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Comparative Analysis of the Influence of the Kind and Amount of Two Ferromagnetic Nanoadditives on the Structural Properties of Precursor Polyacrylonitrile Fibres

Abstract
A comparative analysis of the influence of two different ferromagnetic nanoadditives on the rheological properties of polyacrylonitrile spinning solutions in DMF, as well as on the porous structure and tensile strength properties of nanocomposite fibres obtained from these solutions, was carried out. A ferromagnetic commercial product of the company Sigma-Aldrich and a product manufactured at the AGH University of Science and Technology, Krakow, Poland were used in this study. The influence of the amount of both types of nanoadditives inserted into the fibre matrix on their structure and tensile strength properties was determined. The uniformity of distribution of the nanoadditive on the fibre surface was estimated on the basis of SEM + EDS investigations.

Key words: *precursor fibres, polyacrylonitrile, nanoadditive, ferromagnetic, tenacity, porous structure.*

Introduction

The development of modern material engineering is primarily concerned with obtaining new kinds of nanocomposites with specific properties. A great number of world scientific centres have conducted investigations with the aim of obtaining nanocomposite fibres to be used as technical composite components in the manufacturing of materials and structures with significantly better properties compared with those obtained with a traditional fibre content. Many works concerning modifications of fibres with different nanoadditives, including ceramic, metallic, and nanometric carbon structures have been recently published [1-5].

Recently, a ferrous oxide (Fe_3O_4) nanoadditive with magnetic properties has found broad application in many branches of biomedical engineering and biotechnology [6]. It is used as a modificator of biological active mixtures, as a substance to increase image contrast in investigations involving magnetic resonance [8, 9], and as a substance to help diagnose and heal cancerous cells [10, 11], among others. The use of this compound for manufacturing precursor polyacrylonitrile [PAN] fibres will allow to obtain carbon fibres with ferromagnetic properties, and their fibrous form will enable the manufacturing of composite materials characterised by anisotropic properties typical for natural tissues, among others. Such composites, considering their morphological structure and good strength properties, may find broad application in injury and oncology surgery. Irrespective of the above-mentioned applications, ferromagnetic carbon fibres may be used as screens (shields) preventing the generation of electrical charges on special measuring apparatuses. In order to obtain PAN precursor fibres with increased strength parameters, the solidification process should be conducted in mild conditions, which means in baths with increased solvent content and low temperature, as well as with the use of negative values of the as-spun-draw ratio. These conditions assure the proceeding of solidification according to the diffusion mechanism, and fibres obtained at such conditions are characterised by a micro-porous structure and increased tensile strength properties. Transformation of the micro-porous structure into a structure which would be a near macro-porous structure or even a pure macro-porous structure is connected with a slight sharpening of the solidification conditions as a result of increasing the temperature of the coagulation bath. In the case of fibres from a PAN nanocomposite, the effect obtained is also connected with the presence of nanoadditives in the fibre matrix [12]. This occurs as the presence of nanoadditives of different chemical structure in the solidificated spinning solution stream causing an interaction of these nanoadditives with the fibre matrix, which acts to decrease the speed of the diffusion process [13]. In order to obtain increased tensile strength properties of the fibres obtained, an appropriate drawing ratio distribution should be used at the drawing stages. Previously, this phenomenon was also confirmed for PAN fibres with a ferromagnetic nanoadditive [14]. The porous structure, tensile strength, thermal and ferromagnetic properties of such fibres not only depend on the structure created at the solidification stage, and the fibre matrix susceptibility to deformation processes, but also on the amount of the nanoadditive inserted into the spinning solution [15]. The type of nanoadditive may also play a part , as the chemical structure of the ferromagnetic sort, its degree of disintegration, and agglomeration influence the surface interaction between the polymer matrix and nanoadditive inserted.

The aim of this work was a comparative analysis of the influence of the type and amount of ferromagnetic nanoadditive on the porous structure and tensile strength properties of PAN precursor fibres. The analysis was carried out using two different nanoadditives.

The susceptibility of the fibre matrix with inserted nanoadditives to the deformation processes at the second drawing stage was also an evaluation criterion. This was connected with the necessity of obtaining different values of the total drawing on which the strength properties of the fibres obtained subsequently depend. On the contrary, the realisation of the investigation at a constant total drawing ratio (preliminary assumed) could lead to obtaining fibres (with a given amount of nanoadditives inserted) with an orientation lower than that which is possible to obtain at different value of the total drawing, which as a consequence would cause erroneous conclusions, creating properties of fibres which are possible to obtain.

