

Comparative Analysis of the Structural Parameters and Strength Properties of Polyacrylonitrile Fibers Containing Ceramic Nanoadditives

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Received 17 April 2006; accepted 11 August 2006

DOI 10.1002/app.25403

Published online 4 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The structural parameters and strength properties of three types of new-generation precursor polyacrylonitrile fibers are comparatively analyzed. These fibers, after the carbonization process, can be used as implants supporting the process of bone reconstruction. They are characterized by a high tenacity ranging from 21 to 41 cN/tex. Tests and measurements have shown that the presence

of nanoadditives causes a clear increase in the degree of fiber crystallinity. Moreover, the tenacity of the fibers can be considerably increased by the grinding of nanoadditive agglomerates with ultrasound. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2346–2350, 2007

Key words: crystal structures; fibers; silicas

INTRODUCTION

One of the rapidly developing branches of modern material engineering is nanotechnology in medicine, which may revolutionize the current methods of healing the most serious diseases.¹ The incorporation of nanoparticles of a biologically active compound such as hydroxyapatite (HAp), silica (SiO₂), or montmorillonite (MMT) into precursor polyacrylonitrile (PAN) fibers makes it possible to obtain carbon fibers with new properties incomparable with those of conventional synthetic fibers. A biocomposite obtained from carbon fibers containing biologically active elements in their structure, such as calcium, silicon, and phosphorus, can become an alternative to other materials used in orthopedics and traumatic surgery. Moreover, the use of nanoparticles may allow us to extend these applications of biodegradable carbon fibers in medicine, as exemplified by the reconstructions of knee joints² and Achilles tendons.³

The use of nanoparticles of SiO₂ and MMT is dictated by the fact that silicon plays an important role in the formation of bone structures, the process of bone calcification, and regeneration after fractures.⁴ On the other hand, the use of nanohydroxyapatite is justified by the fact that it combines well with native bone, its presence facilitates the improvement of interlayer adhesion^{5,6} and stimulates fast growth of bone tissue, and it is very similar to the inorganic portion of bone tissue.⁵ Thus, carbon fibers obtained from a precursor containing any of these nanoadditives can be used to produce implants containing in their structures elements with osteoconductive and osteopductive effects. The beneficial influence of the nanoadditive HAp in carbon fibers on the process of bone-tissue reconstruction has been reported.^{7,8}

It is also known that in addition to their basic biological properties, carbon fibers designed for medical applications should possess high strength and increased porosity. As shown in our previous studies, both the strength and porosity of carbon fibers depend directly on the structure of the precursor fibers that form during their solidification and drawing.^{9,10}

The aim of this research project, directed at the making of precursor PAN fibers containing ceramic nanoadditives (HAp, SiO₂, and MMT), was to find such parameters of the fiber-spinning process that would allow us to produce fibers with a suitable strength for carbonization and increased porosity at the same time. It is known that to produce fibers with increased strength properties, the fiber-solidification process should be carried out according to the diffu-

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Contract grant sponsor: Committee for Scientific Research; contract grant number: 3T08E03328.

Contract grant sponsor: European Social Fund and Polish State (to M.B. through the program "Mechanism WID-DOK"); contract grant number: Z/2.10/II/2.6/04/05/U/2/06.

Contract grant sponsor: Foundation for Polish Science (to MB).

Journal of Applied Polymer Science, Vol. 105, 2346–2350 (2007)
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sion mechanism, whereas fibers with increased porosity are formed when this process proceeds according to the drop mechanism.¹¹ Therefore, tests were performed with selected samples of fibers spun at two extreme values of the as-spun draw ratio, -40 and $+10\%$, which allowed us to obtain fibers with either increased strength or increased porosity. Additionally, for fibers spun with the positive as-spun draw ratio, the solidification conditions were intensified by the temperature of the coagulation bath being raised to 25°C ; this shifted the solidification mechanism toward the drop mechanism. A more detailed analysis of the effects of the spinning parameters on the porous structure and properties of PAN fibers containing the aforementioned nanoadditives is presented in our previous publications.^{12–14}

This article concerns a comparative analysis of the porous and supermolecular structures and strength properties of three types of fibers containing various nanoadditives. The analysis makes it possible to explain how the prescribed fiber properties can be obtained despite the incorporation of non-fiber-forming nanoadditives that reduce the susceptibility to deformation during the drawing stage and therefore adversely affect the strength properties.

