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Influence of Forming Conditions on the Tensile Strength Properties of PAN Fibres Containing a Ferromagnetic Nanoaddition

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Abstract
This article presents the manufacturing conditions of polyacrylonitrile (PAN) fibres with ferromagnetic properties. These properties are obtained as the result of incorporating a Fe_3O_4 nanoaddition into the fibre-grade matter at the stage of preparing the spinning solution. The influence of the solidification conditions and the deformation distribution in the two-stage drawing process on the fibres' tensile strength properties was determined. The supermolecular structure, the porosity, the ferromagnetic properties, and the distribution of the nanoaddition on the surface of the fibres formed under the given conditions were characterised.

Key words: *nanoaddition, ferromagnetics, fibre spinning, fibre drawing, supermolecular structure, porosity.*

Introduction

One of the research directions conducted by many scientific and research centres around the world involves applying materials with special magnetic properties to modern medicine. Many ferromagnetics with grain dimensions of several nanometres and micrometers have found applications in different fields of biomedical engineering and biotechnology [1]. At present they are used as the following substances:

- biological modifiers of active mixtures, with enzymes and antibodies [2 – 5],
- substances used to detect and identify biological compounds and xenobiotics [6],
- substances used to magnify the contrast by visualisation with the use of magnetic resonance, and
- substances used to diagnose and heal tumour cells, among others.

Irrespective of the ferromagnetics application presented above, it is possible to use these compounds to modify polymer fibres, in order to create magnetic properties of these fibres additional to their common features. These magnetic properties, together with the fibrous form of fibres, allow us to form composite materials characterised by property anisotropy which is typical of natural tissues, for example. Carbon fibres manufactured from a precursor, into which an appropriate ferromagnetic nanoaddition was incorporated at the stage of spinning, are one kind of fibre type which might find a broad application in biotechnology, as well as in many fields of medicine.

With the incorporation of a non-fibre-grade nanoaddition into the PAN precursor, fibre matter has been linked in the majority of cases [11, 12] to a decrease in the susceptibility to deformation at the stage of plastification drawing. This results in a decrease in the fibres' tensile strength properties. It should be emphasised that the effect of changing in the strength properties is also linked to the type of the nanoaddition included in the fibre as well as its interaction with the polymer. We indicated in our previous investigations [13] that in the case of using hydroxyapatite (HAp) in powder form with grains of nanometre dimensions, a transformation of the crystalline structure of the fibre matter is possible, which results in higher values of tenacity being achieved. An essential influence on the tenacity value is also shown by the tendency of nanoadditions to agglomeration. The presence of agglomerations in the spinning solutions creates difficulties at the stage of filtration, and influences the porous structure and the strength properties of manufactured fibres. Ultrasonication grinding is a technique which can be applied to prevent agglomeration of nanoadditions. The considerations presented above indicate that obtaining PAN fibres with incorporated ferromagnetic nanoadditions requires a suitable selection of the process parameters and manufacturing intended to obtain a structure which will susceptible to deformation processes while applying drawing already, during the solidification stage; these factors condition the obtention of good fibres' tensile strength properties suitable for the process of their carbonisation.

The aim of our work was to determine the influence of the solidification conditions and the deformation distribution in the two-stage drawing process on the tensile strength properties of PAN fibres including a Fe_3O_4 ferromagnetic nanoaddition. This will enable us to select manufacturing conditions which would be advantageous considering the fibres' strength properties. For the fibres obtained in this way, we established the supermolecular structure, the porosity, and the magnetic properties, and also estimated the uniformity of the nanoaddition distribution on the fibres' surface.

Materials and research methods

Polymer and nanoaddition characteristics

A three-component copolymer containing 93-94% wt of acrylonitrile mer units, 5-6% wt acrylane methyl mer units, and 1% wt alilosulphonian mer units, made by Zoltek Co., Hungary, was used for preparing PAN spinning solutions in dimethylformamide (DMF). The intrinsic viscosity of this copolymer assessed at the temperature of 20 °C in DMF equals 1.29 dl/g. The polydispersity of Mw/Mn = 3.1 was determined by gel chromatography; the estimation was carried out at the Institute of Biopolymers and Chemical Fibres in Łódź, Poland.

A Fe_3O_4 ferromagnetic nanoaddition from Sigma-Aldrich with grain dimensions within the range of 30 nm to 50 nm was used. The nanoaddition was inserted into the spinning solution in an amount of 5% re-calculated in relation to the polymer. Before insertion, the nanoaddition suspension in DMF was subjected to the action of ultrasounds, at a temperature of 20 °C over 2 hours. A Polsonic-3 ultrasonic washer with a power of 2×160 W and a working frequency of 40 kHz was used.

