

EFFECT OF THE TYPE OF NANOADDITION ON THE THERMAL PROPERTIES OF POLYACRYLONITRILE FIBRES

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Thermal properties of precursor polyacrylonitrile fibres containing nanoparticles of additives such as SiO₂, hydroxyapatite and montmorillonite have been examined. The thermal curves of the fibres under investigation obtained by the derivatographic method in air and DSC in a neutral gas atmosphere were interpreted from the point of view of physical and chemical changes in the fibre-forming polymer. Based on the thermogravimetric curves, the coefficients of thermal stability of the fibres were found. It has been found that the thermal stability of PAN fibres is affected by the type of nanoadditives and the value of the as-spun draw out ratio used during fibre spinning.

Keywords: hydroxyapatite, montmorillonite, nanoadditives, polyacrylonitrile, silica, thermal properties

Introduction

Biomaterial engineering is one of the most important incentives for the development of modern restorative surgery and orthopaedics. Depending on the destination of the implant materials, the permanent metal implants or implants made of biodegradable and bioresorbent polymers are used. If there is such a possibility, the metal implant materials are being replaced more and more often by implants made of biodegradable and bioresorbent polymers, for example polylactide [1, 2], polyglycole acid [3] and carbon composites [4, 5]. In this case the biodegradable and bioresorption processes of the implant materials constitute the scaffold for reconstruction and growth of new cells. Carbon fibres used in composites are highly significant among such implant materials. They are used for example in some parts of reconstruction of the knee joints [6] or Achilles tendon [7] (which requires the use of carbon fibres with different characteristics).

A new application of carbon fibres can be their use as a carrier of biologically active compounds incorporated into fibre during the stage of precursor fibre production. The implant of carbon fibres, in addition to appropriate biological properties, should show a high strength and an increased porosity at the same time. It is well known that both the strength and porosity of carbon fibres are directly dependent on the structure of precursor fibres formed during fibre solidification and drawing [8–10].

The incorporation of nanoadditives such as hydroxyapatite (HAp), montmorillonite (MMT) or silica (SiO₂) into precursor PAN fibres makes it possible to produce carbon fibres showing new unparal-

leled properties. Biocomposites produced from carbon fibres containing the nanoadditives will possess in their structure elements with osteoconductive and osteoproduative effects. The use of silica nanoparticles results from the particular role played by silicon in the formation of bone structures, the process of their hardening and regeneration after breaks [11]. Of similar importance may be montmorillonite, which is a laminar silicate with negatively charged layers, whose charges are compensated by the cation incorporated into the interlayer spaces during the modification process [12, 13]. However, the greatest medical significance among those nanoadditives belongs to hydroxyapatite, whose structure is very similar to the inorganic portion of bony tissue [14].

The aim of the present study was to assess the thermal properties of three types of precursor PAN fibres containing nanoadditives dispersed in the fibre-forming polymer. The preparation of carbon fibres from so modified PAN precursor requires the determination of the effects of particular nanoadditives on the thermal changes and stability of the fibres as it is important for the proper selection of carbonisation parameters.

Experimental

Materials

Three types of precursor PAN fibres were used in the study:

- PAN fibres containing 3% of nanohydroxyapatite in relation to the polymer (samples with symbols

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Table 1 Sorption and strength properties of polyacrylonitrile fibres

Sample symbol	As-spun draw ratio/%	Total draw ratio/%	Moisture absorption at 65% RH	Moisture absorption at 100% RH	Water retention/%	Tenacity/cN/tex
PAN M1	-40	923.47	1.82	5.64	7.09	36.90
PAN M2	+10	619.29	1.93	7.05	11.13	29.13
PAN H1	-40	998.04	1.92	8.50	11.78	44.23
PAN H2	0.0	792.04	1.92	11.14	20.54	32.00
PAN S1	-40	1019.06	2.21	8.82	14.61	40.95
PAN S2	+10	781.98	1.80	10.45	24.04	31.67
PAN 1	-40	1054.00	2.44	6.77	7.75	47.34
PAN 2	+10	437.35	2.37	8.02	10.94	40.79

PAN M1 and PAN M2 – polyacrylonitrile fibres containing 3% of montmorillonite nano-particles per polymer, PAN H1 and PAN H2 – polyacrylonitrile fibres containing 3% of hydroxyapatite nano-particles per polymer, PAN S1 and PAN S2 – polyacrylonitrile fibres containing 3% of silica nano-particles per polymer, PAN 1 and PAN 2 – polyacrylonitrile fibres without nano-particles

PAN H1, PAN H2). Nanohydroxyapatite (product of AGH Cracow) showed grains with dimensions from dozen or so to 150 nm measured on the basis of scanning microscope photographs.