EXPERIMENTAL

Spinning solutions were prepared from a PAN terpolymer (Zoltek). The PAN terpolymer had an intrinsic viscosity of 1.29, as determined by the viscosimetric method in dimethylformamide (DMF) at 20°C , and the following composition:

- 93–94 wt % acrylonitrile units.
- 5–6 wt % methyl acrylate units.
- About 1 wt % sodium allyl sulfonate.

The rheological characteristics are given in our previous publication.¹⁵ DMF was used as a solvent. The characteristics of the nanoadditives are given in Table I. Before the addition of the nanoadditives to the spinning solutions, they were treated with ultrasound in a solution of DMF at 20°C for 1 h. The ultrasound washer had the following parameters: an ultrasonic power of 2×160 W, a frequency of 40 kHz, and a heating-system power of 150 W.

Fibers were spun from the polymer solution by the wet-spinning process with a laboratory spinning machine, whose construction made it possible to stabilize the technological parameters at a required level under continuous control. A spinneret with 240 orifices 0.08 mm in diameter was used. The solidification process was carried out in a bath containing an aqueous solution of DMF at a concentration of 50–70%. The drawing process was performed in two stages: in

TABLE I
Characteristics of the Ceramic Nanoparticles

Additive	Grain size (nm)
SiO ₂ (a product from AGH Cracow)*	50–150
Hydroxyapatite (a product from AGH Cracow)*	30–120
Montmorillonite – Nanomer PGW (a product from Nanocor)**	2000

*Product from AGH University of Science and Technology, Cracow, POLAND.

**Product from Nanocor[®], Arlington Heights, IL, USA.

a plasticizing bath (containing an aqueous DMF solution of a low concentration) and in an atmosphere of superheated steam at a temperature within the range of 130 – 140°C . After rinsing, the fibers were dried at 40°C under isometric conditions. The process was performed in accordance with a patent.¹⁶ Three groups of fibers containing particular nanoadditives were tested. For each nanoadditive, the fibers were spun at various values of the as-spun draw ratio and the total draw ratio. Fibers containing no nanoadditive (PW1) were used as a reference sample. The following strength properties and structural parameters were tested and measured: the tenacity at break, degree of crystallinity, crystallite size, total pore volume, and internal surface of the pores.

The degree of crystallinity and the size of the crystallites were determined by the wide-angle X-ray diffraction (WAXS) method. Diffraction patterns were recorded in a symmetrical reflection mode with a Seifert URD-6 diffractometer and a copper target X-ray tube ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 30 mA. Cu K α radiation was monochromatized with a nickel filter. WAXS curves were recorded from 6.5 to 60° in steps of 0.1° . The investigated fibers were powdered and pressed into a sample holder. Samples 1 mm thick with a radius of 2 cm were prepared.

The fiber tenacity was determined according to Polish Standard PN-EN ISO 5079;1999 with the use of an Instron tensile testing machine.

The fiber porosity was determined by mercury porosimetry with a Carlo Erba porosimeter linked to a computer system allowing us to determine the total pore volume, the percentage of pores with dimensions of 5–7500 nm, and the total internal pore surface.

RESULTS AND DISCUSSION

The analysis of the WAXS diffraction curves and the calculation of the crystallinity degree were carried out with the computer program OpiFit^{17,18} according to the procedure described in ref. 19. The sizes of the crystallites were calculated for the direction perpendicular to the family of the (110) lattice planes.¹⁹

The results listed in Table II indicate that the use of ultrasound to grind agglomerates of nanoadditive incorporated into fiber-forming polymers has an

TABLE II
Properties of PAN Fibers With and Without Nanoadditions

Sample ^a	As-spun draw ratio (%)	Total draw ratio (%)	Temperature of the coagulation bath (°C)	Total pore volume (cm ³ /g)	Internal surface (m ² /g)	Crystallite size (Å)	Degree of crystallinity (%)	Tenacity (cN/tex)
PMU1	-40	923.5	15	0.235	30.80	48	55	36.90
PMU4	+10	649.6	25	0.304	19.34	49	47	21.26
UH1	-40	998.0	15	0.168	6.31	45	48	44.23
UH3	+10	885.3	25	0.347	26.31	42	37.5	33.10
PSU4	-40	1019.0	15	0.322	25.52	46	49	40.95
PSU3	+10	761.5	25	0.368	20.22	41.5	38	31.02
PW1	-40	1054.0	15	0.245	33.24	43.5	46.8	47.02