Rheological properties of the spinning solution

The rheological properties of the spinning solution containing 22% of PAN in DMF were assessed with the use of a Rheotest RV rheo-viscometer and an 'H' type cylinder, at shearing rates up to 146.8 1/s, and a temperature of 20 °C. The rheological parameters 'n' and 'k' were determined on the basis of flow curves according to the method described in [14]. We obtained the values of n = 0.965 and k = 25.11.

Fibre forming (spinning and drawing)

The fibres were spun from a solution by the wet method with the use of an extended-laboratory scale spinning machine, which allows the technological parameters to be stabilised at the assumed levels as well as their continued monitoring. A 240-hole spinneret was used with hole diameters of 0.08 mm. The process of the fibres' solidification was carried out in a bath containing an aqueous DMF solution of a concentration within the range of 60% to 70%. The drawing process was realised as a two-stage process, the first in a plastification bath containing an aqueous DNF solution of a concentration of 50%, and the second in preheated steam at a temperature of 135 °C. After rinsing the fibres on line, they were dried under isometric conditions at a temperature from 20 °C to 40 °C.

Properties of the fibres obtained

The tenacity was assessed for a fibre bunch in accordance with Polish standard PN-EN-ISO-268:1997 with the use of an Instron tensile tester.

The fibres' porosity was determined by the mercuric porosimetry method with the use of a Carlo-Erba porosimeter coupled with a computer system, which enabled the determination of the total volume of pores, the percentage share of pores with dimensions within the range from 5 nm to 7500 nm and the total internal surface of pores.

The distribution of the Fe_3O_4 nanoaddition in the fibre was evaluated on the basis of images taken by the JSM 5400 scanning electron microscope with the EDX LINK ISIS dispersion energy analyser of the characteristic radiation made by Oxford Instruments.

Measurements of the magnetic properties were carried out with the use of a vibration magnetometer made by Lake Shore. The measurement results of magnetic properties of PAN fibres with the magnetite incorporated are presented in the following co-ordinate system: magnetisation intensity vs. intensity of the external magnetic field [15].

The degree of crystallinity and the size of the crystalline regions were determined by wide-angle X-ray dispersion (WAXS). The tests were carried out with the use of a URD 6 diffractometer made by Seifert, Germany equipped with a cuprum lamp with radiation emission of a wavelength of λ = 1.54 Å and supply parameters of U = 40kV and I = 30 mA. The radiation was made monochromatic by a nickel filter. The diffraction curves were recorded by the reflection method and the jump mode. The results were recorded within the angle range from 2Θ = 6.5° to 2Θ = 60° at jumps of 0.1°. The fibres tested were powdered with the use of a microtome in order to eliminate the texture, and next pressed into pills with a diameter of about 2 cm and thickness of 1 mm. The tests were carried out at the University of Bielsko-Biała, Poland.

Discussion of the results

Attempting to obtain increased tensile strength properties of the PAN fibres with the share of a Fe_3O_4 nanoaddition incorporated into the fibre-matter, the solidification process was conducted under mild conditions, i.e. at increased solvent content in the bath, up to 60% - 70%, and at low temperatures of 15 °C and 20 °C (for each of the coagulation bath concentrations used). This was advantageous for solidification according to the diffusion mechanism and creation of a structure with a low degree of defectiveness. On the basis of previous experience [16], negative values of the as-spun draw ratio within the range of -50% to 30% were used. The drawing process was conducted as a two-stage process, with the first conducted in a plastification bath with a solvent content of 50% and at a temperature of 70 °C, and the second in preheated steam at a temperature of 135 °C. The technological parameters of both drawing stages were determined in our previous works [11, 12]. In both cases, the deformations used were near the maximum values possible to reach under the conditions used.

