Effect of Spinning Conditions on the Structure and Properties of PAN Fibers Containing Nano-Hydroxyapatite

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Received 16 March 2005; accepted 5 July 2005
DOI 10.1002/app.23464
Published online 9 February 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Spinning conditions for nano-hydroxyapatite-containing precursor polyacrylonitrile (PAN) fibers have been developed and their effects on the structure and properties of nanocomposite PAN fibers have been assessed. The precursor PAN fibers prepared under the developed conditions are characterized by high strength, with their total pore content being at a level of 0.25 cm^3/g. After carbonization, these fibers are designed for use as implants that support and stimulate the process of bone reconstruction. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2881–2888, 2006

Key words: nanoparticles; nanocomposites; hydroxyapatite; polyacrylonitrile fibers

INTRODUCTION

In connection with the more and more often observed complicated bone fracture and degenerative diseases of the bone system, one of the tasks faced by medical field nowadays is the search for new biomaterials that could support and stimulate the process of bone reconstruction. Currently, titanium alloys are of the highest importance in the biomolecular engineering. In addition to their advantages, these alloys show also disadvantages such as a low resistance to abrasion and possible release of abrasion products to biological environment, which reduce their use.[1,2] An alternative solution to titanium alloys may be the use of implants made from polymeric materials, for example, polyglycolide,[3] poly(L-lactide),[4,5] and carbon fibers-based composites.[6–8]

The incorporation of hydroxyapatite nanoparticles could allow one to prepare fibrous form of materials containing in their structure an inorganic, biologically active compound. A convincing argument for the use of hydroxyapatite nanoparticles is the fact that this is one of the most common bioceramic materials[9,10] currently used to coat titanium implants.[11–13] However, the greatest advantage of hydroxyapatite comes from the fact that this is a very similar material to the inorganic portion of the bony tissue.[14,15]

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Journal of Applied Polymer Science, Vol. 100, 2881–2888 (2006)

The carbon fibers designed for implants should show, in addition to the basic biological properties, high strength and increased porosity at the same time. Both these parameters depend directly on the structure and properties of precursor fibers. The formation of polyacrylonitrile (PAN) fibers by the wet process from solution makes it possible to control process parameters so as to obtain required fiber properties.[16–18]

The aim of the present study is to develop a process for the manufacture of a new generation of precursor PAN fibers-containing hydroxyapatite nanoparticles, as well as to assess the effects of basic spinning conditions on the fiber structure and properties. This will allow one to select the best spinning conditions for PAN fibers with high strength and increased porosity at the same time. Such fibers should be a proper precursor for the manufacture of carbon fibers that could be successfully used in reconstructive bone surgery.

MATERIALS AND METHODS

Fibers were prepared from PAN terpolymer of Zoltek with the following composition:

- 93–94 wt % of acrylonitrile units
- 5–6 wt % of methyl acrylate units
- about 1 wt % of sodium allylsulphonate.
- Dimethylformamide (DMF) was used as a solvent. Hydroxyapatite used in the study was provided by the Academy of Mining and Metallurgy (Cracow, Poland); the dimensions of its particles

TABLE I
Characteristics of Polymer and Spinning Solution

Intrinsic viscosity, η (dL/g)	Concentration of solution (%)	Hydroxyapatite content (%)	Rheological parameter, n	Rheological parameter, K
1.29	22%	3%	0.955	32.4

ranged from a dozen or so to 100 nm (determined on the basis of scanning microscope images). The rheological properties of spinning solutions were measured by means of a rotary rheometer, Rheotest RV, at a temperature of 20°C and a shearing rate of 146.8 L/s, using an "H" cylinder. Rheological parameters n and K were found from the flow curves in a logarithmic system. The characteristics of spinning solution determined on the basis of separate measurements[19] are given in Table I.