^a PMU1 and PMU4 were fibers containing 3% MMT (with respect to the polymer mass). UH1 and UH3 were fibers containing 3% HAp (with respect to the polymer mass). PSU3 and PSU4 were fibers containing 3% SiO₂ (with respect to the polymer). PW1 was a fiber without nanoadditives.

effect on the basic technological parameters (the as-spun draw ratio, total draw ratio, and temperature of the coagulation bath) of their degree of crystallinity. This phenomenon has not been observed in previous studies concerning fibers containing HAp,¹⁹ in which the grinding of agglomerates by ultrasound was not used. The changes in the spinning conditions that favor the spinning of fibers with a high strength, that is, increasing the as-spun draw ratio from a negative value (-40%) to a positive value (+10%) and increasing the temperature from 15 to 25°C, bring about a considerable decrease in the degree of crystallinity in all three types of fibers. Fibers with nanohydroxyapatite and nanosilica show almost the same crystallinity degrees at these two extreme values of the as-spun draw ratio: about 49–48 and 38–37.5%, respectively. The sizes of the crystallites are also very similar: 45–46 Å for the as-spun draw ratio of -40% and 42–41.5 Å for the as-spun draw ratio of +10%.

The highest values of the crystallinity degree and the biggest sizes of the crystallites have been observed in PAN fibers containing MMT. In this case, the changes in the spinning conditions influence the crystallinity degree to a lesser extent, whereas the sizes of the crystallites are practically unchanged (Table II). In these fibers, we can also observe a change in the

angular position of the characteristic peak corresponding to MMT. In pure MMT, this peak occurs at about 3.4°, whereas in PAN fibers containing MMT, it is at about 5.55° (Fig. 1). Moreover, the height of this peak is clearly lower than that of MMT. The described changes indicate that some of the MMT stacks are exfoliated into individual layers, whereas in the remainder, the height of the galleries between the aluminosilicate layers has decreased from 26 to about 15.9 Å. Thus, a sort of subsidence of the laminal structure has taken place, and this means that the modifier has been removed from the MMT layers. A similar phenomenon has been observed for a nanocomposite of another fiber-forming polymer.²⁰

For fibers containing nanohydroxyapatite, a clear peak can be observed at an angle of about 32° (Fig. 2). This is a reflex (301), whose appearance in this type of fiber has been already reported in ref. ¹⁹. Its appearance indicates that in the fibers containing HAp, there are formed areas in which macromolecular chains are ordered not only in the direction perpendicular to their axis but also along their axis. Thus, it is a transformation of the mesomorphic structure characteristic of most PAN fibers into a more ordered, typically

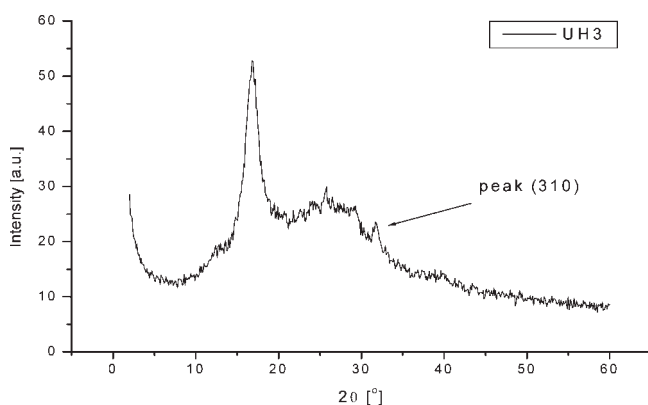


Figure 1 WAXS pattern of the sample containing HAp.

