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# Influence of Coagulation Bath Temperature on the Porous Structure and Strength Properties of PAN Fibres Including Montmorillonite

## Abstract

*An analysis was carried out concerning the influence of coagulation bath temperature on the porous structure and the sorption & strength properties of polyacrylonitrile (PAN) fibres which include montmorillonite (MMT). We stated that fibres formed at a temperature of 25 °C were characterised by maximum tenacity at the level of 19 cN/tex. Obtaining fibres with increased total pore volume up to 0.34 cm<sup>3</sup>/g, which is beneficial for the medical purposes of the carbon fibres obtained from the PAN fibres discussed, requires the solidification process to be conducted in a coagulation bath at a temperature of 35 °C.*

**Key words:** *montmorillonite, nano-addition, polyacrylonitrile fibres, coagulation bath, bath temperature, tenacity, porous properties.*

and increased porosity. The porosity and strength of carbon fibres depends directly on the structure and properties of the precursor fibres, and the formation of PAN fibres spun from a solution by the wet-spinning method enables the selection of process parameters which allow the required fibre properties to be obtained [2, 3].

As a result of our research into the influence of the as-spun draw ratio on the porous structure and the strength properties of PAN fibres with MMT [1], we obtained fibres characterised by a tenacity of a level appropriate for the carbonisation process (about 25 cN/tex). Unfortunately, the fibres we obtained were characterised by too low a total pore volume, at a level of 0.2 cm<sup>3</sup>/g, whereas the assumption of our research work was to obtain PAN fibres including montmorillonite, which would be characterised by both, the increased porosity and the appropriate strength properties and thus enable a successful carbonisation process.

The aim of our current investigation was to obtain fibres characterised by increased total pore volume and to determine the influence of the coagulation bath temperature on the porous structure and the strength properties of these fibres. Considering the aim of our work, as mentioned above, we accepted the use of two values of the as-spun draw ratio (0% and +10%), and 'sharpening' the solidification conditions by increasing the bath temperature within the range of 15-35 °C. (For the purpose of our discussion we will use the following concepts: 'sharp solidification conditions' means high bath temperature, small solvent content, i.e. high

bath concentration; 'soft solidification conditions' means low bath temperature, large solvent content, i.e. low bath concentration). This manner of conducting the fibre solidification process enables us to pass from the diffusive solidification mechanism which was applied in our earlier work [1] to the drop mechanism, which produces fibres characterised by an increased total pore volume.

In extreme cases, the solidification according to the drop mechanism takes place in sharp baths with a small content of solvent. As the result of tearing off the stiff outer layer of the 'film' off the surface of the spinning solution, the coagulation bath penetrates the inner part of the solidified stream, and the further process of mass exchange takes place through the crags and capillaries which appear, and become filled with liquid of changing composition; this process leads up to total polymer precipitation. In contrast, the diffusive mechanism is typical of solidification in soft baths with increased solvent content. This causes the film formed to become elastic and thus able to transform tensions, and the process of mass exchange proceeds according to the mechanism of partial diffusion, through the film which plays the part of a diffusive filter. The solidification conditions may be sharpened as the result of changing the velocity of these processes by increasing the temperature of the coagulation bath.

## Materials and investigation methods

As in previous research works [1, 4, 5], a polyacrylonitrile terpolymer was used,

## Introduction

The paper presented herein describes the continuation of our investigations into obtaining a new generation of polyacrylonitrile (PAN) fibres including dispersed montmorillonite (MMT) in their structure. As we assumed in our earlier investigations [1], the fibres we obtained were destined for carbonisation, and subsequently to be devoted to use in implants which would be able to stimulate rebuilding of the connective tissue. This is caused by the impact effect of the osteoconductive and osteoproduative elements included in the fibre's structure.

Furthermore, it is known that independently of the basic biological features demonstrated by implants manufactured from carbon fibres, they should be characterised by suitable strength

with the trade name Mavilon, manufactured by the Hungarian enterprise Zoltek. The PAN terpolymer was characterised by an intrinsic viscosity of  $[\eta] = 1.29$  dl/g, determined by the viscometric method in DMF, at a temperature of 20 °C.

