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Influence of Fibre Formation Conditions on the Properties of Nanocomposite PAN Fibres Containing Nanosilver

Abstract

The research involved studying the influence of coagulation bath temperature and the as-spun draw ratio on the porous structure and strength properties of PAN fibres containing a silver nanoadditive. The fibres produced are characterised by a strength reaching 45 cN/tex and an increased porosity of up to 0.6 cm³/g. These properties are advantageous when such fibres are a precursor for producing carbon fibres for medical purposes.

Key words: *precursor fibres, polyacrylonitrile (PAN), nanosilver, nanocomposites.*

Introduction

Modifying the polymer matrix with a nanodimensional substance enabled us to obtain a polymer nanocomposite whose properties substantially exceed those of traditional polymers [1, 2]. Depending on the type of polymer applied, and particularly on the modifier introduced, it is possible to equip the nanocomposite with unparalleled features. Using a polymer nanocomposite allows a significant increase in functionality and a range of fibre applications - from technical to medical [3 - 4].

The application of a polyacrylonitrile nanocomposite as a precursor to carbon fibre production enables carbon fibres to assume unprecedented nanoadditive-specific characteristics. Introducing ceramic nanoadditives into a PAN fibre material results in obtaining carbon fibres for use as medical implants displaying osteoconductive and osteoproductive activity [4]. It is presumed that the introduction of nanosilver into precursor PAN fibres would allow us to obtain carbon fibres with antibacterial properties displayed by the nanoadditive introduced into the polymer matrix, which is proved by its numerous medical applications [5, 6]. Active carbon fibres containing silver obtained from different precursors showed antibacterial properties against *Escherischia coli* bacteria and *Staphylococcus aureus* bacteria, and in the future it is predicted that they will used be used in water purifying filters [7 - 9]. However, carbon fibres obtained in such way can also be applied in medicine as material for filling osseous tissue defects; they not only show antibacterial properties but would significantly reduce the possibility of complications after surgery connected with the risk of bacteria infection. Such an effect was observed in the case of endoprosthesis covered with a layer of silver, in which there were no side effects connected with the presence of silver [6]. The lack of toxic action in silver in relation to mammal cells was also stated in work [10], where it was proved that silver is no more toxic than the stainless steel used in medicine.

Taking into account the prospective application of such carbon fibres, it is assumed that their precursor should be characterised, on the one hand, by high strength properties, necessary in the carbonisation process, and conditioning an appropriate level of carbon fibre strength. On the other hand, the precursor should display a porous structure which, although disadvantageous from the point of view of carbon fibre production, is an advantage if such fibres are used as medical implants, because porous materials encourage the adhesion of cells by living organisms [11].

In order to obtain precursor fibres characterised by both high strength and high porosity, one must reconcile antagonistic tendencies of the process parameter's influence on the structure and properties of fibres formed by wet-spinning using the solution method.

The strength properties of precursor PAN fibres are mainly dependent on the material's susceptibility to distortion at the drawing stage and the potential value of the total draw. The aforementioned factors rely heavily on the fibre structure formed during fibre solidification, which is related to the mechanism behind the process.

The solidification occurs in accordance with a diffusion mechanism if the process is conducted with the use of coagulation baths with a low precipitation strength and temperature.

The dripping mechanism of the solidification process occurs in the case of fi-

bre formation with the use of baths with a high precipitation strength, i.e. with a low or zero solution content, or gentle baths in which solidification conditions have been radically intensified by increasing the temperature [12].

Through appropriate control of solidification process parameters with regard to fires formed in mild coagulation baths, it is possible to pass from a diffusion to a dripping mechanism. Such a phenomenon is observed when using a higher coagulation bath temperature, which is related to the acceleration of the mass transfer processes. This effect may be further intensified by using highly positive as-spun draw ratio values during fibre formation. However, applying a negative as-spun draw ratio value is conducive to the formation of a structure susceptible to distortion in the subsequent drawing stages, which is related to the strength properties of fibres.

Taking into account the above-mentioned facts, it may be ascertained that the final properties of fibres formed by wet-spinning from solution are most significantly influenced by the solidification process conditions. The formation of a freshly-solidified fibre structure characterised by high porosity and high susceptibility to distortion in the drawing process requires the solidification process to be conducted with a positive as-spun draw ratio value and mild baths in which solidification conditions are intensified by increasing th temperature. In the case of PAN fibres containing ceramic nanoadditives [13], it was bound with a passage from diffusion towards the dripping solidification mechanism; thus, the fibres obtained were characterised by a macroporous structure.

