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# Effect of Fibre-spinning Conditions on The Properties of Nanosilica-containing Precursor PAN Fibres

**Abstract:**
*Conditions for spinning nanosilica-containing precursor polyacrylonitrile fibres have been developed. The effect of process parameters on the structure and properties of nanocomposite PAN fibres has been assessed, selecting the conditions for the manufacture of two types of precursor fibres with a higher strength or higher total pore volume. It has been found that the incorporation of silica nanoaddition into the fibres results in an increase in fibre porosity, with a simultaneous decrease in the content of the very large pores that cause structural defects in carbon fibres to be produced from these precursor fibres. The resultant carbon fibres will be designed for medical applications.*

**Key words:** *polyacrylonitrile fibres, nanoadditions, precursor fibres*

## Introduction

The modification of manufacturing conditions constitutes a basic procedure for adapting the properties of PAN fibres to their intended applications. Proper control of process parameters makes it possible to solidify fibres thanks to different mechanisms that allow different fibre structures and properties to be obtained. In combination with a proper drawing stage, this leads to highly porous fibres (for textile applications) or to high-strength fibres (precursor fibres) [1].

Entirely new features, without parallel in conventional fibres, can be obtained when the manufacture of fibres uses a nanocomposite whose fibre-forming polymer contains scattered various ceramic nanoparticles (e.g. $SiO_2$), metal oxides or metals [2].

Carbon fibres prepared from such a precursor will show unique properties connected with the type of the nanoaddition which is incorporated. Its selection depends on whether the application of carbon fibres is either technical or medical. In medical applications, it is important that the implant made from such fibres contain elements with osteoconductive and osteoproductive effects. Besides calcium and phosphorus, such a role is also played by silicon [3], which has been used in various forms in biomaterial engineering [4, 5, 6].

Classic precursor fibres should be characterised by high strength, and consequently by a high orientation of structural elements with limited porosity at the same time. On the other hand, when using carbon fibres for medical purposes, it is the increased porosity of precursor fibres that is preferred [7].

Carbon fibres prepared from such a precursor will show the same character of porous structure as that of precursor fibres [8], being simultaneously well assimilable by the mother cells of an organism as collagen fibres [7].

The incorporation of ceramic nanoparticles into a fibre-forming polymer also results in an advantageous increase in fibre porosity, as confirmed by us in other fibre-forming materials [9]. However, the presence of non-fibre forming nanoadditions in spinning solutions can change their rheological parameters [10], and decrease the polymer's susceptibility to deformation during the fibre drawing stage.

The aim of this work is to assess the effect of the basic fibre spinning parameters on the structure and properties of nanosilica-containing precursor PAN fibres, as well as to find out to what extent these properties depend on the incorporated nanoaddition.

An optimisation process, carried out with the use of a computer-aided experiment design system, will make it possible to develop precise conditions for spinning a new generation of precursor PAN fibres with increased porosity and of a strength suitable for carbonisation.

The conditions for manufacturing such precursor nanosilica-containing PAN fibres have not been reported in the literature as yet. It is foreseen that these fibres will be proper precursor fibres for the manufacture of carbon fibres that, while being used as implants, can support the process of bone reconstruction due to the presence of silicon.

## Characteristics of terpolymer and spinning solution

A PAN terpolymer (product by Zoltek) with the following composition was used for fibre preparation:

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

Dimethylformamide (DMF) was used as solvent. The size of the silica nanoparticles used in the experiments ranged from more than 10 to 50 nm (as determined from scanning microscope images). The characteristic of spinning solution determined separately [10] is given in Table 1.

## Fibre spinning

The fibres were spun from solution by the wet process using a spinneret with 500 orifices, each of 0.008 mm in diameter, and a laboratory spinning machine that allowed technological parameters to be stabilised at a predetermined level and continuously monitored.[1] The fibre solidification process was carried out in an aqueous bath containing a DMF solution in water, with a concentration dependent

***Table 1.*** *Characteristics of spinning solution.*

| Intrinsic viscosity η, dcL/g | Concentration of solution, % | Nanosilica content, % | Rheological parameter n | Rheological parameter K |
|---|---|---|---|---|
| 1.29 | 22 | 3 | 0.955 | 33.3 |

