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Influence of Formation Conditions on the Structure and Properties of Nanocomposite PAN Fibres Containing Silver and Hydroxyapatite Nanoadditives

Abstract
An investigation was made into the influence of the temperature of a coagulation bath and value of the as-spun draw ratio on the porous structure and strength properties of PAN fibres containing two nanoadditives. With the presence of hydroxyapatite in nanocomposite fibres, the transformation of paracrystalline regions, existing in fibres without nanoadditives in a crystalline structure, is connected. Carbon fibres were obtained from nanocomposite fibres. The mechanical properties of the carbon fibres obtained are good enough for medical applications. Based on SEM and EDX analyses, it was found that both nanoadditives are evenly distributed on the surface of precursor and carbon fibres.

Key words: *nanocomposite fibres, silver, hydroxyapatite, nanocomposites.*

Introduction

The application of nanotechnology in the production of chemical fibres creates the possibility of obtaining fibres with properties significantly superior to those of classical fibres made of polymers not modified with nanoparticles [1, 2]. When nanocomposite polyacrylonitrile fibres are used to produce carbon fibres, it is possible to improve the properties of those fibres or to give them entirely new characteristics. Carbon fibres obtained from a precursor containing carbon nanotubes have been found to offer higher strength properties than classical carbon fibres [3]. The use of a precursor containing hydroxyapatite as a nanoadditive has made it possible to obtain carbon fibres which support the bone rebuilding processes [2, 4]. It is predicted that the use of a precursor containing a combination of two nanoadditives – hydroxyapatite and silver – will make it possible to obtain carbon fibres which can be used in medicine as a material for filling bone defects. Thanks to the presence of hydroxyapatite in the material, a natural component of bone, it will support the processes of bone rebuilding. The presence of silver in the material of the fibres will cause the implant material to have an anti-bacterial effect as well, which will significantly reduce the probability of post-operative complications relating to bacterial infec-tions, as is evidenced by the numerous applications of silver in medicine [5].

The intended use of this type of carbon fibre means that the precursor from which they are obtained should primarily have high strength so as to make the carbonisa-tion process possible, thus providing sufficient strength to the carbon fibres. Secondly, the precursor should have a porous structure, which, although unfavourable from the point of view of carbon fibre production, is nonetheless desirable if the fibres are to be used as medical implants, as porous materials are better assimilated by living organisms [6]. Obtaining fibres with such a structure and properties requires proper control of the parameters of their production process in order to balance the opposing effects exerted by the process parameters on the structure and properties of fibres spun by the wet process. These issues were considered in [7] for PAN fibres containing silver as a nanoadditive.

The aim of the present work was to investigate the influence of the temperature of the coagulation bath and the value of the as-spun draw ratio on the structure and properties of nanocomposite poly-acrylonitrile fibres containing a combination of the following two nanoadditives: silver and hydroxyapatite.

Materials and methods of investigation

A statistical ternary copolymer of poly-acrylonitrile, produced by Zoltek, a Hungarian company, was used to prepare PAN spinning solutions in dimethylfor-mamide (DMF). The polymer have the following composition:

- 93 - 94% by wt. of acrylonitrile units,
- 5 - 6% by wt. of methyl acrylate units,
- about 1% by wt. of sodium allylsul-phonate units.

The intrinsic viscosity of the copolymer, assayed at a temperature of 20 ºC in DMF, was 1.29 dl/g. Its 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 hydroxyapatite used was obtained from AGH Kraków.

The distribution of nanoparticles of 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 and allows to assess particle sizes characterised by equivalent diameters ranging from 0.6 nm to about 6 μm in aqueous and non-aqueous media.

The rheological properties of spinning solutions were determined using an Anton Paer rotary rheometer. Measurements were carried out in a shearing rate range of $0.2 – 200$ s^{-1} at a temperature of 20 °C. The rheological parameters n and k were determined based on the flow curves.

The tenacity was determined for a bundle of fibres in accordance with Standard

PN-EN-ISO=268:1997, with the use of an Instron tensile tester.

Fibre porosity was assessed by the method of mercury porosimetry 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.

In view of the specific features of the measurement of the total pore volume by the mercury porosimetry method, it was decided to divide the results of the measurement into two values:

- The value of the pore volume corresponding to pores with a radius in the range of 3 - 1000 nm. This range was attributed to the porosity of elementary fibres (the criterion for such a division was an analysis of the cross-sections of fibres obtained without nanoaditives).

- The total pore volume for the test sample (range: 3 - 7500 nm), including the porosity of elementary fibres and that of the fibrous material (e.g. spaces between fibres).

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

The water retention of the fibres obtained was determined using a laboratory centrifuge, which allowed for the mechanical removal of water from fibres 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 fibres with the mass of fibres dried at a temperature of 90 °C.

Photos of fibre cross-sections were taken with a JEOL JSM-5200LV scanning electron microscope. Cross-section preparations were examined by means of the low-pressure technique using a detector of backscattered electrons (the pressure in the sample chamber was within the range of 6 Pa to 270 Pa). An 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.

Assessment of the silver content in fibres was carried out by the method of atom emission spectrometry with inductively coupled plasma (AES-ICP). This method is based on the interpretation of emission spectra emitted by excited atoms and enables the determination of the elemental composition of different samples in a solution state. Calibration of the spectrometer was performed using one-element standards of the ICP class. Prior to analysis, samples were digested in a MLS 1200 system, made by MILESTONE, an Italian company, using micro-wave energy and spectral-pure concentrated nitric acid. The correctness of the results obtained was verified using control samples.

