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Influence of the As-spun Draw Ratio on the Structure and Properties of PAN Fibres Including Montmorillonite

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Abstract
We carried out an analysis of the influence of fibre-forming conditions by wet spinning PAN fibres which include montmorillonite (MMT), on the porous structure, sorption & strength properties of the fibres. The fibres obtained are characterised by a maximum tenacity pf up to 23 cN/tex at a low total pore volume. The presence of Si and Mg in the fibres was confirmed on the basis of images obtained with the use of a scanning electron microscope (SEM), equipped with an energy dispersion analyser of EDX radiation.

Key words: *polyacrylonitrille fibres, nano-additions, montmorillonite, wet spinning, tenacity, porosity.*

Introduction

Carbon fibres and composites including carbon fibres are one of the most widespread groups of biomaterials, which are used in traumatology and orthopaedics. At present, they are applied in the form of threads and rods to the reconstruction of knee joints [1, 2], Achilles tendons [3], and clavicular-shoulder ligaments. Their great biocompatibility and biodegradability allow for further development of this group of biomaterials, and an increase in competitiveness in relation to other polymer materials, such as polylactides [4] or materials obtained from polyglycole acid [5]. The application of different kinds of compounds supporting and stimulating the process of bone reconstruction as carriers in the structure of carbon fibres is one of the latest scientific solutions.

One interesting compound which displays such features is montmorillonite (MMT). By inserting MMT into the structure of polyacrylonitrile precursor fibres, it would be possible to obtain a new generation of carbon fibres, including an inorganic compound in their structure, which should stimulate the process of reconstruction for the connective tissues when the carbon fibres are used as implants. A review of the literature concerning carbon fibres and implants yielded no information about the manufacture of carbon fibres obtained from PAN fibres with MMT. The results of investigations into manufacturing PAN fibres including MMT would have an inventive and cognitive character justified by the information existing about MMT. This compound is commonly used in nano-addition, which should improve the mechanical and thermal properties of composites. It is also applied when obtaining biodegradable polylactides, and thus enables the manufacture of composites with good mechanical and thermal properties [7]. The usability of MMT in medicine, especially in orthopaedics, may be certified by the fact that MMT is a source of silicon and magnesium, chemical elements which manifest osteoconductive and osteoproductive actions.

Apart from the basic biological properties, which should be characterised by implants manufactured from carbon fibres, such implants should also have appropriate tensile strength and increased porosity. As the result of consultations carried out with researchers working on the carbonisation of fibres at the Department of Biomaterials, AGH Krakow, we assumed that the tenacity level of PAN precursor fibres including nano-additions must be about 25 cN/tex. The advantageous influence of fibre porosity, and the presence of another nano-addition in carbon fibres, on the process of tissue reconstruction has been confirmed in work [8]. Both the porosity and tensile strength of carbon fibres depends directly on their structure, and indirectly on the features of precursor fibres. Spinning PAN precursor fibres from solution by the wet method generally allows such a selection of the process parameters, which would ensure that the assumed properties were obtained [9,11].

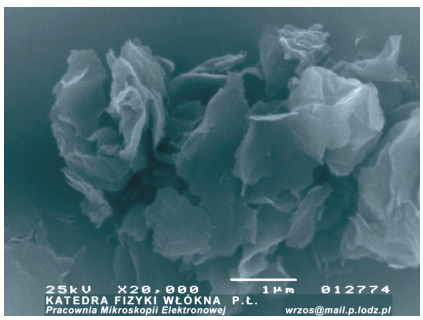

Figure 1. *Photo of montmorillonite (MMT).*

The aim of our research was to determine the influence of the basic process parameters – i.e. the as-spun draw ratio, and the value of the total draw ratio related to the given as-spun draw ratio (which approach the maximum value permitting the fibres to be drawn without disturbances) – on the features of a new generation of PAN precursor fibres, which include montmorillonite. This would allow us to select the most advantageous conditions for forming such PAN fibres, which would have a tensile strength of a level appropriate for carbonisation, namely a tenacity of 25 cN/tex, and the same level of increased porosity. Such fibres would in reality be precursor fibres for obtaining carbon fibres, which would then play an important part in bone surgery.