The present research aims to obtain fibres containing a silver nanoadditive which would display a structure advantageous with regard to the fibre's final use . The objective of this work was to study the influence of coagulation bath temperature and the as-spun draw ratio value on the structure and properties of nanocomposite polyacrylonitrile fibres containing nanosilver.

Research materials and methods

A statistical ternary copolymer of polyacrylonitrile, produced by Zoltek, Hungary, was used to prepare PAN spinning solutions in dimethyloformamide (DMF).

The polymer has the following composition:
■ 93 - 94% by wt. of acrylonitrile units,
■ 5 - 6% by wt. of methyl acrylate units,
■ about 1% by wt. of sodium allylsulphonate units.

The intrinsic viscosity of the copolymer, assayed at a temperature of 20 °C in DMF, was 1.29 dl/g. The polydispersity was determined by gel chromatography and was equal to $Mw/Mn = 3.1$.

Silver nanoparticles of assortment code No. 576832 were supplied by Sigma-Aldrich. Particles under 100 nm were used in our investigations.

The distribution of silver grain size was assayed with Zetasizer Nano-ZS apparatus from Malvern Inc., which uses the technique of dynamic laser light scattering for this purpose. This measuring method is based on Brownian movement of particles immersed in a liquid, which allows to assess particle sizes characterised by equivalent diameters within the range of 0.1 nm to about 6 μm in aqueous and non-aqueous media.

The quantitative distribution of particles in the nano-additive sample was characterised by a maximum with respect to particles, within the range of 28 nm to 190 nm, whose volume percentage was 99.4%. The maximum of this range falls to a size below 100 nm.

The rheological properties of the spinning solutions were determined with use of a Rheotest RV rotary rheometer with an "H" cylinder. Measurements were carried out at a temperature of 20 °C within a shearing rate range of $0.2 - 1.31 \times 10^3$ s^{-1} and shearing stress of $12 - 3 \times 10^3$ N/m^2. The spinning solution applied was characterised by the following rheological parameters: $n = 0.9715$, $k = 26.199$.

Tenacity was determined for a bundle of fibers in accordance with Standard PN-EN-ISO=268:1997, with the use of an Instron tensile tester.

Fiber porosity was assessed by mercury porosimetry method using a Carlo Erba porosimeter linked to a computer system, allowing the determination of the total volume of pores, the volume content of pores with sizes within the range of 5 nm to 7,500 nm, as well as the total internal surface of pores.

Water vapour sorption was determined at 100% RH in accordance with Polish Standard PN-P-04635:1980.

Water retention was determined using a laboratory centrifuge, which allowed the mechanical removal of water from fibers by centrifugation at an acceleration of 10,000 m/s^2. The retention value was determined by comparing the mass of water remaining in the fibers with a mass of fibers dried at a temperature of 90 °C.

Photos of fiber cross-sections were taken with a JEOL JSM-5200LV scanning electron microscope. Cross-section preparations were examined using the low-pressure technique with a backscattered electron detector (the pressure in the sample chamber was within the range of 6 Pa to 270 Pa). Observation was carried out at an accelerating voltage of 25 kV and magnification of 2000× and 5000×. Images were recorded by a Semafor digital system.

