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PAN Precursor Fibres Containing Multi-Walled Carbon Nanotubes

Abstract
The spinning conditions of wet spun polyacrylonitrile (PAN) fibres containing multi-walled carbon nanotubes (MWCNTs) were investigated. On the basis of images from a transmission electron microscope, it was shown that the MWCNTs are well dispersed in the fibre matrix as well as straightened and oriented in the direction of the fibre axis. The presence of MWCNTs in the fibre matter caused an increase in the crystallinity of the precursor fibres and a decrease in their porosity. The tenacity of the composite fibres was lower than that of pure PAN fibres, which was caused by the fact that carbon nanotubes hindered deformation in the drawing stages, resulting in a lower draw ratio possible to be obtained of composite fibres compared to standard fibres. For the PAN precursor fibres obtained a two stage carbonisation process was conducted: The first stage was conducted in an oxidative atmosphere (at 140 °C for 5 hours and then at 200 °C for 6 hours in air). The second stage was conducted in an inert atmosphere (at 1000 °C for 5 minutes in argon atmosphere). The strength of carbon fibres containing MWCNTs obtained shows, in the majority, no significant differences in comparision to reference fibres without MWCNTs. However, the tensile strength was lower.

Key words: *precursor fibres, carbon fibres, PAN, carbon nanotubes, fibre spinning conditions.*

Introduction

Since the 1960s, when the first carbon fibres became commercially available, dynamic growth in their production has been observed worldwide. This is due to the fact that carbon fibres are perfect construction materials, for example for the space, aerospace and motor industries, in view of their characteristic properties: high strength properties (stress at break and Young's modulus) and low density.

Carbon fibres are manufactured mainly through the pyrolysis of carbon-rich organic fibres; however, they can also be obtained by the pyrolysis of carbonaceous gases. It is then possible to make staple carbon fibres [1] or yarn from carbon nanotubes by direct spinning [2 - 4]. However, only carbon fibres obtained by the pyrolysis of organic fibres have so far been produced commercially; the most important organic fibres for this purpose are polyacrylonitrile fibres, coal-tar pitch fibres and cellulose fibres. Due to the distinct chemical structures and properties of the respective types of precursor fibres, the resulting carbon fibres also have different properties. High-strength carbon fibres manufactured from a PAN precursor have a high strength of up to 7 GPa and Young's modulus of 294 GPa – Toray T100 [1]. High-modulus fibres from PAN precursors, in turn, have a strength of 2.5 GPa and Young's modulus of 500 GPa – Toray M50 [1]. Similar strength and Young's modulus values are recorded for carbon fibres based on cellulose fibres (strength: 2.5 GPa, Young's modulus: 517 GPa for Amco Corp. Thornol 75) and for those based on coal-tar pitch fibres (strength: 2.2 GPa, Young's modulus: 820 GPa for Amco. Corp. Thornol P120) [1].

However, it is notable that the strength of currently available carbon fibres is only a fraction of their theoretical strength, assumed to be 1/10 of the Young's modulus value for a material [5]. It is expected that further development of carbon fibres will take place involving obtaining fibres with improved mechanical properties with the use of nanotechnology. In this field composite PAN fibres containing carbon nanotubes (CNT) as precursors for carbon fibres can be used. In the case of PAN fibres containing CNT formed using a dry-wet method, it has been possible to obtain higher-strength precursor fibres in comparison with those without CNT [6,7]. A similar effect was noted for carbon fibres obtained from PAN fibres formed by the wet method from solution [8], by the gel method [9, 10] and from PAN microfibres [11]. A significant increase in strength was also observed for carbon fibres obtained from coal-tar pitch following the incorporation of CNT into the precursor fibre material [12, 13].

Therefore in the present study we tested the effect of manufacturing conditions and the presence of MWCNTs on the structure and properties of precursor PAN fibres obtained using the solution wet spinning method, and of the resulting carbon fibres. The aim of this was to verify the potential of obtaining precursor fibres containing MWCNTs using standard polymer and technology used for the manufacturing of textile fibres. The selection of MWCNTs was carried out on the basis of our previous works in which we investigated the influence of the type of carbon nanotubes on the proprties of PAN fibres [14, 15]. The manufacturing method used in the work for obtaining precursor fibres is one of the most efficient and most widespread methods for the industrial production of precursor PAN fibres. In this study we also tested the effect of the as-spun draw ratio on the structure and properties of precursor PAN fibres over a wide range of parameter values. When highly negative as-spun draw ratios are used, this is favourable for the manufacturing of high-strength PAN fibres [16]. Fibre structures formed in such conditions lead to favourable fibre strength properties at the drawing stage. On the other hand, when highly positive as-spun draw ratios are used, porous (surface-defective) fibres form due to fibre skin cracking under high reception forces. We nonetheless believe that high as-spun draw ratios may contribute to more favourable orientations of carbon nanotubes with respect to fibre axes due to a high longitudinal speed gradient in the zone outside the spinneret, which should result in the increasing tenacity of fibres.