The amount of silver in the fibres was 0.7% compared to the 1% that was introduced into the spinning solution. The amount of hydroxyapatite in the fibres was 2.4% compared to the 3% introduced into the spinning solution.

The decrease in the amount of nanoadditives in the fibres compared to the amount introduced into the spinning solution could be caused by the migration of nanoparticles from the surface layer during particular stages of the fibre formation process.

X-ray measurements were carried out with the use of an URD 6, Seifert diffractometer (Germany) equipped with a copper target X-ray tube (λ = 1.54 Å), operated at U = 40 kV and I = 30 mA. The radiation was monochromised by means of a crystal monochromator. Diffraction curves were recorded using the symmetrical reflection method and the step mode of measurement. The curves were recorded from 2θ = 4° to 60° with a step of 0.1° The fibres investigated were powdered by a microtome to eliminate the fibre texture and then pressed into pills with a diameter of about 2 cm and thickness of 1 mm.

Based on the analysis of the diffraction curves, the degree of crystallinity of the fibres and size of crystallites were determined.

The distribution of the silver nanoadditive on the fibre surface was assessed on the basis of scans performed with the use of a scanning electron microscope (JEOL JSM-5200LV) equipped with an EDX LINK IBIS energy analyser for specific radiation (Oxford Instruments). The EDX (Energy Dispersive X-ray) energy dispersion analyser for specific X-ray radiation enables the qualitative analysis of a microarea with the use of energy from specific X-ray radiation emitted by the sample. The results of EDX analyses can be 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 the specific X-ray radiation (keV) of elements present in the microarea studied. The spectra are obtained from a selected point.

- Element distribution maps with an SEI image: The image of element distribution in a given microarea is obtained by scanning the surface of the material with an electron beam and then monitoring it by means of EDX 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.

The mechanical properties of the precursor fibres selected for the carbonisation process, as well as the carbon fibres obtained, were examined with a universal testing machine (Zwick 1435, Ulm, Germany) equipped with a testXpert version 8.1 program, according to Standard ISO 11566.

■ Fibre formation

Fibres were spun by means of the wet process using a large laboratory spinning machine. A spinneret with 240 orifices, each of 0.08 mm diameter, was used. The spinning solutions used were 22% polyacrylonitrile solutions in DMF containing 1% nanosilver and 3% hydroxyapatite in proportion to the polymer mass. During the preparation of the spinning solution, the nanoadditives were dispersed in the DMF by ultrasound using a Bandelin SONOPULS HD 2200 ultrasound probe for 15 minutes at a temperature of 20 °C.

The conditions of the solidification process were selected on the basis of our earlier work relating to the obtaining of precursor polyacrylonitrile fibres containing various types of ceramic nanoadditives [4] and a silver nanoadditive [7]. Also based on earlier results, the variation in process parameters was limited to a narrow range within which, in the case of fibres containing ceramic nanoaddi-
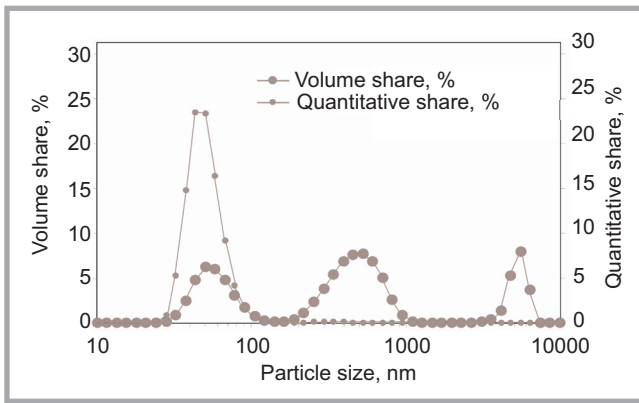
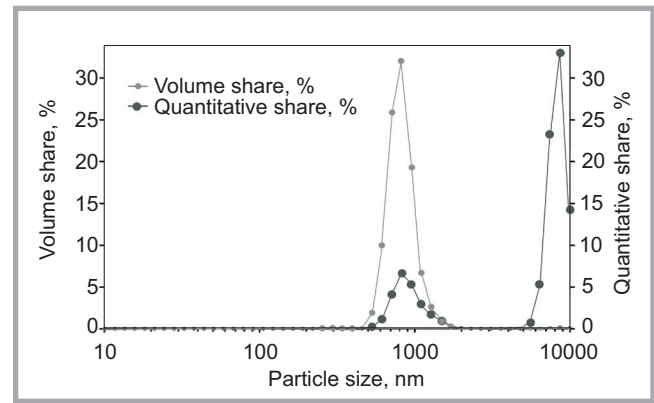*Figure 1. Distribution of silver particle sizes.*

Figure 2. Distribution of hydroxyapatite particle sizes.

tives [4] and a silver nanoadditive [7], it had been observed that the mechanism of the solidification of fibres became more diffusive and less drop-like. The formation conditions were analogous to those described in [7], which investigated the effect of the coagulation bath temperature and value of the as-spun draw ratio on the structure and properties of fibres containing a silver nanoadditive. The use of an analogous range of variation in the parameters of the forming process also enables the determination of the effect of the presence of a system of two nanoadditives – hydroxyapatite and silver - in the material on the structure and properties of the polyacrylonitrile fibres obtained, in order to make a comparison with fibres containing a silver nanoadditive only.