- Fibers were spun by the wet process from the solution, using a laboratory spinning machine that made it possible to stabilize required technological parameters under a constant control. A spinneret with 240 orifices, 0.08 mm in diameter each, was used. Fibers were solidified in a bath containing an aqueous solution of DMF with a concentration adapted to the given spinning series under investigation. The fiber drawing process was carried out in two stages: in a plasticizing bath and under superheated steam. After rinsing, the fibers were dried at 20–40°C under isothermic conditions. Precisely specified technological parameters are under patent protection.[20]
- Moisture content measurements at 100% RH were carried out in accordance with the Polish standard PN-71/P-04635.
- Water retention (WVR) was measured by relating the weight of retained water after centrifuging a sample for 10 min at an acceleration of 10,000 m/s^2 to the weight of a dry sample. Before centrifuging, fibers were immersed in water containing 1% of Rokafenol NX-3 (a surface-active agent) for 24 h.
- Fiber porosity was determined by the method of mercury porosimetry using a Carlo-Erba porosimeter linked to a computer system, allowing one to determine the total pore volume, percentage content of pores with dimensions from 5 to 7500 nm, and the total internal pore surface.
- Fiber tenacity at break was measured according to the Polish standard PN-85/P-04761/04, using an Instron tensile testing machine.
- The distribution of hydroxyapatite in fiber was assessed on the basis of images taken by a scanning microscope of JSM 5400 with an analyzer of dispersion energy of characteristic radiation EDX LINK ISIS of Oxford Instrument.

RESULTS AND DISCUSSION

The study was aimed at the preparation of precursor fibers with good strength properties and increased porosity suitable for the medical application of the final carbon fibers. To reconcile these apparently opposing tendencies, it would be required to leave the specified by us general principle of manufacturing fibers with increased porosity[21] consisting in fiber solidification under mild coagulation baths where the process conditions have been made more severe by raising their temperature. However, aiming at the preparation of fibers with increased strength, the level of intensity of the solidification conditions was reduced by maintaining the temperature not higher than 25°C. At the same time, instead of using positive values of the as-spun draw out ratio, negative values of this parameter were assumed to facilitate the process of increasing the fiber strength.

To determine the limit of reasonable intensification of the solidification conditions for the two types of baths: a mild bath containing 60% of solvent and a very mild bath containing 70% of solvent, the effect of temperature on the structure and properties of PAN fibers was assessed. The temperature of the mild baths was changed from 7 to 25°C, while in the case of very

TABLE II
Sorption and Mechanical Properties of Fibers Spun in a Mild Coagulation Bath (60% of DMF)

Sample symbol	Temperature (°C)	As-spun draw out ratio (%)	Total draw ratio (%)	Moisture absorption at 100% RH (%)	Water retention (%)	Tenacity (cN/tex)
H8	25	−40	865.5	8.70	18.47	38.65
H7	20	−40	863.2	7.40	15.01	39.60
H9	15	−40	1022.2	8.39	16.59	40.09
H10	10	−40	1014.5	7.93	15.37	38.66
H11	7	−40	1022.2	7.38	15.63	39.66

TABLE III
Sorption and Mechanical Properties of Fibers Spun in a Very Mild Coagulation Bath (70% of DMF)

Sample symbol	Temperature (°C)	As-spun draw out ratio (%)	Total draw ratio (%)	Moisture absorption at 100% RH (%)	Water retention (%)	Tenacity (cN/tex)
H12	7	−40	973.4	7.59	17.35	38.20
H13	10	−40	876.9	10.50	19.68	33.97
H14	15	−40	858.5	10.40	17.35	31.32

mild baths, the use of temperatures over 15°C was inexpedient due to its expected greater influence on the strength properties. The intensification of solidification conditions in both mild coagulation baths by raising their temperatures results in quite slight changes in moisture absorption of the obtained fibers (Tables II and III). The moisture absorption of a hydrophobic fiber-forming polymer depends mainly on the total pore volume, the character of the formed porous structure, and the internal surface of the resultant fibers.[21]

The changes in moisture absorption at 100% RH within quite narrow limits from 7.4 to 10.5%, those in WVR from 15 to 19.7%, and the order of magnitude of these values may suggest that the fibers produced during solidification in both coagulation baths will show also a similar porous structure with a relatively low total pore volume. This seems to be due to the fact that the increase in diffusion rate is rather limited as being connected with the moderate raise in the temperature of the coagulation bath.

