

PREPARATION OF NANOFIBRE MATERIAL CONTAINING SILVER

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The process of producing a carbon fibre material containing silver based on polyacrylonitrile nanofibres is investigated. It is shown that immobilizing silver during the spinning step is a more efficient method than surface modification of the material.

Water conservation has become a major current issue as a result of anthropogenic processes due to constant accumulation of toxic substances and heavy metals in water reservoirs [1, 2]. Moreover, such reservoirs become a favorable environment for the growth of bacteria and viruses. Therefore, the creation of new facilities for the treatment of water returning to the environment, as well as for cleaning and disinfection of drinking water from microbiological contamination, is of principal importance. Promising directions for solving such environmental objectives should include the use of different filtering materials [3, 4], including the fibre materials containing silver, since silver has excellent antibacterial properties [5].

This article presents the results of research on the production of nanofibre materials containing silver and based on polyacrylonitrile (PAN). Access to raw material, the antimicrobial activity of silver, and good filtration capacity of nonwoven nanofibre materials [6] make it advantageous to develop a method for producing this type of material based on silver immobilized in the fibre structure of the polymer.

12% solutions of PAN in dimethylacetamide (DMA) containing silver nitrate were used for electrospinning the fibres, and the reduction of silver ions to metal was combined with the process of thermal oxidation of the fibre. It is noted that addition of AgNO_3 to solutions of PAN in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) is not possible due to formation of a precipitate: a black precipitate in DMF, and a red one in DMSO.

Based on the results of the study of rheological properties of solutions of PAN with silver nitrate [7] and their jet formation ability in an electric field, using “Nanospider™” equipment we found that only solutions of PAN in DMA containing silver nitrate in an amount of not more than 0.5% exhibit the ability to form fibres. Optimal conditions for capillaryless electrospinning were determined for these solutions (solution viscosity: 6.6 Pa·s; electrical conductivity: 232.8 micro Siemens per cm; applied voltage: 35–40 kV; distance between the electrodes: 190 mm), and samples of nanofibre PAN material with silver nitrate content of 0.5% were obtained for further investigations. A significant increase in the viscosity of PAN solutions at AgNO_3 content above 1% makes it impossible to process the solution into nanosized fibre material by electrospinning.

Structuring of the solution in the presence of AgNO_3 complicates the process of obtaining films by the coagulation method, which primarily manifests in substantial morphological change of the film surface. Instead of a uniform, clearly expressed fibrillar nature of the surface with a 10–15 nm microrelief, for the film formed from a PAN solution not containing silver nitrate (Fig. 1a), in the process of depositing films from 1–2% solutions of AgNO_3 a grainy surface layer forms with a microrelief of up to 35–60 nm (Figs. 1c, 1d). Large spherical formations of up to 60–100 nm are visible on the surface micrographs, which can appear due to decreasing diffusion processes in the polymer coagulation because of high viscosity of the solution.

Micrographs of film surfaces – those for the plain film, and for the film containing 0.5% silver nitrate – differ insignificantly, although, according to the 3D-images, microrelief height increases on average by a factor of 4–5 (Figs. 1b, and 2a, 2b).

Since the introduction of silver into the nanosized fibre PAN material provides the possibility of obtaining sorptive carbon fibre filtering materials with disinfectant properties, we investigated the effect of silver particles on the carbonization processes under model conditions.

PAN fibres containing 0.5 wt. % silver particles were obtained by immobilizing silver nitrate into the structure in the fibre spinning solution, and by coating the surface of the fibrous material followed by a reduction of silver ions

