PAN-Based Fibers Modified with Two-Component Ceramic Nanoparticles

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ABSTRACT: The authors determined conditions for manufacturing PAN precursor fibers containing a system of two nanoadditives, montmorillonite (MMT), and hydroxyapatite (HAp) in their structure. The PAN precursor fibers thus obtained are characterized by a tenacity of more than 30 cN/tex and a total volume of pores at the level of 0.29 cm^3/g. Furthermore, it was found that the use of nanoadditives entails the remodeling of the paracrystalline structure of PAN fibers into a strictly crystalline one. This is accompanied by a decrease in spacing between MMT layers combined with their partial exfoliation. The fibers thus obtained, after being carbonized, will be used for medical applications. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2343–2350, 2009

INTRODUCTION

The use of various nanoadditives in the process of chemical fiber production is an innovative method of modifying their properties. It is also possible to impart to them new characteristics that do not exist in regular fibers. Polymer nanocomposites modified with metal particles reveal conductive, semiconductive, and antielectrostatic qualities. The addition of ferromagnetics, such as iron oxides, results in imparting magnetic properties, and the use of TiO_2 changes optic properties. Ceramic nanoadditives (SiO_2 and MMT) are used mostly to enhance their mechanical and thermal characteristics, as well as to reduce nanocomposite flammability.[1] Similar properties are obtained if nanoadditives are added to fiber matrix. However, in the case of fibers, tensile strength depends mostly on the deformability of fiber matrix at the stage of drawing. In the case of fibers formed from solution by wet spinning, the presence of nonfibrogenic nanoadditives such as MMT results in a decreased deformability at the stage of drawing. It is also more difficult to align structural elements with the fiber axis. The lowering of tensile strength depends on the amount of MMT used and the type of its modifier. The authors observed this for fibers from various kinds of fibrogenic matrix.[2,3]

Adding two nanoadditives, montmorillonite (MMT) and hydroxyapatite (HAp), to PAN precursor fibers makes it possible to obtain carbon fibers characterized by new, previously unknown features. Biocomposites obtained from carbon fibers, which contain biologically active elements in their structure, such as silicon, phosphorus, or calcium, may be an alternative for other biomaterials used in orthopedics and traumatology. The use of MMT in composites is justified by the special role played by their components, such as silicon and magnesium, in the formation of bone structures, their calcification, and regeneration after fractures.[4] On the other hand, the use of HAp is advantageous as its structure is very similar to the structure of the inorganic parts of bone tissue.[5–10] Consequently, its presence stimulates rapid bone reconstruction, good joining with the stem bone (the matrix), and contributes to the improvement of interlayer adhesion.[11]

Therefore, implants made of carbon fibers obtained from precursors containing a combination of both of the aforementioned nanoadditives will show osteoconductive and osteoproductive activity.

It is also well known that carbon fibers designed for medical applications should be characterized by suitable tensile strength and, at the same time, by increased porosity, irrespective of their basic biological properties. As our previous investigations have revealed, carbon fiber porosity as well as its tensile strength depend directly on the structure of precursor fibers formed during their spinning and

drawing.[12,13] In turn, this requires the choice of such formation conditions for PAN nanocomposite precursor fibers, which would guarantee increased porosity and tensile strength suitable for carrying out the carbonization process, which means that it should be higher than the assumed value of 25 cN/tex. The authors manufactured PAN fibers containing MMT and HAp nanoadditives[14] which met this condition.

The determination of suitable manufacturing conditions was connected with the use of ultrasound processing to break nanoadditive agglomerates, as well as with working out a compromise between the conditions used for obtaining porous fibers and those for high tensile strength.[14] It was necessary because manufacturing fibers with increased tensile strength properties is connected with conducting the solidification process according to the diffusion mechanism, whereas spinning fibers with increased porosity requires the change of solidification mode into the direction of the drop mechanism.

With this in mind, the authors carried out tests aiming to determine the influence of the basic process parameters on the submolecular and porous structures, as well as to obtain appropriate properties of PAN precursor fibers containing a system of the two nanoadditives (MMT and HAp) in their fiber matrix. This required determining such manufacturing conditions that would make it possible to produce fibers fulfilling the aforementioned criteria. An additional objective was to evaluate the distribution of nanoadditives on the fiber surface.

MATERIALS AND TEST METHODS

Polymer and nanoadditive characteristics

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

HAp, delivered by the AGH University of Science and Technology, Cracow, Poland, was used in the form of particles with dimensions within the range of 10–100 nm (determined on the basis of SEM images).