Materials and research methods

PAN-terpolymer from Zoltek (Hungary), of the following composition, was used for obtaining the fibres:

- 93-94% of weight ?meres of acrylonitrile,
- 5-6% of weight meres of methyl acrylate, and
- about 1% of sodium alilosulphoniane.

Dimethyl formamide (DMF) was used as the solvent.

'Nanomer PGW' montmorillonite, a commercial product of Nanocor, USA, was used for the investigation. The plate dimensions, determined on the basis of photographs obtained with the use of SEM, were within the area of 800 nm × 550 nm (Figure 1). The MMT used was

Table 1. *Characteristic of the spinning solution.*

Intrinsic viscosity η, dL/g	1.29
Concentration of PAN in DMF, %	**22**
Montmorylonite content, %	**3**
Rheological parameter n	**0.953**
Rheological parameter K	**29.9**

characterised by a layered structure with interlayer distances of about 2.3 nm; this were determined on the basis of the position of the first peak in X-ray diffraction patterns of the WAXS type. The X-ray investigations were carried out with the use of a Zeiffert diffractometer, as in work [12]. MMT was homogenised in DMF over 30 minutes at a temperature of 25 °C. The dispersions obtained in this way were added to the spinning solution during its preparing.

The rheological properties of the spinning solutions were assessed with the use of a Rheotest RV rotary rheometer. The measurements were performed within the range of shearing rates up to 146.8 1/s, at a temperature of 20 °C, using the H-cylinder. The n and K rheological parameters determined on the basis of the flow curves drawn in the logarithmic scale, and the characteristics of the spinning solution assessed on the basis of separate tests [13], are presented in Table 1.

The fibres were spun from solution by means of the wet method with the use of a spinning machine of extended laboratory scale [14], which allows for stabilisation of the technological parameters at the assumed level, as well as for continuous supervision and control. The detailed technological parameters are subject to a Polish Patent Application [15]. The change of the as-spun draw ratio was performed by changing the tangential velocity of the first pair of godets (at the output of the fibres from the coagulation bath). A spinneret with 240 orifices of 0.08 mm diameter was used, and the fibres, which were guided through the coagulation bath of a 60% water solution of DMF, were solidified at a temperature of 15 °C. The drawing process was carried out in two stages: in the plastification bath of a 50% water solution of DMF, and in overheated steam at a temperature of 135 °C. Next, the fibres were rinsed and dried within the temperature range of 20-40 °C under isometric conditions.

Moisture absorption at 100% relative humidity (RH) was assessed in accordance with Polish Standard PN-80/P-04635.

Water retention was determined by calculating the relation of the mass of water retained by the fibres after centrifuging the sample over 10 minutes at an acceleration of 10,000 ms^{-2} to the mass of the dry sample, in percent. The fibres were immersed before centrifugation in water with the addition of 1% Rokafenol NX-3 as a surface-active agent.

Fibre porosity was assessed by means of mercury porosimetry using a Carlo-Erba porosimeter linked to a computer system which enabled us to determine the total volume of pores, the percentage content of pores with dimensions ranging from 5 nm to 7,500 nm, and the total area of the pores' internal surface.

The tenacity of fibres was assessed for fibre bundles in accordance with Polish Standard PN-85/P-04761/04 with the use of an Instron tensile tester.

The montmorillonite presence in fibres was estimated on the basis of analysing the elements, which can be determined from pictures obtained by a JSM 5400 SEMr working together with an EDX LINK ISIS dispersion analyser with the characteristic radiation, produced by Oxford Instruments.

The total orientation coefficient was determined by the sonic method, by measuring the propagation velocity of the sonic wave in the fibre tested, and comparing the value obtained with the value characteristic for an isotropic fibre. The measurements were performed with the use of a PPM-5R Dynamic Modulus Tester by the Morgan Co. Inc., USA.