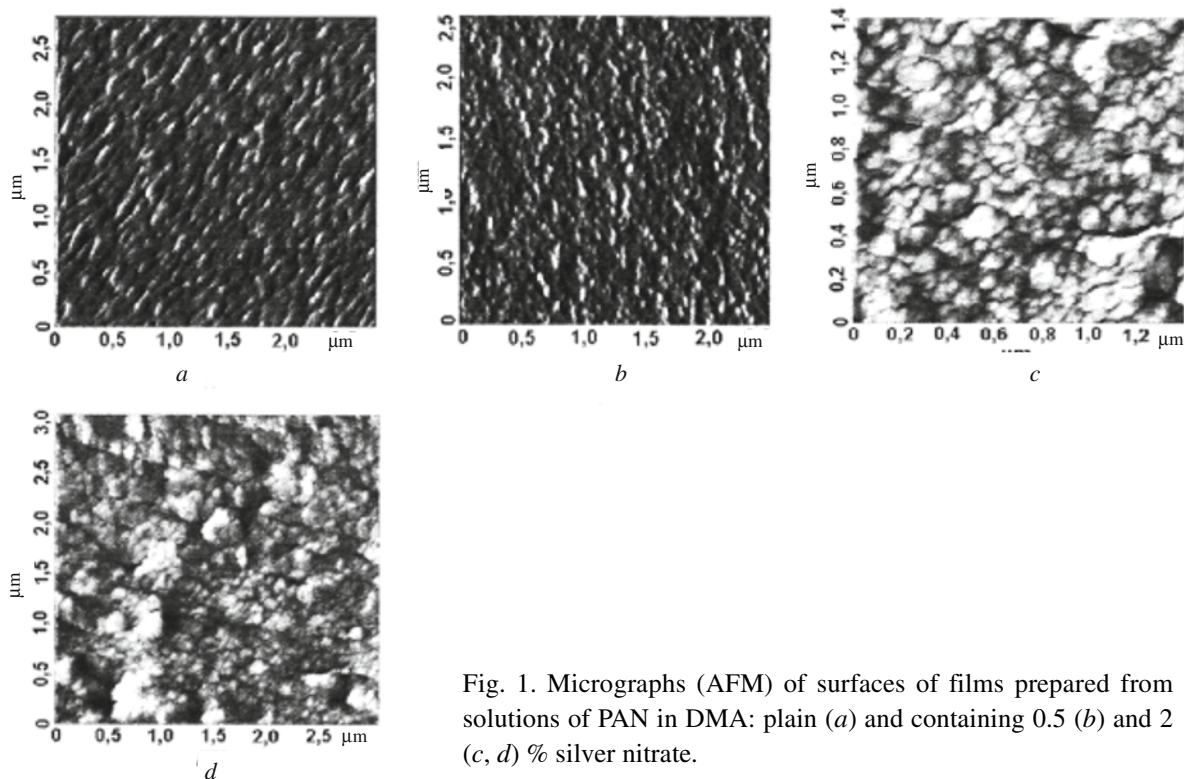


Fig. 1. Micrographs (AFM) of surfaces of films prepared from solutions of PAN in DMA: plain (*a*) and containing 0.5 (*b*) and 2 (*c, d*) % silver nitrate.

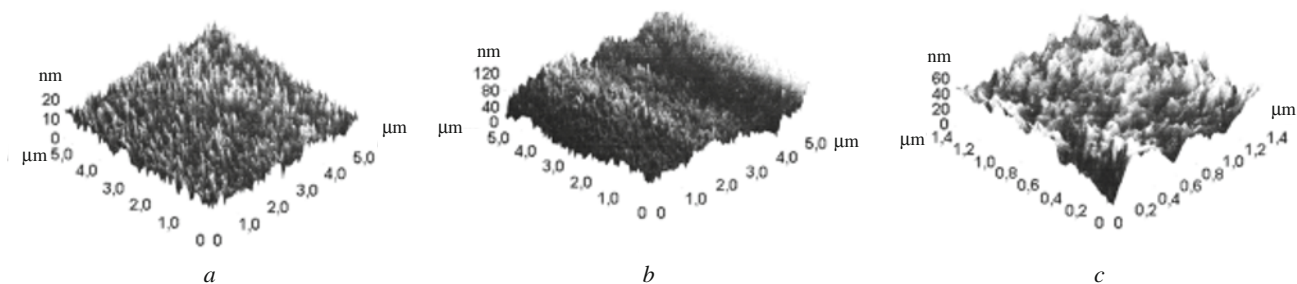


Fig. 2. 3D-images of the surface microrelief for films prepared from solutions of PAN in DMA: plain (*a*) and containing 0.5 (*b*) and 2 (*c, d*) % silver nitrate.

into metal by heat treatment under the conditions of thermal oxidation of PAN. The plain PAN fibre was treated with an aqueous solution of AgNO_3 , and by thermal oxidation under comparable conditions.

