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Comparative Analysis of the Properties of Active Carbon Fibres Obtained from Different Precursors

Abstract
This paper presents the changes to some properties and structural features of four types of polymer fibres and the nonwovens obtained from them during fibre pyrolysis and the following steam activation at a temperature of 850 °C of the carbon nonwovens obtained. The changes in tenacity of the precursor, the carbon, and the active carbon nonwovens as the result of thermal and oxidation processing were tested, among others. We stated that the loss of tenacity mainly takes place during the pyrolysis and the accompanied radical reconstruction of the fibre structure. The activation process, although connected with a further great loss of mass, causes relative significantly small changes in the tenacity of the active carbon nonwovens obtained from viscose and phenolic resin-based fibres, whereas the mechanical properties of active carbon nonwovens obtained from polyacrylonitrile fibres as a precursor decrease even further considerably.

Key words: *polymer fibres, precursor, carbon fibres, active fibres, nonwovens, pyrolysis, tenacity, sorption properties.*

Introduction

The harmonisation of legal standards in the scope of consumer protection against products which could be dangerous for life and health, as well as for the natural environment, is controlled by the New Approach Directives, which has been enforced by the European Union since 1985. The directive 89/686/EEC dictates a duty to achieve certifications for clothing protecting humans against harm to health or life. This responsibility is also related to clothing which protects against chemical products. Such clothing must be characterised by the ability to absorb toxic substances from the environment surrounding humans, if this environment may pose a threat for human life and health. In order to meet the regulations resulting from directive 89/686/EEC, clothing which protects against chemical agents should be reinforced with functional layers characterised by a high adsorption dynamic, which would enable the formation of a protective barrier. This kind of situation takes place when the external and internal diffusion velocities of sorbate particles are high, whereas the distance to micro- and meso-pores, which are the places of adsorption, is relatively short.

Active carbons are applied in sorption layers of protective clothing, including in the following forms [1-3]:
- spherical granules with a diameter not greater than 0.5 mm, obtained mostly from synthetic precursor materials, which form a single layer stuck to the textile carrier;
- fine-grained active carbons deposited by scattering on textile fibres; and
- fibrous active carbons in the form of nonwovens, knitted and woven fabrics, which can be manufactured using different kinds of precursor fibres processed by carbonisation.

The aim of our research was to determine the dependencies of strength and sorption properties of the activated carbon nonwovens on the properties of precursor nonwovens used as their raw material.

Precursor materials used in this investigation

Three types of precursor fibres, viscose, polyacrylonitrile and novoloid fibres, were used for our investigations. Classical viscose fibres with a core-skin structure and polynosic fibres with increased strength properties were tested as viscose precursor fibres.

The viscose fibres were manufactured according to different technological processes, which resulted in a differentiated supermolecular structure. The elementary fibril- and macrofibril-structures are barely developed in classical viscose fibres. On the other hand, polynosic fibres have fine, well-differentiated fibriles which are uniformly distributed throughout the whole fibre volume. Polynosic fibres are characterised by a higher degree of polymerisation, a higher value of molecular orientation, and a higher degree of crystallisation. The full characteristic of both types of fibres is given in [4]. Viscose and polynosic fibres produced by Lentzing were used in our research.

In contrast to viscose fibres, polyacrylonitrile fibres are composed of an unbranched linear polymer with features characteristic for thermosetting and quasi-thermoplastic materials (whose melting points are near or even above the temperature at which decomposition starts). Under the influence of temperature, the fibres changes their physical and next their chemical structure. To protect the fibres from decomposing, the PAN fibres needed thermal stabilisation consisting in an intermolecular nitrile chain cyclisation, based on incorporating nitrogen in the rings at a temperature of about 210 °C, and on oxidation which led to dehydration with water release and to intermolecular cross linking. This type of processing, which proceeds at a temperature of about 270 °C, causes transversal cross-linking of the macromolecules and the creation of a ladder structure, and as a final effect the lack of a prematurely decomposing and sometimes melting.

Fibres with the trade name of Anilana (from the former Anilana Co., Poland) were used for our investigations.