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Materials and testing methods

Characterisation of the polymer and nanoadditives used

A polyacrylonitrile terpolymer of Zoltek Co., Hungary was used for manufacturing the fibres. The polymer was composed of 93-94% of acrylonitrile mer units, 5-6% wt of acrrylate methyl mer units, and 1%wt of alilosulfonian mer units.

The intrinsic viscosity of the terpolymer determined at a temperature of 20 C in DMF with an addition of lithium chloride was equal to 1.54 dl/g .

The polidispersity index M_w/M_n determined by the gel chromatographic method at the Institute of Biopolymers and Chemical Fibres, Lodz was equal to 3.2 .

The Fe_3O_4 nanoadditive was inserted into the spinning solutions during their preparation in the form of a suspension in a solvent solution. In order to disintegrate the nanoadditive agglomerations, before inserting the suspension into the spinning solution, it was processed with the use of an ultrasonic device. A Polsonic-3 ultrasonic washer of 2×160 W, with a frequency of 40 kHz, was used at a temperature of 20 °C for 120 min.

The characteristic of the Fe_3O_4 nanoadditive, manufactured at the Biomaterial Department of the AGH University Krakow, is given in ***Table 1***, and a micro photograph taken by a NANOSEM microscope is presented in ***Figure 1***. In order to compare its properties with the characteristic of the nanoadditive made by the Aldrich Company, also used earlier by us, the parameters of the latter are also given in ***Table 1*** and shown ***Figure 1***.

Rheological properties of the spinning solutions

The rheological properties of the 22% PAN solution in DMF with the Fe_3O_4 nanoadditive were determined with the use of a RV Rheotest reoviscometer at shearing rates of up to 146.8 sek^{-1} at a temperature of 20 °C with the use of an "H" cylinder. The rheological parameters, n and k, were assessed on the basis of flow curves according to the method described in [16].

Forming (spinning and drawing) of the fibres

Solutions of 22% concentration of the PAN terpolymer in DMF were used for spinning the fibres. The ferromagnetic nanoadditive was inserted into the spinning solution at an amount of 5, 10, 15, and 20% in relation to the polymer mass. The use of such large amounts of the nanoadditive (not typical in the case of nanotechnology) was aimed at determining the influence of the nanoadditive amount on the character of spinning solutions, especially the susceptibility to deformation, and on the properties of fibres obtained with enormously high nanoadditive contents in the polymer matrix. It could also appear that obtaining appropriate ferromagnetic properties of the carbon fibres obtained from PAN precursor fibres demands an increase in the nanoadditive inserted into the precursor. The fibres were spun with the use of an extended laboratory-scale spinning machine. A 240-hole spinneret with holes of 0.08 mm diameter was used. The solidification process of the fibres was carried out in a bath containing an aqueous solution of DMF with a concentration within the range of 60-70%. The drawing process was realised in two stages: the first in a plastification bath containing an aqueous solution of DMF with a concentration of 50%, and the second in preheated steam at a temperature of 135 °C. Next, thean on-line rinsing process, during which the fibres were dried at a temperature of 20-40 °C at isometric conditions, was carried out.

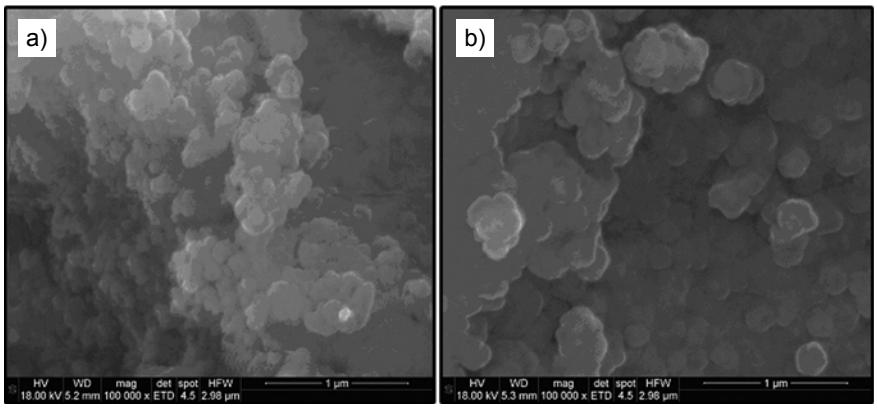

Figure 1. *Macro photos, taken by a NANOSEM electron microscope, of the nanoadditives used: a) made by AGH University, b) made by Sigma – Aldrich.*

