a solidified bath containing a mixture of solvent and water. In the solidified bath, partial desolvation of polymer and separation of phases (precipitation of polymer) take place.

The process of PAN fibers formation is affected by:

- the structure of polymer used for fiber forming mass (percentage share of different types of mers or polymer particles of different masses) and the type of a solvent,
- different conditions of fiber forming process (solidification conditions, configuration of stretching stage, temperature stabilization and drying)

The authors obtained PAN fibers by development and optimization of the manufacturing process of PAN fibers and volume- and surface-modification with the use of metal nanoparticles (Ag, Au) during the fibers forming.

2. Experimental

During the realization phase of the work, polyacrylonitrile (PAN) with the following composition was used:

- 93 wt.% to 94 wt.% acrylonitrile;
- 5 wt.% to 6 wt.% methyl acrylate;
- about 1 wt.% sodium allylsulfonate.

A spinning solution was prepared from the copolymer PAN, dissolved in DMF with an intrinsic viscosity of 1.29 dl/g (determined in dimethylformamide DMF at a temperature of 20 °C). The average weight and number of molecular masses, determined by GPC, using dimethylacetamide (DMAc) as a solvent with the addition of 0.5 % lithium chloride, amounted to Mw = 286988 and Mn = 92577, with the polydispersity index of 3.1

2.1. Preparation of PAN fibers with nanoprecipitated Ag and Au

In the process of fibers formation, in all samples, 23 % of polyacrylonitrile in respect to DMF solvent was used. For the PAN fibers samples with silver (PAN_{Ag}), silver nitrate $AgNO_3$ (POCH, Poland) and ascorbic acid $C_6H_8O_6$ of analytical purity (POCH, Poland) in approximately equimolar amounts 1:1 were used. In respect to the polymer amount 1 % Ag^{+1} was used. For the PAN fibers with gold (PAN_{Au}), chloroauric acid ($HAuCl_4$) POCH, Poland) and ascorbic acid ($C_6H_8O_6$) in molar ratio 1:1.5 were used. The amount of gold in PAN polymer was also 1 %. The fibers were obtained according to Polish Patent application [12].

Rheological properties of the fiber forming fluids were examined using rheoviscometer type Anton Paar, Reolab QC. The properties of the fiber forming fluids were characterized by the following parameters: n – rheological factor called flowing factor (for n = 1 there is a Newton liquid, for n < 1 liquid diluted by shearing, for n > 1 liquid thickened by shearing) and k – consistency factor showing the value of apparent dynamic viscosity at 1 s^{-1} velocity of shearing.

For PAN solution without nanoprecipitates of Ag, those values were: n = 0.96, k = 23.18; for PAN_{Ag} (fluid with PAN fibers containing Ag nanoparticles): n = 0.95, k = 25.73; and for PAN_{Au} (fluid with PAN fibers containing Au nanoparticles): n = 0.94, k = 25.22.

During the fiber pulling process, forming nozzles with 240 holes were used. Each hole was 0.08 mm in diameter. The velocity of the flow from the spinneret channel was $V_{ch} = 1.94$ m/min. Solidification took place in the solidifying medium consisting of 60 % of DMF in 20 °C. Next, plastification in 50 % DMF bath at 70 °C was carried out. Finally, water vapour finishing at 135 °C to 140 °C was performed. Rinsing of the fibers was performed in slanting shafts rinser continuously [13].

2.2. Tests and analysis

Polyacrylonitrile fibers (PAN), polyacrylonitrile fibers doped with silver (PAN_{Ag}) and gold (PAN_{Au}) were obtained. These fibers samples had different colors. PAN fibers were milky-white, PAN_{Ag} had a yellow-gold color and PAN_{Au} pearly-pink one. This means that metallic particles precipitated during the formation of the fibers, gave the fibers their characteristic color, which in turn was dependent on the size and shape of the resulting particles.