Table 1. *Morphological and strength properties of precursor fibres.*

Parameters of precursor fibres	Precursor fibres from:			
	viscose fibres		novoloid fibres	PAN fibres
	classical	polynosic		
Linear density, dtex	4.4	1.7	3.8	3.3
Length, mm	70	38	37	60
Cross-section area, μm^2	227.8	93.1	320.8	314.9
Average breaking force, cN	5.4	7.5	6.0	9.4
Coefficient of variation of breaking force, %	11.1	14.4	20.0	19.0
Tenacity, cN/tex	12.3	44.1	15.9	28.5
Breaking tension, Mpa	236.8	805.5	187.0	298.5

Table 2. *Characterisation of the precursor-nonwovens structure and their strength properties.*

Parameters of precursor nonwovens	Nonwovens from precursor fibres based on:			
	viscose fibres		novoloid fibres	PAN fibres
	classical	polynosic		
Area mass, g/m^2	2159	1330	1776.0	1684.0
Variability coefficient of area mass, %	1.4	2.2	5.5	4.4
Thickness, mm	14.4	10.2	11.0	14.6
Coefficient of variation of thickness, %	3.1	5.2	4.9	9.8
Apparent density, g/cm^3	0.154	0.130	0.161	0.108
Breaking force, N	667	167.0	1850.0	1342
Coefficient of variation of breaking force, %	14.5	22.7	7.9	10.0
Tenacity, cN/tex	0.79	2.52	2.12	1.66
Relative elongation, %	38.1	31.6	23.1	40.6

Table 3. *Percentage mass losses of nonwovens after the pyrolysis and activation processes.*

Type of fibre		Mass loss of nonwoven, in % after the process of		Mass loss of nonwoven during activation, %/min
		pyrolysis	activation	
Based on viscose fibres	Classic	77.6	52.6	1.57
	Polynosic	74.9	42.3	1.29
Based on novoloid fibres		35.1	34.0	0.74
Based on PAN fibres		38.3	47.1	1.07

Novoloid fibres containing at least 85% of a crosslinked novolac were also investigated. This material belongs to the group of amorphous polymers with the highest carbon content, namely about 75% of the total mass. The pyrolysis of these polymers proceeds in a highly cross-linked structure, which in turn is the cause of the strongly disturbed structure of the carbon fibres formed. We used Novoloid fibres produced by Kynol, Japan for the investigation.

The morphological and strength properties of the precursor fibres used are presented in Table 1. The morphological fibre properties were determined in accordance with PN-85/P-04761/02 and PN-82/P-04760 standards. In addition, the cross-section areas were assessed by a computer-aided image analyser. The strength properties were determined in accordance with standard PN-83/P-04602. The breaking tension was also determined.

Carded webs with an area mass of 300 g/m^2 were formed from all the presented fibres. The webs were preliminarily needled at a needling number of 20 cm^{-2}. Next, three webs were joined and needled together double-sided at a needling number of 100 cm^{-2}, and a second packet was prepared in the same way. Both packets were joined together by needling, also at a needling number of 100 cm^{-2}. The webs were needled with the use of needles from Foster with a number of 15×18×36×3RB, at a constant needling depth of 12 mm. The products obtained were used as the precursor nonwovens in further investigations. The area mass and thickness of all kinds of precursor nonwovens were determined in accordance with standards PN-EN-29073-1 and PN-EN-29073-2.

The nonwoven's strength properties were determined using an Instron tensile-tester in accordance with standard PN-88/P-04626. The test results are presented in Table 2.

The webs manufactured during the first stage of the technological process and the needled nonwovens were carbonised and activated with the aim of obtaining active carbon nonwovens. Fibres were sampled from the webs after carbonisation and after activation in order to analyse the changes in the strength properties of carbon fibres.

The pyrolise and activation processes

The fibres included in the webs were pyrolised in a tensionless state accompanied by considerable shrinkage. Carbon fibres from regenerated cellulose, polyacrilinitrile, and phenol resins (novoloid) were obtained by thermal decomposition of the polymeric precursors carried out under non-oxidative conditions in an atmosphere of argon. Regarding the various properties, also thermal, of the materials tested, their thermal and chemical processing required differentiation.

The cellulose decomposition over the first processing stage leads to a decrease in the polymerisation degree, and at the same time to dehydration [5] and the creation of dehydrocellulose [6]. As the cause of thermal degradation of the glycoside rings, tetra-carbon fragments are formed, following by the creation of aromatic structures. The carbon matrix of the fibre is slowly rebuilt in the direction of flat cyclic structures, the graphen layers. The secondary cross-linking during active pyrolysis leads at a temperature over 500 °C to the formation of small aromatic lamellas which contain aliphatic fragments. The increasing carbonisation temperature causes a subsequent ordering of the internal structure, and the creation of parallel packs of graphen layers arranged radially [7].