The changes in moisture absorption of fibers show an upward trend with the increase in the temperature of solidification bath, while the changes in fiber strength go in opposite direction (Tables II and III). The raise in the coagulation bath temperature (intensification of the solidification conditions) is accompanied by the formation of a structure that is less deformable during the drawing stage. This is revealed by a decrease in the fiber tenacity by about 7 cN/tex for fibers solidified in baths containing 70% of DMF. This effect is smaller in the case of fibers solidified in the bath containing 60% of DMF, where the drop in tenacity is about 1 cN/tex.

Generally, the value of tenacity at the level approaching 40 cN/tex should be regarded as high, especially that this concerns fibers from PAN containing a nonfiber-forming nanoadditive.

Based on the performed analysis of the effect of temperature and concentration of the solidification bath, the solidification in mild baths containing 60% of solvent at 15°C can be regarded as most favorable. The PAN fibers containing hydroxyapatite nanoparticles formed under these conditions show a tenacity of 40 cN/tex and also good sorption properties at the same time. Maintaining the aforementioned conditions, the effect of as-spun draw out ratio and the related-fiber deformation during drawing on the porous structure

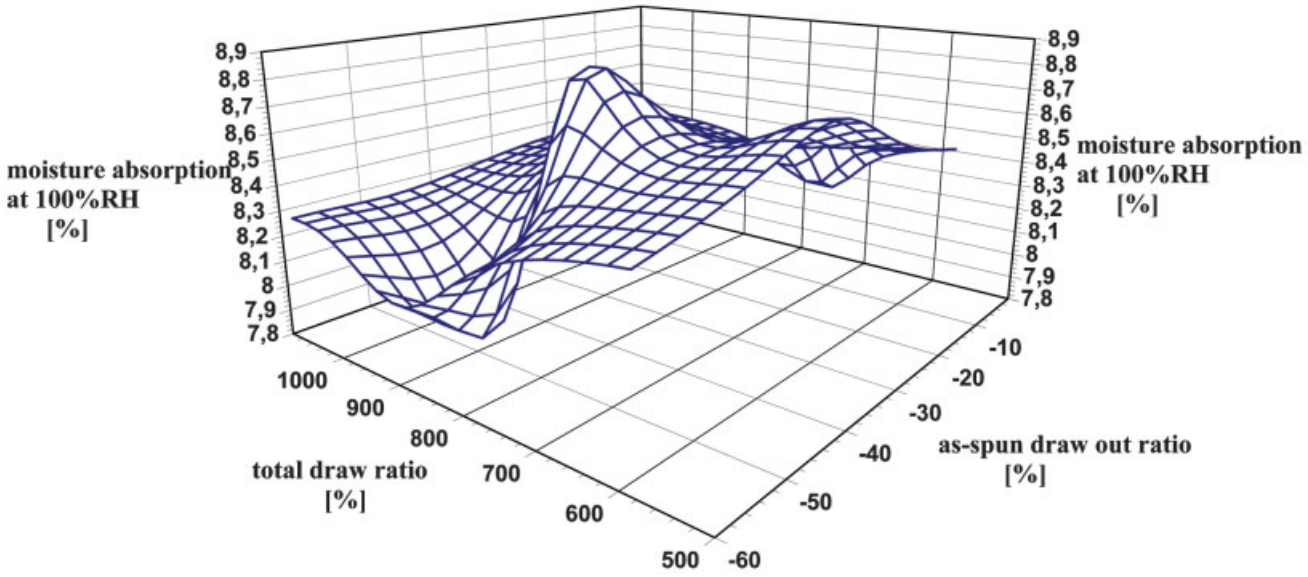

Figure 1 Dependence of moisture absorption at 100% RH on the as-spun draw out ratio and the total draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