Experimental

Materials

A polyacrylonitrile (PAN) therpolymer under the trade name Mavilon (Zoltek, Hungary) was used for the preparation of spinning solutions. The therpolymer was composed of 93 - 94% wt of acrylonitrile mer units, 5 - 6% wt of acrrylate methyl mer units, and 1% wt of alilosulfonian mer units.

Dimethylformamide (DMF) from POCH (Poland) was used as the solvent. As spinning solutions, 22% PAN solutions in DMF containing 1% of MWCNTs per mass of polymer were used.

Multi-wall carbon nanotubes commercially available from Nanostructured & Amorphous Materials Inc. (USA) were used in the experiments. According to the manufacturer, the MWCNTs have high purity (multi-wall carbon nanotubes > 95%, amorphous carbon < 3%, Ni 0.12%, La 0.06%, silica 0.02%), a length in the range 1 – 2 μm, and diameter in the range 10 – 30 nm. The nanotubes were selected based on experimental results reported in [14, 15]. Nanotube images are shown in ***Figure 1***.

Carbon nanotube images were recorded using an FEI Nova NanoSEM 200 scanning electron microscope (SEM) and FEI TECNAI SuperTWIN FEG (200kV) transmission microscope (TEM).

Sample preparation

Fibres were obtained by the wet spinning method using a large laboratory spinning machine. Its design enables the process parameters to be varied over a wide range, stabilised and constantly controlled. The drawing systems provide smooth adjustment of the fibre linear speed and its stabilisation at a desired level between 0.5 and 33 m/min.

The process of PAN fibre soldification was carried out in a coagulation bath which contained water-DMF composition (40:60) at 15 °C.

The drawing process involved two stages: In the first stage, fibres were drawn in a plastification bath (water-DMF 50:50; 70 °C), while in the second drawing occurred in superheated steam at 135 °C.

After the drawing process, the fibres were collected continuously and cross-wound onto a reel. Subsequently the fibres were rinsed and dried at 25 °C in isometric conditions.

Fibre carbonisation was carried out for selected samples. Oxidation involved two stages: the first stage at 140 °C for 5 hours and the second at 200 °C for 6 hours in air. The process was carried out in a low temperature furnace. The heating rate in the oxidation process was 5 °C/min.

The carbonisation process was carried out at 1,000 °C for 5 minutes in an argon atmosphere in a tube furnace, the heating rate of which was 5.5 °C/min.

Research methods

As-spun draw ratio - defines the deformation of the polymer solution stream in a coagulation bath (the relationship between the speed of the polymer solution in the spinneret nozzle and that of the collection of as-spun fibres - fibres before the drawing process).

$$A_R = \left(\frac{V_C - V_S}{V_S} \right) \cdot 100\%$$

A_R – as-spun draw ratio,
V_C – speed of collection of as-spun fibres,
V_S – speed of polymer solution in spinneret nozzle.

Draw ratio - defines the deformation of fibres subjected to the drawing process.

$$R = \left(\frac{V_2 - V_1}{V_1} \right) \cdot 100\%$$

R – draw ratio,
V_1 – speed of fibres on the first pair of drawing geodets,
V_2 – speed of fibres on the second pair of drawing geodets.

Total draw ratio – defines the deformation of fibres in two-stage drawing process.

The tenacity was determined for a fibre bundle according to the PN-EN-ISO-268:1997 standard using an INSTRON strength tester.

$$T = \frac{F}{T_t}$$

T – tenacity, cN/tex,
F – breaking force of fibres, cN,
T_t – linear mass density of fibres – defined as the mass in grams of 1000 meters of fibres

The stress values under which the drawing processes of fibers were implemented were calculated as the ratio of the forces under which the drawing process was carried out and the linear mass of fibres. The force measurement was implemented with the use of a Mesdan Lab ETB-500 tensiometer with a tension range from 1 to 500 cN and accurancy at a level above 1% of the full range of the scale (Italy).

