

# Influence of the Amount of Ferromagnetic Addition on the Rheological Properties of Spinning Solutions, the Structure, the Strength, and Thermal Properties of Polyacrylonitrile Fibres

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**ABSTRACT:** The rheological properties of spinning solutions of polyacrylonitrile in dimethyl formamide (DMF) containing various amounts of a ferromagnetic nanoaddition were investigated. The porous structure, the strength and thermal properties of fibers obtained from these solutions were assessed, as well as the uniformity of the nano-

addition distribution on the fiber surface was estimated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2513–2521, 2008

**Key words:** polyacrylonitril fibers; nanoaddition; ferromagnetics; rheological properties; thermal stability

## INTRODUCTION

The possibility of taking advantage of the unique properties of magnetic polymeric nanoconposites with a content of ferromagnetic nanoparticles was decisive for the growing number of medical applications. Different kinds of ferromagnetics with grain dimensions from nanometers to micrometers have found their application in many fields of biomedical engineering and biotechnology.<sup>1</sup> In the majority of cases they have been used in the following proceedings:

- in immunomagnetic separation, which consists on bond harmful biomolecules by other organic molecules bound with the magnetic nanoparticles<sup>2</sup>;
- in magnetic hypothermia, where the nanoparticles are used for identification and healing of tumor cells<sup>3,4</sup>;
- in medical diagnostic, to visualization cells with the use of nuclear magnetic resonance (NMR).<sup>5</sup>

A broadening of the above-mentioned applications may be inserting magnetic nanoparticles into the

fiber-matter of polyacrylonitrile (PAN) fibers. Carbon fibers obtained from such a PAN precursor would be characterized not only by magnetic properties but also by anisotropy typical for natural tissues. Advantageous is also their increased porosity which is the outcome of the precursor fibers' porosity and the porosity created during carbonisation while manufacturing carbon fibers.<sup>6</sup> To obtain a precursor, which fulfill the demands of increased porosity, and at the same time are characterized by good tensile strength properties requires an appropriate selection of the fiber spinning and drawing conditions.<sup>6</sup> In the case considered, they depend not only on the process parameters of solidification and drawing, which are usual for such fibers, but also on the kind and amount of the nanoaddition inserted.<sup>7</sup> In the majority of cases, incorporating a nonfiber-grade nanoaddition is connected with decreasing the fiber-matter's ability to deformation processes at the stage of drawing.<sup>8–10</sup> Conducting the solidification process under conditions advantageous for formation of a porous structure resulted in obtaining a higher total volume of the pores, and at the same time lowered the tensile strength properties in comparison to PAN fibers without any nanoaddition.<sup>11</sup> The level of the relative strength (tenacity) of PAN fibers also depends on the chemical structure of the nanoaddition incorporated and their mutual interaction with the fiber-matter. In the case of incorporating montmorillonite, an essential importance has the presence of the exfoliation phenomenon of the monmorillonite packets,

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and their orientation in relation to the fiber axis. As we stated in our previous works,<sup>7,12</sup> the reconstruction of the PAN fibers' crystalline structure connected with the nucleation action of the nanoaddition, hydroxyapatite in this case, also influences advantageously the possibility to obtain good tensile strength properties of these fibers.

Research conducted by us<sup>13</sup> into selecting the spinning and drawing conditions of PAN fibers containing a Fe<sub>3</sub>O<sub>4</sub> ferromagnetic addition also confirmed that application of a suitable drawing ratio distribution of the two-stage drawing process advantageously influences the possibility to achieve increased strength properties. At the same time, the solidification process has been conducted under mild conditions, only slightly sharpened as the result of an increase in the temperature of the coagulation bath which was favorable for creation of a structure with a low total volume of pores.

The orientation of the selection of fiber forming conditions to the goal of obtaining increased tensile strength properties of PAN fibers was connected with the need to obtain appropriate magnetic properties of the carbon fibers. Fulfilling this latter condition, might carry with it the increase in the amount of magnetic particles within the matter of the precursor fibers, and that in turn causes a significantly decrease of its strength properties.

The aim of this work is to determine the influence of the Fe<sub>3</sub>O<sub>4</sub> ferromagnetic addition incorporated in the PAN fiber-matter on their structure, and their strength and thermal properties. The knowledge of the nanoaddition's influence on the character of the thermal transformations in PAN fibers is essential while taking into consideration the parameter selection of the carbonisation process of such a precursor. The influence of the amount of the nanoaddition inserted into the spinning solutions on their rheological properties is also within the scope of our work.

## MATERIALS AND RESEARCH METHODS

### Polymer and nanoaddition characteristic

A three-component copolymer containing 93–94% wt of acrylonitrile mer units, 5–6% wt acrylamide methyl mer units, and 1% wt alilosulfonian 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  $M_w/M_n = 3.1$  was determined by gel chromatography; the estimation was carried out at the Institute of Biopolymers and Chemical Fibers in Łódź.