Performing the spinning process of fibres at a solidification which takes place under extremely mild conditions in a bath with a solvent content of 70% results in achieving a tenacity at the level of 30.7 to 32.2 cN/tex in both the 15 °C bath and the 20 °C bath (Table 1). The decrease in the bath's solvent content down to the level of 65% is linked to the creation of a structure which probably undergoes deformation at the stage of drawing influenced by higher tensions, which finally results in achieving higher strength, at the level of 34.68 to 35.1 cN/tex for fibres solidified at 15 °C. Increasing the bath temperature to 20 °C, which is linked to a slight 'sharpening' of the solidification conditions connected with the increase in the rate of the diffusion processes, causes a further increase in the fibres' tenacity to the level of 36.03 cN/tex in the case of applying an as-spun-draw ratio within the range of (-50%), such as for the sample F-32. At a similar susceptibility to deformation (total deformations of 5.2 and 5.5 respectively), the increase in tenacity by about 1 cN/tex in comparison to the sample F-27 (solidified in the same bath, but at 15 °C) is likewise connected with the creation at the solidification stage of a structure which is influenced by the deformation processes under the influence of higher tensions. The susceptibility to deformation processes of the structure formed at the solidification stage, as well as the value of tension under which the drawing process is realised, are decisive factors on the efficiency of the drawing process and the fibres' strength properties. A further 'sharpening' of the solidification process conducted in a bath of solvent content decreased to 60% deepened this effect, leading as a consequence to fibres with a tenacity at the level of 38.00 cN/tex (sample F-38) being obtained. Also, in the case of this concentration of the coagulation bath, a small 'sharpening' of the conditions by increasing the bath temperature up to 20 °C appeared advantageous. At the same time, the highest fibre strength properties are achieved by applying very negative values of the as-spun draw ratio (-50%).

By comparing the tenacity level of fibres solidified in baths with 65% and 60% of the solvent content at temperatures of 15 °C and 20 °C, we see that the most effective 'sharpening' of the solidification conditions can be achieved by increasing the temperature to 20 °C. For lower concentrations of the solidification bath (of 60% DMF), the influence in temperature increase on the fibres' strength properties

__Table 1.__ Fibre forming conditions and properties of fibres obtained from spinning solutions including 5% of Fe_3O_4; Plastification bath: DMF concentration of 50%, bath temperature: 70 °C.

Sample index	Solidification			Drawing in plastification bath, %	Drawing in stream, %	Total draw ratio, %	Total defor-mation	Linear density of fibre stream T_{tex}	Tenacity, cN/tex	Elongation at break, %
	DMF content in bath, %	Bath temperature, °C	As-spun draw out ratio, %							
F-21	70	15	-50	326.4	143.7	939.4	5.20	59.65	32.00	11.67
F-22	70	15	-40	335.2	110.6	860.0	5.76	49.35	31.21	11.69
F-23	70	15	-30	297.6	152.4	903.7	7.02	40.75	30.73	10.74
F-24	70	20	-30	319.1	136.4	890.9	6.93	41.36	30.93	10.94
F-25	70	20	-40	335.6	136.2	929.1	6.17	45.90	32.25	11.01
F-26	70	20	-50	414.0	115.2	1006.4	5.53	52.12	31.69	11.62
F-27	65	15	-50	384.0	116.6	948.3	5.24	51.66	35.11	9.98
F-28	65	15	-40	319.3	143.6	921.3	6.13	45.15	34.87	10.29
F-29	65	15	-30	289.9	134.8	815.6	6.41	42.73	34.68	10.50
F-30	65	20	-30	262.0	162.2	849.2	6.64	42.70	34.20	10.75
F-31	65	20	-40	303.6	150.0	908.7	6.05	47.53	35.22	11.13
F-32	65	20	-50	399.9	123.7	1017.8	5.59	51.85	36.03	11.11
F-33	60	15	-50	404.7	119.9	1010.1	5.55	52.35	34.48	10.58
F-34	60	15	-40	357.2	117.4	893.9	5.96	50.33	32.16	10.92
F-35	60	15	-30	316.1	124.1	832.7	6.53	42.80	35.29	10.75
F-36	60	20	-30	323.9	116.8	819.2	6.43	43.63	34.89	10.71
F-37	60	20	-40	387.2	108.8	917.5	6.10	45.60	37.05	10.63
F-38	60	20	-50	400.6	121.8	1010.1	5.55	51.15	38.00	11.04

__Table 2.__ Fibre forming conditions and properties of fibres without and with nanoaddition drawn by various deformation distribution between the two drawing stages. __Where:__ 1) value of drawing in the first stage related to the value of maximum drawing, 2) sample without nanoaddition. Solidification bath: DMF concentration of 60%, bath temperature of 20^0C, as-spun draw ratio of –50%. Plastification bath: DMF concentration of 60%, bath temperature of 20 °C.