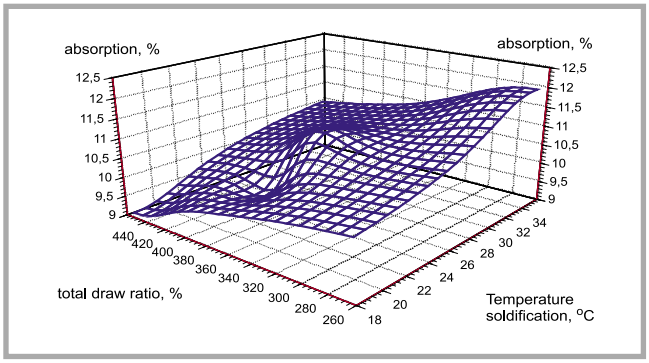


*Figure 1. Dependence of moisture absorption at 100% RH on the temperature of soldification bath and total draw ratio.*

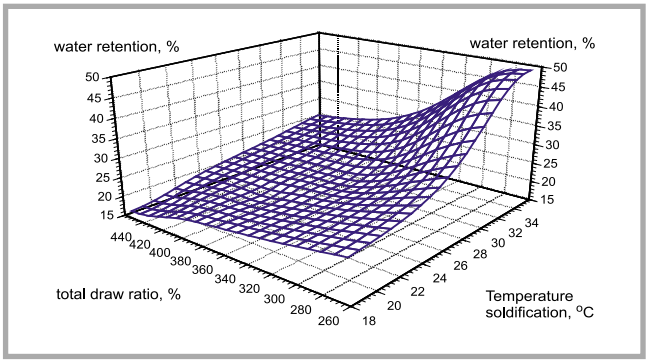


*Figure 2. Dependence of water retention on the temperature of soldification bath and total draw ratio.*

on the given series of experiments. The fibre drawing process was performed in two stages; in plasticisation and under superheated steam. After rinsing, the resultant fibres were dried at a temperature of 40°C under isothermal conditions.

## Measurement and test methods

Moisture absorption at 65% and 100% RH was measured in accordance with Polish Standard PN-71/P-04635. Water retention was determined by the centrifugal method. A sample of fibres was soaked with distilled water containing a surface-active agent (Rokafenol Nx-3 with a concentration of 0.1%) and left for 24 h. The sample was then centrifuged for 10 min at an acceleration of 10,000 $ms^{-2}$.

Fibre porosity was assessed by the method of mercury porosimetry, using a Carlo-Erba mercury porosimeter linked to a computer system that allowed the total volume of pores, the percentage content of pores with dimensions ranging from 3 to 7500 nm and the total internal surface of pores to be measured.

Fibre tenacity and elongation at break were determined according to Polish Standard PN-85/P-04761/04 with the use of an Instron tensile testing machine.

## Results and Discussion

The deformability of a fibre-forming material during drawing depends on the structure created in the fibre solidification process. Undoubtedly, the addition of non-fibre forming nanoadditives to the spinning solution causes this deformability to decrease. On the other hand, the present study was aimed at the preparation of precursor PAN fibres with increased porosity and a possibly high level of strength that would be suitable for the carbonisation process. Thus, in order to make these opposed tendencies compatible, preliminary experiments were required to assess the effect of the temperature of the solidification bath on the fibre's porous structure and properties. This is because temperature is a basic parameter, whose changes make it possible (according to the general principle of highly porous fibre formation) to shift from the diffusion mechanism to the dropwise mechanism [1].

Taking into account the boundary conditions of a stable fibre spinning process as determined during preliminary experiments, two series of experiments were carried out with a variable value of as-spun draw-out ratio ranging from –50 to +50% and related variable fibre deformation during the drawing stage.

In the first series, aimed at obtaining increased strength properties, the solidification process was carried out under typical mild conditions in a coagulation bath containing 60% of solvent at a low temperature of 16°C.

In the second series, aimed at preparing fibres with an increased porosity, the solidification process was performed in a bath containing 70% of solvent at a temperature raised to 23°C.