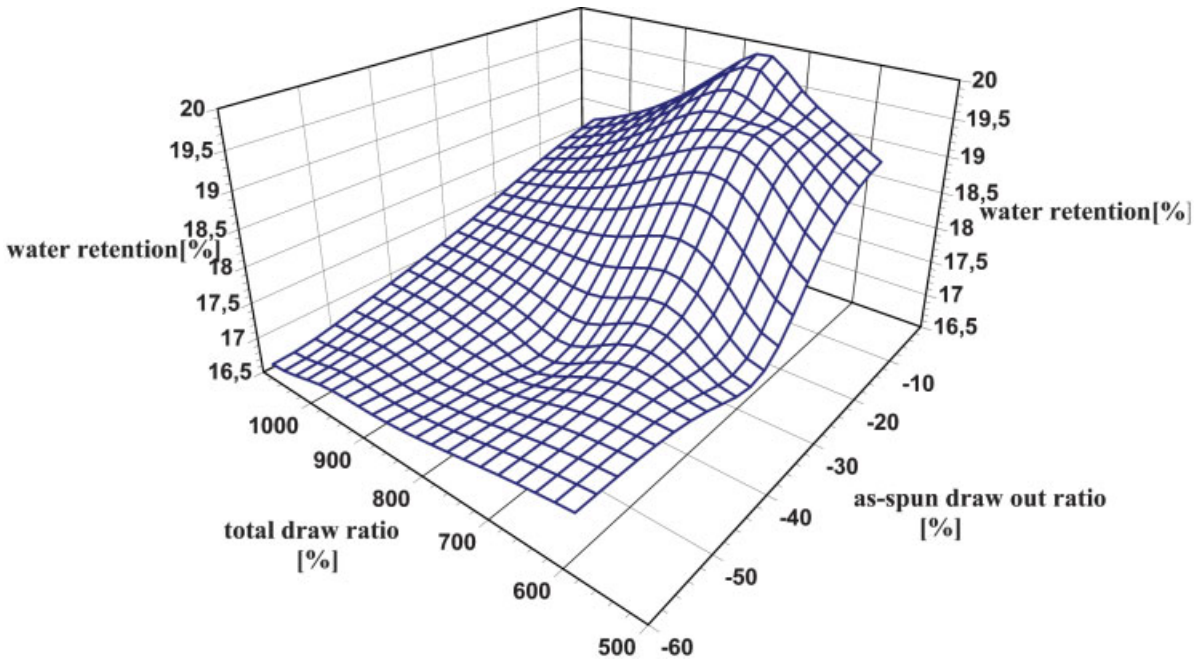

Figure 2 Dependence of water retention on the as-spun draw out ratio and the total draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and properties of fibers was examined. The value of as-spun draw out ratio was changed within a wide range from 0 to −60%, satisfying one of the conditions of the general rule in the formation of fibers with increased strength parameters. At the same time, the value of deformation during drawing was decreased more in relation to maximum values than in previous test series. This created more beneficial conditions to maintain the porous structure formed during the solidification stage with a smaller concentration of structural elements because of the action of tensile stresses.

From the analysis of the structure and properties of fibers spun with variable values of as-spun draw out ration and deformation during drawing, it follows that both moisture absorption at 100% RH and WVR show an upward trend with increase in the as-spun draw out ration (Figs. 1 and 2). A similar character of changes is observed in the total pore content as a