The present work involved two series of experiments aimed at determining the effect of the temperature of the coagulation bath and value of the as-spun draw ratio on the structure and properties of the resulting fibres. Mild coagulation baths were used containing 60% DMF. In the first series the variable process parameter was the temperature of the coagulation bath, within the range of 15 to 35 °C. The value of the as-spun draw ratio was set at +10%, a level favouring the production of a porous structure. In the second series of experiments the variable parameter was the as-spun draw ratio, within the range of –40% to +30%. The temperature of the coagulation bath had a constant value of 25 °C.

The drawing process was carried out in two stages: in a plastification bath (containing 50% aqueous solution of DMF) and in an atmosphere of superheated steam (temperature: 135 °C). The first stage of drawing was carried out with a deformation of approximately 0.7 of

its maximum value, while in the second stage the maximum attainable deformation was used. The process was carried out in this way to obtain the highest possible strength properties – it is known that the strength properties of fibres depend not only on the total deformation but also on the distribution of the draw ratio at particular stages of the process [8]. This rule has also been confirmed for fibres made of the PAN nanocomposite containing a ferromagnetic nanoadditive [9].

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

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 using 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.

▪ Results and disscussion

Characteristication of the nanoadditive and spinning solution

Based on the investigation of the sizes of silver nanoadditive particles (*Figure 1*), it was found that the size distribution of nanoadditive particles is characterised by three maxima associated with the volume fractions of particles of various sizes. The first of them relates to particles in the range 28 – 190 nm, which account for 30.9% of the nanoadditive sample by volume. Subsequent maxima correspond to particles in the ranges 190 – 1100 nm

and 3000 – 6500 nm, which account for 50.4% and 18.6% by volume, respectively. This may be caused by the sporadic occurrence of agglomerates of the nanoadditive.

On the other hand, the number distribution of particles in a sample of the nanoadditive is characterised by a single maximum corresponding to the presence of particles in the size range 28 – 190 nm, which account for a total content of 99.4%.

Analysing the size distribution of particles of hydroxyapatite (*Figure 2*), it is noticed that the distribution curve has two maxima. The first corresponds to the occurrence of particles of a grain size in the range 500 – 2000 nm, which account for approximately 30% by volume. The second maximum probably reflects the presence of agglomerates of hydroxyapatite of more than 5000 nm in size, which probably results from an insufficient degree of powder dispersion in the suspension subjected to measurement. Analysing the number distribution of particles of hydroxyapatite, a single maximum is noted in the range 500 – 2000 nm, which accounts for approximately 98% of the total quantity of particles in the sample.

Based on rheological experiments, it was found that the spinning solution used, with a concentration of 22%, containing 1% silver and 3% hydroxyapatite, had rheological parameters $n = 0.969$ and $k = 28.150$. A polyacrylonitrile solution of the same concentration not containing a nanoadditive had parameters $n = 0.965$ and $k = 25.102$. It can be stated that the solutions analysed are non-Newtonian fluids diluted by shearing without a flow boundary.

Analysis of the influence of the temperature of the coagulation bath on the structure and properties of the fibres

Based on our earlier research on the influence of formation conditions on the structure and properties of polyacrylonitrile fibres containing a silver nanoadditive, it was found [7] that varying the temperature of the coagulation bath in the range 15 – 35 °C caused only slight changes in the deformability of the material at the drawing stage. These do not, however, affect the values obtained for the strength of the fibres. The tenacity of resulting fibres was within the narrow range of 35.2 – 36.7 cN/tex, which was, on average, approximately 5 cN/tex lower than for fibres not containing a nanoadditive formed in analogous conditions. The porous structure of the sample of fibres was of a macroporous nature, the total pore volume of which was greater than 0.4 cm³/g. The high volume fraction of large and very large pores may also result from the presence of scratches and cracks on the surface of the fibres, and may also partly include spaces between elementary fibres.

In the case of fibres containing a combination of two nanoadditives (silver and hydroxyapatite), as in the case of fibres containing only the silver nanoadditive [7], varying the temperature of the solidification bath causes only slight changes in the material's deformability at the drawing stage. These changes have a small effect on the value of fibre tenacity (GH samples in *Table 1*). The maximum difference in tenacity amounts to 6.73 cN/tex, the highest value of which was obtained for fibres formed in a bath at a temperature of 25 °C; these also had the lowest porosity in the series.

A change in the solidification bath temperature results in small changes in the total volume of pores (*Table 1*). Similar changes in the total pore volume occur in the case of fibres that do not contain a nanoadditive (P samples in *Table 1*); the level of this parameter is around 0.3 to 0.2 cm³/g lower.

In the case of fibres containing only a silver nanoadditive the total volume of pores increases with the lowering of the temperature of the coagulation bath [7]. The reason for the varied influence of the coagulation bath temperature on the total pore volume in fibres containing a combination of two nanoadditives, compared with fibres with a silver nanoadditive, can also be found in the presence of the ceramic nanoadditive HAp in the solidifying stream, with its particular effects on the polymer matrix. Its presence is linked to the transformation of the paracrystalline structure of PAN fibre material into a strictly crystalline one [10].