A Fe<sub>3</sub>O<sub>4</sub> ferromagnetic nanoaddition from  $\zeta$ -Aldrich with grain dimensions within the range of

30–50 nm was used. The nanoaddition was inserted into the spinning solution in an amount of 5% re-calculated in relation to the polymer. Before inserting, the nanoaddition suspension in DMF was subjected to the action of ultrasounds, at a temperature of 20°C over 2 h. A Polsonic-3 ultrasonic washer with a power of  $2 \times 160$ 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 rheoviscometer and a "H" type cylinder, at shearing rates up to 146.8 1/s, and a temperature of 20°C.

### Fiber forming (spinning and drawing)

The fibers were spun from a solution by the wet method with the use of an extended-laboratory scale spinning machine which allows to stabilize the technological parameters at the assumed levels and their continues monitoring. A 240-hole spinneret was used with a hole diameters of 0.08 mm. The process of the fibers' solidification was carried out in a bath containing an aqueous DMF solution of a concentration within the range of 60%. The drawing process was realized as a two-stage process, the first stage 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 fibers on line, they were dried under isometric conditions at a temperature from 20 to 40°C.

### Properties of the fibers obtained

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

The fibers' 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 to 7500nm and the total internal surface of pores.

The distribution of the Fe<sub>3</sub>O<sub>4</sub> nanoaddition in the fiber 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.

Assessing the iron amount was performed by the spectrophotometric method with the use of a Specol spectrophotometer made by Carl Zeiss Jena, at a wave length of  $\lambda_{\max} = 474$  nm.

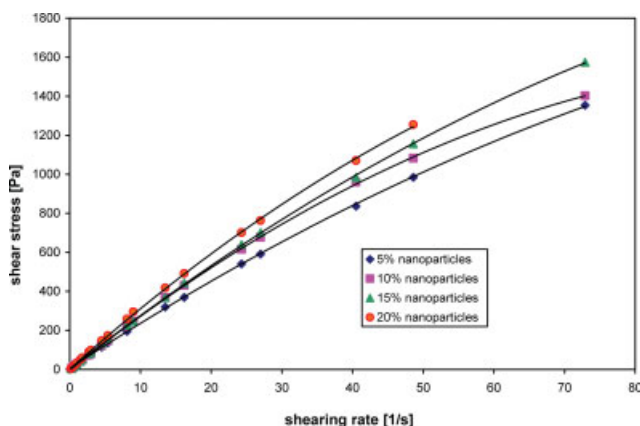
**TABLE I**  
Value of the Rheological Parameters “*n*” and “*k*” of Spinning Solutions with Various Shares of Fe<sub>3</sub>O<sub>4</sub>

Content Fe <sub>3</sub> O <sub>4</sub> in spinning solutions [%]	Rheological parameter “ <i>k</i> ”	Rheological parameter “ <i>n</i> ”
0	27.51	0.9640
5	25.11	0.9647
10	25.84	0.9876
15	27.44	0.9856
20	30.49	0.9962

The thermal analysis of fibers was carried out by means of a derivatograph, using a Paulik–Paulik–Erdey system derivatograph. The derivatographic analysis was carried out in air using weighed portions of 40 mg at a heating rate of 7.9°C min<sup>-1</sup> within the temperature range from 20 to 800°C.

## DISCUSSION OF THE RESULTS

The rheological properties of spinning solutions used for spinning at a constant polymer concentration in the solution of 22% depend on the amount of the nanoaddition incorporated (Table I). With an increase in the amount of Fe<sub>3</sub>O<sub>4</sub> in the spinning solution from 5 to 20% (calculated in relation to the polymer) is connected the increase in the rheological parameter “*k*”, which testify the “consistency” of the solution and the related value of the apparent dynamic viscosity. The increase in the rheological parameter “*n*” is accompanied with this tendency, which in turn testify that the liquid is more similar to a Newtonian fluid with  $n = 1$ . Obtaining values of the rheological parameter  $n < 1$  is typical for liquids “thinned” by shearing. The flow curves (Fig. 1) go through the origin of the co-ordinates, and the shearing stress increases less than proportional with



**Figure 1** Flow curves of spinning solutions containing various amounts of the Fe<sub>3</sub>O<sub>4</sub> ferromagnetic addition. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the increase in the shearing rate. This means that the spinning solutions obtained are non-Newtonian fluids “thinned” by shearing without a flow limit. The increased content of the nanoaddition in the spinning solution does not change the rheological character of this liquid (it further remains “thinned” by shearing), notwithstanding that the rheological parameters “*n*” and “*k*” in the Ostwald de Waele equation change:

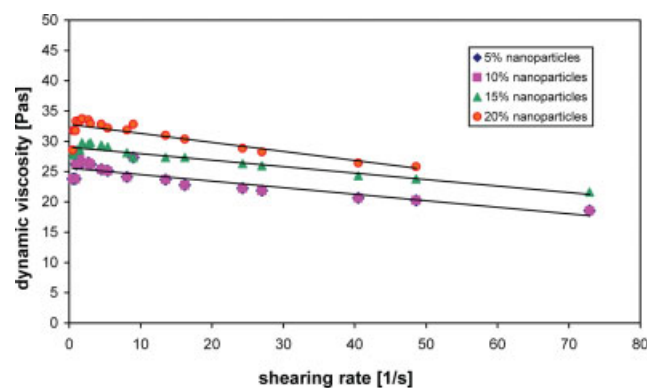
$$\eta = k\gamma^{n-1}$$

where:

- $\eta$ , is the apparent dynamic viscosity, and
- $\gamma$ , the shearing rate
- $n, k$ , rheological parameters

At the same time the solutions tested are characterized by an increase in the apparent dynamic viscosity with an increase in the shearing rate (Fig. 2) which is typical for polymer fluids. However, in all cases this drop is not especially distinctive, which is connected with the presence of the dispersed nanoaddition in the spinning solution. This means that we have to do with a suspension of Fe<sub>3</sub>O<sub>4</sub> in the polymer solution, and this influences the rheological fluid’s properties.

According to our assumption of obtaining increased tensile strength properties of the PAN fibers with different Fe<sub>3</sub>O<sub>4</sub> content, the solidification process we conducted under mild conditions in baths with a 60% content of the solvent, in which the solidification conditions were only slightly “sharpened” as the result of increasing the bath temperature up to the level of 20°C. At negative values of the as-spun draw ratio at the level of -50%, this favorable influenced the solidification process to be performed according to the diffusion mechanism, and the creation of a structure only little defective.



**Figure 2** Changes in the apparent dynamic viscosity as a function of the shearing rate of spinning solutions with various shares of Fe<sub>3</sub>O<sub>4</sub> at a temperature of 20°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE II  
Spinning and Drawing Conditions and the Properties of PAN Fibres Obtained from Spinning Solutions with Various Shares of Fe<sub>3</sub>O<sub>4</sub>

Sample index	Content Fe <sub>3</sub> O <sub>4</sub> in spinning solutions [%] <sup>a</sup>	Solidification				Drawing in bath [%]	Drawing in plastification bath [%]	Drawing in stream [%]	Total draw ratio [%]	Total deformation	Linear density of fibre stream T <sub>tex</sub>	Tenacity [cN/tex]	Elongation at break [%]
		DMF content in bath [%]	Bath temperature [°C]	As-spun draw out ratio [%]	As-spun draw out ratio [%]								
F-41	5	60	20	-50	280.1	210.8	1081.2	5.90	47.80	41.07	11.09		
F-45	10	60	20	-50	280.1	187.2	991.6	5.47	36.58	36.58	11.38		
F-47	15	60	20	-50	280.1	182.8	974.8	5.37	34.70	34.70	11.91		
F-49	20	60	20	-50	280.1	180.3	965.4	5.32	32.28	32.28	12.00		
F-51	0	60	20	-50	280.1	213.8	1092.7	5.96	46.10	46.10	10.95		

<sup>a</sup> % wt calculated in relation to the mass of the PAN polymer.

The drawing process was performed in two stages, the first in a plastification bath with solvent content of 50% and at a temperature of 70°C, and next the second in preheated steam at a temperature of 135°C, under conditions of increasing molecular mobility of the matter's macromolecules. The process parameters accepted were determined in earlier work.<sup>13</sup>

According to our research results,<sup>13</sup> the first stage of drawing was realized at deformations related to a value which equals 70% of the maximum drawing, whereas the second stage of drawing was performed at deformations near the maximum drawing value. Application of such a drawing ratio distribution was advantageous for achieving high tensile strength properties of the fibers. The tenacity of fibers with the smallest amount of nanoaddition incorporated (1.7%) was at a high level of 41.07 cN/tex, which was only by about 5 cN/tex lower than that of fibers without any nanoaddition and formed under analogical conditions (Table II). With the increase in the Fe<sub>3</sub>O<sub>4</sub> amount from 5 to 20% (recalculated in relation to the polymer) incorporated into the spinning solution, a decrease in the ability of the matter to deformation was connected, which in turn resulted in the need to decrease the value of drawing in steam from 210.8% to 180.3%. At a constant drawing value in the plastification bath this was related to a decrease in the total drawing from 1081.2% to 965.4%, and the total deformation from 5.9 to 5.3.