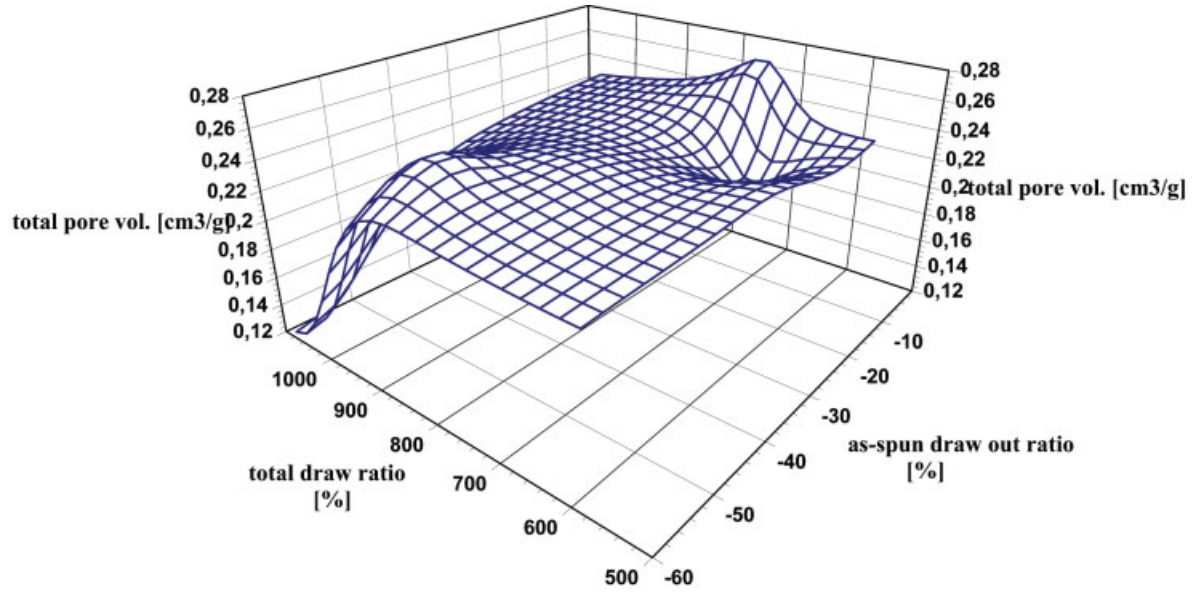

Figure 3 Dependence of total pore volume on the as-spun draw out ratio and the total draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

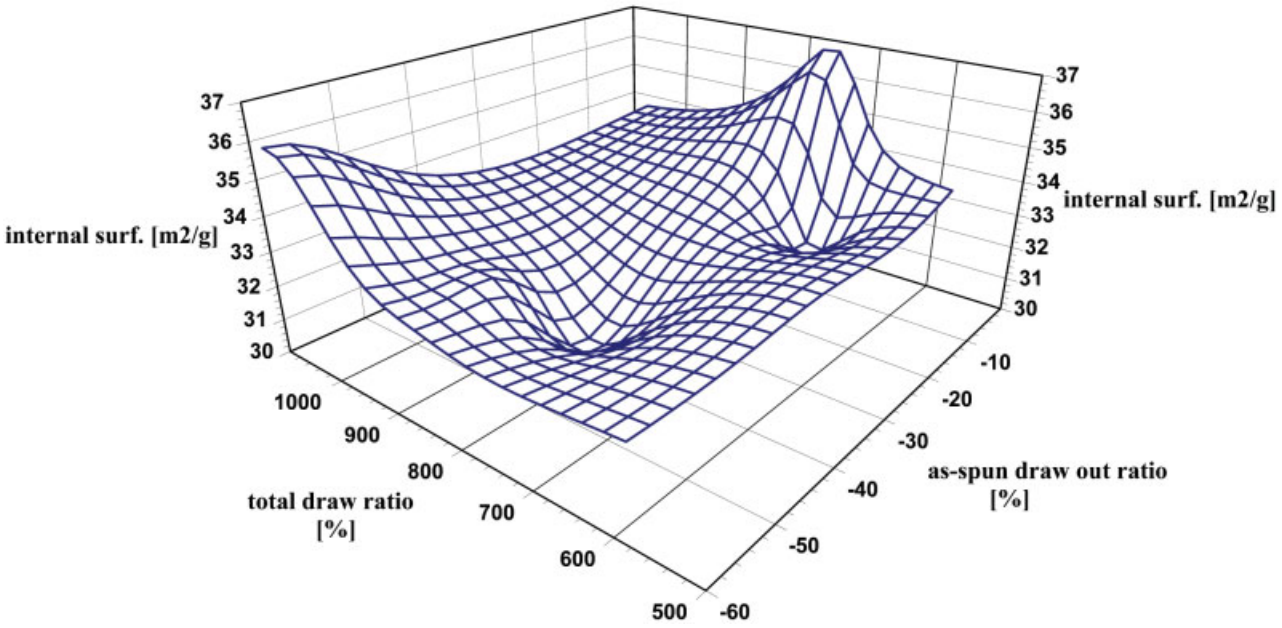

Figure 4 Dependence of the internal surface on the as-spun draw out ratio and the total draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