The distribution curves of pores as a function of their radius for both nanocomposite fibres and fibres not containing a nanoadditive are characterised by a similar run (*Figure 3*). The biggest differences in the run of curves occur in the range of pores with dimensions bigger than 100 nm. In the case of nanocomposite fibres, an increase in the share of pores with the biggest dimensions, in comparison with fibres without a nanoadditive, is observed. However, pores over 1000 nm are indicative of the porosity of the fibrous material, for which the spaces between fibres as well as the cracks and gaps on the surface of the fibres are responsible, since at cross-sections of the fibres (*Figure 4*), pores with dimensions over 1000 nm are not observed.

Table 1. Spinning conditions and properties of fibres obtained; GH – samples of PAN fibres containing silver and hydroxyapatite, P – samples of PAN fibres without a nanoadditive.

Sample symbol	Temperature of coagulation bath, °C	Total draw ratio, %	Tenacity, cN/tex	Elongation at break, %	Total volume of pores, cm³/g	Volume of pores in the range 3 - 1000 nm, cm³/g	Internal surface, m²/g	Crystallinity, %	Crystallite size D_{110}, nm	Interplanar distance d_{110}, Å
GH1	35	832.41	36.86 ± 1.15	12.29 ± 0.57	0.723	0.246	17.055	51	4.7	5.3
GH2	30	780.61	33.18 ± 1.18	11.99 ± 0.74	0.667	0.278	48.105	-	-	-
GH5	25	848.35	39.91 ± 2.89	11.88 ± 0.99	0.595	0.266	18.759	53	4.8	5.3
GH3	20	840.31	33.80 ± 1.5	10.23 ± 0.78	0.673	0.296	52.943	-	-	-
GH4	15	785.88	36.98 ± 1.68	11.12 ± 0.72	0.670	0.274	36.348	61	5.4	5.3
P6	35	729.58	40.44 ± 1.14	13.61 ± 0.42	0.413	0.177	21.967	56	4.9	5.3
P3	25	844.31	39.12 ± 2.85	11.23 ± 0.53	0.316	0.172	23.369	53	4.7	5.3
P5	15	824.64	41.00 ± 1.49	11.38 ± 0.38	0.405	0.205	30.960	57	4.8	5.3

Table 2. Spinning conditions and properties of fibres obtained; GH – samples of PAN fibres containing silver and hydroxyapatite, P – samples of PAN fibres without a nanoadditive.

| Sample symbol	As-spun draw ratio, %	Total draw ratio, %	Tenacity, cN/tex	Elongation at break, %	Total volume of pores, cm³/g	Volume of pores in the range 3 - 1000 nm, cm³/g	Internal surface, m²/g	Crystallinity, %	Crystallite size D_{110}, nm	Interplanar distance d_{110}, Å
GH6	30	775.41	38.15 ± 1.25	11.61 ± 0.88	0.334	0.173	22.599	56	4.8	5.3
GH5	10	848.35	39.91 ± 2.89	11.88 ± 0.99	0.595	0.266	18.759	53	4.8	5.3
GH7	0	910.67	38.22 ± 2.32	12.72 ± 0.74	0.750	0.458	70.367	-	-	-
GH8	-10	800.65	42.94 ± 1.75	13.48 ± 0.68	0.476	0.123	14.233	58	5	5.3
GH9	-40	1022.36	51.37 ± 2.13	14.95 ± 0.69	0.290	0.109	21.564	56	5.2	5.3
P4	30	798.45	38.32 ± 2.39	10.83 ± 0.41	0.508	0.220	25.145	48	4.5	5.3
P3	10	844.32	39.12 ± 2.85	11.23 ± 0.53	0.316	0.172	23.369	53	4.7	5.3
P2	-10	908.32	46.31 ± 1.52	12.72 ± 0.39	0.302	0.102	5.914	49	4.5	5.3
P1	-40	999.59	50.17 ± 1.89	14.71 ± 0.51	0.493	0.360	44.970	57	4.8	5.3
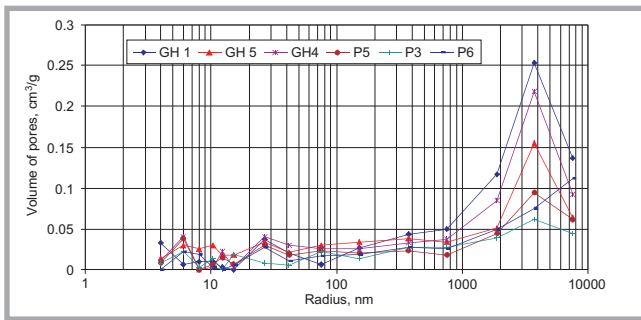
Figure 3. *Relationship between pore volume proportions in the function of their radius.*
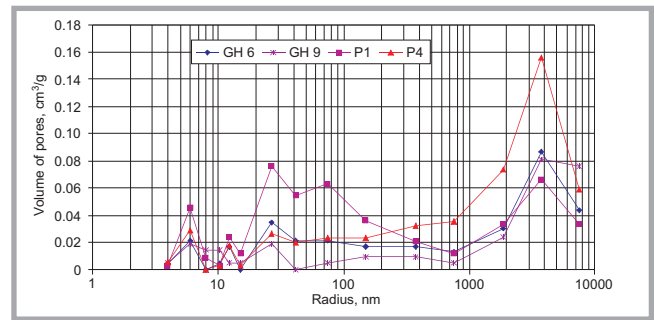

Figure 5. *Relationship between pore volume proportions in the function of their radius.*

Analysing the shape of the cross-sections of fibres formed in baths of different temperatures, we find that in the case of all fibres in the series, the cross-sections are close to being circular, which indicates that during fibre formation, the size of the solvent stream *(js)* took a smaller value than the size of the non-solvent stream *(jn)*. Example cross-sections of fibres are shown in *Figure 4*.