Nanomer PGW MMT, a commercial product of Nanocor (USA), was used for the investigation. Their plate dimensions, determined on the basis of photograms obtained with the use of SEM, have been in the range of 800 nm × 550 nm. The MMT used was characterized by a layered structure with interlayer distances of about 2.3 nm, which was determined on the basis of the position of the first peak in X-ray diffraction patterns of the WAXS type.

Fiber formation (spinning and drawing)

Spinning solutions containing 22% of PAN in DMF and 3% (calculated in relation to the polymer) of each nanoadditive were used for producing fibers.

The nanoadditives (after their dispersion by ultrasounds) in the form of a suspension in a solvent were introduced into the spinning solution over the preparation period. The spinning solution used for spinning had the character of a non-Newtonian fluid thinned by shearing, without a flow limit. The rheological parameters were determined to be $n = 0.978$ and $k = 26.94$.

Fibers were spun from a solution by the wet method with the use of a large-scale laboratory spinning machine, which makes it possible to stabilize technological parameters at desired levels and monitor them. A 240-hole spinneret with hole diameters of 0.08 mm was used. The process of fiber solidification was carried out in a bath containing an aqueous DMF solution with a concentration of 60%. The drawing process was conducted as a two-stage process, the first stage in a plastification bath containing an aqueous DNF solution at a concentration of 50%, and the second one in superheated steam at a temperature of 135°C. After rinsing the fibers on line, they were dried under isometric conditions at a temperature of 20–40°C.

Test methods

Tenacity was assessed for fiber bundles in accordance with the Polish Standard PN-EN-ISO-268:1997 with the use of an Instron tensile tester.

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

The distribution of MMT and HAp nanoadditives in fibers was evaluated on the basis of images taken with a JSM 5400 scanning electron microscope with an EDX LINK ISIS dispersion energy analyzer of the characteristic radiation, produced by Oxford Instruments.

The degree of crystallinity and the size of crystallites were determined by means of wide-angle X-ray diffraction (WAXS) method. Diffraction patterns were recorded in a symmetrical reflection mode using a URD-6 Seifert diffractometer and a copper
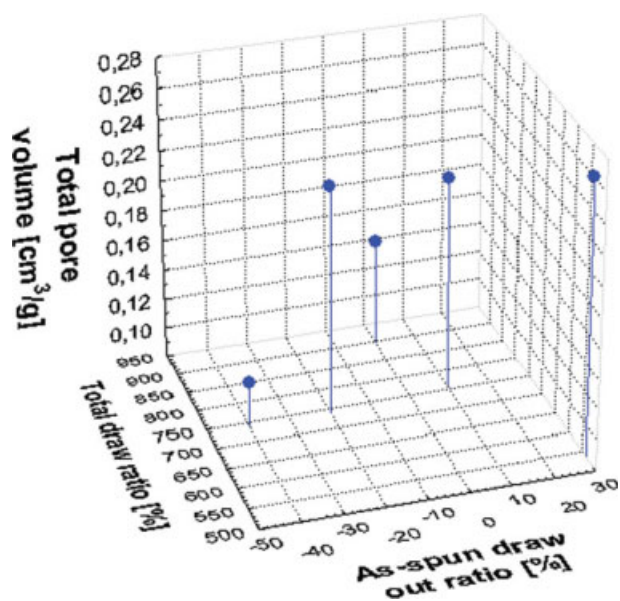
Figure 1 Dependence of the total volume of pores on the as-spun draw ratio and the total drawing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

target X-ray tube ($\lambda = 1.54$ Å) operated at 40 kV and 30 mA. Cu Kα radiation was monochromized with a Ni filter. WAXS curves were recorded in the range from 6.5 to 60°, with an increment of 0.1°. The investigated fibers were powdered and pressed into a sample holder. One-millimeter-thick samples with a radius of 2 cm were prepared. The analysis of the WAXS diffraction curves and the calculation of crystallinity degree were carried out by means of the computer program OpiFit,[15,16] using a procedure described in Ref. 17.