A significant decrease in the temperature of maximum decomposition rate (an average of 300 deg) was revealed from the derivative curves describing the decomposition of nanosized fibre samples containing silver by thermal oxidation in an inert environment. As a consequence, in the early stages of thermolysis a heat resistant polymer degradation product is formed, which provides a higher yield (20–40 %) of carbon fibre at carbonization temperatures of 750–900 °C. As seen from the table, for the carbonization temperatures 750–800–900 °C the yield of carbon fibre for the case of silver nitrate immobilization is 62–59–54%, which is higher than the corresponding values for the nanofibre PAN material not containing silver, 57–54–46% respectively (Figs. 3 and 4). The method of surface modification of the material by treatment with a solution of AgNO_3 to enhance the carbonizing ability of the PAN nanofibre is less effective (see Table 1), which explains the less uniform distribution of silver in the fibre. Higher efficiency of the method of introducing silver into the fibre at the spinning stage proves this. The presence of silver particles in the standard PAN fibre also increases its carbonizing ability.

During thermolysis in air, silver particles showed no effect on the coking processes. There is only a slight shift towards a lower temperature of the maximum decomposition rate v_{max} (by 50 degrees), and its increase (small for a nanofibre material, and almost two-fold for the standard PAN fibre).

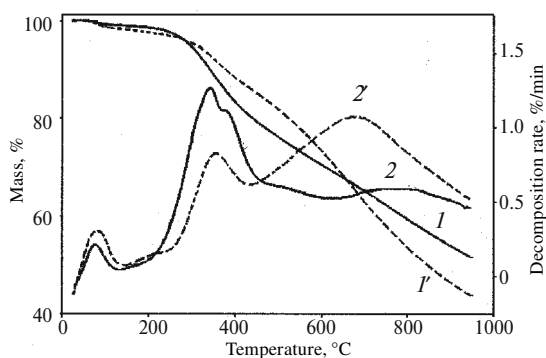


Fig. 3.

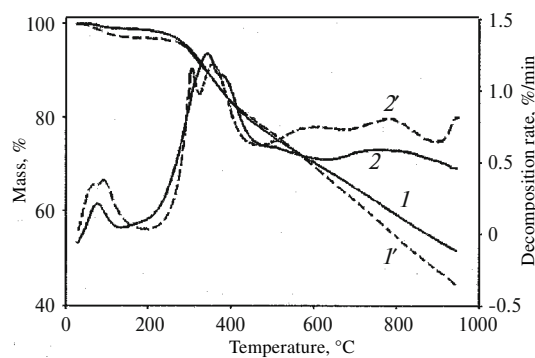


Fig. 4.

Fig. 3. TG (1, 12) and DTG (2, 22) curves for PAN nanofibre materials after thermal oxidation (in an inert environment): 1, 2 – containing silver (immobilization of AgNO_3 in the fibre through the spinning solution); 12, 22 – initial.

Fig. 4. TG (1, 12) and DTG (2, 22) curves for PAN nanofibre materials after thermal oxidation (in an inert environment) and containing silver particles: method of introducing AgNO_3 : 1, 2 – immobilization in the fibre through the spinning solution; 12, 22 – applied to the

Table 1. TGA Data for PAN Materials After Thermal Oxidation Containing Silver Nitrate.

Method of introducing AgNO_3		v_{\max} , %/min.	$t_{v_{\max}}$, °C	Coke residue, %, at a given temperature, °C					
				400	600	700	750	800	900
<i>Inert medium</i>									
Nanofibre material	Initial	0.8	676	88	73	63	57	54	46
	Immobilization into the fibre at the spinning step	1.3	343	83	71	65	62	59	54
	Surface modification	1.2	355	83	70	62	58	55	48
Standard fibre	Initial	0.9	700	90	76	68	64	60	50
	Surface modification	0.9	385	89	77	72	68	66	59
<i>Air environment</i>									
Nanofibre material	Initial	4.8	601	80	11	3.0	3.0	3.0	3.0
	Immobilization into the fibre at the spinning step	6.5	545	81	5.2	4.7	4.7	4.7	4.7
	Surface modification	5.4	556	82	8.3	3.2	3.2	3.2	3.2
Standard fibre	Initial	5.8	655	89	34	0.6	0.6	0.6	0.6
	Surface modification	15.7	608	87	40	3.5	3.5	3.5	3.5

Thermal oxidation conditions: temperature of 280 °C for 20 min in air.

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