Nanomer PGW, a trade product from Nanocor, was used as montmorillonite, being formed from plates with dimensions of about 800 nm × 550 nm, which were determined on the basis of photos taken by a scanning electron microscope. The interlayer distances, at the level of 2.3 nm, were assessed on the basis of the position of the first peak in the X-ray diffractograms of the WAXS type.

The X-ray investigations were carried out with use of a diffractograph from Zeiffert, as in work [6].

MMT was the subject of homogenisation at 1500 rpm in DMF, over 30 minutes, and at a temperature of 25 °C. Next, while preparing the spinning solution, the suspension prepared was added to it to an amount of 3% in relation to the polymer mass.

The fibres were formed by the wet spinning method using a great-scale laboratory-spinning machine [7], which enabled the stabilisation of technological parameters at a pre-set level, as well as their continuous supervision. The change of the as-spun draw ratio was performed by changing the rotary velocity of the first godet pair at the fibres' outlet from the coagulation bath. A spinneret of 240 orifices with diameters of 0.08 mm was used. The fibres' solidification process was conducted in a bath including a 60% aqueous solution of DMF at a temperature within the range from 15 to 35 °C. The drawing process was realised in two stages: in a plastification bath including a 50% aqueous solution of DMF at a temperature of 70 °C, and in an atmosphere of preheated steam at a temperature of 135 °C. Next, after rinsing, the fibres were dried at a temperature within the range of 20 to 40 °C under isometric conditions. The linear density of the fibres obtained was within the range of 39.8 – 67.9 tex in dependence on the formation conditions.

Moisture sorption was tested in accordance with Polish Standard PN-80/P-04635.

Water retention was determined by relating the mass of water retained by the fibres, after centrifugation over 10 minutes

with acceleration of 10,000 ms<sup>-2</sup>, to the mass of the dry sample, and presented in per cent. Before centrifugation, the fibres were immersed over 24 hours in water with the addition of a surface-active compound (1% of Rokafenol NX-3).

The porosity of fibres was assessed by the mercury porosimetry method with the use of a Carlo-Erba porosimeter connected to a computer system, which enabled the determination of the following parameters: the total pore volume, the percentage content of pores distributed in groups of dimension ranges within the total range from 0 to 7500 nm, and the total internal surface of the pores.

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

## Results and discussion of the results obtained

The conditions of conducting the solidification process according to the diffusion mechanism results in obtaining fibres with a small-pore structure and a low total pore volume. Sharpening the solidification conditions (in soft baths with solvent content of 60%) by increasing the temperature to the level of 35 °C enables the passage from the diffusion mechanism to the drop mechanism, as it is known that temperature is the basic parameter upon which the velocity of mass exchange processes depends [7].

The fibres' sorption parameters achieved and assessed by us result from the porous structure formed over the stage of PAN fibres' solidification, which as precursor fibres determine the porosity of carbon fibres.

On the basis of an analysis of the change into sorption properties as a function of the temperature of the coagulation bath, for fibres formed under the as-spun draw ratio at the level of 0.0%, we can state that with the increase in temperature a general tendency of an increase in retention is noted (at the extreme course of humidity sorption changes at 100% RH), as is an increase in the retention value of the fibres tested. However, it should be stated that the increase in water retention is more distinct. The greatest value of humidity sorption at 100% RH demonstrates fibres formed at a temperature of

25 °C, whereas fibres formed at 35 °C are characterised by the greatest water retention (See Table 1).

The type of changes in the fibres' sorption properties, mentioned above, result from sharpening the soft coagulation bath by increasing its temperature, as an increase in the temperature of the coagulation bath leads to an increase in the velocity of diffusion processes. As is visible in Table 1, the temperature of the coagulation bath has a significant effect not only on the structure formed over the stage of solidification, but also on the structure's susceptibility to deformation over the drawing stage. Considering the fibres' ability to achieve a drawing ratio at the level of 500%, the most favourable temperature of solidification is 25 °C.