- PAN fibres containing 3% of nanosilica in relation to polymer (samples with symbols PAN S1, PAN S2). This silica (product of AGH) was characterised by particle size ranging from 50 to 100 nm determined by the method of electron microscopy.
- PAN fibres containing 3% of montmorillonite in relation to polymer (samples with symbols PAN M1 and PAN M2). Montmorillonite – Nanomer PGW of Nanocor – had lamella dimensions of about 800-550 nm determined by the method of electron microscopy. The distance between packages was determined on the basis of the position of the first peak in X-ray diffractograms WAXS and amounted to 2.3 nm.

For comparison, also PAN fibres with no nano-additives were used, marked with symbols PAN 1 and PAN 2, with different values of as-spun draw out ratio.

All the spinning solutions were prepared from PAN terpolymer of Zoltek with the following composition:

- 93–94% by mass of acrylonitrile units,
- 5–6% by mass of methyl acrylate units,
- about 1% by mass of sodium allylsulphonate.

Dimethylformamide (DMF) was used as solvent. Fibres were spun by the wet process from solution with the use of laboratory spinning machine operating with stable technological parameters under a continuous control. A spinneret with 240 orifices, 0.08 mm in diameter each 2 was used. The fibre solidification process was carried out in a bath containing an aqueous solution of DMF. The drawing process was performed in two stages: in a plasticizing bath and under superheated steam. After rinsing, the fibres were dried at 20–40°C under isometric conditions. Precise values of the technological parameters are under patent protection [15].

Characteristics of fibres are given in Table 1.

The fibres under investigation were spun with negative and positive values of as-spun draw out ratio. The solidification process was carried out in mild baths with an increased content of solvent at a low temperature. This allowed us to run the process according to the diffusion mechanism and to obtain fibre strength at a level suitable for the carbonisation process. Considering the use of carbon fibres, the precursor fibres should show an increased porosity. Therefore, there were also used positive values of the as-spun draw out ratio, as typical conditions for the preparation of porous fibres. As the conditions of solidification excluded the shift of solidification mechanism towards the drop-wise mechanism, the range of changes in porosity was limited to 0.2–0.3 cm³ g⁻¹. In conformity with this are changes in moisture absorption ranging from 1.80 to 2.44% at 65% RH and from 5.64 to 11.14% at 100% RH as well as the changes in water retention within the range 7.09–24.04%. At the same time, there was confirmed the previously found regularity that lower strength of fibres spun with a positive as-spun draw out ratio is accompanied by their higher sorption properties resulting from both the total pore volume and the character of porous structure.

Measurement and test methods

The effect of porosity on the thermal properties of fibres from other fibre-forming polymers [16], including also nanoadditive-containing fibres was discussed in our previous papers [17, 18].

Fibre porosity was measured by means of a Mercury Porosimeter of Carlo-Erba linked with a computer system to register the numerical values of the measured parameters. The determinations included: the total pore volume, total internal surface, volume of capillary group with a defined radius and pore percentage content. This method allows one to

determine the pore percentage content with given ranges in the capillary set with sizes of 5–7500 nm.

Moisture absorption at 65 and 100% RH was determined by the desiccator method according to the Polish Standard PN-71/P-04801.

Water retention was measured by the centrifuge method. Fibre samples were immersed in distilled water containing a surface-active agent (Rokafenol Nx-3 in an amount of 0.1%) for 24 h and then the absorbed water was centrifuged off for 10 min at an acceleration of 10000 m s⁻².

Fibre tenacity and elongation at break were measured according to the Polish Standard PN-85/P-04761.04, referring the breaking force to the fibre linear density in text.

The thermal analysis of fibres was carried out by means of a derivatograph, and differential scanning calorimetry (DSC), using a Paulik–Paulik–Erdey system derivatograph and DSC-204 microcalorimeter of Netzsch. The derivatographic analysis was carried out in air using weighed portions of 40 mg at a heating rate of 7.9°C min⁻¹ within the temperature range from 20 to 800°C. In the case of microcalorimetry the measurements were performed in inert gas, using weighed portions of 2.5 mg at a heating rate of 10°C min⁻¹ within the temperature range from 30 to 600°C.