Sample index	Drawing in plastification bath		Drawing in stream, %	Total draw ratio, %	Total deformation	Linear density of fibre stream, T_{tex}	Tenacity, cN/tex	Elongation at break, %
	%	x1)						
F-38	400.6	1.0	121.8	1010.1	5.5487	51.15	38.00	11.04
F-39	355.2	0.9	151.9	1046.6	5.7331	47.35	39.94	11.34
F-40	321.9	0.8	170.2	1039.9	5.6975	48.52	40.20	11.11
F-41	280.1	0.7	210.8	1081.2	5.9039	47.80	41.07	11.09
F-42	239.0	0.6	226.0	1005.1	5.5236	50.07	38.92	11.61
F-51 2)	280.1	0.7	213.8	1092.7	5.9615	46.72	46.10	10.95

is more apparent, and the increase in this factor is at the level of 3.5 cN/tex (the sample F-33 compared with F-38).

To summarise, we can state that in the case of fibres with incorporated ferromagnetic nanoadditions, the small ‘sharpening’ of the solidification conditions (as result of increasing the temperature) in mild baths is connected with an increase in the PAN fibres’ strength properties. This non-typical effect can be caused by the influence of the nanoaddition on slowing down the diffusion processes, resulting in the creation of a structure which would be susceptible to deformation processes under the action of higher tensions. This causes an increase in the fibres’ strength at similar values of the total drawing.

Considering the strength properties, advantageous conditions of spinning PAN fibres with a Fe_3O_4 nanoaddition consist in conducting the solidification process in baths with a solvent concentration of 60%, at a temperature of 20 °C, and at a negative as-spun draw ratio at the level of -50%. At the same time, the values of deformation at the two-stage drawing should be near to the maximum values.

With the goal of further increasing the fibres’ strength properties, we tested the influence of the drawing ratio distribution in the two-stage drawing process on the fibres’ tenacity, as it is already known that a suitable deformation distribution in the multi-stage drawing process is decisive for the fibres’ features, and not just the value of the total drawing.

Taking into account these considerations, for fibres spun under the conditions selected by us, the drawing process was performed by applying deformations related to the value of 0.6 – 0.9 of the maximum drawing value at the first drawing stage, and deformations near the maximum at the second stage were carried out in preheated steam.

With a gradual decrease in the drawing performed in the plastification bath from 400% to 280%, the possibility of increasing the drawing in preheated steam from 121.6% to 210.6% (0.7 of the maximum value) was raised; this resulted in an increase in the fibres’ strength properties by 3 cN/tex. Fibres drawn as described above were characterised by a high tenacity of up to 41.07 cN/tex (sample F-41, see Table 2). A further decrease in the deformation value of the first drawing stage to a value related to 0.6 of the total drawing, notwithstanding the fact that at the second stage it was possible to achieve higher

***Table 3**. Percentage shares of pores, parameters of porous structure of PAN fibres with a Fe_3O_4 nanoaddition and without nanoaddition.*

Set of pores, nm		Share of pores, %	Total share of pores, %	Share of pores, %	Total share of pores, %
		F-51 (without nanoaddition)		F-41 (5% Fe_3O_4)	
Very great	7500	11,93	53,08	29,92	62,21
	3750	32,92		25,20	
	1875	8,23		7,09	
Great	750	5,35	16,05	3,15	10,24
	375	5,76		7,09	
	150	4,94		0	
Middle	75.0	4,53	16,06	3,94	5,51
	41,7	4,12		0.00	
	26,8	5,35		1,57	
	15.0	2,06		0.00	
Small	12,3	1,23	14,81	0,79	22,05
	10,3	2,88		3,15	
	8.0	3,70		8,66	
	6.0	7.00		9,45	
	4.0	0.00		0.00	
Total volume of pores, cm^3/g		0.238		0.144	
Total internal surface of pores, m^2/g		15.39		11.47	

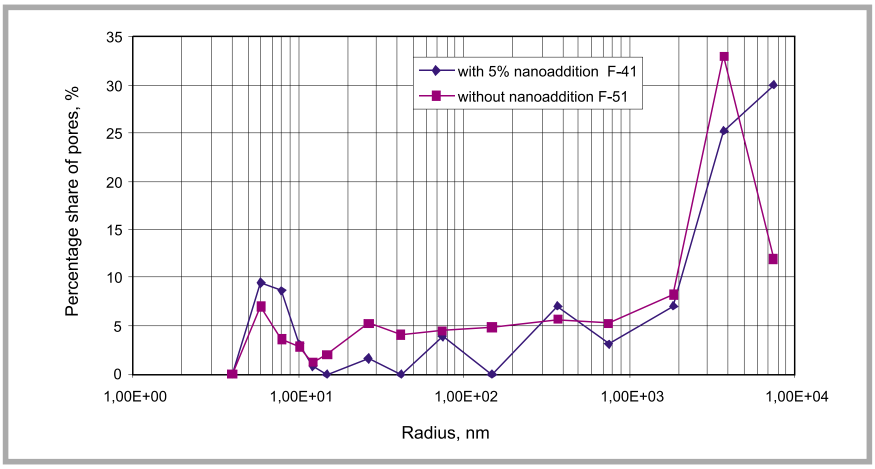

***Figure 1.** Dependence of the percentage shares of pores as a function of their radii for PAN fibres without and with a nanoaddition.*