The fibres formed at the highest solidification bath temperature of 35 °C (PM 16) are characterised by a total pore volume increased up to 0.34 cm<sup>3</sup>/g and an internal surface at the level of 60.39 m<sup>2</sup>/g (Table 2). The porous structure formed under these conditions is also characterised by a high percentage content (73%) of small and medium pores, and limited to 8.1% of very great pores, which are the source of structural defects in carbon fibres obtained from such precursor fibres (Table 2). The small-pore-structure character, as well as the limited content of pores with the greatest dimensions, is a very advantageous phenomenon when considering that the precursor fibres are intended for obtaining carbon fibres for medical applications. However, the tenacity on the level of 16 cN/tex may be accepted as the lower limit of the precursor fibres' usability for the carbonisation process, the real test of applying such fibres in manufacturing carbon fibres would be the successful result of their carbonisation. This means that the temperature of the solidification bath at the level of 35 °C is a boundary condition for sharpening the moderate soft coagulation baths.

The highest tenacity within this research series, of 19 cN/tex (Table 1), is demonstrated by fibres solidified in a coagulation bath at a temperature of 25 °C. Unfortunately, their total pore volume is at a low level of 0.2 cm<sup>3</sup>/g (Table 2). In order to produce fibres approaching greater porosity, a test series was carried out under a higher as-spun draw ratio value, at the level of +10%.

On the basis of an analysis of the sorption properties of fibres formed under the as-spun draw ratio of +10% as a function of the coagulation bath temperature, we can state a dependency similar to that for fibres formed under the as-spun draw ratio of 0.0%. With the increase in the coagulation bath's temperature, a general tendency was observed for the humidity sorption at 100% RH to increase, as likewise the water retention. As in the previous test series, the greatest humidity sorption at 100% RH demonstrates fibres formed at a temperature of 25 °C, whereas fibres formed at the temperature of 35 °C are characterised by the greatest water retention (Table 3). The fibres

formed at the highest temperature are characterised by a total pore volume of 0.34 cm<sup>3</sup>/g and an internal surface of 63 m<sup>2</sup>/g (Table 4). They are also characterised by a small-pore structure with a significant predominance of small and medium pores within the range of about 77% (Table 4). At the same time, the disadvantageous content of very great pores in the structure obtained is limited essentially to about 6%.

Applying an as-spun draw ratio at the level of +10% caused a slight decrease in tenacity, compared with the fibres formed by 0.0% of the as-spun draw ratio. Fibres formed at a temperature of

20 °C are characterised by the highest tenacity value of 17.93 cN/tex, whereas sharpening of the solidification conditions by increasing the temperature to 35 °C caused a decrease in tenacity to the level of 15.60 cN/tex (Table 3).

Considering both test series, the insertion of montmorillonite into the fibre-forming polymer caused a decrease of its susceptibility to deformation over the drawing stage. Fibres without montmorillonite, which were solidified under similar conditions as those with montmorillonite, could be processed under significantly higher deformations over the drawing stage than the latter fibres (sample PW 2 compared with PM 7). This resulted in a higher value of tenacity, at the level of about 21 cN/tex (Table 3). In contrast, in the case of PAN fibres with MMT, the tenacity below 17 cN/tex is probably the lowest boundary of application of these fibres for the carbonisation process. The essential decrease of the fibre-forming polymer's susceptibility to deformation over the drawing stage, which results in significantly lower tenacity values, is probably connected with the phenomenon of agglomeration of the inserted nano-addition.

The advantageous influence of montmorillonite is visible in the case of the porous structure's formation. Despite the lower total pore volume in fibres with montmorillonite formed under the same solidification conditions as fibres without nano-addition, the structures obtained have a small-pore character. Achieving such a structure is extremely advantageous considering the further processing of the polyacrylonitrile fibres, as it is known that great and very great pores may be the source of structural defects in the final product, the carbon fibre.