The distribution of the silver nanoadditive on the fibre surface was assessed on the basis of scans made with the use of scanning electron microscopy (SEM JSM 5400) equipped with an EDX LINK IBIS energy dispersion analyser for specific radiation (Oxford Instruments). The EDX (Energy Dispersive X-ray) energy dispersion analyser for specific X-ray radiation enables qualitative analysis of a microarea with the use of energy from specific X-ray radiation emitted by the sample. The results of EDX analyses are presented as follows:
■ EDX spectrum – a graph presenting the relationship between the element peak intensity (number of calculations per second – cps) and the energy of quantums of specific X-ray radiation (keV) of elements present in the microarea studied. The spectra are obtained from a selected point.
■ Element distribution maps with SEI image: The image of element distribution in a given microarea is obtained through scanning the surface of the material with an electron beam and then monitoring, by means of EDX, the emitted energy lines of the specific X-ray radiation of the elements studied.
■ EDX linear analysis consists in recording the intensity variation of the specific X-ray radiation of elements along a selected line of electron beam movement in the microarea studied.
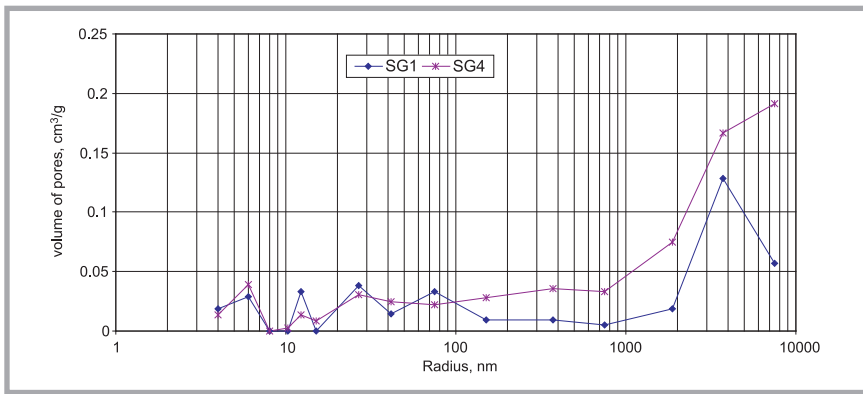
Figure 1. *Relationship between pore volume proportions in the function of their radii for the fibre samples SG1 and SG4.*
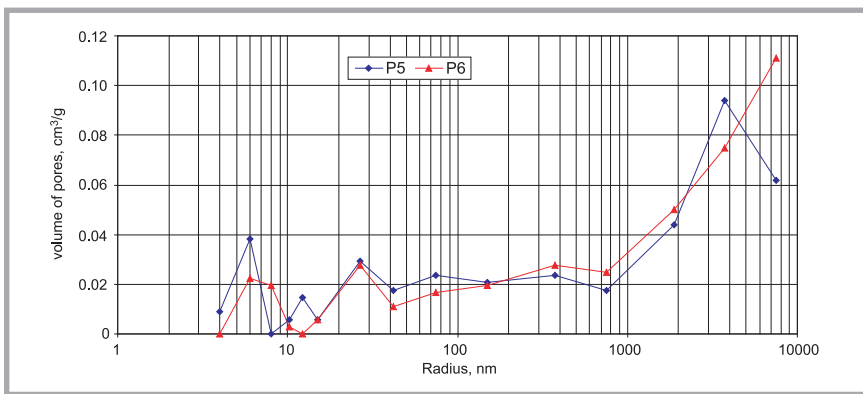

Figure 2. *Relationship between pore volume proportions in the function of their radii for the fibre samples P5 and P6.*

Fibre formation

Fibres were formed by wet-spinning from solution using a commercial-lab spinner. We used a 240-hole spinnered with a hole diameter of 0.08 mm. As spinning solutions we used 22% solutions of polyacrylonitrile in DMF containing 1% of nano-silver in relation to the polymer mass. The nanoadditive was ultrasonically dispersed in DMF with the use of a Sonopuls HD 2200 sounder (Bandelin) over the period of 30 minutes at a temperature of 20 °C during the spinning solution preparation.

The conditions of the solidification process were devised on the basis of our previous work concerning the manufacturing of precursor PAN fibres containing various ceramic nanoadditives [13]. That research aimed at obtaining fibres characterised by an increased porosity of about 0.30 cm^3/g and a strength necessary for conducting the carbonisation process, exceeding 25 cN/tex.

The present work consisted in conducting a two-study series with the purpose of determining the influence of coagulation bath temperature and the as-spun draw ratio value on the structure and properties of fibres obtained with the use of mild coagulation baths containing 60% DMF. In the first series the coagulation bath temperature was the variable, ranging from 15 to 35°C. The as-spun draw ratio value was constant and amounted to +10%, which is a value conducive to porous structure formation. In the second study series, it was the as-spun draw ratio value that was the variable, with a variation ranging from -40 to +30%. The coagulation bath temperature was constant and amounted to 25 °C, which was determined on the basis of the first study series.

The drawing process was conducted in two stages: in a plastification bath (containing a 50% water solution of DMF), and in an atmosphere of overheated steam (at a temperature of 135 °C). The first drawing stage was conducted at a distortion value of about 0.7 of its maximum value, whereas the second stage was realised at the maximum value of distortion. Such a realisation of the distortion process aimed at obtaining as high strength properties as possible. It is a fact that the strength properties of fibres depend not only on the total distortion value but also on the appropriate distribution of drawing at consecutive stages of the process [13]. This regularity has also been confirmed in the case of nanocomposite PAN fibres containing a ferromagnetic nanoadditive [14].

After the forming process, the fibres were rinsed and dried in isometric conditions at a temperature of about 20 °C.

Carbonisation of fibres

In order to check the possibility of producing carbon fibres from the precursor obtained, the carbonisation process was performed on the sample selected.