drawing values, even at the level of 226%; this already caused a decrease in tenacity down to 38.92 cN/tex (sample F-42). The tenacity decrease by 2 cN/tex caused that the tenacity was similar to those obtained while conducting the drawing process at maximum deformations in both stages. Considering the strength properties of PAN fibres with a Fe_3O_4 nanoaddition, it is advantageous to perform the drawing process under the following conditions:

- applying a deformation decreased to 0.7 of the maximum value at the first drawing stage in the plastification bath, and
- applying drawing near the maximum in the preheated steam.

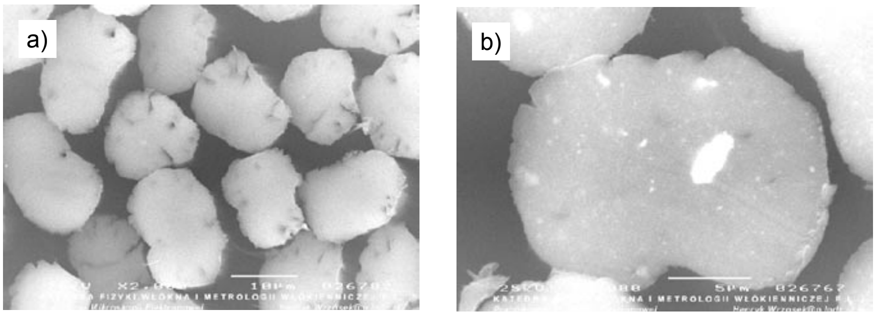

***Figure 2.** Cross-sections of fibres without nanoaddition and with a 5% nanoaddition; a) fibres without nanoaddition (F-51), b) fibres with a Fe_3O_4 nanoaddition (F-41).*

From a comparison of the strength properties of fibres drawn as described above with the properties of fibres without a nanoaddition (sample F-51 with F-41), it appears that with the presence of the ferromagnetic nanoaddition in the fibre-matter, a decrease of the tenacity value by 5.03 cN/tex occurs (Table 2). This suggests that at analogous drawing ratio distribution and similar values of the total drawing, not only may the orientation of the structural elements decide the fibres' strength properties, but also the supermolecular and porous structure. However, at significantly smaller total volume of pores of 0.144 cm^3/g of the fibres with Fe_3O_4 nanoaddition, in comparison with the porosity of fibres without any nanoaddition, which are characterised by a total volume of pores at the level of 0.238 cm^3/g, and small differences in the internal surface of 11.47 m^2/g and 15.39 m^2/g respectively (Table 3), their tenacity is lower by about 5 cN/tex (compared to fibres without nanoaddition). The character of the porous structure of both types of fibres is similar. The curves of pores distribution as a function of their radii (Figure 1) for fibres without nanoaddition are characterised by the existence of a small maximum within the range of small pores (which is related to their percentage shares) and a distinctive maximum within the range of very great pores, whereas for fibres with a ferromagnetic the percentage share of very great pores increases successively. However, it seems very improbable that the higher share content of very great pores of above 3750 nm, and at the same time the total volume of pores (nearly half the value as for the fibres without nanoaddition) could be the only reasons for the decreased strength properties. The summarised percentage share of great and very great pores, at the level of 70% – 72% for both types of fibres, entitle them to qualify as macroporous structures. This is advantageous considering the medical application of carbon fibres manufactured from such a precursor. The creation of a porous structure with such a character was connected with a slight 'sharpening' of the solidification conditions, as the result of applying a temperature of the solidification bath at 20 °C. In the case of fibres with a nanoaddition, they were advantageous for obtaining increased tensile strength properties and a lower total volume of pores. On the con-