Fibre porosity was determined using mercury porosimetry with a CE Instruments Pascal 440 porosimeter coupled with a computer system, which can determine the total pore volume, pore size distribution (range: 5 – 7500 nm) and total internal area of pores. This technique allows to get results with an accurancy at the level of about 4% (UK).

The degree of crystallinity and size of crystalline areas were determined by wide-angle X-ray scattering (WAXS). The testing was carried out using a Seifert URD 6 diffractometer according to the method described in [15]. The technique used for crystallinity measurements allows to get results with an accurancy at the level of 3% (Germany).

The compensation stress of the fibres was measured using a TA Instruments DMA Q800 dynamic thermomechanical analyser (DTMA). The testing involved measurements of fibre stress on heating to 150 °C in isometric conditions [17] (USA).

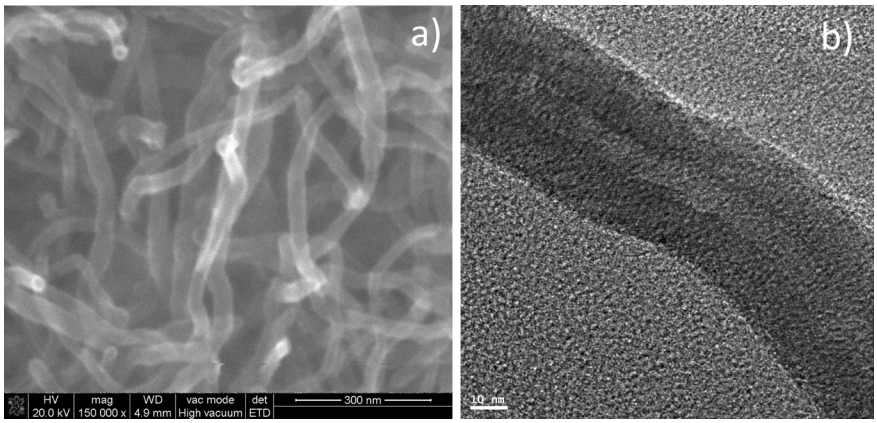

Figure 1. *Images of the multi-wall carbon nanotubes used in the experiments, recorded using (a) SEM, (b) TEM.*

The mechanical properties of carbon fibres were measured using elementary fibres with a Zwick model 1435 strength tester (Germany).

The distribution of carbon nanotubes in the PAN fibre material was analysed based on images recorded using an FEI TECNAI SuperTWIN FEG (200kV) (USA) transmission microscope. Thin-foil preparations for transmission microscope observations were obtained using a LEICA microtome (fibers embedded in the matrix were cut into slices at a pitch of 50 nm) (Germany).

Observations were carried out using diffraction contrast in the bright field mode and with phase contrast (High Resolution Electron Microscopy, HREM).

Thermal properties were determined based on DTA and TG analyses. Thermal measurements were carried out using a TA Instruments SDT 2960 tester (USA), which enables simultaneous measurements of sample mass changes (TG curve) and recording of thermal effects (DTA curve) associated with the changes. Samples weighing approx. 5 – 6 mg were placed in cylindrical platinum crucibles and heated at a linear temperature increase of 10 °C/min. The measurements were conducted in an oxidising atmosphere (synthetic air, water content < 15 ppm) at a flow rate of 100 cm^3/min.

A QMD 300 ThermoStar quadrupole mass spectrometer (Bazlers) with an ion source (70 eV) was used for the analysis of gaseous decomposition products. The spectrometer was coupled on-line with the SDT apparatus by a heated quartz capillary (up to 200 °C), enabling gaseous decomposition products to be recorded upon their formation. Measurements were also conducted using the scan system (ionic currents were recorded for M/z values in the range 10 – 50).