Analysis of the influence of the as-spun draw ratio on the structure and properties of fibres

Analysis of the influence of the as-spun draw ratio on the structure and properties of nanocomposite fibres containing two nanoadditives shows that when the as-spun draw ratio moves from positive to negative values, there is an increase in the deformability of the fibre material at the drawing stage, from 775 to 1022% (*Table 2*). These changes in deformability are in accordance with general rules relating to fibres spun by the wet method. Corresponding values for fibres not containing a nanoadditive lay in the narrow range 798 – 999%, while those for fibres containing only a silver nanoadditive were in the range 698 – 1093% [7]. The changes in deformability at the drawing stage described are accompanied by an increase in the tenacity of the fibres, from

38.15 to 51.37 cN/tex. These values are, on average, approximately 5 cN/tex higher than those for fibres containing only a silver nanoadditive, formed in analogous conditions [7], which are also similar to the strength values for fibres not containing a nanoadditive. This phenomenon is probably due to the change in the crystalline structure of the fibres resulting from the presence of hydroxyapatite in the material. As has already been indicated above, the presence of this nanoadditive in the material of polyacrylonitrile fibres causes a change in the supramolecular structure of the fibres, from para-crystalline to strictly crystalline [10]. A similar effect resulting from the presence of this nanoadditive has been observed in the case of fibres containing a combination of montmorillonite and hydroxyapatite [4]. In addition, the presence of hydroxyapatite in the material of the fibres led to an increase in the strength of fibres of this type compared with fibres containing only montmorillonite as an additive.

Analysing the influence of the as-spun draw ratio on the porous structure of the resulting fibres, it is noticed that the total pore volume reaches the highest value (0.75 cm³/g) for fibres formed at an as-spun draw ratio equal to 0%. Similar changes are observed in the case of the porosity of fibres in the range up to 1000

nm. When fibres are formed with either a positive or negative value of the as-spun draw ratio, the values of the total pore volume and volume of pores with a radius of up to 1000 nm decrease to around 0.3 cm³/g and 0.1 cm³/g, respectively. Moreover, as the as-spun draw ratio changes from a value of 0% in the positive or negative direction, there is a change in the porous structure of the fibres. Fibres formed at a zero as-spun draw ratio are characterised by a large content of pores of a small and medium range (*Figure 5*). In the case of fibres formed at an as-spun draw ratio of +10% or –10%, the maxima previously observed in the size distribution of pores for small and medium pores tend to vanish.

Analysing the influence of the as-spun draw ratio on the porous structure of fibres not containing a nanoadditive, one can observe that the highest values of the total pore volume and volume of pores with a radius up to 1000 nm are observed for fibres formed at the extreme as-spun draw ratios applied. The value of the pore volume for these fibres in the range up to 1000 nm reaches 0.36 cm³/g, compared with a value of 0.102 cm³/g for fibres formed at a pull-out of –10%. The changes in the pore volume values described are accompanied by variations in the nature of the porous structure. When the as-
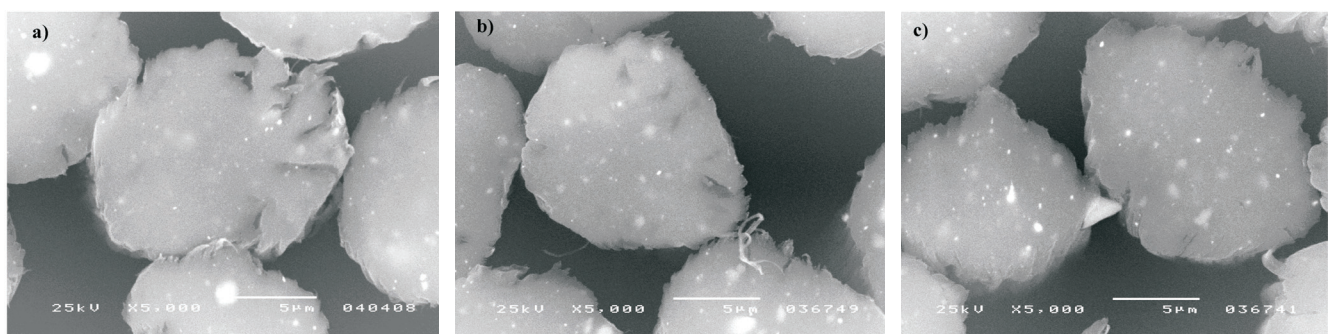

Figure 4. *Cross-sections of nanocomposite fibres spun at various temperatures of the coagulation bath a) 35 °C – GH1, b) 25 °C – GH5, c) 15 °C – GH4.*

spun draw ratio changes from negative to positive values, there is a change in the content of pores of particular sizes (*Figure 5*). In the case of fibres formed at an as-spun draw ratio of –40%, the content of small and medium pores is the highest in the experimental series. When the as-spun draw ratio changes in the positive direction, there is a fall in the contributions from small and medium pores, accompanied by a change in the relative position of the curves in the higher ranges of pore size. The curve corresponding to fibres formed at an as-spun draw ratio of +30% reaches the highest level in this range, which also coincides with the highest total pore volume of these fibres in the series. This type of variation in the porous structure with respect to the as-spun draw ratio is typical in the case of PAN fibres formed under fairly mild conditions of solidification.