The pyrolysis of polyacrylonitrile fibres leads to the elimination of nitrogen, and at higher temperatures causes cyclisation [8] with the subsequent liberation of hydrogen cyanide and formation of graphen planes, which begin to create packets with sharp edges, initially isolated. At a higher temperature, within the range of 1200 °C, this process leads to further orientation in the turbostratic

structures [9-13]. Within the range of low processing temperatures, such as those maintained in our investigations, the fibres have regions located directly near the surface which are distinguished from other regions by a significantly better arrangement of their graphen layers. The layers are larger and of greater radii of the plane curvature, whereas the core is markedly more poorly oriented [14]. In the temperature range from 600 °C to 800 °C, at a relatively low internal orientation (which is essential considering the relatively easy activation by oxidation gases), the inner parts of the fibres include significant amounts of free spaces and cracks (the so-called Morozov cracks) which form structural discontinuities. In addition, during pyrolysis some tensions of internal origin appear at the edges of the arranged regions [15]. The fibres exhibit significant amorphous regions in the core part. This kind of structure, and the accompanying significant reactivity which already exists, enable the process of oxidative activation to proceed with the creation of a porous structure.

Depolymerisation, dehydration and cracking take place accompanied by the release of non-cyclic fragments such as the result of heating the novoloid fibres during pyrolysis at temperatures of about 500 °C. A significantly spatially cross-linked polymer is created, composed from aromatic cores and non-aromatic cyclic compounds [16]. At further heating, above the temperature of 800 °C, hexagonal carbon layers are created which form packets as an effect of the dehydrogenation. Bands of highly arranged hexagonal packets of the matrix structure maintain the initially non-oriented supermolecular structure of the spatially cross-linked polymer with macro-pores, which compose the free spaces between the bands. Carbon is amorphous, and does not crystallise even at temperatures above 3000 °C; considering its shape, such carbon is
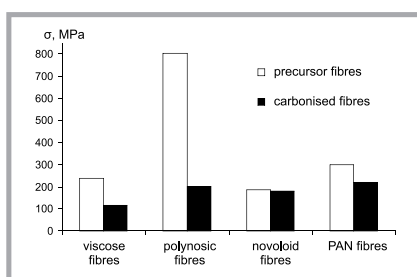

Figure 1. *Strength properties of precursor and carbon fibres.*

Table 4. *Strength properties of carbon fibres.*

Parameters of carbon fibres	Type of fibres based on:			
	viscose fibres		novoloid fibres	PAN fibres
	classical	polynosic		
Average breaking force, cN	1.1	1.0	5.2	4.7
Coefficient of variation of breaking strength, %	47.0	50.0	22.0	28.8
Breaking tension, MPa	115.0	201.1	180.3	220.5
Cross-section area, μm^2	100.0	50.2	229.4	213.1

often designated as glassy carbon. The novoloid fibres, thanks to their chemical structure, are characterised by the lowest reactivity and ability to oxidation and thermal decomposition.

To avoid the overlapping of the various processes which take place during the pyrolysis, the fibre processing was conducted during a slow temperature increase in the reaction zone of about 3 °C/min. The pyrolysis of all raw materials, independently of the carbonisation degree, was interrupted at the same final temperature, freezing the rebuild carbon structure at the level of 600 °C. The choice of this temperature was principally motivated by the degree of rebuilding the structure of the mother carbon matter (the matrix) and by the fibre's reactivity. On one hand, this temperature is already above the zone of active polymer pyrolysis; on the other, the degree of the internal orientation is low enough to enable the creation of developed porous structures.

The activation process was carried out with the use of a periodically-working chamber reactor in an atmosphere of vapours and gases emitted from the processed fibres and those of an argon gas stream. After achieving the final temperature, the samples were conditioned at a constant temperature to the decay of the decomposition reaction, and were next cooled.

The process of carbon oxidation during the activation of the nonwovens depended to a great degree on the state of the carbonisation advancement and the state of the fibres' internal structure orientation.

Despite the fact that a further increased pyrolysis takes place during heating to the activation temperature, the reactivity of carbon fibres is to an essential degree dependent on the final temperature of the pyrolysis, which proceeds during the slow temperature progression.

The carbon fibres were activated at a temperature of 850 °C allowing for carbon oxidation with a velocity value lying on the boundary of the kinetic and diffusion characters of the activation process. The carbon preparations, whose composition and structure had been frozen at the level of the final pyrolysis temperature, are heated over a short time during the preliminary stage of activation up to the activation temperature at a speed often greater than 100 °C/min. Thus, the further pyrolysis and carbon structure rebuilding proceed at great speed, which results in a deepening of the carbonisation process.