function of both the spinning process parameters (Fig. 3). A different character of changes in the internal surface (Fig. 4) corresponds with high contents of small pores in fibers formed with extremely negative values of as-spun draw out ratio. The range of changes in sorption properties (similarly in the previous test series) is narrow and limited to analogous limits. This is due to the formation of a porous structure with relatively minor differences in the total pore volume within the range from 0.125 to 0.26 cm^3/g.

Such an order of magnitude of this structural parameter does not justify one to regard these fibers as those with increased porosity. The sorption properties of fibers from a hydrophobic polymer depend on both the total pore volume and the character of porous structure.

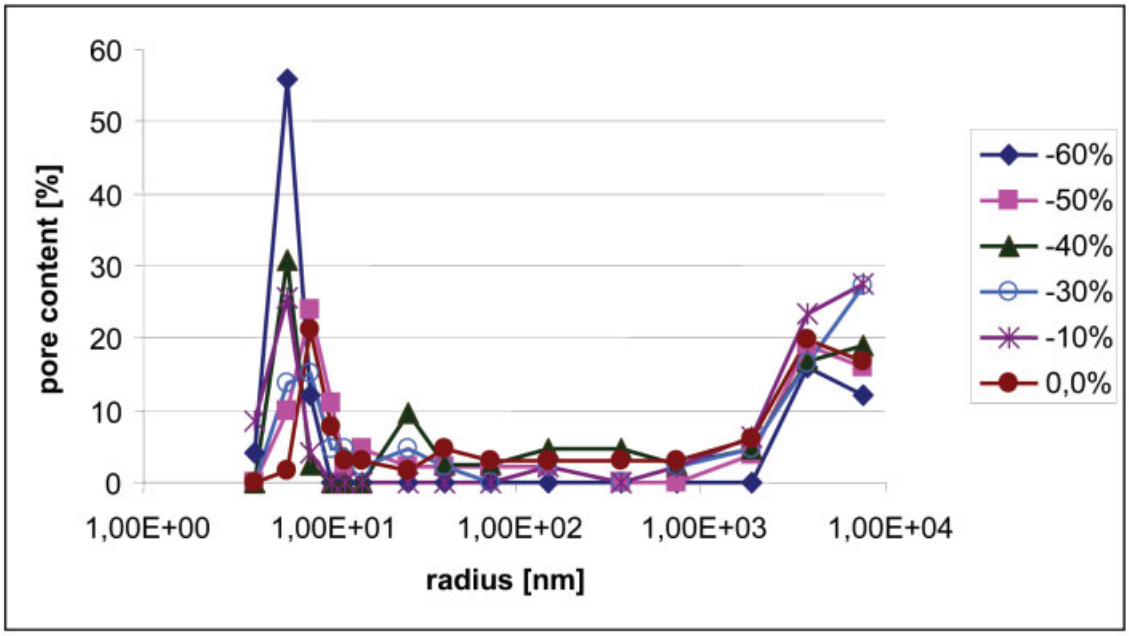

Figure 5 Dependence of the percentage content of pores on their radius. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Percentage Contents of Pores in Fibers Spun with Variable Values of the As-Spun Draw Out Ratio

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)
H5	−60	1074.0	72.00	0.0	0.0	28.00
H1	−50	887.6	47.23	11.59	2.33	38.82
H6	−40	887.6	33.33	14.28	11.90	40.48
H2	−30	583.9	37.91	9.09	4.54	48.46
H3	−10	717.3	38.30	0.0	4.26	57.44
H4	0	765.9	33.34	12.13	9.09	42.43

The pore distribution curves (Fig. 5) of fibers spun with variable values of as-spun draw out ratio are characterized by a clear maximum within the range of small pores and with limited contents of medium-sized and large pores, and they show a considerable content of very large pores that in extreme cases approaches 57% (Table IV). The content of very large pores is disadvantageous due to the fact that they can be a source of structural defects in carbon fibers obtained from such a precursor.