Table 1. *Spinning conditions and fibre properties CT 1 - 13: fibres with 1% MWCNTs; C 1 - 4: reference fibres.*

Sample symbol	As-spun draw ratio, %	Draw ratio, %		Total draw ratio, %	Tenacity, cN/tex	Elongation at break, %
		plastification bath	steam			
CT 1	-60	314	155	957	41.82 ± 1.27	14,66 ± 0,77
CT 2	-50	312	142	896	40.58 ± 1.02	14,22 ± 0,43
CT 3	-40	266	163	862	42.55 ± 1.66	12,88 ± 0,55
CT 4	-30	267	165	873	41.69 ± 1.76	12,77 ± 0,53
CT 5	-20	269	152	831	40.98 ± 1.75	12,44 ± 0,51
CT 6	-10	243	162	799	37.26 ± 1.33	11,91 ± 0,49
CT 7	0	245	166	816	37.67 ± 1.16	11,15 ± 0,42
CT 8	+10	226	181	817	36.44 ± 1.23	10,40 ± 0,35
CT 9	+20	235	175	822	36.38 ± 2.23	10,09 ± 0,53
CT 10	+30	238	165	796	37.02 ± 1.75	10,41 ± 0,39
CT 11	+40	221	161	740	36.86 ± 1.57	9,92 ± 0,41
CT 12	+50	224	148	705	32.09 ± 1.61	9,61 ± 0,51
CT 13	+60	227	146	704	32.94 ± 1.64	9,41 ± 0,44
C 1	-60	386	152	1128	51.19 ± 1.97	13,69 ± 0,52
C 2	-40	366	140	1019	47.61 ± 1.90	12,38 ± 0,49
C 3	-20	313	151	939	45.31 ± 1.74	11,17 ± 0,49
C 4	+60	251	133	719	35.45 ± 1.46	9,81 ± 0,61

Results and discussion

On the basis of the research results it can be stated that the stress involved in the fibre soldification process increases as the as-spun draw ratio changes from negative to positive values (***Figure 2***). This is

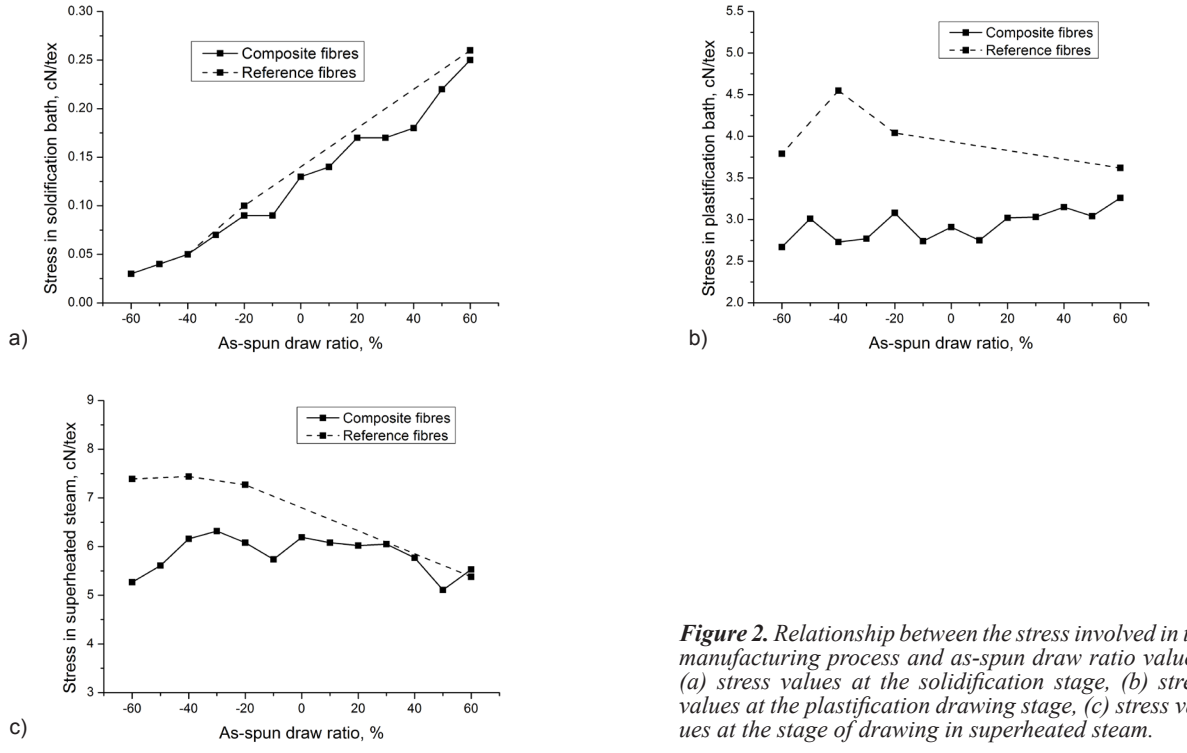

Figure 2. *Relationship between the stress involved in the manufacturing process and as-spun draw ratio values: (a) stress values at the solidification stage, (b) stress values at the plastification drawing stage, (c) stress values at the stage of drawing in superheated steam.*