Discussion of the results obtained

The aim of our work was to obtain PAN precursor fibres (including montmorillonite) which would be characterised by appropriate strength features, allowing for further processing into carbon fibres, and by increased porosity. As resulted from our earlier investigations [16, 17] in obtaining PAN precursor fibres with other nano-additions, which are advantageous considering the fibres' strength properties, fibre solidification is conducted in a mild coagulation bath, which means at a temperature of 15 °C. Using such mild solidification conditions would be in accordance with conducting the process according to the diffusion mechanism, and obtaining a structure which would be susceptible to deformation during the drawing stage. The fibres obtained should be characterised by a regular fine-porous structure, with a limited number of large and very large pores, which are indeed structural defects.

Unfortunately, inserting montmorillonite in the fibre matter causes an impact decrease of the material's susceptibility to deformation during the drawing stage, when compared to fibres without a nano-addition (sample PW 1 in Table 2).

From the analysis of the fibre structure and the features of the fibres spun under various values of the as-spun draw ratio and various deformations during the

Table 2. *Structural parameters and features of PAN fibres with montmorillonite and of the reference sample without MMT; PM 1 – PM 7 fibres including 3% of MMT in relation to the polymer, PW 1, PW 2 fibres without MMT.*

Sample denotation	As-spun draw ratio, %	Total draw ratio, %	Area of internal pores surface, m^2/g	Total pore volume, cm^3/g	Degree of total orientation	Tenacity, cN/tex	Elongation, %
PM 1	-60	430.87	21.95	0.08	0.51	16.6	11.27
PM 2	-50	575.09	14.97	0.05	0.50	21.5	10.55
PM 3	-40	606.63	2.45	0.05	0.50	23.7	11.62
PM 4	-30	552.65	--------	-------	0.52	19.3	8.99
PM 5	-10	457.09	17.81	0.08	0.60	17.6	8.41
PM 6	0.0	422.14	35.35	0.18	0.52	16.1	7.52
PM 7	10	453.42	28.00	0.12	0.57	15.7	7.18
PW 1	-40	1054.03	33.24	0.24	0.79	47.3	11.51
PW 2	10	437.35	33.86	0.39	0.64	40.8	11.02

Table 3. Moisture sorption at 100%RH and water retention of PAN fibres including MMT.

Sample denotation	As-spun draw ratio, %	Total draw ratio, %	Moisture sorption at 100% RH, %	Water retention, %
PM 1	-60	430.87	6.20	14.83
PM 2	-50	575.09	6.90	14.19
PM 3	-40	606.63	6.30	10.95
PM 4	-30	552.65	7.58	17.39
PM 5	-10	457.09	7.23	18.69
PM 6	0.0	422.14	8.02	17.96
PM 7	10	453.42	7.83	18.84

drawing stage, it results that moisture sorption at 100% RH and water retention indicate increasing tendencies to change in the as-spun draw ratio towards higher values (Table 3).

In the case of fibres spun under negative values of the as-spun draw ratio, the differences between the values of moisture sorption at 100% RH of fibres including MMT, and those of fibres without MMT (sample PW 1 is characterised by the sorption at 100% RH of the level of 6.34%) are in principle not great. Slightly greater differences in moisture sorption occur when spinning the fibres under zero and positive as-spun draw ratios. Significantly greater differences occur in the case of water retention, which is smaller in the case of fibres without MMT, and amount respectively to 8.6% for fibres spun under negative as-span draw ratios (sample PW 1) and 13.3% for fibres spun under positive as-spun draw ratio (sample PW 2). The small range of changes in the sorption properties is firstly connected with the very poorly developed porous structure, which is characterised by relatively small differentiation of the total pore volume within the range of 0.05 cm^3/g to 0.18 cm^3/g, and the small value of the internal pores' surface area (Table 2). Such low fibre porosity is above all connected with conducting the solidification process in a mild coagulation bath at low temperature. We can expect that if the solidification conditions is made 'more severe' by increasing the bath temperature, the solidification mechanism will change from the diffusive to the droplet-mechanism, which is quite different; this would allow higher porosity values to be obtained.

It is also known [18] that the sorption properties of fibres which are spun from hydrophobic matter including other nano-additions significantly influence the character of the porous structure formed, and not the total pore volume alone.