The fibres were oxidised in a two-stage process at a temperature of 140 °C for 5 hours, and next at a temperature of 200 °C for 6 hours in air. The carbonization process was performed at a temperature of 1000 °C for 5 minutes in an argon atmosphere.

Table 1. *Properties of fibres formed at a constant as-spun draw ratio value of +10%; SG 1 - 5 – PAN fibres containing nanosilver, P 5 - 6 – PAN fibres without nanoadditive.*

Sample symbol	Temperature of coagulation bath, oC	Total draw ratio, %	Tenacity, cN/tex	Elongation at break, %	Moisture absorption at 100% RH, %	Water retention, %	Total volume of pores, cm³/g	Total internal surface, m²/g
SG1	35	745.4	35.66 ± 1.58	11.42 ± 0.70	9.62	18.85	0.395	33.891
SG2	30	844.3	35.80 ± 1.56	11.01 ± 0.83	8.92	15.88	0.488	35.142
SG5	25	817.0	35.21 ± 1.58	11.50 ± 0.84	9.00	13.95	0.484	20.820
SG3	20	856.5	35.43 ± 1.87	9.83 ± 0.79	8.88	16.87	0.716	21.934
SG4	15	765.2	36.67 ± 1.52	11.14 ± 0.70	9.56	10.54	0.686	34.334
P6	35	729.6	40.44 ± 1.14	13.61 ± 0.42	-	-	0.414	21.967
P5	15	824.6	41.00 ± 1.49	11.38 ± 0.38	-	-	0.405	30.960

The carbonisation of the fibres was performed in the Department of Biomaterials of University of Science and Technology in Cracow, Poland.

Discussion of results

On the basis of research on the influence of coagulation bath temperature on the structure and properties of nanocomposite PAN fibres, it may be ascertained that as the coagulation bath temperature varies in the range of 15 - 35 °C, minor changes in the material's susceptibility to distortion in the drawing process can be observed; however, they do not affect the strength values of fibres, which result from the different temperatures of the solidification process, on which the speed of the mass exchange processes and the structure produced at this stage are dependent. Generally, the susceptibility of the material to deformation processes during the drawing stage and the resulting tenacity of the fibres are significantly dependent on the strukture formed at the solidification process. However, in the range of the change in process parameters under investigation, at a positive as-spun draw-out ratio value, it is not reflected in high fibre tenacity values obtained. The strength values of the fibres obtained vary only in the very narrow range of 35.2 - 36.7 cN/tex (**Table 1**), and the elongation at break values fall by between 9.83% and 11.50%. Similar variations in susceptibility to deformation processes are observed in the case of fibres without a nanoadditive; however, in this case, the tenacity values range from 39 to 41 cN/tex. The elongation at break for these fibres amounts to 11.38% to 13.81%. Slightly lower tenacity values were obtained for nanosilver-enriched fibres, probably resulting from the presence of a non-fibrogenous nanoadditive in the material, which might affect the smaller amount of secondary bonds

formed between polymer macromolecules.

In the analysis of the porous structure of nanocomposite fibres and fibres without nanoadditives, it may be noted that, regardless of the process realisation temperature, all fibres are characterised by a macroporous structure with over 50% participation of large and very large pores (**Figures 1** & **2**) [12]. A high share of the latter can also result from the presence of scratches and gaps on the surface of fibres, which is also shown by the characteristics of the lateral cross-section (**Figure 3**), which has often an irregular edge line. This range also partly contains spaces between elementary fibres, which, in the opinion of some authors, is connected with the specification for marking porosity by the mercury porosimetry method [16].

Analysing the values of the total volume of pores of fibres obtained, it can be noticed that with a change in the temperature of solidification, significant variations in this value appear. Therefore, it may be assumed that, in accordance with the main presumption, the application of a positive as-spun draw ratio value contributed to obtaining a macroporous structure, characteristic of the dripping mechanism of solidification.

Another important fact is that in the case of nanocomposite fibres, values of the total pore volume are highest for fibres formed in baths with the lowest temperatures, and lowest for fibres formed in baths with the highest temperature (**Table 1**). This fact stems from the volume proportion of large and very large pores increasing as the coagulation bath temperature falls. The drop in the total pore volume observed, despite the intensification of solidification conditions (resulting from an increase in the coagulation bath temperature), might be due to the change in the thickness, density, and flexibility
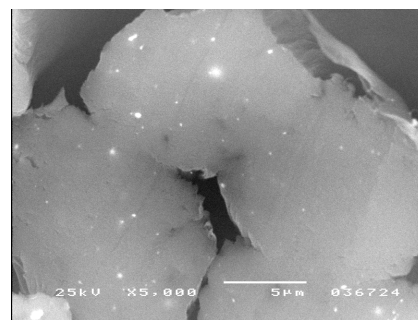