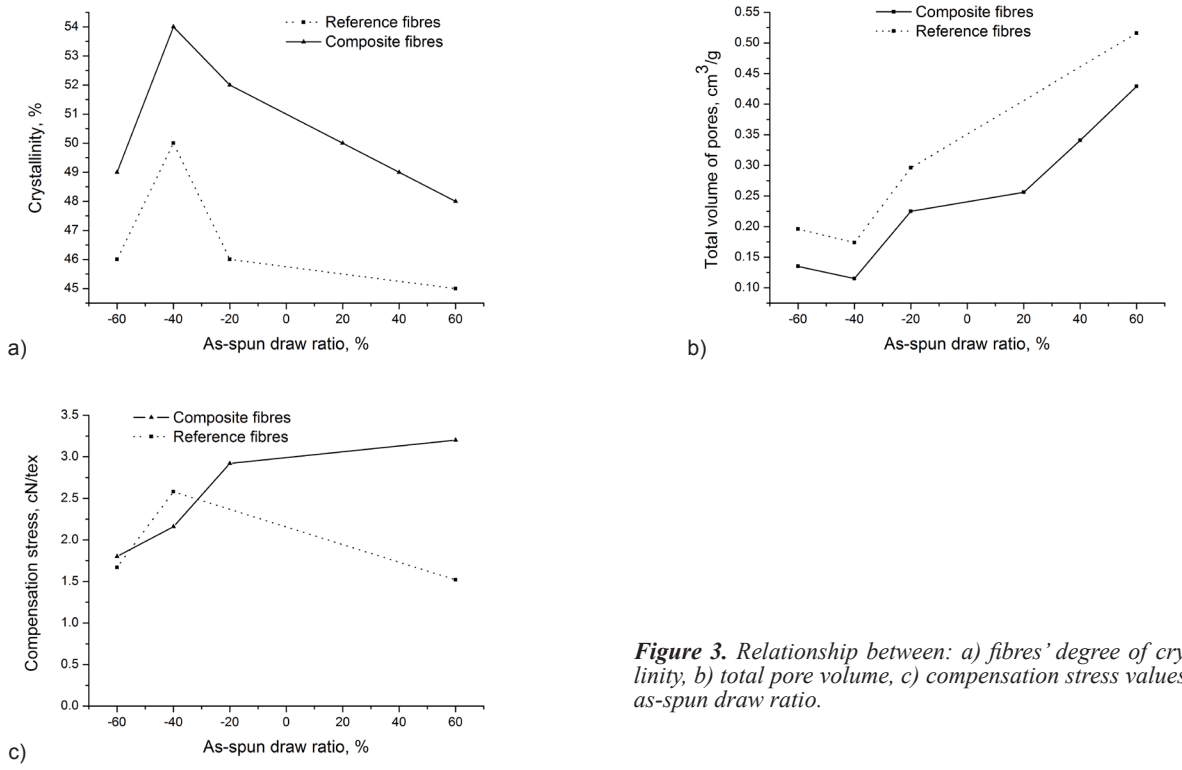

Figure 3. *Relationship between: a) fibres' degree of crystallinity, b) total pore volume, c) compensation stress values and as-spun draw ratio.*

related to the collection force acting on the fibres, which can be applied to both fibres containing carbon nanotubes and those with pure PAN fibres.

Depending on the as-spun draw ratio values used, as-spun fibres had different structures, which became evident at the drawing stage. The draw values in the plastification bath achievable for fibres formed using extremely negative as-spun draw ratios were the highest within the experimental series under investigation. When the as-spun draw ratio changed towards positive values, the fibres became less susceptible to deformation processes (***Table 1***), which was seen for both composite fibres and pure PAN fibres. It is notable, however, that the total draw ratio values achievable and stress values involved in the drawing process for fibres with MWCNTs were significantly lower than for reference fibres, which may indicate that the carbon nanotubes incorporated into the material hindered the fibre drawing process. This in turn may be substantiated by the fact that lower deformation values at the plastification drawing stage, associated with as-spun draw ratios changing from negative to positive values, were accompanied by an increase in the stress involved in the drawing process. This may suggest that carbon nanotubes were incorporated into the fibres in an oriented fashion when positive as-spun draw ratios were used, and thus increased the strength of the as-spun fibres.