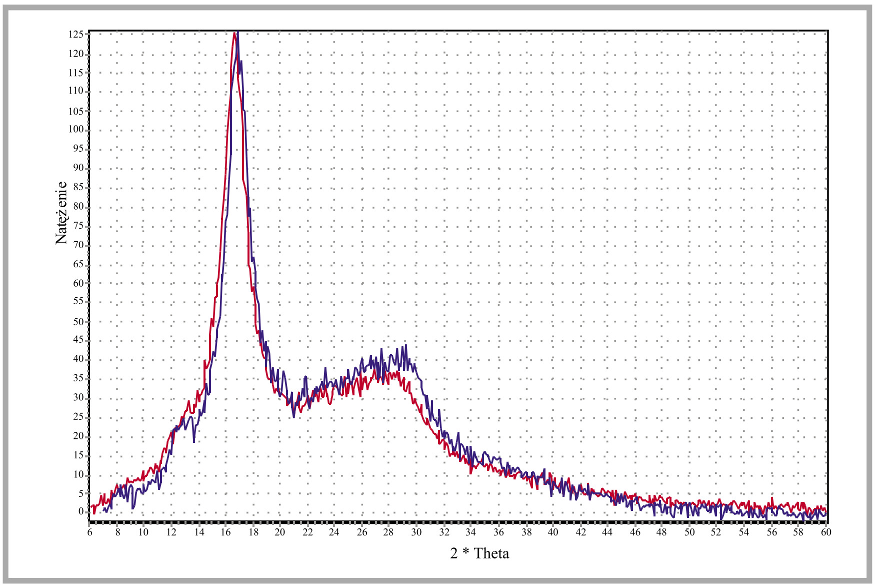

Figure 3. *Comparison of the diffractograms of PAN fibre without nanoaddition - sample F-51 (red line) and PAN fibre with a* Fe_3O_4 *nanoaddition –sample F-41 (blue line).*

trary, fibres without a nanoaddition (in accordance with the general regularities [15]) were favourable to the creation of a structure with higher porosity. On the photos of the fibre, cross-sections small amounts of very great radially positioned capillaries are visible (Figure 2).

Both types of fibres are differentiated only insignificantly by the content of the para-crystalline phase at comparable dimensions of crystallites. These values are equal to 49% and d = 43 Ĺ respectively for fibres without a nanoaddition, and to 47% and d = 44 Ĺ for fibres with a Fe_3O_4 nanoaddition. The comparison of the diffractograms of both fibre types is presented in Figure 3. Considering the above-mentioned data, we may suppose that the presence of Fe_3O_4 nanoparticles in the fibre-matter could cause the formation of a structure with a smaller number of secondary bonds between macromolecules than in the case of PAN fibres without nanoaddition. This is probably the main cause of the lower strength properties of PAN fibres which include nano-Fe_3O_4.

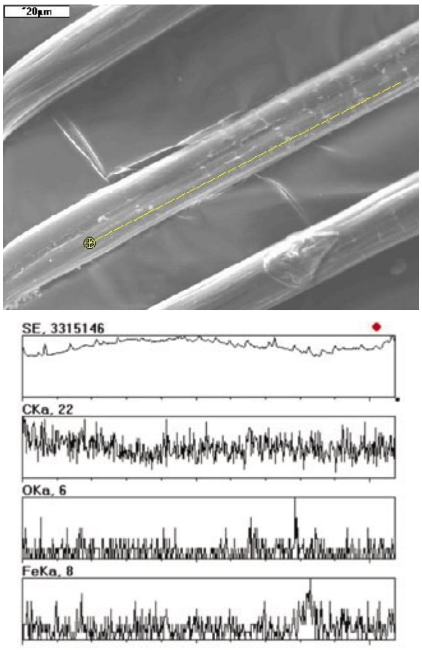

Figure 4. *Linear EDS analysis of the surface of PAN fibres with a* Fe_3O_4 *nanoaddition – sample F-41.*

It was possible to confirm the presence of nanoaddition in PAN fibres and estimate its distribution on the fibres' surface and through their cross-sections thanks to SEM+EDS X-ray microanalysis. On the basis of the linear analysis presented for sample F-41 in Figure 4, it appears that irrespective of the presence of carbon atoms on the fibres' surface, which are characteristic for the fibre matter, iron and oxygen atoms originating in the incorporated nanoaddition can also be indicated. The dependencies obtained and presented in Figure 4 are concerned with the straight-line segment marked on the fibre sample, and confirm the presence of Fe_3O_4 on this fibre segment; what is more, its character proves the uniform distribution of the nanoaddition.

On the basis of the mapping presented in Figure 5, i.e. a map of concentrations of the elements which make up the sample, we can state that the nanoaddition is distributed uniformly on the fibres' surface. On the basis of SEM photos (Figures 6 and 7 see page 24), we also can state that the nanoaddition distribution along the fibres' cross-section is relatively uniform, although greater agglomerates appear sporadically.