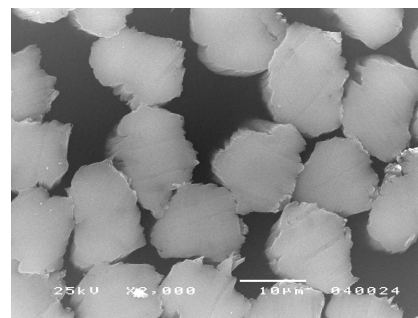***Figure 3.*** *Cross-section of SG4 fibres.*

Figure 4. *Cross-section of P5 fibres.*

of the polymer membrane formed on the freshly-solidified fibre. In the case of fibre formation in a coagulation bath with a higher temperature, as a result of solidification process acceleration, the skin is characterised by a very limited thickness and density but with a high flexibility [12]. In the case of fibres formed in a low-temperature coagulation bath, a more distinct, thick structure of the skin-core type is formed, characterised by high density and low flexibility. During fibre formation, a rigid membrane may become fractured, which explains the macroporous structure and increased porosity of fibres formed in a low-temperature coagulation bath. Such an influence of temperature on the total pore volume was also noted in the case of highly porous fibres formed at a positive as-spun draw ratio value [12]. However, in the case of the solidification mechanism passing

Table 2. *Properties of fibres formed at a constant coagulation bath temperature of 25^0C; SG 5 - 10 – PAN fibres containing nanosilver. P 1, P4 – PAN fibres without nanoadditive.*

| Sample symbol	As-spun draw ratio, %	Total draw ratio, %	Tenacity, cN/tex	Elongation at break, %	Moisture absorption at 100% RH, %	Water retention, %	Total volume of pores, cm³/g	Total internal surface, m²/g
SG10	+30	689.0	33.08 ± 1.31	10.13 ± 0.74	9.36	19.95	0.473	25.999
SG5	+10	817.0	35.21 ± 1.58	11.50 ± 0.84	9.00	13.95	0.484	20.820
SG6	0	880.3	38.83 ± 1.34	12.54 ± 0.56	9.68	9.59	0.541	18.740
SG7	-10	931.3	39.64 ± 1.84	11.95 ± 0.37	7.86	9.21	0.572	18.788
SG8	-20	989.7	42.88 ± 1.55	12.15 ± 0.67	7.97	8.10	0.553	27.030
SG9	-40	1093.1	45.36 ± 1.87	14.07 ± 0.53	8.09	8.12	0.661	42.517
P4	+30	798.4	38.32 ± 1.39	10.83 ± 0.41	-	-	0.508	25.145
P1	-40	999.6	50.17 ± 1.89	14.71 ± 0.51	-	-	0.493	44.970
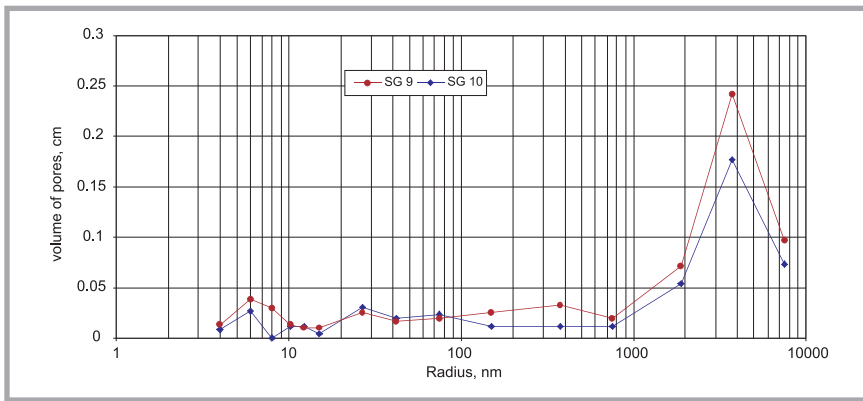
Figure 5. *Relationship between pore volume proportions in the function of their radii for the fibre samples SG9 and SG10.*
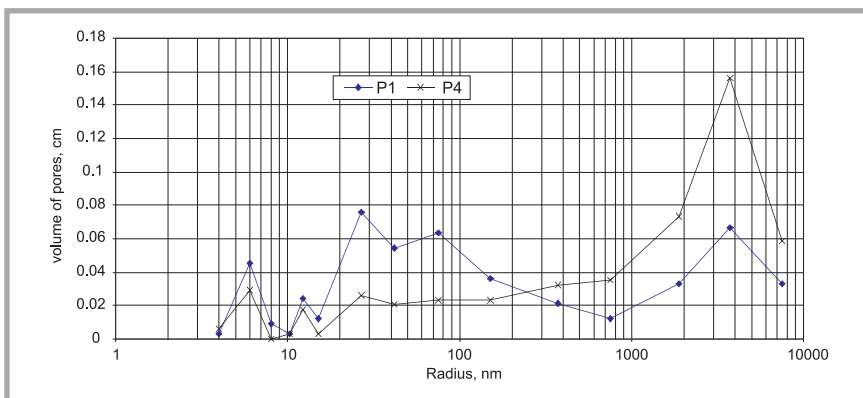