The effect of this change in the drawing conditions is a decrease by 8.8cN/tex in the tensile strength properties of fibers with the highest nanoaddition amount of 12%. At a similar content of the paracrystalline phase within the range of 47–49% and the value of crystallites within the range of 43–44 Å for fibers without a nanoaddition and fibers obtained from spinning solutions with a 5% content of Fe<sub>3</sub>O<sub>4</sub> (recalculated in relation to the polymer),<sup>13</sup> it seems that for the tensile strength properties are decisive, apart from the orientation of the structural elements, mainly the number of the secondary bonds between the macromolecules of the fiber-matter. With incorporating greater amounts of Fe<sub>3</sub>O<sub>4</sub> probably is con-

TABLE III  
Content of Fe<sub>3</sub>O<sub>4</sub> in Fibres Obtained from Spinning Solutions with Incorporated Various Amounts of Fe<sub>3</sub>O<sub>4</sub>

Sample index	Content Fe <sub>3</sub> O <sub>4</sub> in spinning solutions [%] <sup>a</sup>	Content Fe <sub>3</sub> O <sub>4</sub> in fibres [%] <sup>a</sup>
F-41	5	1.698
F-45	10	5.544
F-47	15	8.739
F-49	20	12.132

<sup>a</sup> The percent value calculated in relation to the polymer.

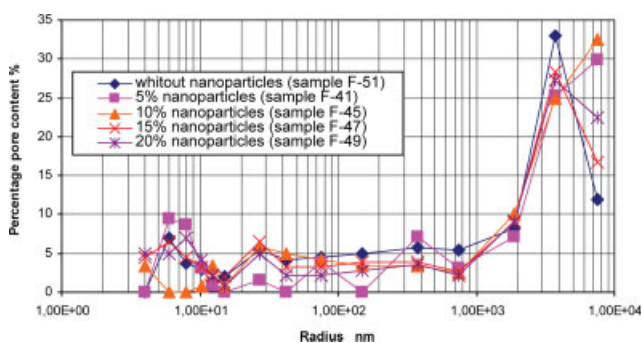
**TABLE IV**  
**Percentage Shares of Pores in PAN Fibres with Various Contents of the Nanoaddition**

Sample symbol	Total pore volume [cm <sup>3</sup> /g]	Internal surface [m <sup>2</sup> /g]	Percent contents of pores [%]			
			Small pores 4–12.3 [nm]	Medium pores 12.3–75 [nm]	Large pores 75–750 [nm]	Very large pores 750–7500 [nm]
F-51	0.238	15.40	14.81	16.06	16.05	53.08
F-41	0.144	11.47	22.05	5.51	10.24	62.21
F-45	0.150	5.74	7.49	15.83	9.16	67.50
F-47	0.167	14.67	20.66	14.85	10.32	54.19
F-49	0.154	13.70	23.09	9.80	8.40	58.74

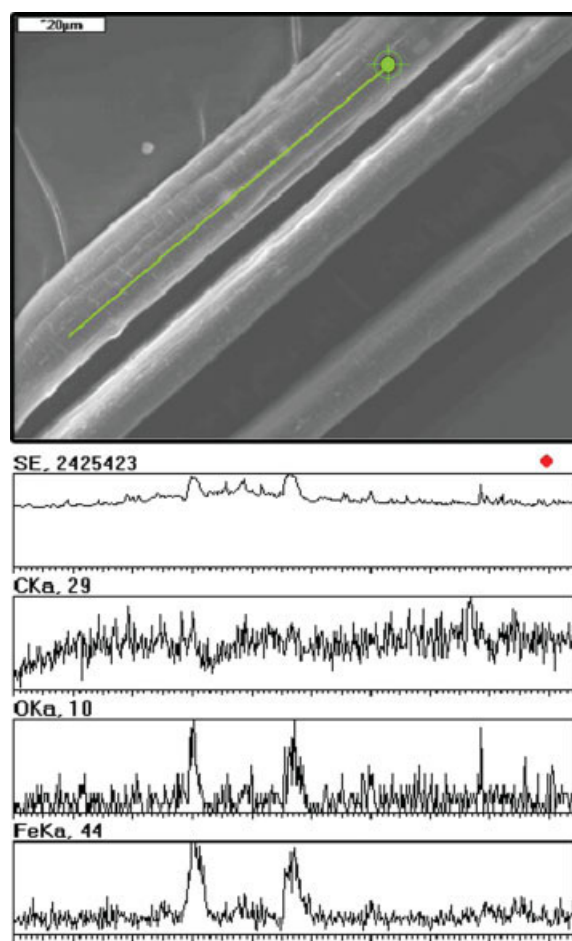
nected the creation of a structure with a smaller number of secondary bonds, and at the same with lower strength properties. The level of tenacity within the range of 32.2 cN/tex may be further considered as a high, especially at such high amount of the nanoaddition incorporated into the spinning solution. The nanoaddition presence in the solidified stream of the spinning solution influences proceeding of the mass exchange processes, as well as the ability to deformation of the fiber-matter at the plastification drawing stage. The incorporation into the spinning solutions such great amounts of the nanoaddition (20% recalculated in relation to the polymer) was connected with the fact that during the process of rinsing the fibers, the nanoaddition was washed out from the fiber-matter. We may assume that the cause of this phenomenon was the dissolution of a layer, probably of polysaccharide, which covered the Fe<sub>3</sub>O<sub>4</sub> particles. This assumption sounds credibly as ferromagnetic nanoadditions dedicated for medical application are commonly covered by the producers with a layer most often of dextrane. As the result of removing this layer, the amount of nanoaddition in the fiber-matter (assessed by an analytical method) decreases (Table III). The fact of remaining of a relative larger nanoaddition amount after rinsing those fibers which contained an increased amount incorporated into the spinning so-