Considering the essential time factor, it is believed that the chemical processes, which proceed in a solid body with considerable speed, are disadvantageous, especially in the case of subsequent reactions such as the pyrolysis and carbonisation processes, based on structure arrangement and cyclisation. While carrying out the experiments, we tried to manufacture the active fibres by means of a procedure which would provide a similar specific surface, as determined by us using the BET method. At an equal activation temperature of 850 °C, this became possible by changing the activation time, and thus compensating for the differences in the fibre reactivity.

The percentage mass losses of nonwovens after the pyrolysis and activation processes are presented in Table 3.

Analysis of fibres' strength properties after pyrolysis and activation

Single fibres were sampled from the webs obtained after carbonisation, and then their strength properties were tested. The breaking force and the elongation at break were determined, and the breaking strength calculated. The tests were carried out at a velocity of 2 mm/min for fibres of an initial length of 5 mm. The fibre cross-section area was analysed with the use of a computer-aided image analyser. The test results are listed in Table 4 and shown in Figure 1.

It was not possible to determine the tensile properties of active carbon fibres as the fibres selected from webs were too fragile. Because of this circumstance, the active carbon strength properties was only analysed by using the needled nonwovens as samples.

Analysis of nonwovens' properties after pyrolysis and activation

The structure and properties of the carbon nonwovens after the carbonisation and activation processes was characterised by carrying out tests in accordance

with the methods described in the second chapter. The test results are presented in Tables 5 and 6.

In order to enable a deep analysis of the structural processes which take place during carbonisation and activation, the percentage changes of the area masses of nonwovens and the changes in strength of the samples after carbonisation and activation in relation to precursor nonwovens were listed additionally. The results presented in Tables 3 and 7 are based on the test results shown in Tables 5 and 6.

Table 5. Structure and strength characterisation of carbon nonwovens.

| Parameters of carbon nonwovens | Type of fibres based on: | | | |
| | viscose fibres | | novoloid fibres | PAN fibres |
	classical	polynosic		
Area mass, g/m2	913	672	1545	1629
Coefficient of variation of area mass, %	5.2	2.4	3.9	2.8
Thickness, mm	9.5	7.6	10.4	7.3
Coefficient of variation of thickness, %	3.2	3.8	4.3	2.9
Apparent density, g/cm3	0.096	0.088	0.149	0.221
Breaking force, N	8.8	20.8	60.0	227.5
Coefficient of variation of breaking force, %	8.6	1.4	23.5	3.7
Tenacity, cN/tex	0.018	0.052	0.078	0.290
Relative elongation, %	15.8	18.3	4.3	14.2

Table 6. Structure characterisation of active nonwovens.

| Parameters of active carbon nonwovens | Type of fibres based on: | | | |
| | viscose fibres | | novoloid fibres | PAN fibres |
	classical	polynosic		
Area mass, g/m2	643	479	1280	1144
Coefficient of variation of area mass, %	29.7	14.9	2.8	5.7
Thickness, mm	8.7	7.2	9.5	6.7
Coefficient of variation of thickness, %	16.0	6.0	2.3	5.3
Apparent density, g/cm3	0.080	0.067	0.135	0.179
Breaking force, N	5.6	12.0	49.8	55.0
Coefficient of variation of breaking force, %	51.5	18.0	3.8	9.6
Tenacity, cN/tex	0.015	0.050	0.078	0.093
Relative elongation, %	10.0	12.8	5.0	9.0

Table 7. Percentage strength loss of nonwovens after the pyrolysis and activation processes.

| Type of fibre based on: | | Strength loss in % of nonwovens after: | |
		pyrolysis	activation in relation to the pyrolysed samples
viscose fibres	classic	97.8	11,8
	polynosic	97.5	19.2
novoloid fibres		96.3	0.3
PAN fibres		82.5	68.0

Table 8. Results of X-ray investigations.

| Type of fibre based on: | | Degree of crystallinity, % | | |
		precursor fibres	carbon fibres	active fibres
viscose fibres	classic	45.8	structure substantially amorphous	flat graphen structures mainly perpendicular to the fibre axis
	polynosic	49.8		
novoloid fibres		amorphous structure		
PAN fibres		35.4		

Characterisation of the supermolecular structure of the precursor, carbonised, and activated fibres

The X-ray investigations (WAXS) of precursor fibres were carried out with the use of a HZG-4 diffractometer with CuKα radiation, at an accelerating voltage of 30 kV and an anode current intensity of 20 mA. The carbon fibres were tested with the use of a URD-6 Seifert diffractometer. CuKα radiation was also used; an accelerating voltage of 40 kV and an anode current of 30 mA were applied. The diffractograms were carried out within the diffraction angle range from 4 to 40 degrees by the step method, with steps of 0.1 degree and an impulse counting time of 10 s.