RESULTS AND DISCUSSION

The authors were determined to obtain fibers that would be both characterized by increased porosity and a suitably high value of tenacity, so to reconcile

two opposite fundamental rules related to producing either highly porous or very strong fibers, the solidification process was carried out under mild conditions, in a coagulation bath with a solvent content of 60% and at a low temperature of 15°C. To obtain an increased total volume of pores, the range of changes of the draw-out ratio, which for high-strength fibers normally has only minus values, was increased by positive values, which are characteristic for obtaining fibers with increased porosity. For the sake of comparison, fiber samples were also spun in optimal conditions determined on the basis of tests on fibers containing particular nanoadditives.[14]

On the basis of an analysis of the porous structure, we determined that introducing a system of two nanoadditives into the spinning solution and conducting the spinning process at negative values of the as-spun draw ratio made it possible to obtain fibers with a total volume of pores within the range of 0.11–0.3 cm^3/g. However, carrying out the spinning process at a positive value of the as-spun draw ratio entailed a small increase in the total volume of pores, to the level of 0.26 cm^3/g (sample PKM 5). The total volume of pores, being a function of the as-spun draw ratio, and total drawing is characterized by an extremum in the form of a maximum for the highest as-spun draw ratio used (Fig. 1). The order of magnitude of this structural factor qualifies these fibers only to the group of increased porosity. The fibers obtained also have a relatively small total internal surface (Table I). Conducting the solidification process at optimum conditions, determined for fibers containing MMT or HAp, respectively, caused an insignificant increase in the total volume of pores up to the level of 0.29 cm^3/g, and in the internal surface of pores up to 26.48 m^2/g. However, this level of porosity was lower than that obtained for fibers without a nanoadditive (sample PW2), which had a total volume of pores of 0.39 cm^3/g.

Pore distribution curves (Fig. 2) are characterized by a distinct maximum within the range of very

TABLE I
Tensile Strength Properties and Porous Structure of Fibers, which Include 3% of Montmorollonite and 3% of Hydroxyapatite, and Fibers Without Any Nanoaddition

Sample symbol	As-spun draw out ratio (%)	Total draw ratio (%)	Total pore volume (cm^3/g)	Internal surface (m^2/g)	Tenacity (cN/tex)	Elongation at break (%)
PKM 1	−40	739.69	0.11	11.40	27.81	13.55
PKM 4	−20	740.73	0.23	6.23	32.12	13.25
PKM 2	0.0	898.45	0.15	18.25	39.65	10.59
PKM 3	+10	760.56	0.22	24.78	33.12	11.62
PKM 5	+30	540.25	0.26	20.89	22.05	10.22
PKM X	+10	520.69	0.29	26.48	30.95	9.45
PW 2	+10	437.35	0.39	33.86	40.80	11.02

PW 2: fibers without nanoaddition formed in a coagulation bath at a temperature of 25°C; PKM X: fibers spun at optimum conditions in a coagulation bath at a temperature of 25°C.
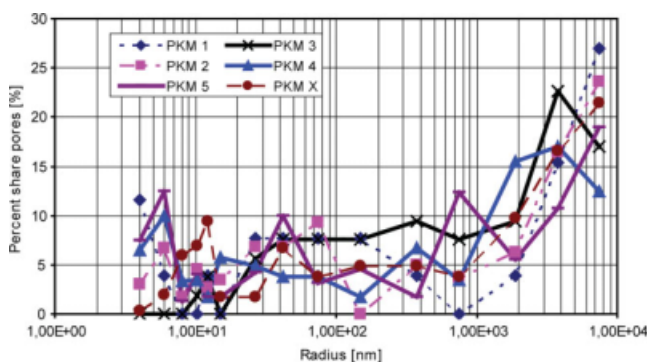
Figure 2 Dependency of the percentage share of pores as a function of their radius, expressed in logarithmic scale, for fibers which include two nanoadditions (3% of MMT and 3% of HAp). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

large pores or by a successive increase of such pores, both at a smoothened content of small and medium pores arising the level of 46%. The content of large and very large pores in the porous structure thus formed can even reach the level of almost 50% (Table II). Fibers spun at an as-spun draw ratio of +10% show the highest amount of such pores.

In the case of fiber sample PKM X formed at optimum conditions determined for fibers with one nanoadditive, the content of pores from the aforementioned range rises to almost 48% and is similar to the content of sample PW2 without a nanoadditive. Such a high content of very large pores, with dimensions within the range of 750–7500 nm corroborates the macroporous character of the structure created.