The magnetic properties of the PAN fibres obtained are connected with the presence of the Fe_3O_4 nanoaddition incorporated into the fibre matter. The dependences of the magnetisation intensity as a function of the external magnetic field intensity for a sample containing Fe_3O_4 with nanometre-grain dimensions and for PAN fibres with incorporated

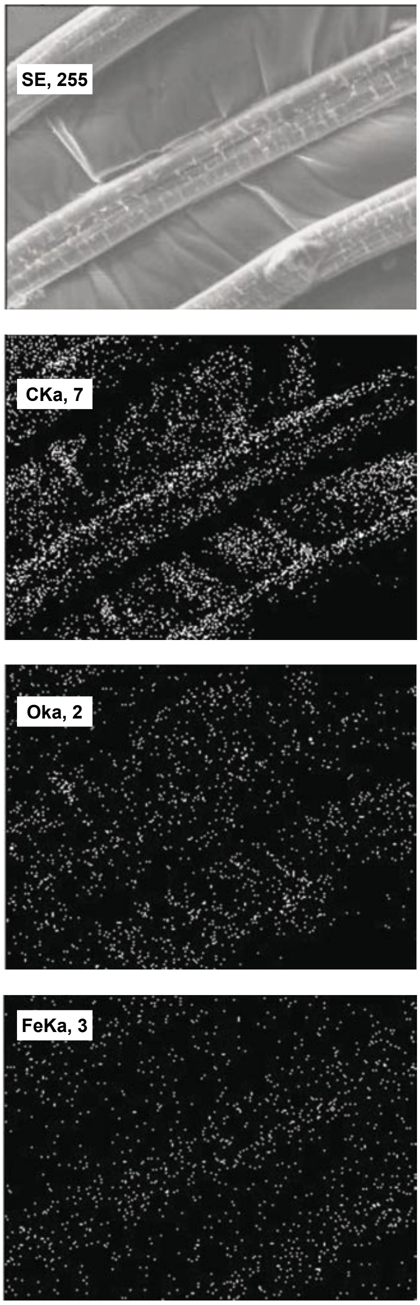

Figure 5. *EDS mapping of the surface of PAN fibres with a* Fe_3O_4 *nanoaddition (sample F-41).*

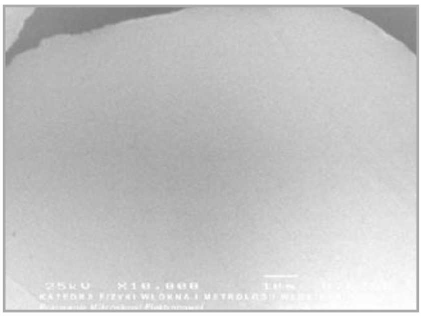

Figure 6. *Fragment of the cross-section of a polyacrylonitryle fibre without a nanoaddition (sample F-51); any addition is visible in the cross-section.*

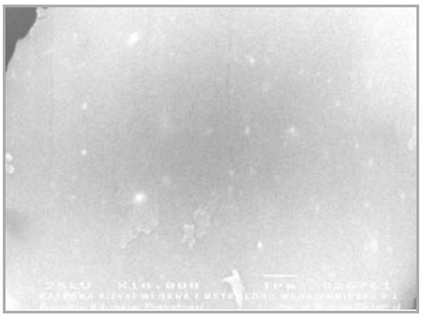

Figure 7. *Fragment of the cross-section of a polyacrylonitryle fibre with a Fe_3O_4 nanoaddition (sample F-41); clearly visible are nanoaddition agglomerates.*

5% of this nanoaddition are presented in Figure 8. These dependences indicate the presence of the magnetite nanoparticles in the polymer structure. By comparing the shape of magnetisation curves for a pure magnetite and the composite fibre, we can state with great probability that introducing the magnetite particles into the spinning solution, followed by formation of the fibre by spinning and drawing, do not change the properties of the magnetite itself.

Summary

1. Obtaining PAN fibres with ferromagnetic properties (including a Fe_3O_4 nanoaddition) and increased tensile strength properties, which would ensure the carbonisation process of these precursor fibres without special difficulties, requires the following process conditions to be applied:
   - dispersion of the nanoaddition in the solvent by ultrasound processing before inserting it into the spinning solution,
   - a slight 'sharpening' of the solidification conditions as the result of a temperature increase of the moderately mild coagulation bath,
   - conducting the drawing process as a two-stage process at a deformation decreased to 0.7 of the maximum value in the first stage, and near to the maximum in the second stage.