It was noticed, based on the evaluation of the drawing process in superheated steam, that the resulting deformation values for both nanocomposite fibres and those without nanoadditives were similar (***Table 1***). Furthermore the stress involved at this stage for fibres without MWCNTs was slightly higher than for the composite fibres (***Figure 2***).

It follows from the investigation of strength properties of the resulting fibres that changes in the as-spun draw ratio from positive to negative values led to higher fibre tenacity, related to the increase in the total draw ratio achievable in both drawing stages (***Table 1***). It is notable that tenacity values for fibres containing carbon nanotubes were lower compared to those without nanoadditives, most likely caused by the incorporation of carbon nanotubes into the fibre structure at the solidification stage, which hinders deformation processes at the drawing stage and leads to lower strength properties. Furthermore the highest differences in fibre strength are seen for fibres spun at an as-spun draw ratio of -60% (nanocomposite fibres 41.82 cN/tex, reference fibres 51.19 cN/tex), and the lowest for fibres spun at an as-spun draw ratio of +60% (nanocomposite fibres 32.94 cN/tex, reference fibres 35.45 cN/tex). This may result from the fact that a high longitudinal speed gradient for fibres spun using highly positive as-spun draw ratios may lead to the orientation of nanotubes along the fibre axis. Therefore such nanotubes most likely do not constitute a hindrance at the drawing stage, which is evidenced by the fact that the difference in total draw ratio values between nanocomposite and reference fibres was 15% for fibres spun at an as-spun draw ratio of +60%, while the difference in tenacity was 2.5 cN/tex. These differences were approx. 170% and approx. 10 cN/tex, respectively, at an as-spun draw ratio of -60%.

On the basis of the analysis of elongation at break values, it can be stated that with a change in the as-spun draw ratio from positive to negative values, the value of the elongation at break increases. The presence of carbon nanotubes causes no significant changes in elongation at break values in comparison to the reference fibres.

It follows from our supramolecular structure studies that irrespective of the fibre spinning process conditions used, fibres containing MWCNTs have higher crystallinity values compared with reference fibres (***Figure 3.a***). The effect of an in-