Considering the shape of the cross-section of the fibres obtained, it is noted that when the value of the as-spun draw ratio moves from positive to negative values, the shape of their cross-section changes from circular to bean-like (*Figure 6*), which indicates a change in the ratio of the solvent stream *(js)* to that of a non-solvent stream *(jn)*. The bean-like shape of a cross-section is typical when *js/jn* > 1, which means that during a bi-directional mass exchange, the stream *js* is dominant. Meanwhile, a circular cross-section is typical when *js/jn* ≤ 1, where the non-solvent stream is larger than the solvent one.

For fibre sample GH 9, characterised by the highest tenacity value, carbonisation was attempted. The carbon fibres obtained were characterised by a tensile strength of 469 MPa in comparison to 419 MPa for precursor fibres. The value of the Young Modulus of carbon fibres is 89 GPa in comparison to 8.2 GPa for precursor fibres. The quite low values of tensile strength and Young modulus result from the fact that the process of carbonisation was conducted at a temperature of 1000 °C. Such properties of carbon fibres are good enough for medical applications.

Influence of formation conditions on the supramolecular structure of the fibres

The diffraction curves of the fibres investigated were analysed by means of the computer program WAXSFIT [11]. In the first stage, a linear background
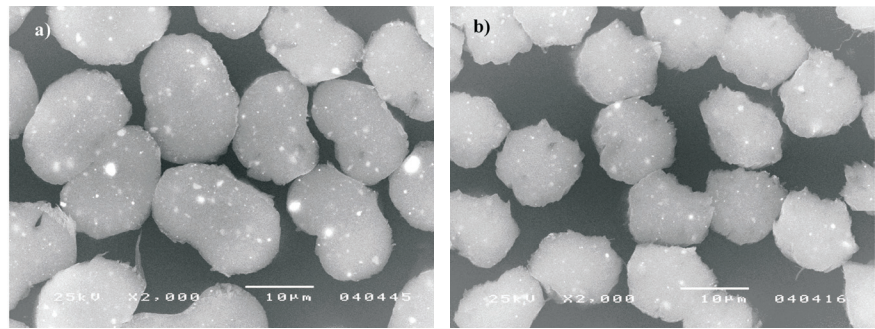

Figure 6. Cross-sections of nanocomposite fibres spun at various values of the as-spun draw ratio: a) -40% – GH9, b) +30% – GH6.

was determined based on the intensity level at small and large angles and subtracted from the diffraction curve. Then the curves of all the samples were normalised to the same value of integral intensity scattered by the sample over the whole range of the scattering angle recorded in the experiment. Next the diffraction curves were resolved into crystalline peaks and amorphous components. For this aim, a theoretical curve was constructed composed of functions related to individual crystalline peaks and amorphous halos. The theoretical curve was fitted to the experimental one using a multicriterial optimisation procedure and hybrid system which combines a genetic algorithm with Powell's classical optimisation method [12]. Both the crystalline peaks and amorphous halos were represented by a linear combination of Gauss and Lorentz profiles. The amorphous component was approximated using two broad maxima located at $2\theta \approx 24°$ and $2\theta \approx 41°$.

The calculations were performed assuming the unit cell dimensions of PAN given by Stefani [13]. According to Stefani, the unit cell of PAN is orthorhombic with dimensions of a =10.2 Å, b = 6.1 Å and c = 5.1 Å. The degree of crystallinity was calculated as the ratio of the total integral intensity comprised in the crystalline peaks to the total integral intensity scattered by the sample over the whole range of the measurement, after the background subtraction.

From the unit cell dimensions of PAN, the interplanar distances d_{hkl} for different families of lattice planes were calculated. Next, using Bragg's law, the 2θ angular positions of crystalline reflections related to the lattice planes were calculated. In this way, the Miller's indices of the crystalline peaks observed in the WAXS patterns were established.

The sizes of crystallites were determined from the width at the half height of the strongest peak (110) in the diffraction curves of the fibres using Scherrer's formula:

$$D_{110} = \frac{\lambda}{w \cdot \cos\theta} \qquad (1)$$

where w – width at the half height of a peak related to (110) lattice planes, λ - the wavelength of X-rays, 2θ - scattering angle.

Examples of the diffraction curves of PAN fibres resolved into crystalline peaks and amorphous components are shown in *Figures 7* and *8. Figure 7* corresponds to the fibre without nanoadditives (sample P1), while *Figure 8* corresponds to the fibre containing silver and Hap (sample GH1).

In the second figure one can see the (301) peak localised at 2θ ≈ 31.9°, which is absent in the diffraction curve of the fibre formed of pure PAN. This effect has already been described in our earlier studies [10] on the influence of nano-hydroxyapatite on the structure of PAN fibres. It was shown that this peak indicates the transformation of paracrystalline regions in PAN into better ordered, typically crystalline regions. The presence of HAp causes the macromolecular chains of PAN to be ordered not only in the direction perpendicular to their axes but also in the direction parallel to the axes. For this reason, the WAXS patterns of fibres containing Hap show diffraction peaks with the third Miller index [l] equal to non-zero. It was suggested [10] that the ordering occurs because of the epitaxial growth of PAN crystallites on the HAp grains.