lution, may suggest its more uniform distribution over the fiber cross section. In the case of smaller amounts, the nanoaddition may be placed mainly in the layers near the surface, which facilitates its removing.

The decrease of the fibers' strength properties with the increase in the amount of the ferromagnetic nanoaddition incorporated in the fiber-matter is accompanied with a small increase in their porosity (Table IV). The total volume of pores is at a relative



**Figure 3** Dependency of the percentage shares of pores as a function of their radius for PAN fibers with various percentage shares of the incorporated ferromagnetic. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** Linear EDS analysis of PAN fibers containing Fe<sub>3</sub>O<sub>4</sub> (sample F-49). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

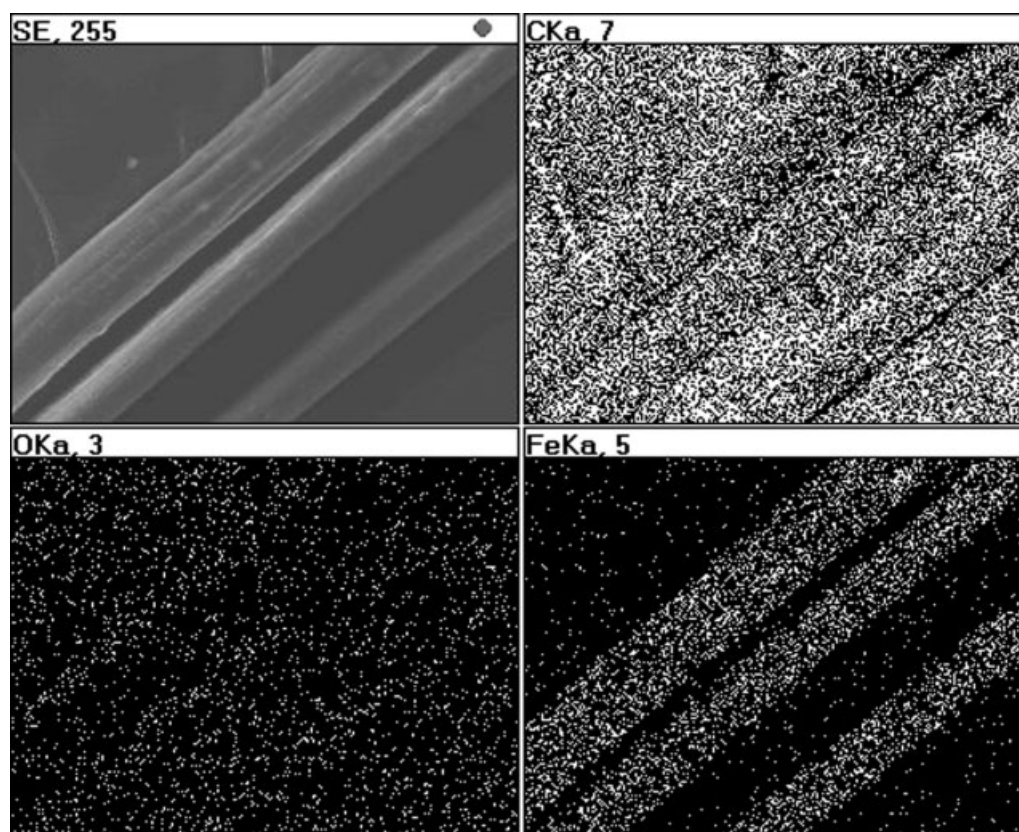


Figure 5 Map EDS analysis of PAN/Fe<sub>3</sub>O<sub>4</sub> fiber surface (sample F-49).