The pore dimensions' distribution curves (Figure 2 and 3) of fibres with MMT addition, spun under various negative as-spun draw ratios (Figure 2), as well as under positive as-spun draw ratios (Figure 3), are characterised by the occurrence of a distinct maximum in the range of small- (pores with dimensions of 4-12.3 nm) and medium-sized pores (pores with dimensions of 12.3-75 nm); this explains the higher values of moisture sorption at 100% RH of these fibres compared to the fibres without MMT. On the other hand, the lower value of water retention in fibres without MMT (samples PW 1 and PW 2) are connected with the small contents of middle-sized pores from the upper end of the range, and large pores (pores with dimensions of 75-750 nm) from the beginning of this range, which are all able to retain water after it has been mechanically removed. At the same time, in the case of fibres without MMT, a clearly visible, disadvantageous maximum appears within the range of very large pores (pores with dimensions of 750-7,500 nm), which certify numerous structural defects. From the point of view of further processing the PAN fibres obtained, the decrease of large and very large pores is very advantageous, as it means the structural defects of the carbon fibres have finally been removed.

Inserting MMT into the fibres caused a decrease in the fibres' tenacity of over 50%, when compared with fibres without MMT (Table 2). Such a decrease of tenacity may be connected not only with a worse susceptibility to deformation during drawing, but most probably also with agglomerations of montmorillonite packs which occur in the fibre matter, since the obtention of increased strength features of nano-composites [6] is connected with the process of MMT exfoliation in the polymer matrix. An explanation of the influence of the dispersion kind of MMT in the fibre matter (exfoliation or intercalation) on the strength properties of PAN fibres is the subject of another publication [19]. The influence of various nano-additions on the crystalline structure of fibres on the basis of WAXS X-ray investigations is also discussed in that paper.

As in our previous works [16, 17], the significant influence of the basic parameters of the spinning process is visible, namely, the as-spun draw ratio and the total draw ratio on the tenacity and elongation at break. We obtained the highest tenacity

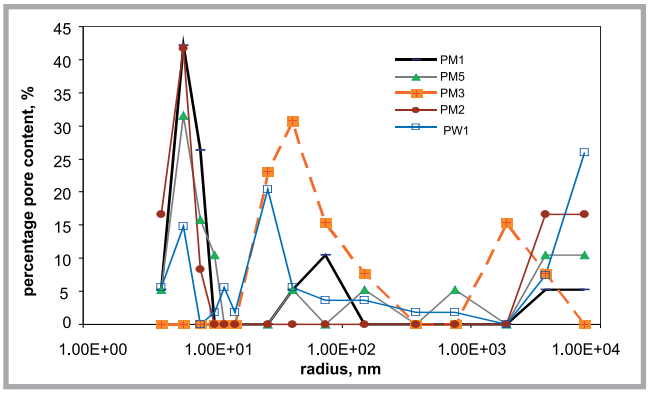

Figure 2. Dependence of the percentage pore content on the pore radius, presented in logarithmic scale, for fibres spun under negative as-spun draw ratio.

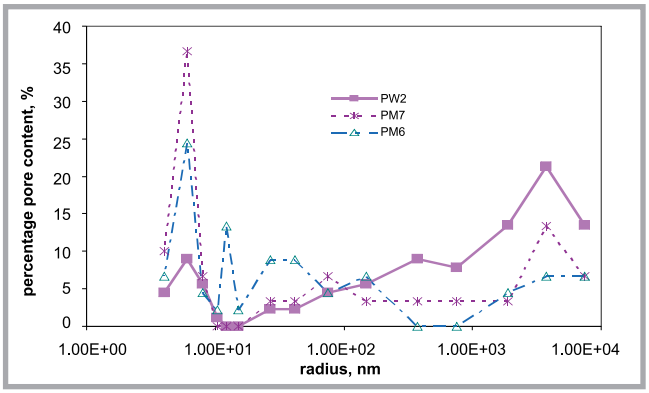

Figure 3. Dependence of the percentage pore content on the pore radius, presented in logarithmic scale, for fibres spun under positive as-spun draw ratio.