Results and discussion

Analysing the obtained derivatograms of the fibres under investigation, one can observe that during heating from room temperature up to 800°C the fibres undergo complex physical and chemical processes (Figs 1–3,

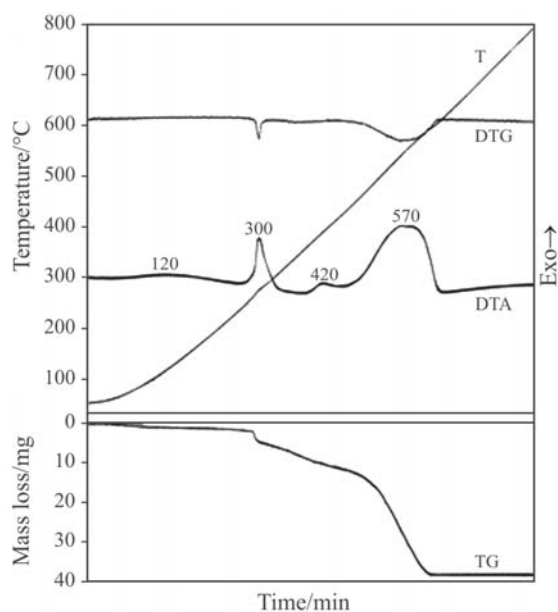


Fig. 1 TG, DTG, DTA and *T* curves of fibres from PAN containing hydroxyapatite

Table 2). Within the temperature range from 30 to 270°C, the DTA curves of all examined samples of PAN precursor fibres show a broadened exothermic peak that is connected with water desorption and dehydration. As it follows from the thermogravimetric curves, the amount of absorbed water in fibres is low and amounts to 1.25–3.75%, which is consistent with the values of moisture absorption at 65% RH (Table 1). The fibres containing nanomontmorillonite and nano-