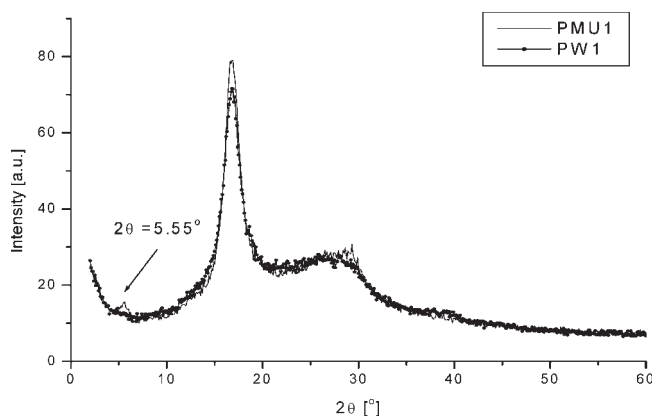


Figure 2 WAXS patterns of a sample containing the nano-additive MMT (PMU1) and a sample without the nano-additive (PW1).

crystalline structure. This process probably takes place in the PAN crystallites, which are formed because of epitaxial growth on the HAp grains. A detailed explanation of this problem is given in ref. 19.

Peak (301) does not appear in the diffractograms of fibers containing nanoparticles of MMT or SiO₂. Thus, we can conclude that the crystallites that are present in those fibers are of a lower quality and are characterized by a lower degree of perfection, which undoubtedly reduces their strength with respect to that of fibers containing HAp (Table II).

The relatively high degree of crystallinity and the degree of overall orientation at a level up to 0.8 of the fibers under investigation are accompanied by good tenacity, which increases to 30 cN/tex, with the exception of fibers containing MMT spun at the positive as-spun draw ratio, which facilitates the formation of higher porosity. High structural parameters and strength properties of precursor fibers are important as there is a close relationship between the crystalline structure and tenacity of precursor fibers and the tenacity of the carbon fibers obtained from the former.^{9,10} From an examination of the porous structure of the fibers, it follows that in fibers containing nanoparticles of SiO₂ or MMT, the grinding of agglomerates with the use of ultrasound increases the total pore volume. As shown in previous studies,^{12,14} the fibers that are not treated with ultrasound to grind agglomerates have lower values of this parameter. On the other hand, for fibers containing HAp spun at a negative value of the as-spun draw ratio, we can observe a slight decrease in the total pore volume.

In all the fibers under investigation, a considerable effect of the fiber-forming conditions on the total pore volume can be observed. If the fiber-solidification process is carried out according to the diffusion mechanism (a negative value of the as-spun draw ratio and a low temperature of the coagulation bath), it is possible to obtain the total pore volume within the range of 0.16–0.32 cm³/g, with the highest values being obtained for PAN fibers containing nanosilica.

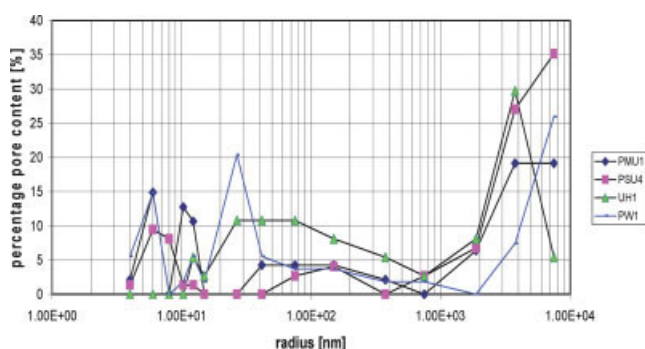


Figure 3 Size distribution of the pores. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

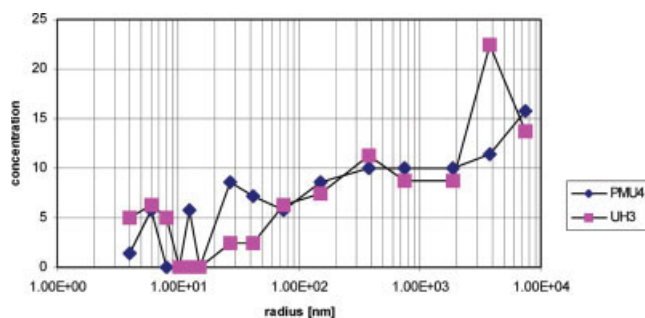


Figure 4 Size distribution of the pores. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

On the other hand, the transformation of the diffusion mechanism of solidification into the drop mechanism (a positive value of the as-spun draw ratio and increased temperature of the coagulation bath) allows us to obtain fibers with a total pore volume within the range of 0.30–0.37 cm³/g, with the highest values being obtained for PAN fibers containing nanosilica (Table II). Such an order of magnitude of this structural parameter, however, does not allow us to rate these fibers among highly porous fibers, but they can be rated as fibers with an increased porosity.