Table 6. *Relationship between pore volume proportions in the function of their radiifor the fibre samples P1 and P4.*

from diffusion to dripping (as a result of intensifying the solidification conditions through increasing the coagulation bath temperature), we observe a reverse tendency in the change in the total pore volume. At the same time, the nature of the porous structure is transformed into that of macroporosity.

A different influence of temperature on the direction of changes in the total pore volume of the nanocomposite fibres obtained, in comparison to traditional PAN fibres, might also stem from the presence of nanosilver in the solidifying spinning solution stream, which substantially affects the speed of the fibre solidification process by slowing it down significantly. Such a proposition is proved by the occasional occurrence of agglutinated fibres (***Figure 3***) observed on cross-sections of nanocomposite fibres formed in a coagulation bath at a temperature of 15 °C, which was not observed in the case of fibres without a nanoadditive formed in analogical conditions (***Figure 4***).

While analysing the sorptive properties of fibres obtained, we might note that humidity sorption values at 100% RH fall within the narrow range of 8.88 - 9.62%. These values are caused by the share of pores capable of moisture absorption according to the principle of the capillary condensation phenomenon. Mainly the first maximum on the graph presented in ***Figure 2*** corresponds to the volume share of such pores. At a similar height of this maximum for fibres obtained in extreme temperatures of coagulation baths, similar values of this coefficient are expected. In the case of a predominant share of such pores in the structure of fibres (typical of a microporous structure), they mainly determine the value of the inner surface, which for the fibres researched was in the range of 20 - 35 m^2/g.

In the case of water retention values of fibres obtained, it is observed that they undergo changes depending on the temperature in which they are solidified. Higher values of this parameter are displayed by fibres formed in a bath with a higher temperature, which corresponds to a higher proportion of medium-sized and large pores from the beginning of this range (***Figure 1***).

The study of the influence of the as-spun draw ratio value on the structure and properties of nanocomposite PAN fibres was realised by conducting a solidification process in a coagulation bath at a temperature of 25 °C. Because of the similar strength values of the fibres, the temperature was selected on the basis of the structure of fibres obtained and the possibility of conducting a stable formation process. In the case of using lower coagulation bath temperatures, excessive mitigation of the solidification conditions disturbed the process by producing occasional fibre agglutination. On the other hand, the use of higher temperatures in the solidification baths was not necessary,because the macroporous structure had already been obtained in all cases.

On the basis of research on the influence of the as-spun draw ratio on the structure and properties of nanocomposite PAN fibres containing a silver nanoadditive, it may be ascertained that variation in the as-spun draw ratio from positive to negative values entails an increase in the material's susceptibility to distortion processes at the drawing stage from 689% to 1093%, respectively (***Table 2***). In the case of fibres without a nanoadditive, these values fall within the narrow range of 798 - 999%. Changes in susceptibility to distortion at the drawing stage, related to the variation in the as-spun draw ratio, are accompanied by an increase in the tenacity of both these types of fibres - from 33.08 to 45.36 cN/tex, and from 38.32 to 50.17 cN/tex, respectively. This phenomenon is in agreement with general rules for fibre formation using the wet-spinning from solution method, and it confirms the fact that the strength properties of fibres are mainly influenced by the value of deformation at the drawing stage, depending on the relevant as-spun draw ratio and fibre structure formed at the solidification stage. elongation at break values for both types of fibres fall within the approximate range of 10 - 14%.