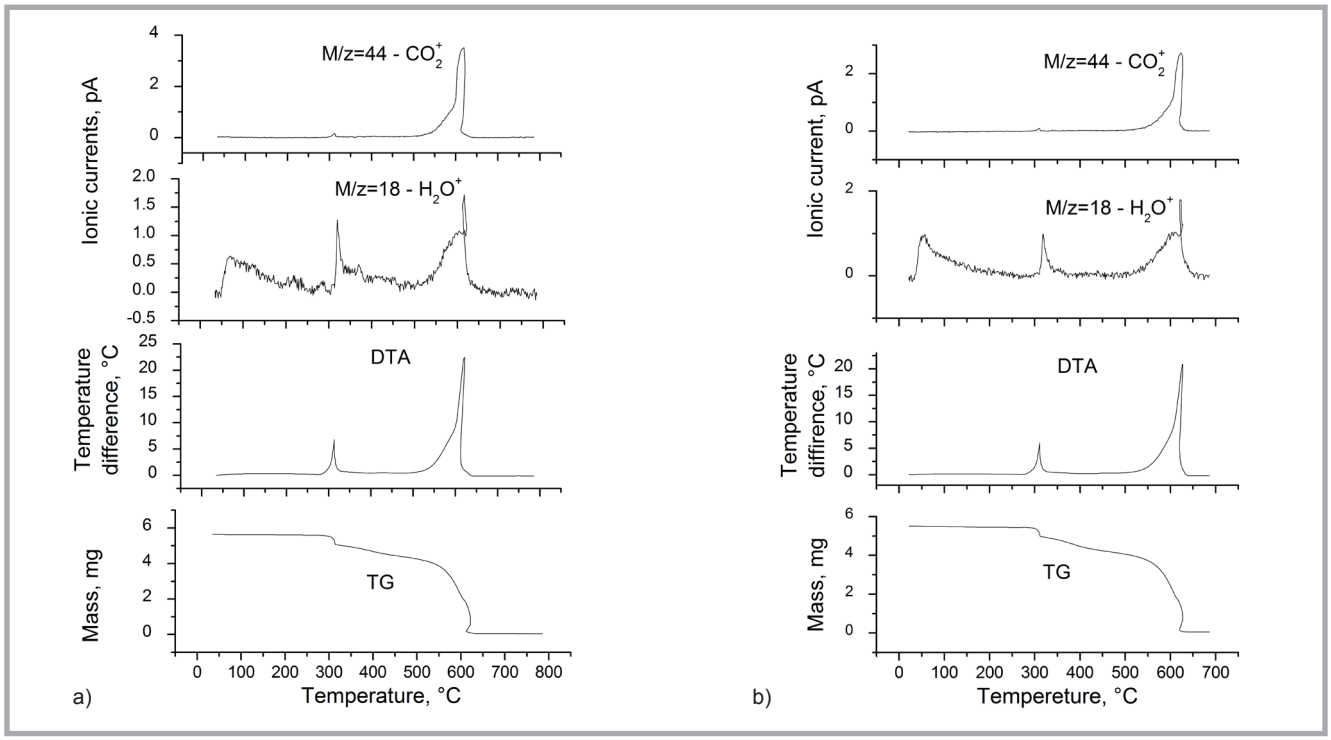

Figure 4. *DTA and TG thermal curves and analyses of gaseous thermal decomposition products for: (a) fibres with 1% MWCNTs and (b)reference fibres; TG is the sample weight, mg, DTA the temperature difference, and M/z the ionic currents (M/z=18, H2O$^+$; M/z=44, CO_2^+).*

creased degree of crystallinity in PAN fibres is related to the presence of carbon nanotubes in the material, as reported previously in the literature [15]. Analysis of the results for the degree of crystallinity of nanocomposite fibres showed that fibres formed at an as-spun draw ratio of -40%, that is, those with the highest specific strength value in the experimental series under investigation, also had the highest degree of crystallinity. Furthermore the presence of carbon nanotubes did not lead to any rearrangements of the fibre material's crystal lattice, because the interplanar distances did not change; the value of 5.3 Å was identical for all test samples (reference and composite fibres).

Tests of the porous structure of the resulting fibres showed that the total pore volume of composite fibres is lower than that for reference fibres spun in similar conditions (***Figure 3.b***). Furthermore when the as-spun draw ratio changed from positive to negative values there was a decrease in this parameter, and a very low value of 0.115 cm^3/g was obtained for fibres spun at an as-spun draw ratio of -40%.

Tests were conducted for the resulting composite fibres and reference fibres to determine compensation stress values, that is, stress values at which fibres when heated (during carbonisation) do not shrink or elongate. It was found based on the studies that when negative as-spun draw ratios are used, compensation stress values for fibres with MWCNTs and reference fibres are similar. When positive as-spun draw ratios are applied, composite fibres have significantly higher compensation stress values than reference fibres (***Figure 3.c***).

It was found based on tests of the thermal properties of the resulting fibres that the presence of carbon nanotubes did not lead to significant changes in the process of thermal decomposition of the heated fibres (***Figure 4***). This is important for the fibre oxidation process because it shows that the first stage of obtaining of carbon fibres can be carried out in the same conditions as for the traditional precursor.

Tests were performed for the resulting nanocomposite fibres to determine the dispersion of MWCNTs in the precursor fibre material. Longitudinal section images were recorded for fibres formed using extreme as-spun draw ratio values (-60% and +60%) ***Figure 5***. The dispersion of MWCNTs in the fibre material, evaluated using TEM images, was found to be uniform (***Figure 5***). The MWCNTs were also established to be relatively well stretched and oriented along the fibre axis. It is notable that no significant differences were found in the orientation of MWCNTs in fibres formed in radically different conditions, which may indicate that MWCNTs are oriented not only as a result of the significant deformation of a liquid polymer stream during the solidifi-

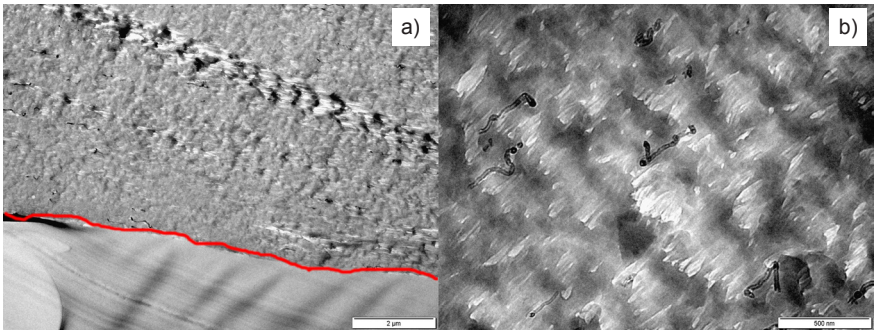

Figure 5. *Longitudinal section images of fibres with MWNT spun at the as-spun draw ratio of: (a) -60% and (b) +60% . Red line – edge of the fibre.*