Investigation of microstructure of the fibers and analysis of their elemental composition were made using SEM, LEO 435 VP by LEO (Zeiss + Leica), equipped with X-ray microanalysis system (EDS) Rontec, GmbH.

Dynamic light scattering (DLS) was used to determine the size and distribution profile of Ag and Au particles in the dispersions. The Particle Sizing System NICOMP 380, a product of Nicomp, (Santa Barbara, USA) was used. This technique can be used to determine the size distribution profile of small particles in a suspension or polymers in a solution.

The absorption (A) of obtained fibers was measured with the Ocean Optics QE65000 spectrophotometer. The absorption spectrum was measured in the wavelength range of 200 nm to 700 nm. To perform the tests, the samples were dissolved in DMF.

To analyze the elemental composition of obtained fibers, the tests using Energy Dispersive Spectrometry (EDS) were performed. Microprobe detector resolution was 133 eV and the window area was 10 mm^2.

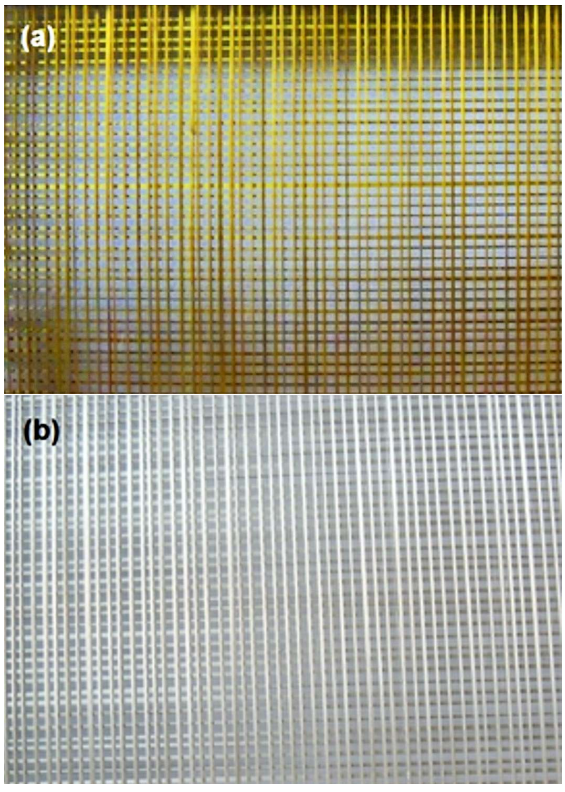

Fig. 1. Weft fabric prototypes (1.5 mm × 1.5 mm grid size) for the test connected with protective properties against electromagnetic radiation: (a) PAN fibers with silver nanoparticles, (b) PAN fibers with gold nanoparticles.

The measurements of PEM transmission losses in the frequency range of 2.5 GHz to 3.5 GHz were carried out at the accredited (by the Polish Accreditation Centre) Research Laboratory of Radiolocation, Commanding Systems, Radiolocation Fighting and Microwave Technique of the Military Institute of Technical Armament in Zielonka near Warsaw. The examined samples are presented in Fig. 1. PAN fibers with nano- or microparticles of gold and silver were the basis for weft fabric. To achieve this, the bundles of fibers having the linear mass comparable to PAN fibers without modification, were placed in parallel and in perpendicular scheme at a distance of 1.5 mm from each other using special wooden frames. The fibers did not interweave with each other (layer of fibers in parallel scheme was placed on the layer in perpendicular scheme). Each bundle of fibers was strictly

connected to the frame so as not to change the distance between the bundles during the tests.

Electromagnetic shielding effectiveness (SE) is defined as a logarithm of the ratio of power incident on the sample to the power measured behind the sample, in dB units. Therefore it can be expressed by equation:

$$SE = 10\log\frac{P_1}{P_2} \tag{1}$$

where P_1 is power incident on the tested sample (mW), P_2 is power measured behind the tested sample (mW).

SE is widely discussed in literature and used for fast comparison of shielding properties of different materials and structures [14–16].