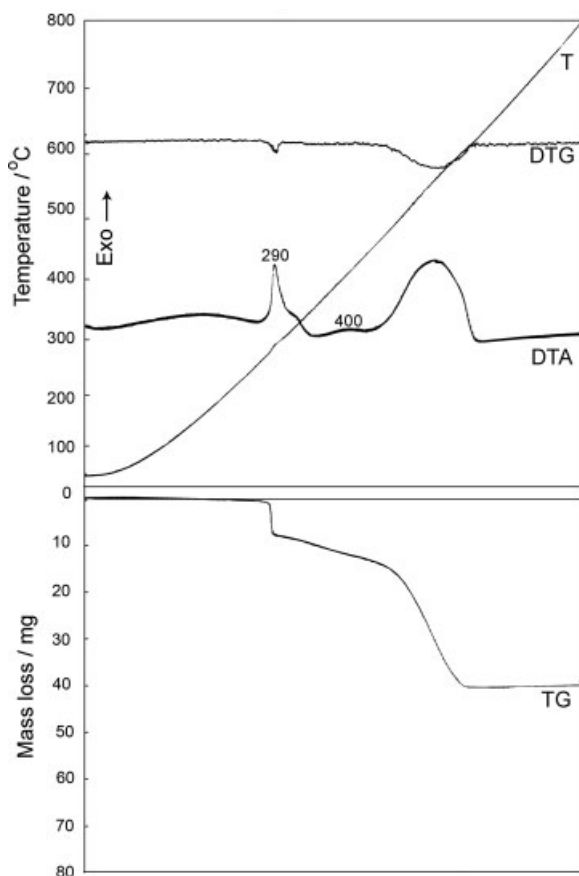
low level and depending on the amount of the Fe<sub>3</sub>O<sub>4</sub> nanoaddition is within the range of 0.14 cm<sup>3</sup>/g to 0.16 cm<sup>3</sup>/g, whereas the internal surface is at the level within 11.46 m<sup>2</sup>/g to 14.67 m<sup>2</sup>/g. An exception is the sample F-45 containing 5.5% of Fe<sub>3</sub>O<sub>4</sub> with an internal surface of 5.7 m<sup>2</sup>/g which is connected with a low amount of small pores at the level of 7.5%.

For all the types of fibers the level of these both factors is lower in comparison to PAN fibers without nanoaddition, spun and drawn under similar conditions. So, we can assume that in this case a slightly “sharpening” in the solidification conditions was advantageous for the creation of a porous structure. On the other hand, incorporation of the nanoaddition caused an inhibition of the diffusion processes, which revealed a decrease in the total volume of pores and the internal surface. At the same time, the character of the porous structure of all types of fibers is similar. At a quantitative predominance of the summarized share of great and very great pores above 60% (Table IV), the structure created may be described as a macroporous. The curves of the pore distribution as a function of its diameter (Fig. 3) are characterized (without the curve for the sample F-45 with a 5.5% of the of Fe<sub>3</sub>O<sub>4</sub> content) by the existence of a small maximum within the range of small pores, and a distinct maximum within the range of very

great pores. The existence of the latter, notwithstanding that it may be responsible for the presence of structural defects in the carbon fibers, may also be advantageous considering their medical applications, as it should favor re-sorption processes of the carbon fibers.

The indication of the nanoaddition presence in the PAN fibers and the estimation of the distribution uniformity on the fiber’s surface and through their cross section is possible thanks to the SEM + EDS X-ray microanalysis. From the linear analysis presented in Figure 4 for the sample F-49, it results that independently on the typical for this fiber-matter presence of carbon atoms, also iron and oxygen atoms are presented originating in the incorporated nanoaddition. The diagram obtained (Fig. 4) is connected to the straight line segment marked on the fiber’s surface, and confirmed the presence of Fe<sub>3</sub>O<sub>4</sub> on the fiber segment tested, whereas its character and the presence of the both maxima confirms that occasionally agglomerates occur on the fiber’s surface background of the even distributed nanoadditions. Such agglomerate-centers are also visible on the marked tested segment.

On the basis of the mapping presented in Figure 5 (i.e., a map of concentrations of the elements which compose the sample) also can be stated that the