Analyzing the tensile strength properties of the fibers obtained, we can state that the susceptibility of fiber matrix to deformation at the stage of drawing plays the main role in obtaining high tensile strength. Considering the test series analyzed, the highest value of tenacity was obtained at an as-spun draw ratio of 0% and a total drawing within the

range of 898%, whereas the lowest value was obtained at an as-spun draw ratio of +30% and a total drawing of 540%. The changes of tenacity as a function of the as-spun draw ratio and total drawing has an extremum character with a maximum of this factor located at the zero level of the as-spun draw ratio (Table III). Forming fibers according to optimum conditions determined for particular nanoadditives made it possible to obtain fibers characterized by a tenacity of 30 cN/tex (Table III). For comparison, the tenacity of fibers containing only HAp or MMT is 33.10 cN/tex and 29.26 cN/tex at a porosity of 0.34 cm^3/g and 0.30 cm^3/g, respectively. The values of tenacity obtained for fibers containing both nanoadditives are lower by 9 cN/tex than for fibers characterized by the highest value of tenacity in the series tested, and lower by 10 cN/tex, as compared with fibers that do not contain a nanoadditive. This is understandable considering the as-spun draw ratios used and the increased temperature of the coagulation bath, as a result of the mild solidification conditions caused by the bath temperature increased to 25°C. The assumed increase in porosity to 0.29 cm^3/g was obtained at a decrease of tensile strength properties, which were still considerably higher than the assumed level of 25 cN/tex.

Elongation at break for fibers formed at a broad range of as-spun draw ratios was within the range of 10–13.5%. These values are slightly higher than for fibers containing either MMT or HAp, which is connected with obtaining lower total drawing values. By comparing the structures and properties of fibers with a system of two nanoadditives (PKM sample) with those containing only one type of nanoadditive and formed at optimum conditions (samples PMU 4 and UH 3; see Table III), it is clearly visible that although the deformability of fiber matrix was decreased by adding 6% of non-fiber-grade nanoadditives into it, the total volume of pores as well as tensile strength of the fibers are

TABLE II
Characterization of the Porous Structure of PAN Fibers, which Include Two Nanoadditions and PAN Fibers Without Any Nanoaddition (PW 2 Sample)

Sample symbol	As-spun draw out ratio (%)	Total draw ratio (%)	Percent contents of pores (%)			
			Small pores 4–12.3 (nm)	Medium pores 12.3–75 (nm)	Large pores 75–750 (nm)	Very large pores 750–7500 (nm)
PKM 1	−40	739.69	19.24	23.07	11.54	46.15
PKM 4	−20	740.73	25.05	18.08	12.00	44.87
PKM 2	0.0	898.45	18.80	26.30	8.63	46.27
PKM 3	+10	760.56	5.66	20.76	24.53	49.05
PKM 5	+30	540.25	26.99	19.15	18.70	35.16
PKM X	+10	520.69	24.66	14.03	13.51	47.72
PW 2	+10	437.35	20.22	8.99	22.48	48.31

PW 2: fibers without nanoaddition formed in a coagulation bath at a temperature of 25°C; PKM X: fibers spun at optimum conditions in a coagulation bath at a temperature of 25°C.

Sample symbol	As-spun draw out ratio (%)	Total draw ratio (%)	Total pore volume (cm^3/g)	Internal surface (m^2/g)	Tenacity (cN/tex)
UH 3	+10	649.61	0.30	19.34	29.26
PMU 4	+10	885.35	0.35	26.31	33.10

similar. This may result not only from the orientation of the structural elements and layers of MMT along the fiber axis but also the character and perfection of the supramolecular structure created, as well as the dispersion of MMT in the fiber matrix.

To confirm this hypothesis, an X-ray investigation (WAXS) was carried out for fibers formed at two values (−40% and +10%) of the as-spun draw ratio.

On the basis of analysis of the results, one can conclude that using negative values of the as-spun draw ratio was advantageous for obtaining slightly higher degrees of crystallinity at the level of 48% and crystallite sizes within the range of 44 Å (sample PKM 1) than in the case of using positive values of the as-spun draw ratio (sample PKM 3 characterized by a degree of crystallinity of 47% and crystallite dimensions of 43 Å). In both cases, which were recorded on the diffractograms presented in Figures 3 and 4, a peak is visible at the 2θ degree of about 32°. This shows that in fibers with two nanoadditives (MMT and HAp), a transformation of the mesomorphous structure into a typical crystalline structure took place (occurring in PAN fibers).