Our hypothesis that the main cause of the decreased strength properties of PAN fibres including MMT is susceptibility to agglomeration of the nano-addition is confirmed by the results of our investigations into the strength properties of PAN fibres including montmorillonite subjected to the action of ultrasounds before being introduced into the spinning solution. Fibres spun from a solution prepared in this way, and formed under an as-spun draw ratio of +10% and at a temperature of 15 °C, were characterised by a tenacity of 29 cN/tex. The results of these investigations are the subject of our publication [8]. In this latter paper an

**Table 1.** Properties of PAN fibres with 3% of montmorillonite, spun under the as-spun draw ratio of 0.0%.

Sample denotation	Coagulation bath temperature, °C	Total drawing ratio, %	Tenacity, cN/tex	Elongation at break, %	Sorption in air of 100% relative humidity, %	Retention, %
PM6	15	422.14	16.09	7.52	8.02	17.96
PM8	20	391.30	15.89	11.12	10.43	28.17
PM 11	25	501.28	18.97	8.75	11.78	26.43
PM 13	30	420.04	17.61	8.83	8.25	32.20
PM 16	35	427.91	15.91	10.03	9.52	38.89

**Table 2.** Characterisation of the porous structure of PAN fibres with montmorillonite, spun under the as-spun draw ratio of 0.0%.

Sample denotation	Total volume of pores, cm <sup>3</sup> /g	Internal surface of pores, m <sup>2</sup> /g	Percentage content of pores, %			
			small (4-15), nm	medium (15-150), nm	great (150-750), nm	very great (750-7500), nm
PM 6	0.18	35.35	51.10	24.44	6.67	17.78
PM 8	0.30	34.55	24.24	13.51	10.81	43.25
PM 11	0.19	27.80	34.09	34.09	18.18	13.65
PM 13	0.21	46.43	43.39	30.19	7.55	7.55
PM 16	0.34	60.39	43.25	29.73	18.92	8.10

**Table 3.** Properties of PAN fibres with 3% of montmorillonite, and without montmorillonite (sample PW 2), spun under the as-spun draw ratio of 10%.

Sample denotation	Coagulation bath temperature, °C	Total drawing ratio, %	Tenacity, cN/tex	Elongation at break, %	Sorption in air of 100% relative humidity, %	Retention, %
PM 7	15	453.42	15.75	7.18	7.83	18.84
PM 9	20	484.73	17.93	7.01	8.87	23.60
PM 10	25	437.35	16.09	8.62	10.76	29.70
PM 14	30	380.95	15.82	9.68	8.72	33.20
PM 17	35	379.90	15.60	10.33	9.05	43.71
PW 2	15	437.35	40.80	11.02	6.72	10.75

**Table 4.** Characterisation of the porous structure of PAN fibres with montmorillonite and without montmorillonite (sample PW 2), spun under the as-spun draw ratio of 10%.

Sample denotation	Total volume of pores, cm <sup>3</sup> /g	Internal surface of pores, m <sup>2</sup> /g	Percentage content of pores, %			
			small (4-15), nm	medium (15-150), nm	great (150-750), nm	very great (750-7500), nm
PM 7	0.12	28.00	53.34	16.67	6.67	17.78
PM 9	0.16	21.78	31.71	19.52	21.96	26.83
PM 17	0.34	63.01	47.06	30.59	16.47	5.88
PW 2	0.39	33.86	20.22	8.99	22.48	48.31

explanation is also given for the influence of the submolecular structure and the kind of MMT dispersion (exfoliation and intercalation determined by means of the WAXS method) on the level of the strength values of the fibres obtained.

## ■ Conclusions

1. An advantageous transformation of the microporous structure of fibres without any nano-addition into a small-dimension-porous structure of the fibres including montmorillonite is connected with the increase in the temperature of the coagulation bath.
2. Sharpening the solidification conditions by increasing the temperature of the coagulation bath enhances the effect of decreasing the strength properties of PAN fibres, including MMT.

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