The formation of a considerable amount of this type of pores may also be due to the great capability of hydroxyapatite nanoparticles to agglomerate.

Generally, the formed porous structure, however, shows almost a fine-porous character. The total content of small and medium pores approaches 50%, expect for the fibers formed with an as-spun draw out ratio of –10%. On the other hand, when the value of as-spun draw out ratio is zero, the total pore volume and internal surface of fibers assume the highest values. A typically fine-porous character of structure is shown by the fibers spun with the extremely negative values of as-spun draw out ratio, which is clear when considering the use of generally quite mild spinning conditions. Such a structure is obviously accompanied by a high strength of fibers. At the same time, there is maintained the downward trend in the changes of this parameter with increasing as-spun draw out ratio, also found by us previously[22] (Fig. 6). This allows one to obtain higher values of the total draw ratio (Fig. 6). Generally, despite the presence of nonfiber-forming nanoparticles, PAN fibers with hydroxyapatite (formed within the whole range of process parameters) show an increased tenacity at a level of 31–38 cN/tex. The tenacity of these fibers is higher by about 12 cN/tex than that of PAN fibers containing silica nanoparticles, and in the extreme case (sample H5), it is very similar to the values obtained for PAN fibers without any additive of nanoparticles (over 43 cN/tex).[22] Thus, the incorporation of hydroxyapatite nanoparticles into the fiber-forming polymer has not decreased the fiber deformability to the extent observed in the case of PAN fibers containing silica nanoparticles.

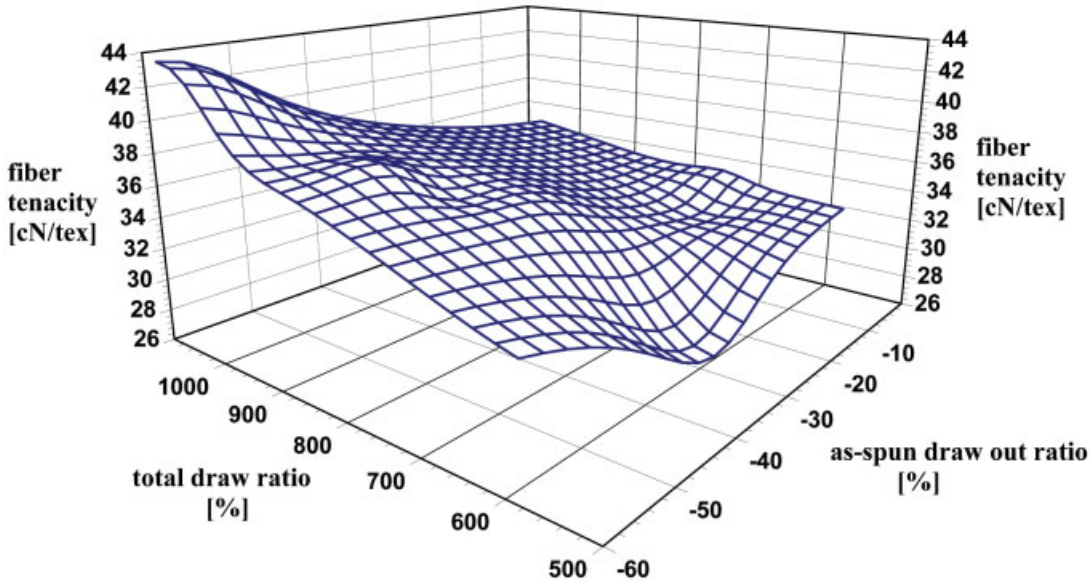

Figure 6 Dependence of fiber tenacity on the as-spun draw out ratio and the total draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