There are several methods of measuring shielding effectiveness. One of them is a method using wave guide applicator, presented schematically in Fig. 2. It consists of a synthesizer sweeper (type HP83640A), scalar analyzer (type HP8757D) and sample holder. During the measurements, the attenuation of the transmitted power of the electromagnetic wave is measured while passing through the sample over the frequency domain.

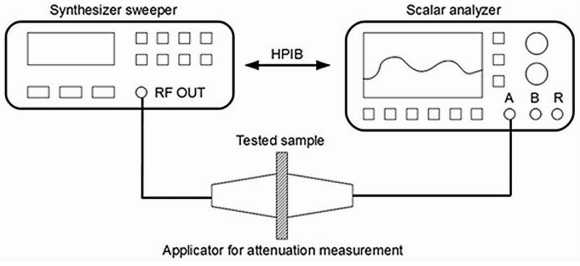

Fig. 2. Stand for measuring transmission losses.

3. Results and discussion

3.1. Evaluation of the surface of the prepared fibers

In order to accurately examine the surface of prepared fibers, observations with a scanning electron microscope were performed. Images analysis showed that there were some differences in the structure of the surface of the tested fibers (Fig. 3).

Silver-doped fiber surface was not significantly different from the surface of the PAN reference fibers. In contrast, on the surface of fibers with gold precipitates distinct spherical objects were observed.

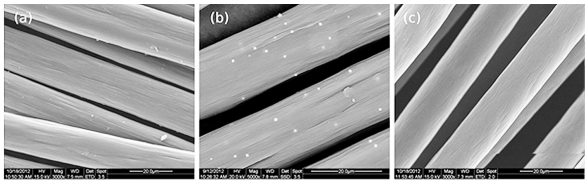

Fig. 3. Surfaces of PAN fibers obtained: (a) with the participation of silver particles (PAN_{Ag}), (b) with the participation of gold particles (PAN_{Au}), (c) the reference fiber (PAN).

3.2. Analysis of the elemental composition of tested fibers

The EDS analysis of the reference fibers revealed that they consist mainly of carbon, nitrogen and oxygen. It results directly from the structure of the polymeric matrix used, which consists of polyacrylonitrile, polymethylmethacrylate and sodium allilosulfonian (Fig. 4).

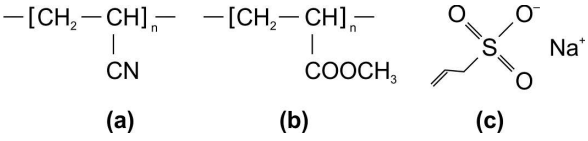

Fig. 4. The particle structure of: (a) polyacrylonitrile; (b) polymethylmethacrylate; (c) sodium allilosulfonian.

The examination of fiber doped with silver and gold nanoparticles using EDS method shows that the elements of which the tested material is composed are very similar to those of reference PAN fiber (Table 1). The main components of the composite are carbon, nitrogen and oxygen. The slight difference in percentage content of the elements results from using ascorbic acid ($C_6H_8O_6$) as a reducing agent. Similarly to the reference fiber case, the contaminations connected with the treatment process occur and can be found in a form of calcium. It was also found that chlorine is present in this sample, which results from using the chloroauric

acid as the gold ions precursor. The proof of gold presence is that it can be found in the EDS spectrum.

Analysis of EDS tests for a fiber doped with silver nanoparticles shows that its elemental composition is typical of PAN fibers. Also in this case the main elements are carbon, nitrogen and oxygen. The difference in percentage content of the elements results from the use of silver nitrate as silver ions precursor in this system. The contaminations resulting from the treatment process also occur but their number is significantly lower compared to the previously described samples. In the case of fiber containing silver nanoparticles we succeeded in obtaining much greater concentration of metal compared to the case of fiber doped with gold, at the same percentage content of metal precursors in the spinning liquid.