Properties of the fibres obtained

Determination of iron in the fibres was performed by the colorimetric method using thiocyanate, with the use of SPECOL 11 apparatus. $Fe[NH_4][SO_4]2 .12H_2O$ salt was used for preparing the standard solution. A working solution was prepared from the solution obtained in order to assess the wave length at which the absorbency value achieves its maximum. The next stage of the analysis was determining the standard curve, measured at an earlier assessed wavelength of $\lambda = 474$ nm. Next, the test samples were prepared with dissolution fibres of an exactly determined mass in concentrated sulphuric acid. Later, after 15 min, the solution prepared was analysed in the presence of the same reference as the standard sample. The iron concentration was calculated on the basis of an equation describing the standard curve. The averages of 3 measurements comprised the results.

The tenacity was assessed for a fibre bundle in accordance with the Polish Standard PN-EN-ISO-268:1997 using an In-

Table 1. *Grain dimensions of the ferromagnetic nanoadditives used.*

Nanoadditive used	Grain dimension, nm
Fe_3O_4 – AGH Kraków	10-20
Fe_3O_4 – Sigma Aldrich	30-50

Table 2. *Values of the rheological parameters n and k of spinning solutions with different amounts of both Fe_3O_4 nanoadditive types and solutions without a nanoadditive.*

Sample symbol	Content of Fe_3O_4, %	Rheological parameter „n"	Rheological parameter „k"
PAN	0	0.97	25,57
AGH 1	5	0.95	38,07
AGH 2	10	0.94	39,72
AGH 3	15	0.92	42,89
AGH 4	20	0.84	67,05
ALDRICH 1	5	0.96	25,11
ALDRICH 2	10	0.98	25,84
ALDRICH 3	15	0.98	27,44
ALDRICH 4	20	0.99	30,49

stron tensile tester. The results presented are the average of 50 measurements.

The porosity of fibres was determined by the mercury porosimetry method using a Carlo-Erba porosimeter linked to a computer system which allows to assess the total volume of pores, the percentage content of pores with diminutions of selected subranges within the range of 5-7,500 nm, as well as the total internal surface of pores.

The distribution of the Fe_3O_4 nanoadditive in fibres was evaluated on the basis of images taken by the JSM 5400 SEN linked to an energy dispersion analyser of characteristic radiation- EDX LINK ISISA of the OXFORD INSTUMENTS COMPANY.

Tests results

Values of the rheological parameters, n and k, of the spinning solutions with different contents of both ferromagnetic nanoadditives, as well as of the spinning solution without any nanoadditive are listed in ***Table 2*** (see page 49). The flow curves of the spinning solutions containing different amounts of the ferromagnetic nanoadditives produced at the AGH University are presented in ***Figure 2***. The changes in the dynamic viscosity as a function of the shearing rate for spinning solutions containing different amounts of the ferromagnetic nanoadditive produced at the AGH University are presented in ***Figure 3***. The tensile properties (tenacity and elongation at break) of fibres with different contents of both ferromagnetic nanoadditives formed at different parameters of the drawing stages are presented in ***Table 3***. ***Table 4*** presents the parameters of the porous structure (total volume of pores , total internal surface of pores, percentage content of small, middle and great pores) of fibres without a nanoadditive and those containing Fe_3O_4. The dependencies of the percentage contents of pores are presented in ***Figures 4*** and ***5*** as a function of their radii of fibres without a nanoadditive and with different amounts of the ferromagnetic nanoadditive. A linear SEM+EDS analysis of fibres containing both types of the ferromagnetic nanoadditive made by Sigma-Aldrich Co and AGH University at an amount of 10% are presented in ***Figure 6*** (see page 52).