A precise explanation of these phenomena is given in Ref. 17. At the same time, a peak originated from MMT displaced to the right from the position at the
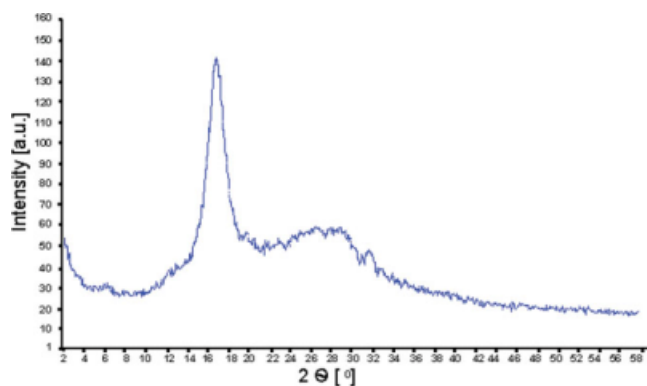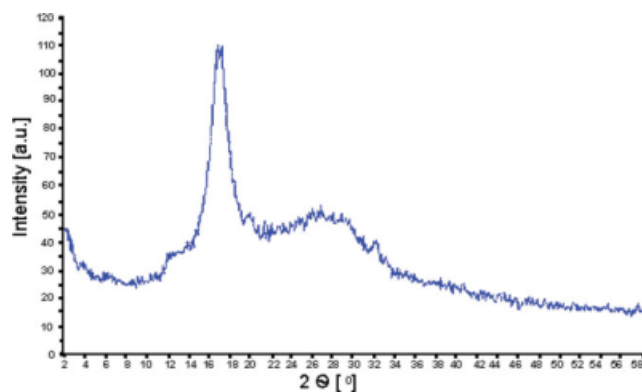

Figure 4 Normalized diffractogram of sample PKM 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

2θ degree of about 3.4° appears on the diffractogram. This fact means that also in this case the distance between MMT layers in some particles decreased forming agglomerates. At the same time, a decrease in peak height shows that part of MMT broke down to particular layers (underwent exfoliation). This phenomenon was described in Ref. 18, which concerns a comparative analysis of the structural parameters of PAN fibers characterized by different nanoadditives (SiO_2, Hap, and MMT).

Figure 3 Normalized diffractogram of sample PKM 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
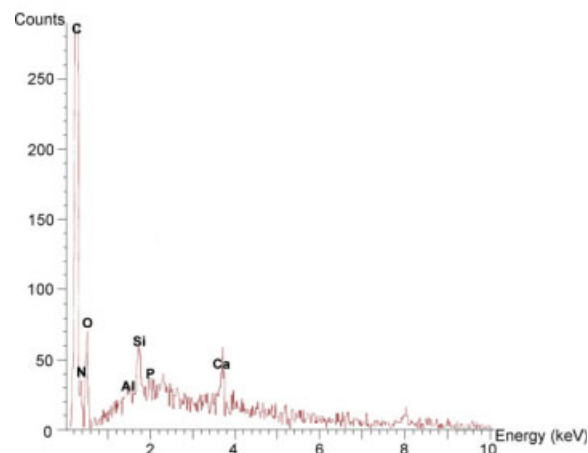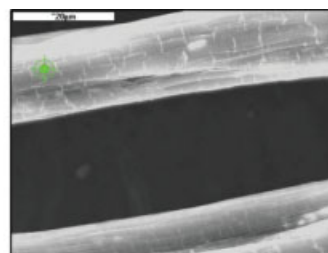
Figure 5 EDS point-microanalysis of PAN fibers including a system of two nanoadditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 EDS linear analysis of PAN fibers including a system of two nanoadditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
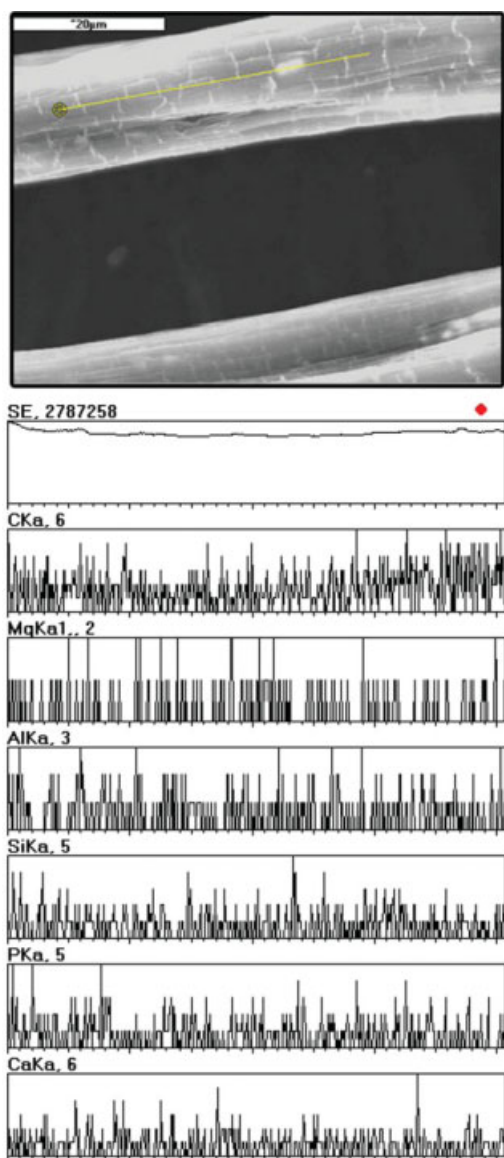
Considering the influence of the presence of two nanoadditives in the fiber matrix of PAN fibers on their tensile strength properties, the following facts should be taken into account. Introducing MMT in the amount of 3% into fiber matrix entailed a decrease in the deformability of this matrix, which resulted in obtaining a tenacity of 29.26 cN/tex of the fibers formed at optimum conditions (Table III). On the other hand, in the case of fibers, which contained 3% of Hap, it was possible to obtain at the stage of drawing a deformation higher by 230% than that of fibers with MMT. Furthermore, the authors observed a decreased inner friction of the system