In the case of carbon fibres, the diffractograms do not have well developed crystalline reflexes, and the small reflexes created probably originated from arranged structures formed secondarily; the remaining part of the matrix is amorphous. Under such conditions, it is not possible to assess the degree of crystallinity and the crystallite size, and the reflexes created at the 2Θ angles of 19.20 and 34.40 may be caused by the graphen planes formed. The distances between the planes calculated according to Bragg's law on the basis of the angles measured were equal to 2.60 Å and 4.64 Å. The carbon fibres obtained on the novoloid-fibre basis are totally amorphous.

The results of X-ray investigations are briefly presented in Table 8.

Porosity characterisation of precursor, carbon, and active fibres

The porous structure of fibres was investigated on the basis of nitrogen adsorption measurements under static conditions. The adsorption isotherms were determined with the use of an ASAP 2010 Micrometrics sorption apparatus at a temperature of −196 °C. The total pore volume V_t, the micro-pore volume V_{mic}, and the meso-pore volume V_{meso} were calculated according to the BJH method. The specific surface area of the pores S_{BET} was calculated by the BET method.

Many classical methods used for porosity determination do not work when applied to precursor and carbon fibres. This is be-
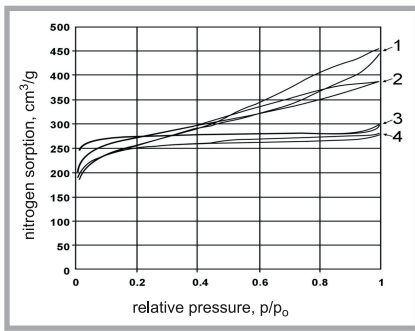
Figure 2. Nitrogen adsorption isotherms at a temperature of – 196 °C for active carbon fibres obtained from the precursors tested; carbon fibres based on: 1 – viscose fibres, 2 – polynosic fibres, 3 – novoloid fibres, 4 – polyacrilonitrile fibres.

cause the formation of nucleus of the porous structures takes place on a level not much greater than the molecular level. Research attempts indicated that the micro-pore and meso-pore systems formed are small and not easily accessible for nitrogen. The nitrogen sorption for precursor and carbon fibres was not greater than 23 cm^3/g within the whole relative pressure range (p/p$_o$), whose result is beyond the boundary of the method's reliability. The greatest total pore volume, but not greater than 0.045 cm^3/g, is shown by the carbon fibres manufactured from viscose. Similarly, the volumes of macro-pores in carbon fibres of radii up to 1000 nm are very small. The total volume was within the range from 0.0175 to 0.0240 cm^3/g.

The determination of pore structure for active carbon fibres was conducted without any problems using the BJH and BET methods. The curves of nitrogen sorption for all types of the active fibres tested are presented in Figure 2, and the porous structure parameters, which were calculated on the basis of the curves' shapes, are listed in Table 9.

All the results presented in this work are related to carbon fibres activated by means of steam. The adsorption isotherms of active fibres manufactured from viscose precursors have a shape which is distinctly different from those of the isotherms obtained at the same temperature for active carbon fibres from novoloid and polyacrylonitrile precursor fibres. In Figure 2, it is clearly visible that the adsorption and desorption branches of the hysteresis loop gradually draw together. In the case of active fibres from viscose, we note a lack of any visible hysteresis for active fibres from novoloid precursor fibres, and a narrow hysteresis

with parallel branches is visible in the case of active carbon fibres obtained from polyacrylonitrile fibres [17-20]. The narrow shape of the hysteresis loop indicates that the capillary condensation of nitrogen in pores is reversible for the similar values of sorption and desorption pressures. Based on these observations, it is possible to conclude that the pores have a cracked character in all the fibres discussed. This hypothesis was confirmed by the scanning tunnelling micrographs.

The porous character of the active carbon fibres is presented, as an example for fibres from viscose, in Figure 3. This figure shows scanning tunnelling (STM) micrographs of an active carbon fibre surface of 100×100 nm area as well as the fibre profile. The crack pores arranged in a system of deep pores cut into the carbon structure, and which are in many places connected mutually and ramified, are characteristic of carbons formed from viscose and polyacrylonitrile. The wedge-shaped cracks have a width at the broader end (adjoining the fibre surface) related to the meso-pores' dimensions, and then become narrower, so that the cracks finally change into micro-pores. It appears that the walls of the carbon matrix structure which forms

the pores have a laminar character of quasi-parallel graphen layers positioned transversally to the fibre axis.