Discussion of the results

The structure and properties of nanocomposite fibres not only depend on the parameters of the solidification or drawing processes but also significantly on the presence of different amounts of ferromagnetic nanoadditives in the spinning solutions and in the solidificated polymer stream. The rheological properties of the spinning solutions may also be influenced by the amount of nanoadditive, its type and dispersion. ***Table 1*** and ***Figure 1*** (see page 49) illustrate that the Fe_3O_4 nanoadditive produced at the AGH University differs in the grain dimensions and the

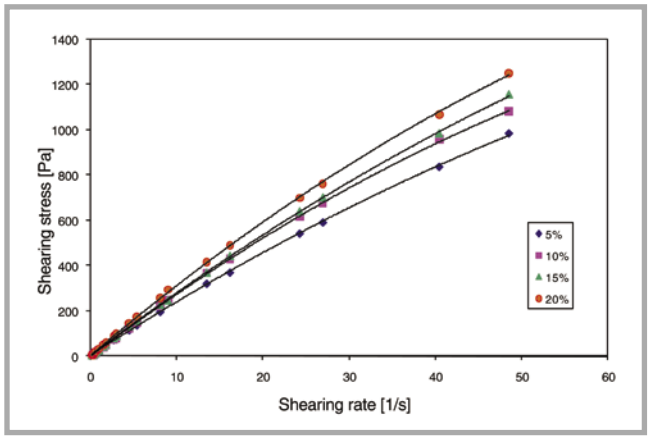

Figure 2. *Flowing curves of spinning solutions containing different amounts of the ferromagnetic nanoadditive synthesised by AGH University.*

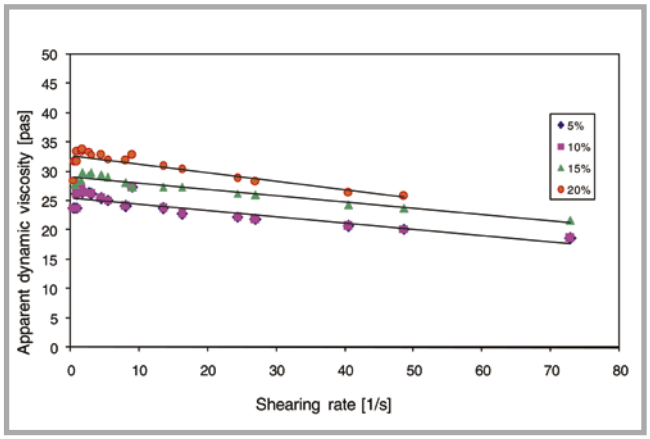

Figure 3. *Apparent dynamic viscosity as a function of the shearing rate of spinning solutions of different amounts of the ferromagnetic nanoadditive synthesised by AGH University .*

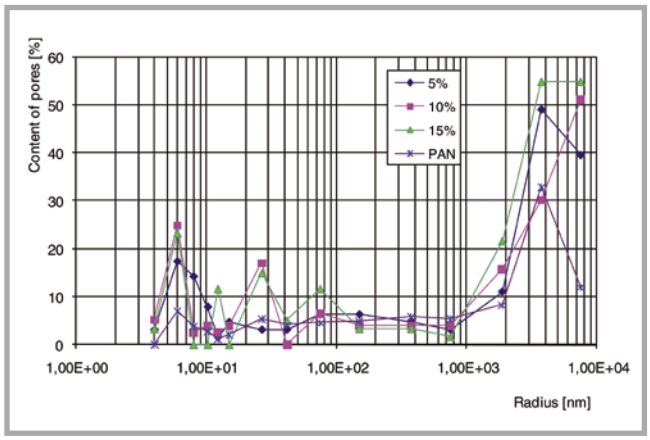

Figure 4. *Dependencies of the content of pores on their radius for fibres without a nanoadditive and with different amounts of the nanoadditive synthesised by AGH University.*

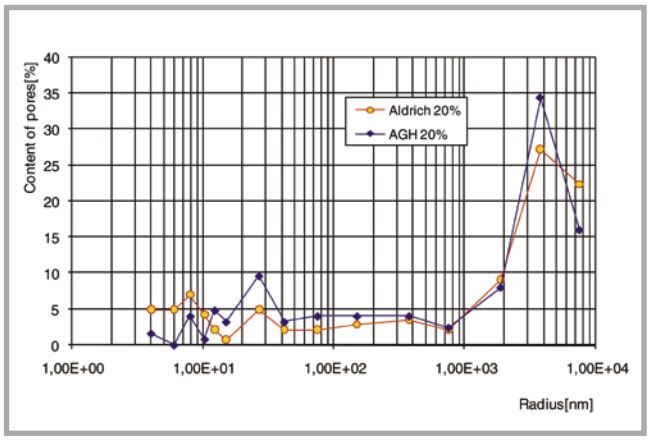

Figure 5. *Dependencies of the content of pores on their radius for fibres with a nonoadditive content of 20% of both types.*