connected with the presence of this nanoadditive in the fiber matrix, as in the case of MMT, the presence of MMT layers hinders the sliding of macromolecules past one another. In the case of introducing a system of two nanoadditives, which are clearly active in different ways, we can assume that the effect obtained will be the result of opposite actions. The deformability of such a system will certainly be influenced also by an increase to 6% of the nonfiber grade content. The deformability decreased and the value of the total drawing possible to be obtained was 520%. However, the tensile strength obtained (30.95 cN/tex) was comparable with that obtained for fibers containing only single nanoadditives and formed at optimum conditions. Therefore, one can assume that the supramolecular structure had a decisive influence on the tensile strength properties of PAN fibers containing both nanoadditives. The introduction of the HAp nanoadditive into the fiber matrix resulted in a transformation of the PAN fiber structure from mesomorphous into a more organized, purely crystalline one; and this transformation was confirmed by our results. This means that a longitudinal alignment of macromolecule chains does occur, and most probably in PAN crystallites which are created by an epitaxial increase of HAp grains.[17] These phenomena are advantageous with respect to obtaining good fiber tensile strength properties. It is also well known that obtaining increased tensile strength properties is connected with the phenomenon of exfoliation of MMT layers and their orientation in line with the fiber axis.[18]

Furthermore, the authors conducted SEM+EDS tests aimed to detect the presence of the nanoadditives introduced to fiber matrix on the surface of polyacrylonitrile fibers. Moreover, on the basis of these tests, the authors also tried to assess the regularity of distribution of particular nanoadditives on the fiber surface. Local analysis (Fig. 5) revealed that apart from characteristic elements coming from polyacrylonitrile, other elements, such as Al, Si, Ca, and P, coming from nanoadditives, were present on the fiber surface. Linear analysis (Fig. 6) shows that on the examined