3.3. Analysis of the size of obtained nanoparticles

To obtain information about the size and size distribution profiles of silver and gold nanoparticles created by in situ method in the fibers, the Dynamic Light Scattering Method was used. The results of the particle size analysis and distribution are shown in Table 2.

The DLS module employs the "rules" of light scattering in order to obtain the number-weighted and volume-weighted diameter distributions from the starting result, which is an intensity-weighted plot. The "volume-weight" is a relative particle volume vs. diameter, "number-weight' means the relative number of particles in a sample run vs. diameter.

The largest percentage of the fine fraction of nanoparticles of silver, in terms of the analysis of volume weight intensity, is in the range of 1.3 nm (68.8 %), and taking into account the analysis of number weight intensity, it is in the range of 1.3 nm (85.2 %).

The largest percentage of the fine fraction of nanoparticles of gold, in terms of the analysis of volume weight intensity, is in the range of 452.3 nm (86.8 %), and taking into account the analysis of number weight intensity, it is in the range of 433.4 nm (96.1 %).

In order to confirm the presence of metal nanoparticles and their size in the fibers, UV-Vis spectroscopy was performed. The results showed that in both cases, it was possible to obtain metal nanoparticles within the PAN fibers. The spectrum obtained for the silver-doped material shows a clear absorption peak at a wavelength of 409 nm, which is characteristic of silver nanoparticles with a size of about 20 nm (Fig. 5) [17]. This result confirms the DLS tests according to which the material contains a fraction of nanoparticles of most significant weight fraction with the size of about 16.7 nm (Table 2).

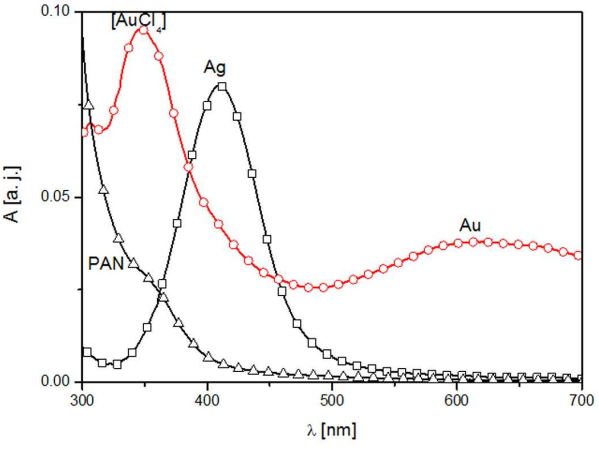

Fig. 5. UV-Vis spectra of PAN fibers and PAN fibers doped with silver or gold (where 'a.j.' stands for relative units).

In case of the sample doped with gold, the UV-Vis spectrum shows two peaks. The one at the wavelength of 350 nm is narrow and the second one at 620 nm is wide (Fig. 5). According to the literature data, the first absorption peak corresponds to the presence of ions $[AuCl_4]^-$ in the system [18] but the second, at a wavelength about of 620 nm, is characteristic of the large particles of gold of about 500 nm [19]. This result is consistent with the SEM observations. The presence of gold ions in the system under study is related to incomplete overreaction of chloroauric acid.

Table 1. The measurement of the elemental composition of PAN pure and doped fibers.

	PAN_{pure}		PAN_{Au}		PAN_{Ag}	
	Element [%]	Atomic percent [%]	Element [%]	Atomic percent [%]	Element [%]	Atomic percent [%]
C	62.14	66.46	72.99	76.63	61.74	66.36
N	29.66	27.21	21.98	19.81	30.94	28.51
O	7.67	6.16	4.28	3.30	5.95	4.80
Ag	–	–	–	–	0.80	0.10
Au	–	–	0.16	0.01	–	–
C:O		10.8:1		23.2:1		13.8:1
C:N		2.4:1		3.9:1		2.3:1

Table 2. The size and particle size distribution of Ag and Au.