For fibers formed at a negative value (Fig. 3) and those formed at a positive value of the as-spun draw ratio (Fig. 4), the curves of the pore size distribution show maxima within the range of large and very large pores, whereas the contents of medium and small pores are rather low. The low content of small pores is also confirmed by a low value of the total internal surface, which is lowest for fibers containing HAp ranging from 6.3 to 26.3 m²/g (Table II). Such a high content of large and very large pores may, however, be disadvantageous because in the case of an improper selection of carbonization parameters, they can be a source of structural defects in the carbon fibers obtained from such a precursor. On the other hand, carbon fibers should show the presence of relatively large pores, which are required for an easier combination of implants with maternal tissues, and slightly lower strength properties of carbon fibers may be of no major importance because of the generally high strength level of the precursor.

The introduction of the stage of agglomerate grinding with the use of ultrasound into the process of making precursor fibers allows us to eliminate the disturbance of the macroscopic structure of the fiber-forming polymer by large agglomerates of nanoadditives. Because of this treatment, the susceptibility of a polymer to deformation during the drawing stage is increased. As a result, the resultant PAN fibers are characterized by high values of tenacity even though they contain various non-fiber-forming nanoadditives (Table II). The value of the tenacity is, however,

clearly dependent on the basic technological parameters of fiber spinning, mainly on the as-spun draw ratio and the total draw ratio: for fibers formed at a negative value of the as-spun draw ratio, it is considerably higher (36.9–44.2 cN/tex) than that of fibers formed at a positive value of the as-spun draw ratio (21.2–33.1 cN/tex). Such a trend of changes is consistent with the generally accepted principles of spinning high-tenacity and highly porous fibers.¹¹ However, the increase in the tenacity resulting from the replacement of the positive value with the negative value of the as-spun draw ratio is fully correlated with the increase in the degree of crystallinity that takes place at such a change in the fiber-spinning conditions (Table II). This means that the higher tenacity of fibers formed at a negative as-spun draw ratio is connected not only to the lower content of pores but also to a better order of the macromolecular chains in the fiber-forming polymer in comparison with that of fibers formed at a positive as-spun draw ratio.

Because of the use of ultrasound for the grinding of agglomerates of the nanoadditives incorporated into the fiber-forming polymer, the strength properties of these fibers have been made considerably similar to those of fibers without nanoadditives (PW1), and at the same time, the porosity of the fibers has been significantly increased, with the exception of MMT-containing fibers, which despite a higher degree of crystallinity and larger crystallite sizes, show a clearly lower tenacity. This is most likely due to the fact that the exfoliation of MMT stacks takes place only to a limited extent and at the same time there occurs the previously mentioned phenomenon of gallery subsidence between the aluminosilicate layers. As a result, agglomerates are formed that are considerably larger (Table I) than those observed in the case of the two remaining nanoadditives. Because of the low value of the ratio of the external surface to the volume, these agglomerates are weakly linked with the polymer matrix, and this consequently adversely affects the strength of the fibers.

CONCLUSIONS

The introduction of the stage of nanoadditive agglomerate grinding with ultrasound in the process of making composite PAN fibers results in a considerable increase in the susceptibility of the polymer to deformation during the drawing stage. The fibers made by this process are characterized by a considerably higher tenacity (>33 cN/tex at the as-spun draw ratio of –40%) than the fibers made without the stage of ultrasonic treatment.

Such a high tenacity of PAN fibers containing nanoadditives makes them perfect precursors for the production of a new generation of carbon fibers designed

for implants supporting the process of bone reconstruction because of the presence of elements with osteoproduktive and osteoconductive effects.

The incorporation of nanoadditives into the spinning solution brings about a beneficial increase in the crystallinity degree of PAN fibers obtained from such solutions. At the same time, for fibers containing nano-hydroxyapatite, the mesomorphic structure, which is characteristic of fibers containing no nanoadditive, transforms into a more ordered crystalline structure.

The clear increase in the tenacity of the fibers, observed after the replacement of the positive as-spun draw ratio with a negative value, is connected not only to the lower content of the pores but also to a better order of the macromolecular chains in the fiber-forming polymer in comparison with the fibers formed at a positive as-spun draw ratio.

In all three PAN fibers containing nanoadditives, we can observe a change in the character of the formed porous structure with respect to its macroporosity. This effect may be beneficial because of the better assimilability of implants obtained from carbon fibers with such properties.

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