fiber segment the distribution of nanoadditives on the fiber surface is quite regular. However, there is also a larger concentration of nanoadditives, which indicates MMT and HAp agglomeration. The map of characteristic elements (Fig. 7) shows the presence of areas with regular nanoadditive distribution in the examined area. It also needs to be stressed that in the presented mapping there exist areas with a greater concentration of elements coming from MMT or nano-HAp, which may indicate the process of agglomeration, in spite of the use of an ultrasound scattering process.
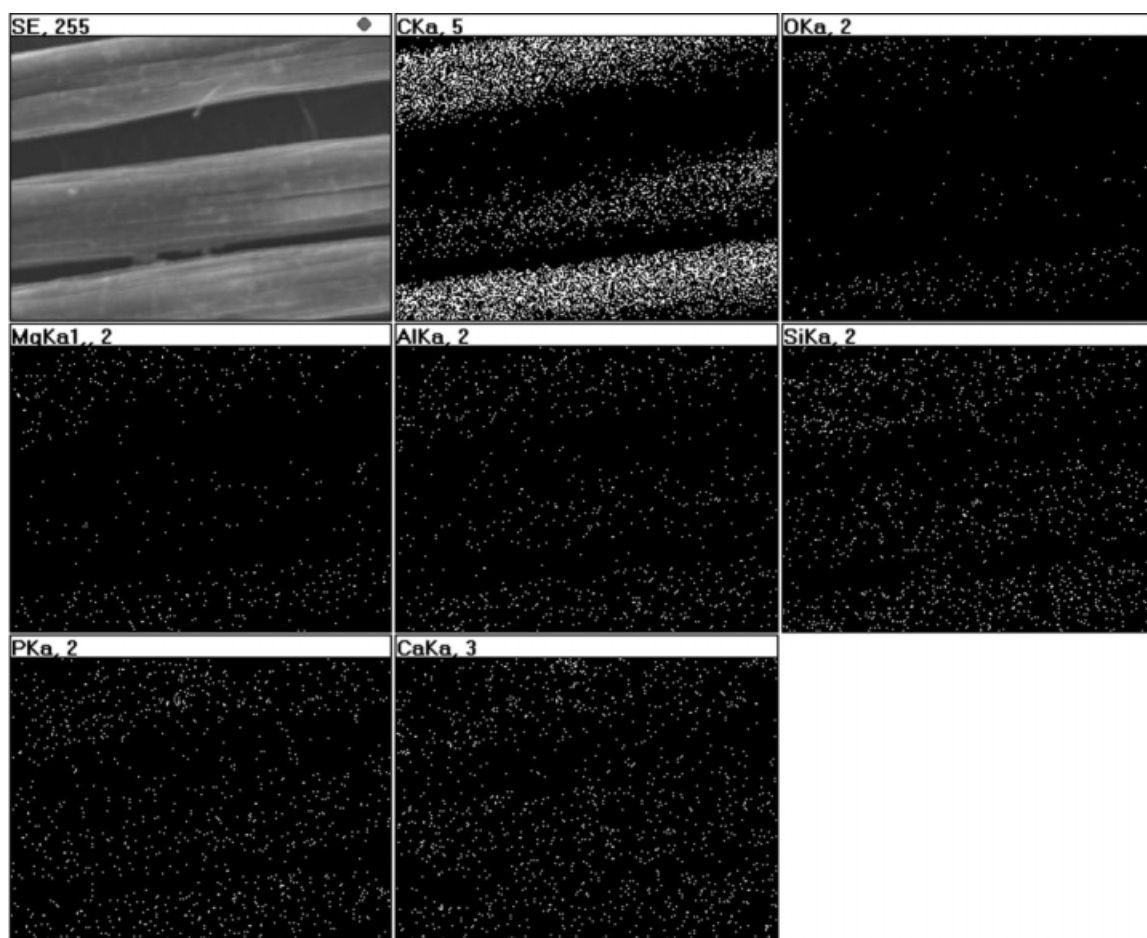
Figure 7 Scanning microphotographs with a distribution map of characteristic elements.

SUMMARY

- Conducting the solidification process at mild conditions makes it possible to obtain PAN nanocomposite fibers including two nanoadditives characterized by an increased tenacity of about 40 cN/tex and a low total volume of pores at the level of 0.15 cm^3/g at an as-spun draw ratio of 0%, or, alternatively, fibers with an increased total volume of pores of 0.26 cm^3/g and a tenacity lower by 3 cN/tex than the level of 25 cN/tex assumed while fibers are formed at a positive value of the as-spun draw ratio of +30%.

- By using harsher solidification conditions in mild coagulation baths (by increasing their temperature), the authors obtained an increase in the total volume of pores of up to about 0.3 cm^3/g at a tenacity of 30 cN/tex. These are the same forming conditions as for fibers including a 3% content of particular nanoadditives.

- In spite of the total content of nanoadditives in the spinning solution, which increased to 6%, fibers containing MMT and HAp in the fiber matrix are characterized by tenacity comparable with that of fibers formed at optimum conditions and containing only a single nanoadditive. This is probably connected with the transformation of the crystalline structure, which takes place during fiber formation, and a partial exfoliation of MMT layers. The order of magnitude of the total volume of pores is also comparable. This has corroborated the previously formulated hypothesis.

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