**Figure 6** TG, DTG, DTA, and T curves of fibers from PAN without nanoparticles (sample F-51).

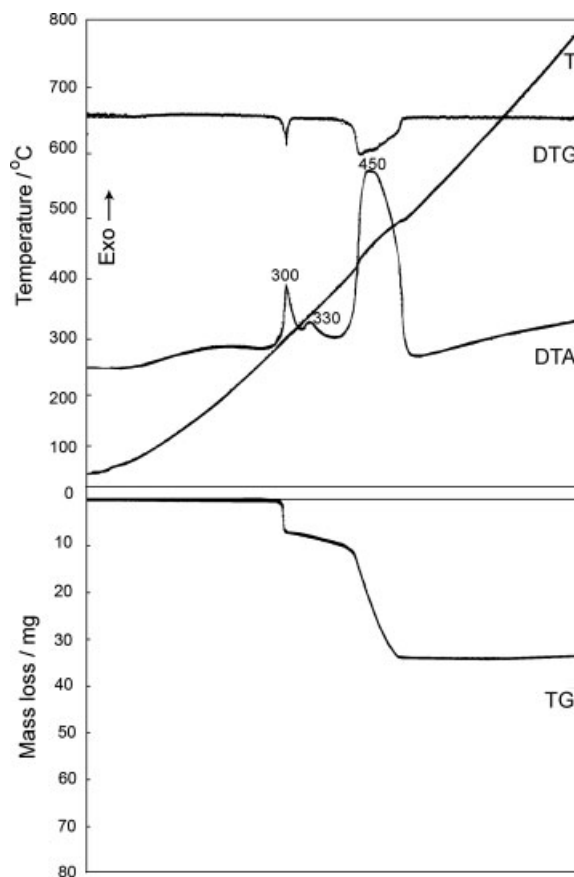
nanoaddition is uniform distributed on the fiber's surface.

The magnetic properties obtained by PAN fibers are connected with the presence of the  $\text{Fe}_3\text{O}_4$  nanoaddition in the fiber-grade matter. In our previous investigations we indicated that almost with the insertion of a 5%  $\text{Fe}_3\text{O}_4$  nanoaddition into the spinning solution, the creation of magnetic properties of the spun PAN fibers is connected.<sup>13</sup> The influence of the amount of the incorporated nanoaddition on the fibers' magnetisation degree will be the subject of an independent further publication. This will allow us to choose an appropriate amount of the nanoaddition incorporated into the precursor fibers which would be necessary to reach the assumed magnetic properties of the carbon fibers manufactured from them.

From the derivatographic analysis results that the presence of the  $\text{Fe}_3\text{O}_4$  nanoaddition in the PAN fibers does not change the character of its thermal transformations (Figs. 6 and 7). An exothermic peak occurs on the DTA curve of the PAN fibers at a temperature of  $T = 290^\circ\text{C}$ , which is the result of cyclisation and dehydrogenation processes connected with the creation of a cyclic structure. These processes are

clearly visible also on the DTA curves of fibers including a nanoaddition content and its presence does not influence significantly the temperature at which this peak occurs (Table V). At the maximum temperature of the cyclisation processes a distinct jump of mass loss appears on the TG curves of the samples tested, caused by the release of volatile substances, such as  $\text{NH}_3$ ,  $\text{CO}$ , and  $\text{HCN}$ , among others which are formed as the result of creating carboxyl and hydroxyl groups, and ether bridges between carbon atoms of the methyl groups. The jump of mass loss is the greatest in the case of fibers containing of 8.74% and 12.13% of the nanoaddition.

Incorporation of the nanoaddition causes that the process of further intermolecular crosslinking, which is accompanied by creating carbon structures, appears as a distinctive exothermic peak at a temperature of  $T = 330^\circ\text{C}$  (Fig. 7). In the case of PAN fibers without a nanoaddition this peak occurs within a more extended temperature range, is more broadening and its maximum appears at the temperature of  $T = 400^\circ\text{C}$  (Fig. 6). The above-mentioned processes are accompanied by a slowly mass loss of the sample, which after finishing the processes is equal to about 27% and is independent on the  $\text{Fe}_3\text{O}_4$  amount.



**Figure 7** TG, DTG, DTA, and T curves of fibers from PAN containing  $\text{Fe}_3\text{O}_4$  (sample F-47).

TABLE V  
Results of Thermal Analysis of Polyacrylonitrile Fibres

Sample index	Cyclization		Oxidation				Thermal stability indicator		
	$T_C$ [°C]	$\Delta m_C$ [%]	$T_C$ [°C]	$\Delta T$ [°C]	$\Delta m_o$ [%]	$dc/dT$ [mm]	$T_5$ [°C]	$T_{50}$ [°C]	$T_{800}$ [%]
F-51	290	18.70	565	455–615	100.00	10	270	520	0.0
F-41	290	18.70	480	420–530	92.50	10	280	460	7.5
F-45	300	9.25	500	435–530	87.50	15	295	490	16.5
F-47	300	20.00	450	385–500	88.75	16	290	440	12.5
F-49	290	22.50	450	370–500	87.50	16	255	435	15.0

$T_C$ , temperature of the maximum rate of the cyclisation processes;  $\Delta m_C$ , mass loss of the sample at the temperature  $T_C$ ;  $T_o$ , temperature of the maximum rate of oxidation;  $\Delta m_o$ , mass loss of the sample after the end of the oxidation processes.