In the analysis of the influence of the as-spun draw ratio on strength properties, it must be remembered that in the case of wet-spinning from solution fibre formation, the external layer's structure and compuctness is primarily determined by relaxation processes occurring after the spinning liquid leaves the spinning nozzle channel and by the external stress related to the take-up strength. If deeply negative as-spun draw ratio values are applied, the process of solidified poly-
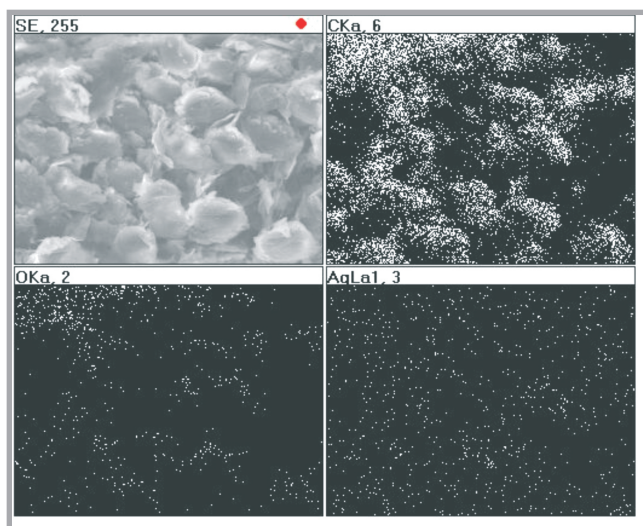
Figure 7. *Carbon, oxygen and silver distribution evaluated by EDS analysis of SG9 precursor fibres cross-sections.*

Figure 8. *Carbon, oxygen and silver distribution evaluated by EDS analysis of SG9 carbon fibre cross-section.*

mer layer accumulation is stretched in time, whose structure is not very compact. Upon leaving the nozzle channel, relaxation processes become very distinct (stream expansion is strong), and the structure thus formed is weakly-oriented, lacking a system of pores and channels. This structure yields easily to deformationn processes at the drawing stage, which is evident in the highest total draw value of SG9 nanocomposite fibres formed at an as-spun draw ratio of -40%. If deeply positive as-spun ratio values are used, the layer of freshly-solidified polymer is compact, and the external stress applied causes microfracturing and the formation of a system of pores and channels which limit further fibre drawing processes (and might lead to elementary fibre breaking).

When analysing the porous structure of nanocomposite fibres obtained, it may be observed that changes in the as-spun draw ratio from positive to negative values are accompanied by an increase in the total pore volume (***Table 2***). This effect may be due to the presence of the silver nanoadditive in the fibre material, which may cause the formation of empty spaces around the nanosilver in the drawing process. This hypothesis may be confirmed by the fact that the greatest total pore volume was displayed by fibres for which the total draw value was lowest (***Table 2***). What is more, these fibres were characterised by the greatest proportion in the series of pores below 100 nm in size (***Figure 5***), which is smaller than the dimensions of the nanoadditive introduced. The presence of pores with such dimensions caused a significant change in the value of the inner surface of the fibres, which was also the highest in this research series, equal to 42.517 m^2/g.
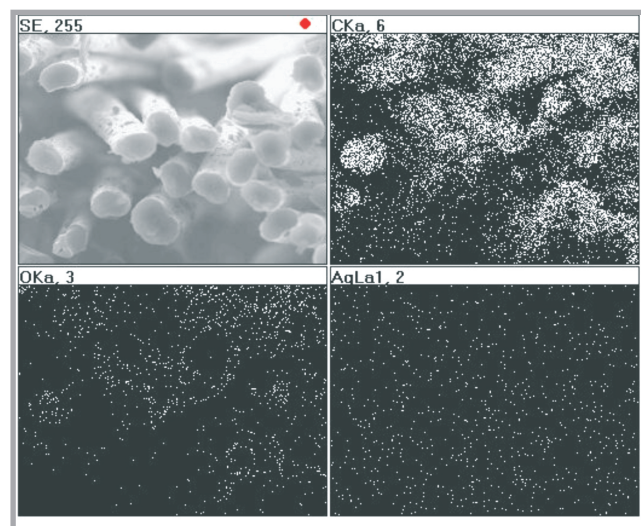
Simultaneously, the porosity of fibres may be influenced by the effect of external skin fracturing caused by high drawing stress.

When comparing the porous structure of fibres obtained without a nanoadditive (***Figure 6***) and the structure of nanocomposite fibres (***Figure 5***) formed at a negative as-spun draw ratio value, it may be stated that fibres without a nanoadditive display a microporous structure. However, the macroporous structure of nanocomposite fibres may be related to the presence of a nanoadditive in their material.