ability to agglomerate in comparison with the nanoadditive of the Aldrich Company used in our previous investigations [15]. The ferromagnetic grains are smaller, whereas the ability to agglomerate can be estimated as greater. This tendency, estimated by microscopic images, was also visible after the ultrasonic disintegration stage of the agglomerations in the solvent. According to our assumptions, the smaller ability of the Aldrich Co. Nanoadditive to agglomerate may be caused by the surface modification applied by the producer, who unfortunately does not give any information on this subject. On the basis of rheological investigations carried out by us, we observed that at similar concentrations of the spinning solutions and similar amounts of the nanoadditives included in them, they differ significantly in their rheological parameters, n and k, depending on the kind of nanoadditive. The solutions, which include the Fe_3O_4 of the Aldrich Co., are very similar to Newtonian liquids (the rheological parameter n increases with anincrease in the nanoadditive amount). This is accompanied by a small increase in the rheological parameter k, but only above concentrations of 15%. Below this nanoadditive amount, the parameter k has values which are lower than those of a solution without any nanoadditive [15.] On the other hand, the solutions which include Fe_3O_4 made at AGH University are typically non-Newtonian, which means that with an increase in the nanoadditive amount, the character of non-Newtonian liquids is stronger. For boundary amounts of the ferromagnetic additives, of about 20%, the parameter n = 0.84 ***(Table 2)***. In comparison with these values, the spinning solution which includes 20% of the Aldrich Co. nanoadditives was characterised by a parameter n of 0.996 and parameter k of 30.49 . This latter parameter, which is for solutions with Fe_3O_4 made at AGH University, is characterised by a tendency to significantly increase with an increase in the nanoadditive amount. This is mirrored by the flow curves presented in ***Figure 2***. They have a shape typical for non-Newtonian liquids thinned by shearing without a flow limit. This means that the shearing stress increases less than proportionally with an increase in the shearing rate, and the curves cross the origin of the coordinate system. The changes in the apparent dynamic viscosity as a function of the shearing rate are characteristic for polymer liquids ***(Figure 3)***. From this figure it is visible that the spinning solution which includes 20% of the nanoadditive has a shape mostly similar to polymer liquids. Considering the well-known interpretation of thinning by the shearing mechanism [17], we can assume that in the case of the AGH University nanoadditive, in a non-moving liquid, the phenomenon of an increase in the effective dimensions of entangled macromolecules immersed in a non-moving continuous phase created by the solvent is clearly apparent. We can assume that this is caused by the presence of greater nanoadditive agglomerations in the entangled macromolecules of great dimensions. The phenomenon of straightening the chains with an increasing shearing rate may be hindered due to substantial friction in such a system. The effect obtained is similar to that in the case of an increase in the polymer molecular mass. The character of changes in the rheological parameters presented above, confirms the presence of mutual interactions between the nanoadditive and polymer macromolecules. The rheological character of these liquids also influences the proceeding of the deformation processes at the drawing stages. At identical conditions of the solidification process and deformation at the first drawing stage of 290.1%, the deformation during drawing in steam was characterised by different tendencies of changes for both ferromagnetics discussed. In the case of the Aldrich Co. nanoadditives, the deformation during drawing in steam systematically decreased with an increase in their content in the spinning solution of up to 20%. On the other hand, in the case of the AGH University nanoadditives, the smallest values of deformation were obtained at 5% and 10% of their content in the spinning solution. Their increase to 15% and 20% causes a

Table 3. *Spinning and drawing conditions and tensile strength properties of fibres without a nanoadditive and with different contents of nanoadditives of both types.*