The results presented in Figure 3 and in Table 9 indicate that the porous structure of active carbon fibres obtained from a viscose precursor has a mixed character, which means that on the one hand active fibres have significant amounts of micropores, comparable to and even greater than the micro-pore value in fibres from other precursors, while on the other hand also having great amounts of meso-pores. This observation is confirmed in [21 - 24]. The ratio of micro- and mezzo pores is within the range from 1.14 to 2.24. The total volume of all types of pores can be even greater than 0.8 cm^3/g for fibres obtained from viscose. The steeply increasing adsorption branch indicates a very broad pore dimension span, from small micro-pores to the greatest macro-pores. The pores are mostly wedge-shaped.

Active fibres obtained from polyacrylonitrile [6, 25] also have a micro-porous character with a ratio of micro-pores to meso-pores of 3:1 (see Table 9). The micro-pores already show a substantial dimension span, which also indicates the flat shape of the isotherm in the p/p$_o$ range from 0.01 to 0.3.

Table 9. Parameters of the porous structure of active fibres.

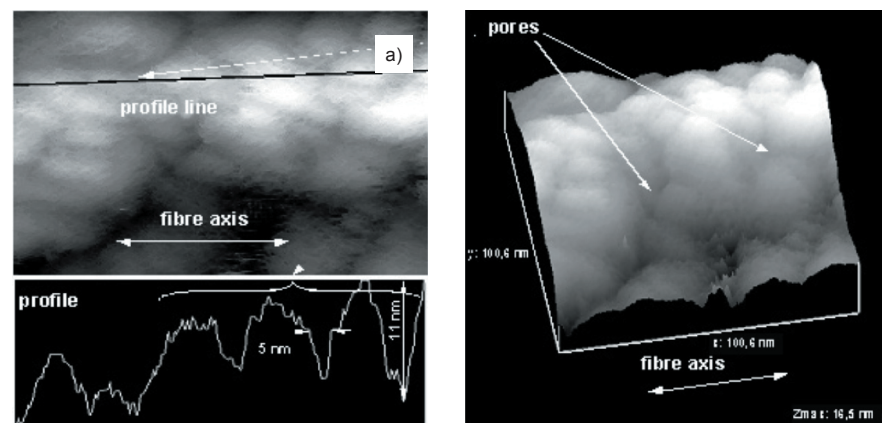| Type of fibre based on:		Pore volume, cm3/g				V$_{mic}$/ V$_{meso}$	Specific surface area S$_{BET}$, m^2/g	Average pore diameter d, nm
		Micropore (2 nm>d) V$_{mic}$	Mesopore (2nm<d< 50nm) V$_{mez}$	total V$_{sum}$= V$_{mic}$+ V$_{mez}$	Macropore (50nm <d) V$_{mac}$			
Viscose fibres	Classic	0.440	0.387	0.824	0.334	1.14	824	4.00
	Polynosic	0.489	0.218	0.707	0.296	2.24	862	3.28
Novoloid fibres		0.387	0.055	0.442	0.135	7.03	918	1.93
PAN fibres		0.320	0.106	0.426	0.096	3.02	859	1.98

Figure 3. Scanning tunnelling (STM) micrographs of an active carbon fibre obtained from viscose precursor: a) the fibre longitudinal profile along the black line, b) surface of 100 nm × 100 nm area.

The adsorption isotherm of carbon products obtained from novoloid fibres has the most rectangular shape, which indicates a remarkable micro-porous structure, and the practical absence of any pores with greater dimensions. The ratio of micro-pores to meso-pores is greater than 7:1 (see Table 9, page 83).

■ Discussion of results

The analysis of the strength properties of precursor fibres and the carbon fibres obtained from them indicates that for all types of precursors, with the exception of phenolic resin-originated fibres, a decrease in the carbon fibre breaking tension occurs in relation to precursor fibres; this is shown in Figure 1 (page 81). For fibres obtained from the phenolic resin, the strength value of carbon fibres practically did not change in relation to the precursor fibres.

From Figure 1 we can state that the breaking tension value of the carbon fibres obtained depends on the kind of precursor fibres. Carbon fibres obtained from a polyacrylonitril precursor are characterised by the highest value of breaking tension. Carbon fibres from polynosic fibres have strength values lower by about 10%. Carbon fibres from phenolic resin precursors are characterised by a strength lower by a further 10%. The smallest tension values were measured for carbon fibres obtained from a precursor belonging to viscose fibres of the first generation; these values were 50% smaller than those for the carbon fibres from a polyacrylonitril precursor. The test results obtained for carbon fibres manufactured from precursors differentiated by molecular and supermolecular structure indicate that the strength features of carbon fibres are influenced not only by the molecular structure of the primary polymer but also its supermolecular structure. This is why investigations should be aimed at determining the optimal parameters of the supermolecular structure of the primary polymer, which essentially influences the course of the carbonisation process, as well as the strength properties of carbon fibres with increased sorption properties obtained by means of this process.