From the changes in sorption properties versus the temperature of coagulation bath and the total draw ratio (Figures 1 and 2), it follows that the increase in temperature results in both increased moisture absorption at 100%RH and considerably increased water retention of the fibres examined. Such changes in the fibres' absorption properties results from the fact that the mild coagulation bath was made severe by raising its temperature. The increase in temperature leads to the increase in the rate of diffusion processes, and the stream of diffusing non-solvent (water) gains more and more advantage over the stream of diffusing solvent (DMF) from the spinning solution stream introduced into the bath. Thus, the ration of both streams increases with increasing temperature. The value of this ratio influences the shape of the fibre cross-section and the increase/decrease in its size. As a rule, the increase in the coagulation bath temperature results in the latter phenomenon. The course of these processes also depends on the thickness and elasticity of the outer layer (skin), which is a kind of diffusion filter

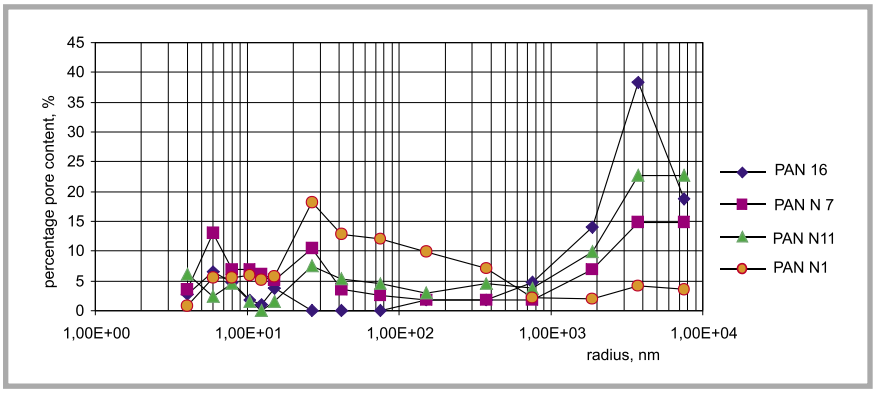


*Figure 3. Curves of pore distribution versus pore radius.*

***Table 2.*** *Characteristics of the porous structure of PAN fibres (spun under various conditions) containing silica nanoparticles in comparison to that of fibres without this addition.*

| Sample symbol | Total pore volume, $cm^3/g$ | Internal pore surface, $m^2/g$ | Percentage content of pores | | | |
|---|---|---|---|---|---|---|
| | | | Small 4-12.3 nm | Medium 12.3 - 75 nm | Large 75 - 750 nm | Very large 750 - 7500 nm |
| PAN N11 | 0.24 | 18.27 | 14.40 | 18.95 | 11.37 | 55.31 |
| PAN N1 | 0.60 | 63.78 | 22.79 | 48.52 | 19.05 | 9.63 |
| PAN N7 | 0.19 | 27.18 | 36.53 | 21.74 | 5.22 | 36.52 |
| PAN 16 | 0.15 | 10.25 | 16.81 | 3.74 | 8.41 | 71.03 |

PAN 16 – fibres without silica nanoparticles spun under the same conditions as sample PAN N7.

***Table 3.*** *Sorption and strength properties of nanosilica-containing PAN fibres.*

| Sample symbol | As-spun draw out ratio, % | Total draw ratio, % | Moisture absorption at 100% RH, % | Water retention, % | Tenacity, cN/tex |
|---|---|---|---|---|---|
| PAN N8 | -50 | 516.8 | 9.93 | 20.39 | 19.07 |
| PAN N7 | -20 | 546.9 | 9.70 | 16.39 | 26.73 |
| PAN N6 | 20 | 449.6 | 9.96 | 15.56 | 27.54 |
| PAN N5 | 50 | 443.3 | 20.21 | 20.21 | 25.19 |
| PAN 16 | 20 | 582.2 | 6.80 | 7.90 | 31.12 |

through which the processes of mass exchange pass.

The fibres spun at the highest temperature of the coagulation bath at a level of 35°C (PAN N1) show a total pore volume increased to 0.6 $cm^3/g$ with a very beneficial character of their distribution curve (Figure 3).

The porous structure produced under these conditions is characterised by a high total content of small and medium-sized pores, amounting to 71.3% with a content of very large pores limited to 9.3%; such large pores are a source of structural defects in carbon fibres (Table 2). Both the fine-porous character of the fibre structure and the limited content of very large pores are very beneficial, considering the fact that the precursor fibres are to be used to manufacture carbon fibres designed for medical applications.