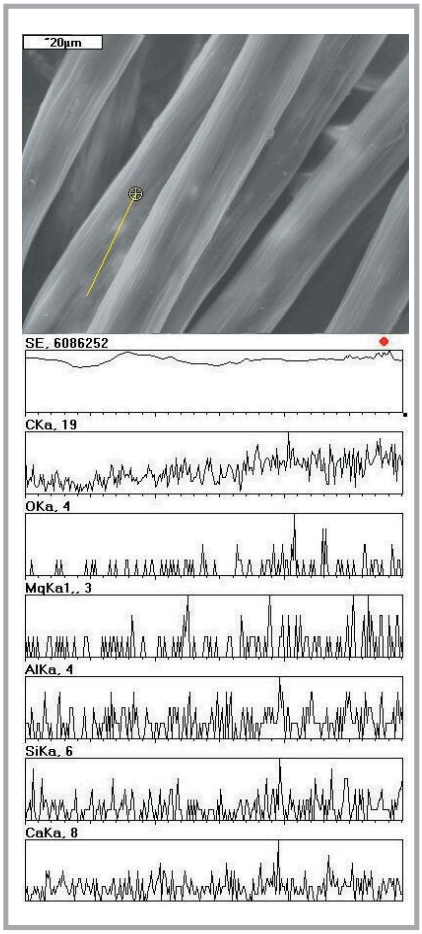

Figure 4. *SEM photo of PAN fibres with MMT, and the distribution of selected elements along the fibre segment indicated in the photo; the following elements are indicated (from above): S, C, O, Mg, Al, Si, and Ca.*

values under an as-spun draw ratio of -40% (Table 2). In contrast, the lowest values of tenacity were displayed by fibres spun under the mostly negative and the positive values of the as-spun draw ratio. This relation is not unexpected, as it is known [14] that applying positive values of the as-spun draw ratio does not create favourable conditions for obtaining increased strength properties. Exceeding the negative border limit of the as-spun draw ratio is connected with a decrease in of the fibres' strength features. This results from the shape of the 3-D dependency of tenacity on the as-spun draw ratio and the total draw ratio, which is characterised by a maximum, as we observed in our previous investigations [16, 17].

The changes of strength properties as a function of both process parameters is in accordance with the decrease of the total orientation determined by the sonic method, based on the relation of the sonic wave propagation velocity in the tested fibre to the respective velocity in a non-oriented fibre. Fibres without MMT spun under both negative and positive values of the as-spun draw ratio are characterised by significantly higher values of the total orientation degree, as in fibres with MMT (Table 2). An influence on the value of this factor is held not only by porosity, but also the presence of the layered nano-addition, which is an obstacle for the propagation of the sonic wave. This was why we only considered this method as a comparative method for the fibres spun under various as-spun draw ratios.

The presence of montmorillonite in the fibres is confirmed by the images obtained by the SEM linked with a X-ray analyser, which identify the presence of such elements as Si, Mg, and Al in the fibre matter (Figure 4). However, the amounts of these elements along the fibre segment tested are small, as is indicated by the small differences in the peaks of the EDX analysis. This is caused by the amount of MMT introduced into the fibre-grade matter (3% in relation to the polymer mass).

Considering the significant decrease in tenacity of the fibres with MMT, compared with those without MMT, as well as the very low total pore volume, further modification of the spinning process conditions is necessary. The modification should be directed to reconcile the two opposing tendencies of the total pore volume influence and the porosity character on the fibres' tenacity. The results of these investigations will be the subject of a subsequent publication.

Conclusions

1. Notwithstanding the mild conditions of solidification, the PAN fibres with montmorillonite obtained, with small total pore volume, are characterised by a tenacity slightly below the value of 25 cN/tex which we accepted. This is caused by a significant decrease in the susceptibility to deformation at the stage of drawing by the fibre matter which includes dispersed non-fibre-grade MMT.

2. With the presence of MMT in the fibre-grade matter, an advantageous change in the porous structure is connected, manifested by a decrease in very large pores, which are the source of structural defects in carbon fibres.

Acknowledgment

We would like to thanks Mrs. Kamila Wrońska for putting her test results at our disposal, which were concerned with the fibres' sorption properties and total orientation obtained within the scope of her M.Sc. thesis, a research work financially supported within the frame of grant 3T08E03328.

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Received 29.11.2005 Reviewed 20.01.2006