	Intensity-weighted		Volume-weighted		Number-weighted	
Elements	Diameter [nm]	[%]	Diameter [nm]	[%]	Diameter [nm]	[%]
Ag	1.3	3.7	1.3	68.8	1.3	85.2
	3.5	22.4	3.1	30.4	3.0	14.7
	16.7	73.9	14.7	0.8	13.9	0.1
Au	10.5	2.0	9.3	1.3	8.8	0.2
	280.3	30.6	244.1	11.9	236.1	3.7
	438.2	67.3	452.3	86.8	433.4	96.1

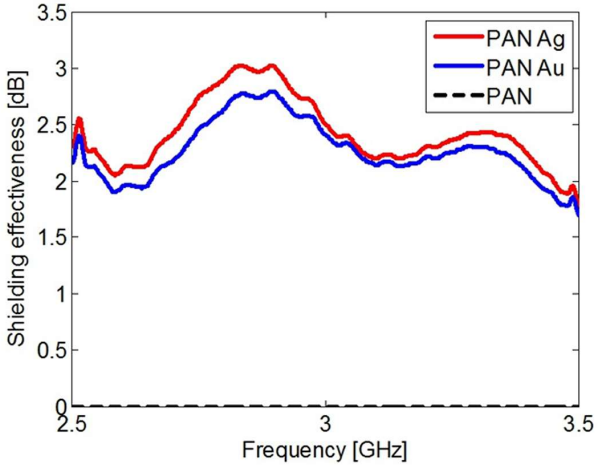

Fig. 6. Shielding effectiveness of PAN_{Ag}, PAN_{Au} and pure PAN fibers.

3.4. Measurement of electromagnetic field shielding properties

The results of shielding effectiveness (SE) of the studied fibers are presented in Fig. 6.

Analyzing the experimental results one can say that SE curves are quite flat over the considered frequency range and present small values of shielding properties (around 2.5 dB). The value of SE for Ag sample is slightly higher compared with Au sample.

The average values of shielding effectiveness over a frequency range of 2.5 GHz to 3.5 GHz for the samples are as follows: $SE_{PAN\,Ag} = 2.42$ dB and $SE_{PAN\,Au} = 2.27$ dB.

Fibers with Au and Ag nanoprecipitations lead to dispersion of electromagnetic radiation which results in the shielding properties. In future, the works will be directed to much higher concentrations of Au and Ag additives to achieve the percolation threshold of nanoprecipitations in order to form conductive paths. Thanks to the fiber formation process the conductive paths will be created in the whole volume of fibers [20]. Also the concentration of nanomodifications in volume can be reduced (compared to the surface modifications)

because the conduction paths can be created in the volume of whole fibers not only on their surface.

4. Conclusions

It is possible to form a PAN nanocomposite/hybrid, whose fibers are characterized by similar durability to PAN fibers but possess new properties. The obtained PAN fibers and the PAN fibers modified by nano- and microparticles of Ag and Au have similar physical properties. They do not differ significantly in shapes, as shown in the SEM images, however, the fibers have different colors. Mechanical strength of the fibers doped with metallic particles (PAN_{Ag} and PAN_{Au}) during static stretching was not worse than that of undoped fibers (PAN). The examination of metallic nanoparticles doped fibers showed the presence of these substances in the samples. Analysis of EDS tests showed that despite using the same amounts of the metal ions precursors, the amount of silver in the element-doped fiber was significantly greater than the amount of gold in the corresponding sample. DLS and UV-Vis analyses indicated a difference between the sizes of metallic precipitates. The largest percentage amount of the fine fraction of silver nanoparticles was in the range of 1.3 nm and the largest percentage amount of the same fraction of particles of gold was in the range of over 430 nm.

The PAN_{Ag} and PAN_{Au} fibers possess specific features regarding electromagnetic radiation absorption activity.

The authors are convinced that the results obtained during the planned research will considerably contribute to the development of textronics discipline. It is planned to make and/or modify fibrous materials that would be suitable for clothing as well as construction of textronics sensors or relays.

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