However, the increase in the coagulation bath temperature from 18 to 35°C leads to an adverse drop in fibre tenacity from 23 cN/tex to 16 cN/tex for the highest temperature of solidification (Figure 4).

The fibre tenacity at the level mentioned above can be regarded as being the lower limit of fibre suitability for the carbonisation process. The temperature of 35°C can be thus treated as a boundary condition to be set for moderately mild coagulation baths. In order to obtain a higher fibre strength, it was decided to carry out the solidification process in milder baths with a solvent content increased to 60% and 70%.

From the analysis of the effect of the as-spun draw out ratio and the total draw ratio on fibre tenacity, it follows that the use of mild solidification conditions (series I), in accordance with the assumption, makes it possible to obtain a tenacity up to 27.5 cN/tex. The character of changes in this indicator versus the parameters examined shows an extreme course (Figure 5). High values of fibre tenacity are obtained with an as-spun draw out ratio of -20 and 20%. On the other hand, the lowest tenacities are shown by the fibres spun with the extremely negative and positive values of the as-spun draw out ratio. At the same time, these fibres show the highest values of moisture absorption at 100% RH in the series and water retention, respectively 9.9% and 20.3%. Generally, however, the range of changes in moisture absorption versus as-spun draw out ratio is low, at levels of 0.5% for moisture absorption at 100% RH and 5% for water retention (Table 3). As is seen, the changes in fibre strength and absorption versus the as-spun draw out ratio and the total draw ratio show contrasting trends (Table 3). The use of an as-spun draw out ratio of -20% is beneficial, as it allows one to obtain somewhat higher moisture absorption and simultaneously high fibre strength. The fibres spun under these conditions (sample PAN N7) show a fine-porous structure with a beneficial high maximum in the pore distribution curve within the range of small and medium pores (Figure 3). However, the total pore volumes at levels of 0.19 $cm^3/g$ and internal surface 27.18 $m^2/g$ do not explain why these fibres are included in the group of fibres with increased porosity. However, these values are higher than those for fibres without silica nanoparticles spun under the same conditions (Table 2).

Fibres containing nanosilica also show the beneficial character of pore distribution within the range of large/very large pores, in comparison with that of fibres without this addition (sample PAN 16). The content of very large pores in nanosilica-containing fibres has been reduced considerably, which is of great importance as these

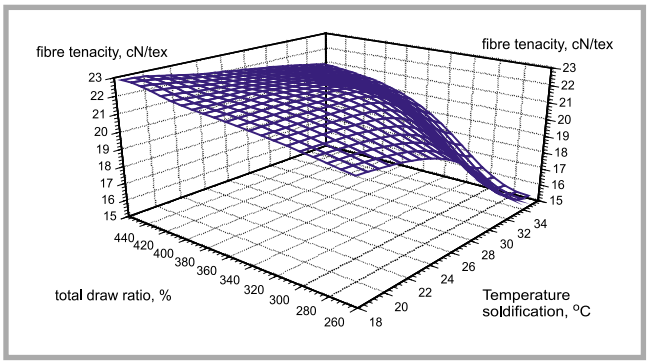


***Figure 4****. Dependence of tenacity on the temperature of soldification bath and total draw ratio.*

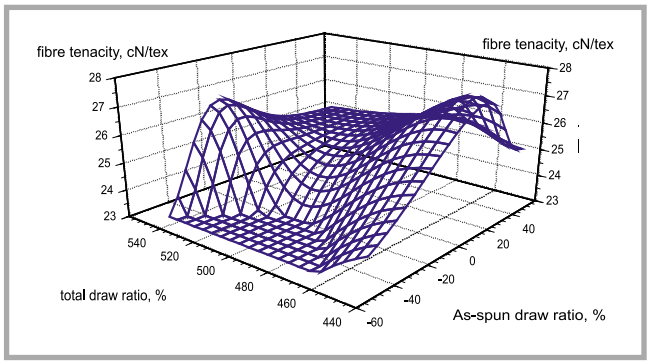


***Figure 5.*** *Dependence of tenacity on the as-spun draw out ration and total draw ration (concentration of soldification bath: 60%).*