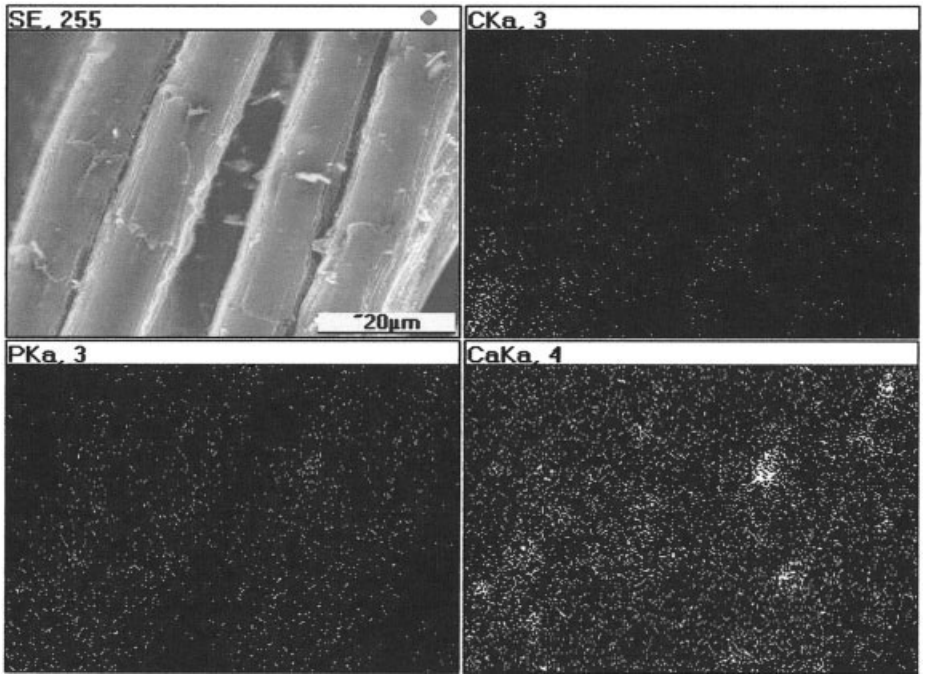

Figure 7 EDS analysis of PAN/HAp fiber surface.

Because of the requirements (concerning high strength and increased porosity) imposed on the precursors of carbon fibers designed for medical applications, the most beneficial conditions of fiber spinning are those that include the use of a mild coagulation bath containing 60% of solvent at a temperature of 15°C and moderately low values of as-spun draw out ratio. PAN fibers containing hydroxyapatite nanoparticles obtained under these conditions show a high tenacity at a level of 35.4 cN/tex, with the total pore volume increased only to 0.25 cm^3/g.

These fibers are characterized by very beneficial uniform distribution of non-hydroxyapatite in the polymer as confirmed by the ESM images (Fig. 7), illustrating the distribution of element such as C, Ca, and P. The appearance of greater clusters seen in the case of Ca may be connected with the tendency of the nanoadditive towards agglomeration.

Taking into account the fact that fibers with a high strength have been obtained, it is still possible to continue the modification of fiber-spinning conditions to increase fiber porosity through more beneficial pore distribution. It also seems possible to increase the content of hydroxyapatite in the fiber-forming polymer. The results of such examinations will be the subject of subsequent papers.

CONCLUSIONS

1. A process has been developed for the preparation of a new generation of PAN fibers containing hydroxyapatite nanoparticles, with the total pore volume at a level of 0.25 cm^3/g and a high tenacity of 35.4 cN/tex being suitable for the carbonization process.
2. The incorporation of hydroxyapatite nanoparticles into spinning solutions does not cause any significant decrease in the polymer susceptibility to deformation during the stage of plasticizing drawing.
3. The uniform distribution of hydroxyapatite nanoparticles in the precursor PAN fibers should be beneficial from the point of view of the stimulation of cell growth.

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