By analysing the sorptive properties of fibres obtained, one might note that humidity sorption values at 100% RH are contained in the narrow range of 7.86 - 9.68%. Water retention values range from 8.12% to 19.95% for fibres formed at extremely negative and extremely positive as-spun draw ratio values , respectively. Variations in the value of this parameter comply with the participation of medium-sized and large pores from the beginning of this section, whose proportion displays a growing tendency parallel to changes in the as-spun draw ratio from negative to positive values. The value of water retention is dependent not only on the character of the porous structure but also on the total volume of pores. It also agrees with the known influence of this parameter on the variation in the water retention value.

On the basis of the quantitative analysis performed with the use of the ICP-MS method, the content of silver in the fibres was determined, as equal to 0.6%,
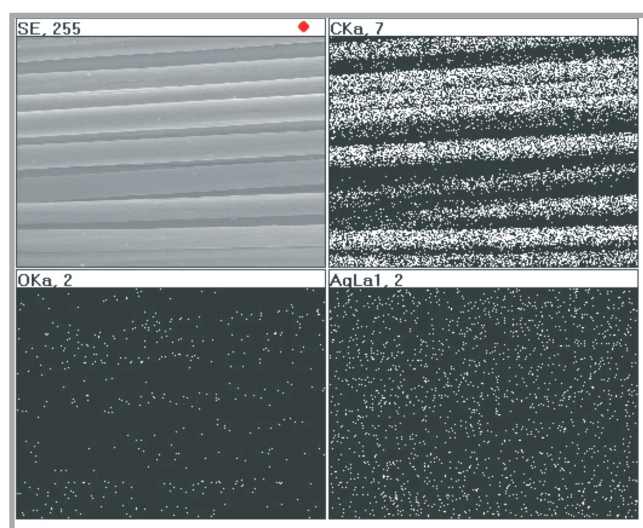

Figure 9. *Carbon, oxygen and silver distribution evaluated by EDS analysis of SG9 carbon fibres longitudinal sections.*
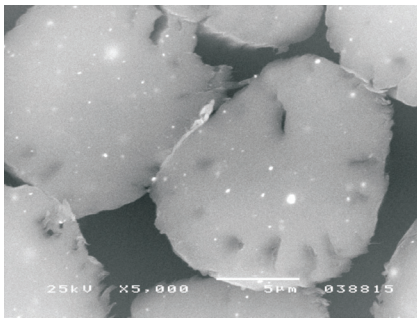
Figure 10. *Cross-section of SG9 precursor fibres.*

Figure 11. *Cross-section of SG9 carbon fibres.*

at the amount of nanoadditive added to the spinning solution, equal to 1% to the polymer mass. A lower content of silver in the fibres may result from migration of nano-silver from the surface of fibres as a consequence of the contact of fibres with the drawing elements of the spinner.

For the SG9 fibre sample, characterised by the highest tenacity value, carbonisation was attempted . With regard to precursor fibres and carbon fibres obtained from them, an assessment was made concerning the distribution of the silver nanoadditive on their surface and in a section. On the basis of the section analysis, it was determined that the nanoadditive is evenly dispersed in the fibre material. This is evident at equally arranged points, illustrating the occurrence of silver in the area observed (*Figure 7*).

When analysing element distribution maps prepared for cross-sections (*Figure 8*) and longitudinal (*Figure 9*) of carbon fibres, we observe an even distribution of points corresponding to nanosilver occurrence in the fibre material.

On the mapping there is a visible presence of a small amount of oxygen most probably coming from air contained in the

sample. Performing the process of carbonization in an atmosphere of inert gas at a temperature of 1000 °C excludes the presence of silver oxide in carbon fibres.

As a significant porosity was obtained in precursor fibres (visible in *Figure 10*), which is preserved in carbon fibres (*Figure 11*), and bearing in mind the fact there is an increase porosity as a result of the carbonisation process, the selection of conditions for producing PAN fibres is performed taking into consideration the tenacity properties of the carbon fibres obtained from them.

■ Conclusions

On the basis of research on the influence of fibre formation conditions on the properties of nanocomposite PAN fibres, the following may be ascertained:
- Variation in the as-spun draw ratio from positive to negative values entails a substantial increase in the tenacity of fibres (by 12.3 cN/tex), accompanied by changes in porosity.
- The macroporous structure of nanocomposite fibres obtained in the range of process parameter variation applied (solidification bath temperature and the as-spun draw ratio value) is characteristic of a solidification mechanism and similar to a dripping one.
- The presence of nanosilver in PAN fibre material resulted in only a minor (about 10%) decrease in tenacity properties in comparison to fibres without a nanoadditive.
- The possibility of obtaining carbon fibres containing silver, implemented in the form of a nano-additive for precursor fibres, was stated.
- The equal distribution of the nanoadditive in precursor fibres is reflected in its equal distribution in carbon fibres.

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