An analysis of the changes to the nonwoven properties after the carbonisation and activation processes indicates that the carbonisation and activation of phenolic resins and polyacrylonitril fibres is the most efficient method, whereas the lowest efficiency is observed while manufacturing carbon fibres from viscose fibres (see Table 6, page 82). These results among others reveal the differentiated character of the process of chemical transformations through which the precursor fibres must go during their carbonisation and subsequent activation processes.

It should be stated that during the thermal processing of polymers without oxygen access, thermal decomposition of molecules occurs over the first stage of the process, which differs for the particular polymers. During this decomposition, the primary fibre structure is converted (Figure 1).

The crystalline fibre structures also decompose, and a considerable mass loss results in a volumetric shrink. A total chemical molecule reconstruction occurs as the effect, and the reconstruction of the fibre's carbon matrix also follows. These phenomena proceed mainly as subsequent processes and reactions, which mainly depend on the temperature, and which proceed gradually over a range of some hundreds of degrees Centigrade, from the decomposition temperature to a temperature within the range from 1200 to 1500 °C [26, 27]. As a result of these processes, the tensile properties of carbon fibres increase considerably.

The destructive processes overlap with the recombination of the carbon structures, which remained after the pyrolysis, and lead to cyclisation with the creation of ordered graphen layers, the basic structures of the carbon matrix which are growing all the time.

In the manufacturing technologies for active carbon fibres, the basic aim is to obtain high-defective structures of the carbon matrix, which include partially ordered carbon fragments as their structural skeleton. The surfaces which surrounded the free spaces between the graphen layers, together with the vacant, burned-out spaces between the more resistant fibre fragments, sometimes reaches even more than 2000 m²/g [6, 21, 22, 24].

Obtaining such a structure is possible only thanks to the fact that local chemical and physical differences exist within the structure of the carbonised fibre. Fibres heated to relatively low temperatures, such as those described in this article, are in the initial stage of structure organisation, and are thus characterised by high chemical reactivity [25, 28, 29] and a significant share of the amorphous phase. The fibres' mechanical strength at this phase of thermal transformations is individualised, and certainly very low.

The process of fibre activation which leads to the formation of pores is connected with the selective gasification of significant amounts of the carbon matter, which often exceed 50% of the total mass. On one hand, the activation temperature of 800-900 °C leads to an increase in the fibre strength; on the other, the gasification of notable fibre fragments decreases the strength of the active fibres.

The fibres' structure condition after pyrolysis, which is advantageous from the point of view of the fibres' sorption properties, caused an drop of over 40 times in the fibre strength in the case of fibres obtained from cellulose. This was caused by the change of the carbon fragments' arrangement from axial to radial, among others [29]. In addition, the tensions in fibres which appeared during the pyrolysis increase during the preparation of the nonwoven, and cause cracks and defects in the fibre to appear. Tensions also appear as the result of temperature gradients over the fibre thickness, leading to an irregular collapse throughout the entire fibre matter and an increase in the number of internal cracks. Usually, thinner fibres are characterised by a lower decrease in the strength properties (this also applies to fibres obtained from polynosic fibres, irrespective of the influence of their internal structure).

The greatest decrease in strength during activation was observed for polyacrylonitrile fibres, which have nitrogen heteroatoms built into the carbon matrix structure. This is probably caused by the exposition of the quaternary nitrogen (N-Q) built into the aromatic rings as the result of carbon gasification, its release from the rings and reactivity in the oxidative activation environment [28]. Contrary to what happens during heating, the place of nitrogen in the graphen structures in HT and HMT technologies is not replaced by carbon atoms, and the defective rings are more susceptible to the action of the oxidisers (H_2O and CO_2). Increases in the reactivity and the oxidation rate caused by nitriding and amoxidating the fibres from viscose and brown coal were also observed [31, 32]. This process also caused a decrease in mechanical strength. The observations made are confirmed by

the results obtained. The highest fibre strength after the pyrolysis, which results from the ladder structure of the stabilised precursor fibres, and which is maintained to a great degree during the pyrolysis and activation processes, allowed for the maintenance of the highest mechanical strength of the final fibres also. The lack of reorientation of the graphen structures created is essentially conducive to this, as it takes place in the case of fibres originated in cellulose.