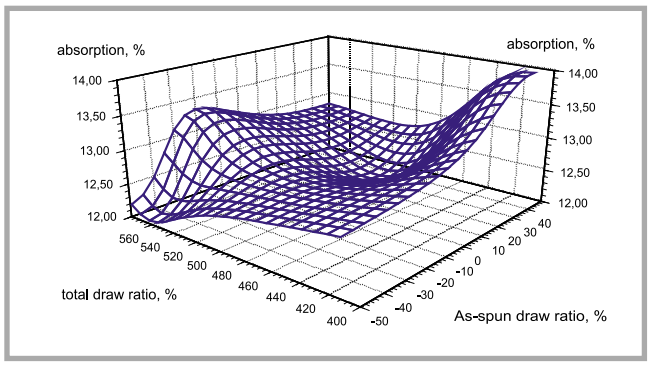


***Figure 6.*** *Dependence of moisture absorption at 100% RH on the as-spun draw ratio and total draw ratio (concentration of sodification bath 75%).*

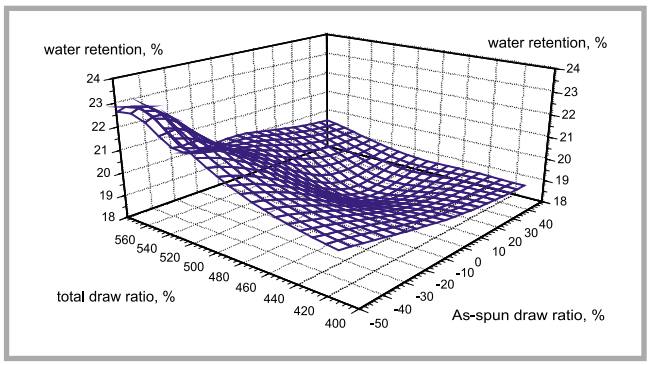


***Figure 7.*** *Dependence of water retention on the as-spun draw out ratio and total draw ratio (concentration of soldification bath 70%).*

fibres are designed for carbonisation.

However, the incorporation of nanosilica into the fibre-forming polymer results in the decreased deformability of such a polymer during the drawing stage. Fibres without nanosilica which are solidified under the same conditions could be subjected to considerably higher deformation during drawing, which resulted in their tenacity being higher by about 9.7 cN/tex (sample PAN N7). With similar deformations, the difference in tenacity values was about 4.4 cN/tex.

Analysing the effect of nanosilica on the character of the porous structure formed, we may assume that the difference in the total pore volumes as well as in the types of structure are associated with different courses of the solidification process.

With the same process parameters (temperature and bath concentration), the different courses of solidification were due to different coagulation capabilities of spinning solutions. The solution containing nanosilica coagulated to a 'weaker' degree, and the effect was thus similar to that under mild conditions of solidification. The structure created is typical for such solidification conditions, and being fine-porous it is characterised by a considerable content of small and medium pores (Table 2). Despite quite a low content of total pore volume and internal surface, this was connected with higher sorption values and twice as high retention. As is known [1], these indicators also depend on the character of the porous structure which is created. Hence the usefulness of these indicators is also important in the analysis of the properties of precursor fibres.

The use of milder coagulation baths under intensified solidification conditions by increasing their temperature up to 21°C (series II) resulted in fibres with increased porosity, and consequently increased moisture absorption. The moisture absorption at 100% RH shows an upward tendency versus the as-spun draw out ratio and the total draw ratio, reaching the highest value for the extremely positive as-spun draw out ratio (Figure 6). The different character of changes versus both parameters is shown by the value of retention (Figure 7). Generally, however, both parameters assume their values at a higher level, which is connected with a higher total pore volume, as well as with different contents of particular types of pores. The higher values of retention of 20-23% are connected with increased contents of large and very large pores within the initial portion of this range (sample PAN N11). The content of the latter, despite being undesirable, is however lower by about 22% than that for fibres without nanosilica (sample PAN 16).

The tenacity of 23.5 cN/tex is at an appropriate level for precursor fibres. As in the case of mild solidification conditions, the same effect of nanosilica is also observed on the decrease in fibre deformability during the drawing stage. The tenacity values of fibres without nanosilica are comparable in both cases. The fibres drawn with maximum deformations show a tenacity of 41-41.5 cN/tex, while the fibres drawn with the same deformations as those of nanosilica-containing fibres have a tenacity of 31.5 cN/tex (Figure 8).