2. The PAN fibres, which include a ferromagnetic nanoaddition, obtained under the selected conditions, are characterised by a macroporous structure with a small total volume of pores within the range of 0.144 cm^3/g, uniform distribution of the nanoaddition in the fibre matter, a content of the paracrystalline phase at the level of 47% and crystallite dimensions within the range of 44 A, and tenacity at the level up to 41 cN/tex, which is appropriate for conducting the carbonisation.

3. The investigations into the magnetisation degree of the fibres in a external magnetic field show that the fibres' magnetic properties are connected with the presence of the ferromagnetic nanoaddition in the fibre-matter. The magnetic properties of the ferromagnetic particles do not change while spinning and drawing the fibres.

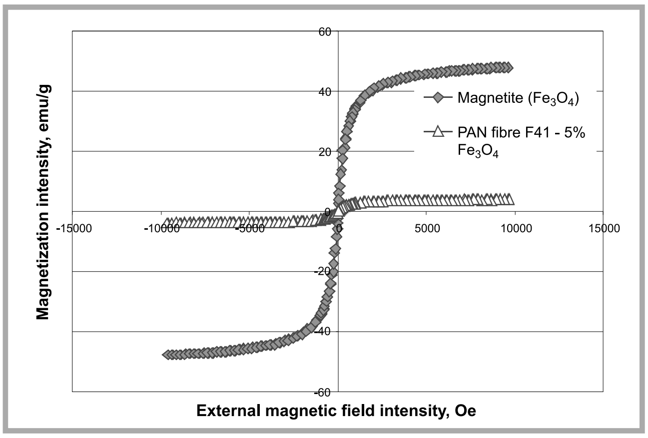

Figure 8. *Dependence of the magnetisation intensity as a function of the external field intensity for a sample of pure magnetite (Fe_3O_4) nanoaddition and for fibres including a 5% Fe_3O_4 nanoaddition.*

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References

1. *Šafařik I., Šafaříková M.; Monatshefte für Chemie 2002, 133, 737.*
2. *Matsunaga T., Kamiya S.; Appl. Microbiol. Biotechnol. 1987, 26, 328.*
3. *Matsunaga T., Kawasaki M., Yu X., Tsujimura N., Nakamura, N.; Anal. Chem. 1996, 65, 3551.*
4. *Nakamura N., Matsunaga T.; Anal. Chem. Acta 1993, 281, 585.*
5. *Sestier C., DaSilva M. F., Sabolovic D., Roger J., Pons J. N.; Electrophoresis 1998, 19, 1220.*
6. *Kriz C. B., Radevik K., Kriz D.; Anal. Chem. 1996, 68, 1966.*
7. *Yeh T. C., Zhang W. G., Ildstad S. T., Ho C.; Magn. Reson. Med. 1995, 33, 200.*
8. *Bulte J. W. M., de Cuyper M., Despres D., Frank J. A.; J. Magn. Magn. Mater. 1999, 194, 204.*
9. *Brusentsov N. A., Gogosov V. V., Brusentsova T. N., Sergeev A. V., Jurchenko N. Y., Kuznetsov A. A., Kuznetsov O. A., Shumakov L. I.; J Magn. Magn. Mater. 2001, 225, 113.*
10. *Jordan A., Scholz R., Maier-Hauff K., Johannsen M., Wust P., Nadobny J., Schirra, H., Schmidt H., Deger S., Loening S., Lanksch W., Felix R.; J. Magn. Mater. 2001, 225, 118.*
11. *Mikołajczyk T., Boguń M., Kowalczyk A.; Fibres & Textiles in Eastern Europe 2005, vol. 13, No 3, pp. 30-34.*
12. *Boguń M., Mikołajczyk T., Kurzak A., Błażewicz M., Rajzer I.; Fibres & Textiles in Eastern Europe 2006, Vol. 14, No 2, pp. 13-16.*
13. *Mikołajczyk T., Boguń M., Błażewicz M., Piekarczyk I.; J. Appl. Polym. Sci. 2006, 100, 2881.*
14. *Mikołajczyk T., Boguń M.; Fibres & Textiles in Eastern Europe 2005, Vol. 13, No 1, pp. 28-31.*
15. *Wójcik M., Nowicka K., Mikołajczyk T., Chmist J., Figiel H., Błażewicz S.; 'Preliminary Study on Polyacrylonitrile - based Fibres Magnetite Nanoparticles for Biomaterials Engineering', Engineering of Biomaterials, No 58-60, IX, 2006.*
16. *Mikołajczyk T.; 'Modification of the Manufacturing Process of Polyacrylonitrile Fibres', Scientific Buletin of Technical University of Lodz, 1997, No 781, Scientific Theses Z 243.*

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