The amorphous character of the novoloid fibres also leads to an amorphous or small-crystalline carbon fibre with a strongly developed micro-pore system. Such fibres are homogeneous and compact [33 – 35], which is also caused by the highest (considering all the types of fibres we used) elemental-carbon content in the polymer. This results in the significant mechanical strength of the fibres, as well as its smallest loss during activation. The small graphen layers which are formed are isotropic, which in turn causes the spatial arrangement existing in the fibre to remain very stable, and they contribute to maintaining a relatively high tensile strength even at high degassing degrees during activation. The relative lowly oxidation speed also has an advantageous influence on maintaining the fibres' considerable tensile strength (see Table 7)

The mechanism of strength changes in fibres from viscose is slightly different. As was shown earlier, the greatest strength loss has taken place as the result of pyrolysis, during which the breaks of the oxygen bridges of the cellulose chains caused a total reconstruction of the structure. The secondary arrangement of the matrix structure after its formation, and the aromatisation with the creation of graphen layers, cause a change in the internal orientation of the fragments which compose the carbon matrix, from axial in the precursor fibres to radial [30], in which the graphen layers are arranged perpendicularly to the fibre axis [27], as was mentioned before. This was proved by STM photos as well as by other investigations [7, 36]. The above-mentioned layers are mutually linked by hydrogen bonds or by oxygen bridges, which are significantly weaker compared with the C-C type bonds in the graphen layers. Thus, the weakest connected fragments of the matrix structure are decisive for the fibre strength. The bonds between layers are further weakened during ac-

tivation, thanks to the gasification of a considerable part of the carbon matter connected with formation of crack pores, mainly as spaces between the layers. The strength decrease during activation is significantly smaller than during the pyrolysis, and it does not exceed 20% (see Table 7). Similar results were obtained and discussed in paper [37].

We should especially emphasise the existence of a very essential factor, the porous structure of active fibres formed over the activation. The fibre strength is inversely proportional to the volume of the pores formed. For standard viscose fibres, polynosic fibres, and polyacrylonitrile fibres, in which great graphen layers, excellently oriented, are formed, and in which wedge-shaped crack pores are dominant, the strength decreases proportionally to the amount of pores and to its size. The greater the amount of mesopores, the smaller the V_{mik}/V_{mez} ratio (Table 9), and so the greater the pore width (as indicated by the increasing angle of the adsorption isotherm branch within the range of $p/po < 0.3$, characteristic of supermicro- and meso-pores), and the lower is the strength of the active fibres. The different character of the structure and the pores formed of the phenol-originated fibres, also mentioned above, causes the fibre strength-decrease during activation to be insignificant.

■ Conclusions

1. A rapid, significant drop in the strength of nonwovens occurs during the pyrolysis and carbonisation of the nonwovens obtained from all fibres. It is caused by the thermal decomposition of polymer molecules resulting in the disintegration of the primary fibre structure, and increases additionally upon an increase in the internal tensions connected with the fibre's collapse during its rapid mass loss and by the internal temperature gradients.
2. A visible, although significantly smaller further decrease in the fibre strength is connected to a great extent with the increase in porosity, especially with the growth of great pores during gasification of over 50% by weight of the primary fibre mass.
3. The strength drop differentiation and its final values are connected with the differentiated decomposition mechanism for the particular precursor fibres during the pyrolysis, and

the rebuilding of the fibres' carbon structures while heating the fibres to the temperature of 850 °C and during activation.
4. The following structural features of active carbon fibres obtained using different precursor fibres plays the most important role in determining tensile properties.
   ■ The building of a radial spatial orientation occurring in the graphen fragments of fibres obtained from cellulose and their partial gasification along the weakest planes which connect the fibre results in the greatest strength losses during the pyrolysis and activation processes.
   ■ The relatively stabile amorphic novoloid fibres do not cause any greater strength changes over gasification.
   ■ The processes of the formation of cyclic layer structures in polyacrylonitrile fibres (dehydrogenation and denitrogenation) along the fibre axis, as well as the formation of significant amounts of slit pores which are also axially positioned, both of which are distributed within a significant temperature range, lead to the highest relative strength, thanks to the significant participation of the main forces of the C-C bonds of the graphen layers in achieving the fibres' strength.

It should be emphasised that the processes of rebuilding the carbon matrix structures of the investigated fibres occurred during the initial phase of heating to 850 °C, and proceed chaotically as the result of the activation character (lack of fibre stretching). This is the reason that significant strengths of the fibres and nonwovens cannot be attained by the presented processes.

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