Sample symbol	Content of Fe_3O_4 in the spinning solution, %	Content Fe_3O_4 in the fibres, %	Drawing Instil, %	Total drawing, %	Total deformation	Tenacity, cN/tex	Elongation of break, %
F-51	0	0	213.8	1092.7	5.9615	46.10	10.95
F-60 AGH	5	2.28	165.6	909.3	5.0449	34.86	10.48
F-61 AGH	10	7.45	160.2	888.9	4.9430	33.75	12.91
F-62 AGH	15	10.75	174.9	944.8	5.2220	32.87	13.62
F-63 AGH	20	12.82	188.8	997.7	5.4864	32.37	14.83
F-41 ALDRICH	5	1.698	210.8	1081.2	5.9039	41.07	11.09
F-45 ALDRICH	10	5.544	187.2	991.6	5.4558	36.58	11.38
F-47 ALDRICH	15	8.739	182.8	974.8	5.3719	34.70	11.91
F-49 ALDRICH	20	12.132	180.3	965.4	5.3251	32.28	12.00

** The fibres were solidified in a bath of 60% DMF content at a temperature of 20 °C at an as-draw-ratio of –50% – at the first drawing stage, the fibres were drawn in a plastification bath of 50% DMF content at a temperature of 70 °C and drawn at a level of 280%.*
*** In order to compare, deformation values at the drawing stage and the properties of fibres containing the Aldrich Co. nanoadditive [15] are presented in the table.*
**** The coefficients of variation of the breaking force (tenacity) were within the range of V_F = 2.7-4.0%, whereas the coefficients of variation of the elongation at break were within the range of V_ε = 4.0-6.4%*

Table 4. *Porous structure of fibres without a nanoadditive and that of those containing Fe_3O_4.*

Sample symbol	Total volume of pores, cm^3/g	Total internal surfers of pores, m^2/g	Percentage content of pores [nm]			
			small 4-15, nm	middle 15-75, nm	large 75-750, nm	very large 750-7500, nm
F-51	0.238	15.397	14.81	16.06	16.05	53.08
F-60 AGH	0.176	16.694	25.22	9.9	8.1	56.76
F-61 AGH	0.176	18.003	22.39	15.67	6.72	55.22
F-62 AGH	0.210	15.982	18.26	15.08	3.97	62.70
F-63 AGH	0.219	10.828	11.20	20.00	10.40	58.40
F-49 ALDRICH	0.154	13.698	23.09	9.80	8.40	58.74

** Sample F-51 are fibres without nanoadditive.*

relative increase in the deformation possible to be obtained (the highest at 20% of Fe_3O_4). Such different proceedings may be connected with a different influence of the amount of both nanoadditives on the rheological parameters described before. It should be emphasised that at 20% of the nanoadditive in the spinning solutions, we obtained similar deformation values at the drawing stage for both kinds of ferromagnetic: 180.3% for the Aldrich Co. nanoadditive and 188.8% for the AGH University nanoadditive, as well as similar values for the tenacity: 32.28 cN/tex and 32.37 cN/tex, respectively ***(Table 3)***.

The content of iron in the fibres obtained was also similar: 12.13% for the Aldrich Co. nanoadditive ***(Table 3)*** [15] and 12.80% for the AGH University nanoadditive. In the case of a lower content of the latter ferromagnetic, the content of iron in the fibre was higher than in the case of the Aldrich Co. Fe_3O_4 ***(Table 3)***. The content of ferromagnetic in the fibre is in close connection with its interaction with the polymer matrix. In the case of the AHG University Fe_3O_4, the interactions were distinctly higher, which was presented in the analysis of rheological properties of the spinning solutions. The content of iron permanently included in the fibres is influenced by the occurrence of a migration phenomenon, especially from the surface layer. This caused that at higher deformations, fibres were obtained with a higher content of the external layer from which the migration of Fe_3O_4 could occur. The agglomeration of this nanoadditive may also influence the effect obtained.