From the comparative analysis of both series performed for variable values of as-spun draw out ratio and total draw ratio under different solidification conditions, it follows that the fibres containing nanosilica and spun under milder conditions are characterised by improved strength properties (with fine-porous structure) and decreased porosity in comparison to the fibres solidified in a milder bath, in which the coagulation conditions were made more severe by raising its temperature. In the second case, the fibres show a total pore volume higher by 1.4 times, and a tenacity lower only by 3 cN/tex, despite the fact that they have lost the fine-porous character of their structure.

Considering the requirements concerning increased porosity which have been imposed on the precursors of carbon fibres designed for medical applications, the following fibre-forming conditions can alternatively be regarded as beneficial:

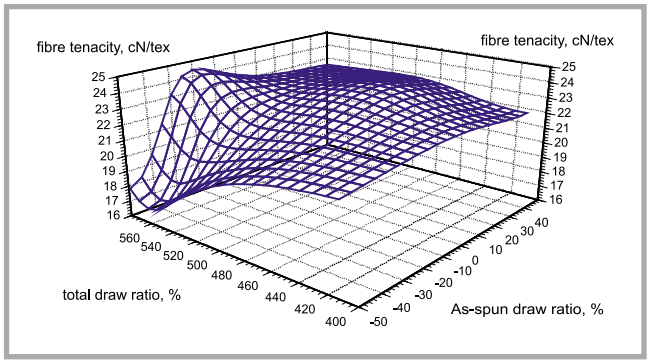


***Figure 8.*** *Dependence of tenacity on the as spun draw out ratio and total draw ratio (concentration of soldification bath 70%).*

*Table 4. The structural parameters and strength properties of the above precursor PAN fibres containing nanosilica and designed for carbonisation.*

| Sample symbol | Total pore volume, $cm^3/g$ | Internal pore surface, $cm^2/g$ | Tenacity, cN/tex |
|---|---|---|---|
| PAN N1 | 0.60 | 63.78 | 16.5 |
| PAN N11 | 0.24 | 18.27 | 23.4 |
| PAN 7 | 0.19 | 27.18 | 26.7 |
| PAN16 | 0.15 | 19.25 | 31.1 |

- the use of very mild coagulation baths (with a solvent content of 70%), in which the solidification conditions have been made severe by raising their temperature up to 21°C.
- the use of moderately mild coagulation baths (with a solvent content of 50%), in which the solidification conditions have been made more severe by raising the temperature up to 35°C.

The fibres spun according to the first variant are characterised by a tenacity of 23- 25cN/tex, with their porosity at rather a low level of 0.25 $cm^3/g$. The use of the second solidification principle makes it possible to obtain highly porous fibres with a total pore volume above 0.6 $cm^3/g$. Their tenacity of 16.5 cN/tex can be regarded as a boundary value that classifies the fibres for processing into carbon fibres.

The solidification of fibres under typical mild conditions (in coagulation baths with an increased solvent content and at low temperatures) makes it possible to obtain nanosilica-containing precursor PAN fibres with a tenacity increased to 26.5-27 cN/tex, and a total pore volume lower than 0.2 $cm^3/g$, but with a beneficial fine-porous structure and an internal surface at a level of 27 $m^2/g$.

The structural parameters and strength properties of the above precursor PAN fibres containing nanosilica designed for carbonisation are given in Table 4.

The final choice of proper precursor will be possible on the basis of in vivo tests of carbon fibres.

## Conclusions

- Conditions for manufacturing a new generation of precursor PAN fibres containing nanosilica have been developed. The fibres show an increased porosity and a tenacity that is suitable for the carbonisation process. As the final carbon fibres to be produced from the precursor will contain silicon, they should support the process of bone reconstruction.
- The control of parameters of the fibre-spinning process makes it possible to obtain precursor PAN fibres containing nanosilica with either an increased tenacity of 25 cN/tex and considerably lower porosity, or with an increased porosity, beneficial distribution of pores and a tenacity of 16 cN/tex that is at the limit of processing into carbon fibres.
- The addition of nanosilica into spinning solutions changes their coagulation capabilities, and decreases the deformability of the fibre-forming polymer during the plasticising drawing stage.
- The incorporation of nanosilica into precursor PAN fibres results in a beneficial increase in fibre porosity, and a simultaneous decrease in the content of very large pores that are a source of structural defects in carbon fibres.

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