The results of X-ray diffraction investigations and calculations are given in *Tables 1* and *2*. As can be seen, it is dif-
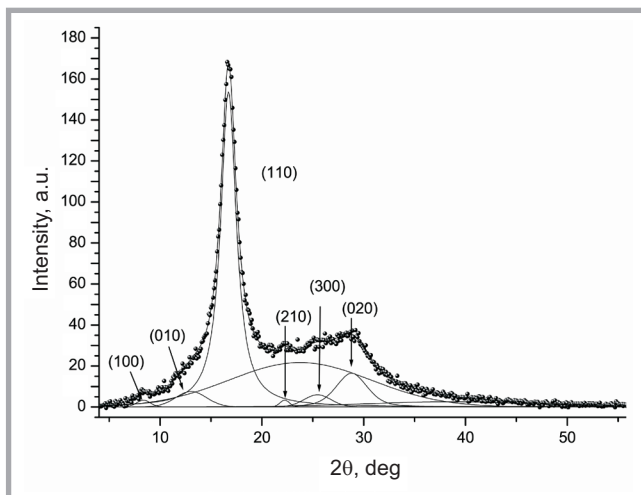
Figure 7. *WAXS curve of a PAN fibre without nanoadtitives - sample P1, resolved into crystalline peaks and amorphous components.*
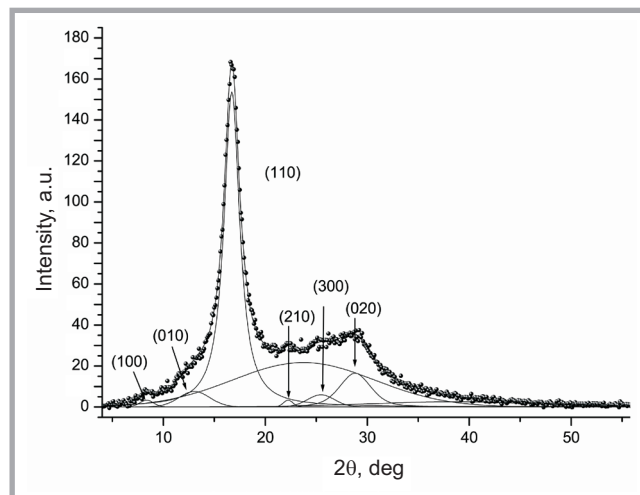

Figure 8. *WAXS curve of a PAN fibre containing two nanoadditives - sample GH1, resolved into crystalline peaks and amorphous components.*

ficult to find a clear relationship between the crystallinity values of fibres containing nanoadditives and the crystallinity of fibres obtained from pure PAN. However, concerning the sizes of crystallites, one can state that generally the sizes are slightly larger in the fibres with nanoadtitives. No changes in the average interplanar distances d_{100} were noticed, which indicates that the presence of the nanoadditives do not influence the density and perfection of the crystalline phase.

The results obtained can be explained by the fact that each of the two nanoadditives influence the crystalline structure of PAN fibres differently. Our earlier investigations of PAN fibres containing only Hap [4] showed that this nanoadditive results in a slight increase in PAN crystallinity as well as in the size and perfection of crystallites. On the other hand, in the case of PAN fibres containing only nano-silver [14], we observed a decrease in the crystallinity but no changes in the size of crystallites.
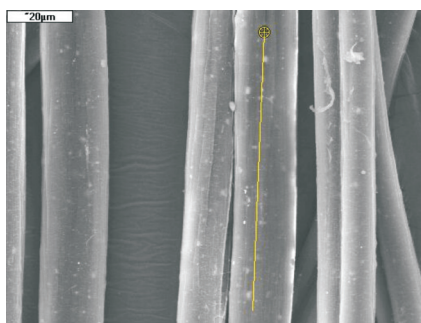

Figure 9. *Longitudinal view of SG 9 fibres (see also **Figure 10**).*

Analysing the influence of the temperature of the coagulation bath on the crystalline structure of the fibres, one can state that in the case of fibres containing the nanoadditives, both the crystallinity and the size of crystallites clearly decrease with an increasing bath temperature. Such behaviour may be caused by the enhanced intensity of the mass exchange processes between the fibre volume and the bath at higher temperatures. In the case of fibres without nanoadditives, changes in the structural parameters are small and do not exceed the limits of experimental error. Apparently, in these fibres the intensity of the mass exchange processes is not so high and does not influence considerably the crystallisation of the polymer.

Considering the influence of the as-spun draw ratio on the crystalline structure of the fibres investigated, one can notice that for both fibres containing and not containing the nanoadditives, a slight increase in the size of crystallites can be observed when the as-spun draw ratio changes from positive to negative values, which is probably caused by the fact that such changes in the as-spun ratio are accompanied by an increase in the total draw ratio of the fibres (see ***Table 2***). Consequently, the orientation of the polymer chains and their ability to crystallise increase. However, the total crystallinity does not change systematically because during drawing, the smaller and imperfect crystallites are destroyed, and only bigger crystallites can grow due to such a mechanism.

SEM analysis of nanocomposite fibres

For fibre sample GH 9, characterised by the highest tenacity value, carbonisation was attempted. With regard to the 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.