The character of tenacity changes indicates a clear tendency of decreasing with an increase in the amount of nanoadditive inserted into the fibre matrix, from 5% to 20%; however, this decrease is small and is equal to about 2 cN/tex. On the other hand, significantly greater differences in the tenacity, within the range of 11.2-13.7 cN/tex ***(Table 3)***, were noted by us in comparison with fibres formed at identical conditions, but without any nanoadditive. This is mainly connected with the decreased susceptibility to deformation processes due to the presence of non-fibre grade nanoadditives in the fibre matrix. They decrease the possibility of connecting neighbourhood macromolecules by secondary bonds and creates structural defects which, as a consequence, leads to a decrease in the tensile strength properties of the fibres. This is accompanied by an insignificant increase in the total volume of pores within the range of 0.176-0.219 cm^3/g together with an increase in the amount of ferromagnetic inserted into the fibres ***(Table 4)***. However, this level is insignificantly higher in comparison with the range of changes in this parameters in the case of fibres including Aldrich Co. Fe_3O_4 [15], for example, values for 20% of the nanoadditive content were given. At the same time, these values are slightly smaller in comparison with those obtained for fibres without a nanoadditive, for which this macrostructural parameter is equal to 0.238 cm^3/g. This phenomenon was exposed by the influence of the nanoadditive presence in the solidified polymer stream on the inhibition of the mass exchange rate. A similar regularity occurs in the case of the total internal surface of pores, which was observed for fibres with a higher content of the AGH University nanoadditive, within the range of 10.8-18cm^3/g. The porous structure obtained with both types of ferromagnetic can be described as macro-porous, as the summary content of large and very large pores exceeded 60% ***(Table 4)***. The distribution curves of pores as a function of their radii also have a similar shape and are characterised by the presence of two low maxima within the ranges of small and medium pores, and a distinct maximum within the range of very large pores irrespective of the amount of nanoadditives inserted ***(Figure 4)***. An example of a pore distribution curve for fibres which contain 20% of the ferromagnetic content for both types of nanoadditive is presented in ***Figure 5***.

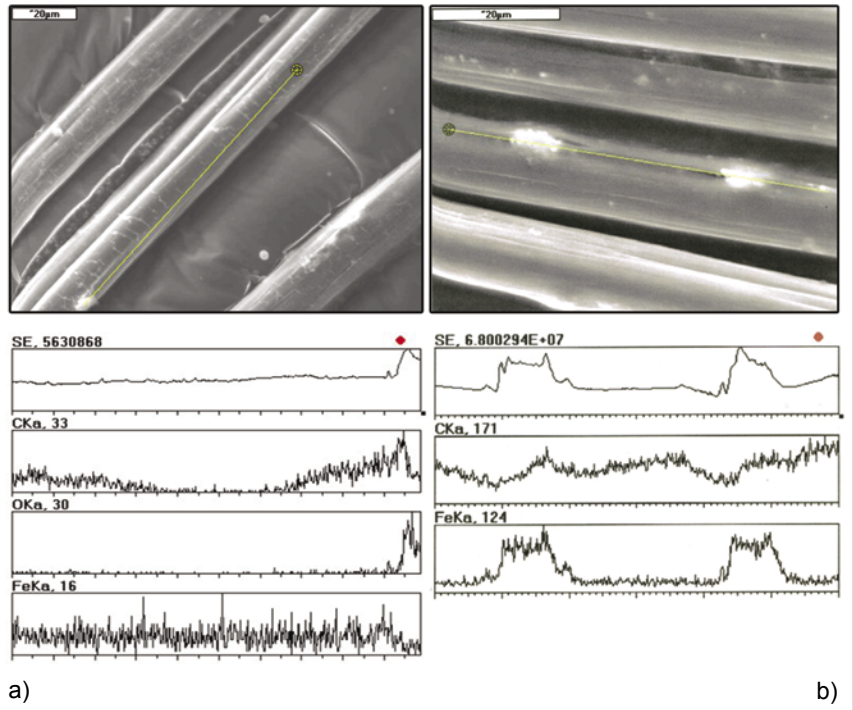

Figure 6. *Linear analysis SEM+EDS for fibres containing 10% of both types of nanoadditive; a) made by SIGMA-ALDRICH Co, b) made by AGH University.*

In the case of both types of nanoadditive, together with the increase in the percentage content of the nanoadditive in the fibres, an increase in the elongation at break was observed. The increase was more distinct in the case of fibres which contained the AGH University nanoadditive ***(Table 3)***. On the other hand, essential differences occur in the distribution of both nanoadditives analysed on the fibre surface. As can be seen from the fibre surface analysis presented in ***Figure 6***, fibres which contain the AGH University ferromagnetic at an amount of 10%, inserted in the spinning solution, are characterised by the presence of great agglomerates along the marked surface segment. This is related to the presence of distinctive peaks originating from iron, which can be seen on the chart obtained from the SEM+EDS linear analysis. In comparison with this, fibres which contain Aldrich Co. nanoadditives are also characterised by nanoadditive agglom-

erations, which however are significantly smaller than those occurring in the previous case. On this basis we can assume that the susceptibility to agglomerate is greater in the case of the AGH University ferromagnetic. This difference in the behaviour of both ferromagnetics is probably connected with the custom that in the majority of cases, trade products with a ferromagnetic nanoadditive are modified with polysaharydes (for example, dextrin) in order to prevent their agglomeration. Unfortunately, the producer of our ferromagnetic did not popularise such information .