We also indicated a distinctive influence of the nanoaddition presence in the tested fibers on the oxidation processes of PAN fibers. With an increase in the  $Fe_3O_4$  amount a decrease occurs in the initial temperature  $T_0$  of the oxidation processes, as well as a decrease in their maximum rate. What is more, they proceed in a significantly narrower temperature range, and their rate after exceeding 1.7% of the nanoaddition content in the fiber-grade matter is evidently higher (Table V). The result of the oxidation process is a great loss of the mass of the fibers tested, even up to 100% in the case of a sample without any nanoaddition. With the increase in the  $Fe_3O_4$  content in the fiber, the mass loss of the sample caused by the thermooxidation processes decreases thanks to the high thermal stability of the nanoaddition used (Fig. 8).

The thermal stability of the fibers tested was estimated on the basis of the  $T_5$  and  $T_{50}$  factors. It was stated that the amount of nanoaddition from 1.70% to 6.74% increases the fibers' thermal stability, determined by the value of  $T_5$ . On the other hand, the value of  $T_{50}$  decreases with the increase in the  $Fe_3O_4$  content in the fiber. The highest values of the  $T_5$  and  $T_{50}$  thermal stability factors were stated in the case of the sample containing 5.54% of  $Fe_3O_4$ . In the case of this sample we stated also the smallest mass loss connected with the cyclisation of the sample, the highest temperature of the maximum oxidation rate, and the narrowest temperature range of these processes. At the same time these fibers are characterized by the smallest area of the internal surface with a total volume of pores comparable to other samples. This may suggest that an optimum exists of the amount of nanoaddition incorporated into the fiber which influences advantageously the fibers' thermal properties.

## CONCLUSIONS

1. The incorporation of a ferromagnetic nanoaddition of up to 20% into the spinning solution of PAN in DMF does not influence a change of the

rheological character of the fluid. It remains further a non-Newtonian fluid "thinned" by shearing, and only the rheological parameters "n" and "k" change their values.

2. With the incorporation of 5–20% of the nanoaddition into the spinning solution, a decrease of the fiber-matter's ability to deformation at the stage of drawing is connected which is displayed by a decrease of the value of the total drawing from 1081% to 965.4%.
3. With the increase of the  $Fe_3O_4$  nanoaddition content in the PAN fiber-matter from 1.7 to

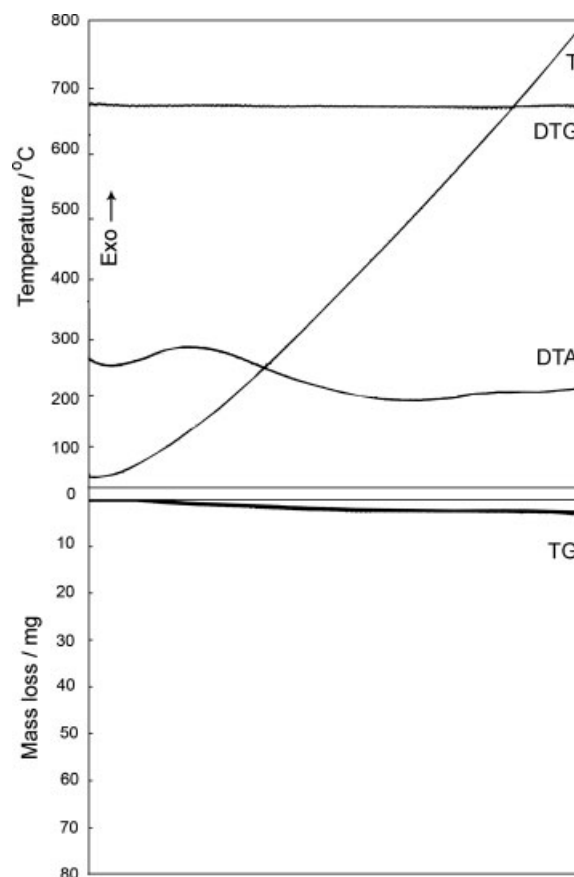


Figure 8 TG, DTG, DTA, and T curves of nanoparticles  $Fe_3O_4$ .



12%, a decrease is connected in the tensile strength properties by 8.8 cN/tex which is accompanied by a slightly increase in the total volume of pores and the internal surface.

4. A uniform distribution of the  $\text{Fe}_3\text{O}_4$  nanoaddition incorporated into the fiber-matter was stated on the surface of the PAN fibers.
5. Incorporating of a nanoaddition into the fiber-grade-matter influences essentially the oxidation processes of the PAN precursor fibers. The increase in the  $\text{Fe}_3\text{O}_4$  content causes a decrease in the initial temperature of these processes, as well as in the temperature of their maximum rate. What is more, the oxidation processes proceed within a significantly higher temperature range in comparison to fibers without any nanoaddition.

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