Figure 9 is an SEM image showing a lengthwise view of the fibres analysed. On the basis of the linear EDX analysis of the fibre image shown in ***Figure 9***, one can state that the nanoadditives are distributed on the surface of the fibres evenly enough, as indicated by the intensity of the characteristic x-ray radiation of the elements registered along a selected line of the travel of the electron beam in the microregion analysed (***Figure 10***). However,
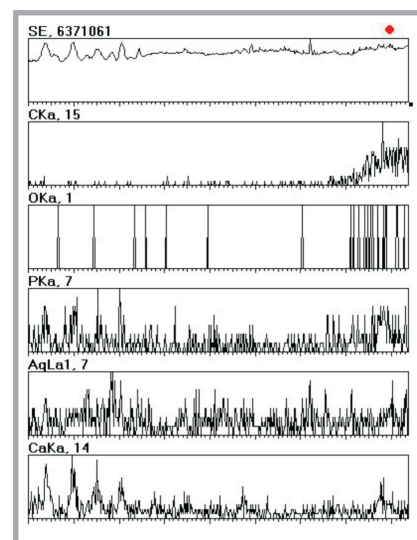

Figure 10. *EDX linear analysis of GH 9 fibres.*
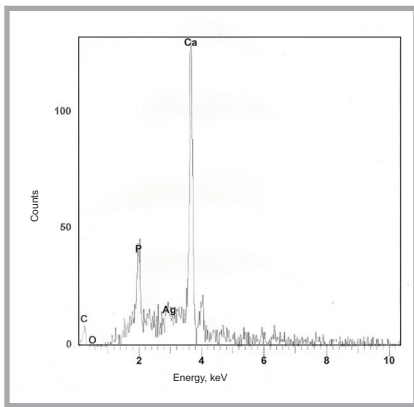
Figure 11. *EDX point analysis of GH 9 fibres.*
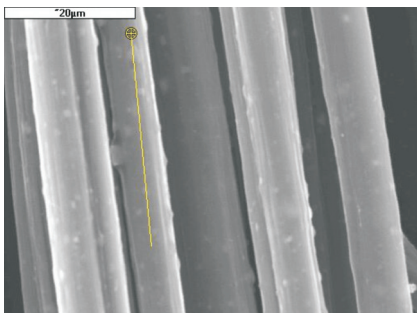

Figure 12. *Longitudinal view of GH 9 carbon fibres (see also Figure 14).*

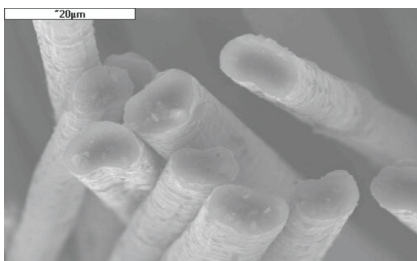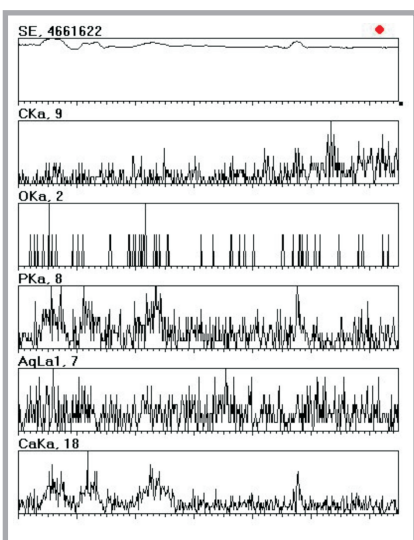**Figure 13.** *Cross-section of GH 9 carbon fibres.*

Figure 14. *EDX linear analysis of GH 9 carbon fibres.*

there are bright points visible on the surface (***Figure 9***) and on the cross-section of fibres (***Figure 6***). EDX point analysis of one of these points showed quite a high concentration of calcium and phosphorus (***Figure 11***), which are elements forming hydroxyapatite, showing that hydroxyapatite agglomerates are present.

The EDX analysis of carbon fibres showed that the distribution of characteristic elements on the surface and in the cross-section of the fibres is even enough. Similar to the precursor fibres, there are some agglomerates of hydroxyapatite. ***Figure 12*** is an SEM image showing a lengthwise view of the carbon fibres analysed. ***Figure 13*** is an SEM image showing a cross-section of carbon fibres. In ***Figure 14***, an EDX linear analysis of those fibres is shown.

■ **Conclusions**

1. Based on the investigation of the effect of formation conditions on the properties of nanocomposite PAN fibres containing a combination of two nanoadditives, the following conclusions can be drawn:
   - Variation of the coagulation bath temperature over the range 15 – 35 °C leads to a change in the nature of the resulting structure produced at the solidification stage and in its deformability at the drawing stage. With an increasing coagulation bath temperature, the decrease in crystallinity and the size of crystallites are connected. Carrying out the process in mild baths at a temperature of 25 °C makes it possible to obtain high deformation at the drawing stage, resulting in the production of fibres with a tenacity approaching 40 cN/tex.
   - When the as-spun draw ratio changes from positive to negative values, there is a significant (13.22 cN/tex) increase in the tenacity of the fibres, accompanied by changes in their porosity and an increase the crystallite size.
2. The presence of a combination of two nanoadditives in the material of PAN fibres caused an increase in the strength of the fibres as compared to those containing only the silver nanoadditive. The strength of fibres containing a combination of two nanoadditives was similar to that of fibres without a nanoadditive.

3. Based on SEM and EDX analyses, it was found that both nanoadditives are evenly distributed on the surface of the precursor and carbon fibres obtained.

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