An analysis of the ferromagnetic properties of fibres which contain the nanoadditive made at the AGH University will be the subject of a further publication.

Conclusions

1. Inserting ferromagnetic nanoadditives in PAN precursor fibres does not change the rheological character of these liquids. They remain non-Newtonian liquids thinned by the shearing rate, without a flow limit. The values of the rheological parameters n and k depend on the amount of nanoadditives inserted into the spinning solution, and their character which is connected with the interactions between the polymer macromolecules.
2. For both ferromagnetic nanoadditives compared, the different influences of their amount in the spinning solution on the proceeding of deformation processes at the drawing stage were noted,
3. The increase in ferromagnetic nanoadditives within the ranges analysed by us is connected with a decrease in the tenacity of fibres by about 14 cN/tex in comparison to that of fibres without a nanoadditive.
4. On the fibre surface we noted moderately evenly distributed nanoadditives of both kinds and agglomerates of significantly large dimensions.
5. Taking into account the high amounts of the ferromagnetic nanoadditives which should be inserted into the fibres, as well as a fibre tenacity of 32 cN/tex, which is appropriate for the carbonisation of the precursor fibres, we recommend the application of the nanoadditive made at AGH University as more beneficial, inserted into the spinning solution at an amount of 20%.

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References

1. *Sinha Ray, S.:Okamoto, M. Prog Polym Sci 28, 2003, 1539.*
2. *Zhang, Z.; Zhang, L.; Wang, S.; Chen, W.; Lei, Y. Polymer 42, 2001, 8315.*
3. *Liu, Z.T.; Lu, D.S.; Guo, Z.Y. Appl Catal A 118, 1994, 163.*
4. *Hong, Y.; Li, D.; Zheng, J.; Zou, G. Nanotechnology 17, 2006, 1986.*
5. *Deki, S.; Nabika, H.; Akamatsu, K.; Mizuhata, M.; Kajinami, A.; Tomita, S.; Fujii, M.; Hayashi, S. Thin Solid Films 408, 2002, 59.*
6. *Šafařik, I.; Šafaříková, M Monatshefte für Chemie 2002, 133, 737.*
7. *Kriz, C.B.; Radevik, K.; Kriz, D. Anal Chem 68, 1996, 1966.*
8. *Yeh, T.C.; Zhang, W.G.; Ildstad, S.T.; Ho, C. Magnet Reson Med 1995, 33, 200.*
9. *Bulte, J.W.M.; de Cuyper, M.; Despres, D.; Frank, J.A. J Magn Magn Mater 194, 1999, 204.*
10. *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 225, 2001, 113.*
11. *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 Magn Mater 225, 2001, 118.*
12. *Boguń, M.; Mikołajczyk, T. "PAN Nanocomposite Fibres Including a System of Two Nano-additions in their Fibre Matter" J Appl Polym Sci – w druku.*
13. *Boguń, M. "New Generation Precursor PAN Fibres Containing Ceramic Nanoaddition" Doctoral Thesis, Technical University of Lodz, 2007.*
14. *Mikołajczyk, T.; Boguń, M.; Kurzak, A.; Wójcik, M.; Nowicka, K. Fibres Text East Eur 15(3), 2007,19.*
15. *Mikołajczyk, T.; Janowska, G.; Wójcik, M.; Boguń, M.; Kurzak, A. "Influence of the Amount of Ferromagnetic Addition on the Rheological Properties of Spinning Solutions, the Structure, the Strength and Thermal Properties of Polyacrylonitrile Fibres" J Appl Polym Sci – w druku.*
16. *Mikołajczyk, T.; Boguń, M. Fibres & Textiles in Eastern Europe13(1), 2005, 28.*
17. *Ferguson, J.; Kembłowski, Z. ,,Reologia stosowana płynów", Wydawnictwo Marcus sc, Łódź, 1995.*

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