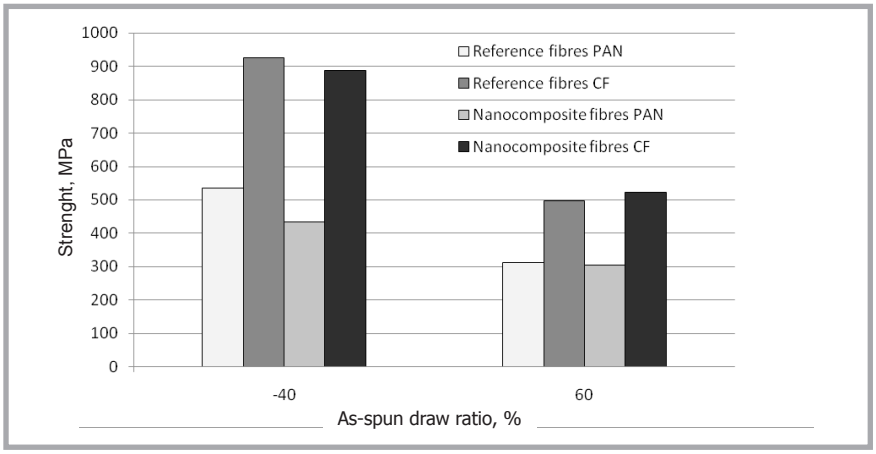

Figure 6. *Precursor (PAN) and carbon fibres (CF) tensile strength.*

cation process, but also during the drawing process at high deformation.

Carbonisation experiments were performed for the resulting nanocomposite fibres and for reference fibres. The fibres selected for the carbonisation process included those spun using an as-spun draw ratio of -40% (highest tenacity, the highest degree of crystallinity and lowest porosity) and at an as-spun draw ratio of +60% (fibres spun with the highest longitudinal speed gradient during the solidification process).

It was found based on the resulting strength properties of the carbon fibres that higher strengths were obtained for fibres prepared from a precursor formed at an as-spun draw ratio of -40% (fibre precursors with higher tenacity) (***Table 1, Figure 6***), which is consistent with literature data on the preparation of carbon fibres from a PAN precursor, because the strength of carbon fibres is generally related to that of the precursor fibres. The relationship between the strength of the precursor composite and reference fibres was confrimed in the case of carbon fibres prepared from precursors spun at anas-spun draw ratio of -40%. However, in the case of carbon fibres from precursors formed at an as-spun draw ratio of +60%, the strength of carbon fibres prepared from composite PAN fibres was slightly higher than that for carbon fibres prepared from the reference precursor. Data shown in literature [9 - 11] reports the beneficial effects of the presence of carbon nanotubes in the fibres matrix in the case of the application of a high deformation of fibres in the solidification stage (dry-wet spinning or melt spinning). In the case of the wet spinning of fibres, deformation in the solidification stage is minor, which results in a lack of the significant increase in the strength of precursor and carbon fibres expected.

Conclusions and summary

We have shown in this work that the presence of MWCNTs in PAN fibre material leads to a reduced total pore volume in the fibres and an increased degree of crystallinity. Furthermore we found that the presence of carbon nanotubes in the amount of 1% did not lead to changes in the fibres' thermal properties; therefore, the carbonisation process of such fibres may be performed in similar conditions as for standard PAN fibres.

We also showed, based on the resulting fibre longitudinal section images, that carbon nanotubes are oriented along the fibre axis irrespective of the as-spun draw ratio used.

The results obtained show that the presence of MWCNTs in the PAN fibre material unfortunately leads to the reduced susceptibility of the fibre material to deformation processes at the drawing stage, which may cause the obtaining of fibres with lower tenacity in comparison to those without the nanoadditive. Also in our research it was found, based on the results, that in contrast to our assumptions the presence of MWCNTs did not lead to improved properties either for the precursor fibres or for the carbon fibres obtained from those precursors.

Acknowledgments

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