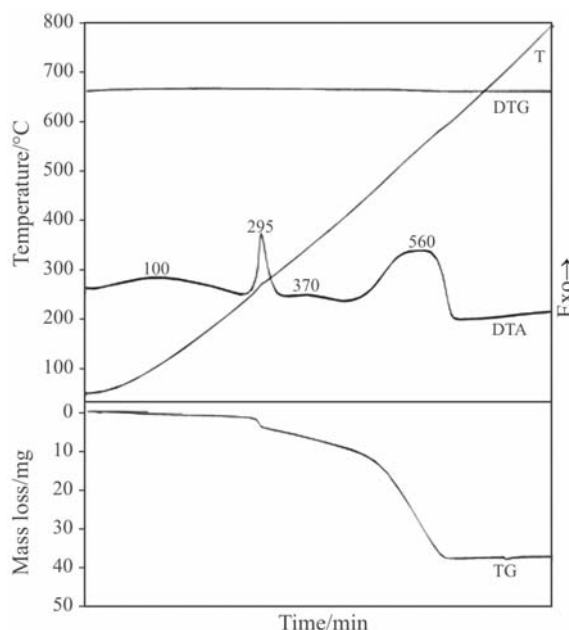


Fig. 2 TG, DTG, DTA and *T* curves of fibres from PAN containing montmorillonite

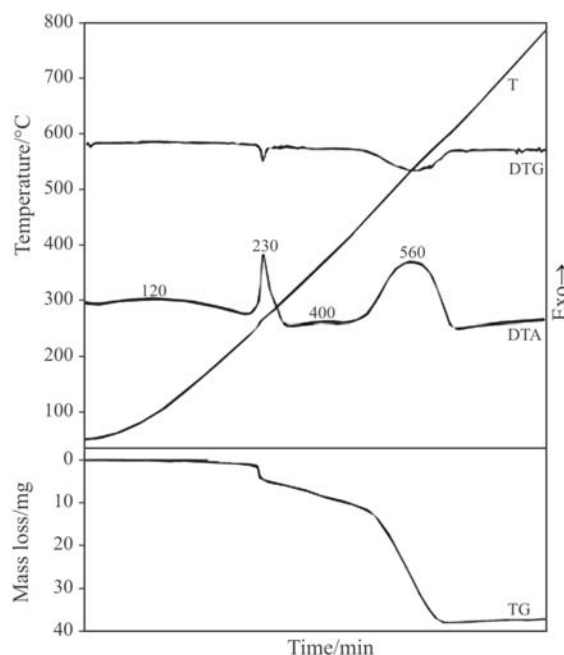


Fig. 3 TG, DTG, DTA and *T* curves of fibres from PAN containing silica

Table 2 Results of thermal analysis of polyacrylonitrile fibres

Sample symbol	Water desorption and dehydration		Cyclization		Further thermal decomposition with the formation of carbon structures		Oxidation		Residue at $T=800^{\circ}\text{C}/\%$		Thermal stability indicator	
	$\Delta T/^{\circ}\text{C}$	$\Delta m/\%$	$\Delta T/^{\circ}\text{C}$	$\Delta m/\%$	$\Delta T/^{\circ}\text{C}$	$\Delta m/\%$	$\Delta T/^{\circ}\text{C}$	$\Delta m/\%$	$T_s/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$		
PAN M1	40–250	2.50	270–330	12.50	390–420	20.00	460–630	92.50	290	550		
PAN M2	30–270	3.75	270–320	12.50	350–400	22.50	440–620	97.50	280	530		
PAN H1	40–260	3.75	260–330	15.00	380–440	27.50	470–630	97.50	290	540		
PAN H2	40–240	3.75	240–330	22.50	370–420	30.00	450–620	98.75	270	510		
PAN S1	40–250	2.50	250–330	16.25	360–420	25.00	450–620	97.50	280	510		
PAN S2	40–250	2.50	250–330	15.00	360–420	22.50	460–630	93.75	280	530		
PAN I	40–240	1.25	260–340	22.50	370–430	30.00	450–620	100.00	270	520		
PAN 2	40–230	2.50	250–330	25.00	350–410	32.50	450–600	100.00	270	510		

Δm – calculated in relation to the initial sample mass, T_s – temperature corresponding to a 5% mass loss, T_{50} – temperature corresponding to a 50% mass loss

hydroxyapatite show higher mass losses resulting probably from the evaporation of water combined not only physically, but also chemically with those nano-additives (Fig. 4). A lower mass loss is observed in fibres containing nanosilica, as the quantity of water combined with this nanoadditive is the lowest (Fig. 4). In all the cases of the fibres under consideration, the water evaporation is accompanied by the release of residual solvent remaining in fibres. In the case of MMT, as found in papers [19–22], the presence of the exothermic peak at about 150°C is connected with the dehydration process.

Within the temperature range 240–340°C the DTA curves of the examined fibres show an exothermic peak that results from cyclisation and dehydrogenation processes, which is connected with the formation of rink structure. This process is clearly visible in the DSC curves of the examined fibres, with its maximum under the atmosphere of neutral gas being slightly shifted towards higher temperatures (Fig. 5). At the maximal temperature of cyclization processes, the TG curves show a distinct, stepwise mass loss amounting to 25% (sample marked with symbol

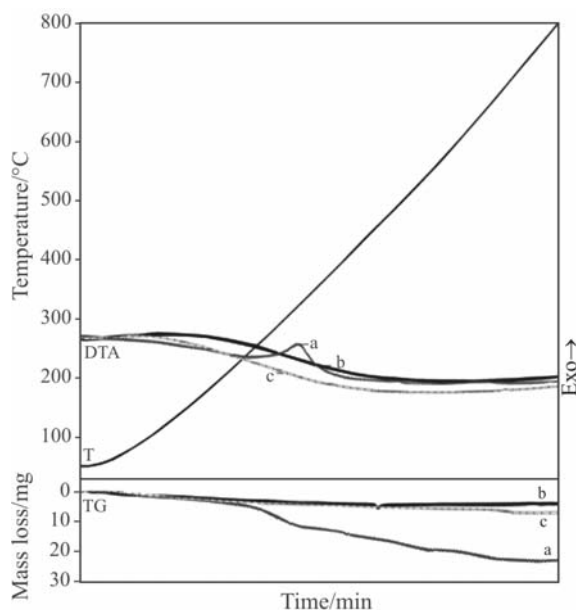


Fig. 4 TG, DTA and T curves of a – montmorillonite, b – silica, c – hydroxyapatite

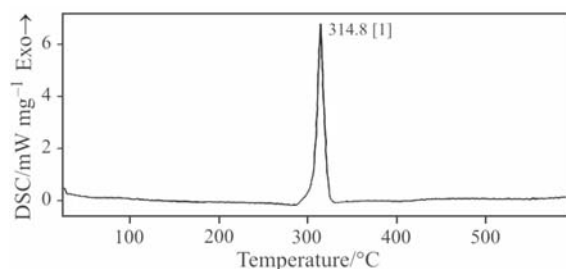


Fig. 5 DSC curves of fibres from PAN containing montmorillonite

PAN 2). It is due, first of all, to the emission of volatile compounds, such as NH_3 , CO , HCN , resulting from the formation of carboxyl and hydroxyl groups and ether bridges between carbon atoms of methyl groups. The mass loss at this temperature depends clearly of the type of nanoadditive incorporated into fibres. In our opinion, this results from the adsorption processes of the mentioned above gaseous products on the surface of nanoadditive. This is confirmed by the fact that in the case of MMT-containing fibres, the mass loss is lower, which is associated with the specific laminar structure of montmorillonite.

The process of further intermolecular cross-linking is revealed by a slight, broadened exothermic peak within the temperature range 350–440°C (Figs 1–3), which is accompanied by the formation of carbon structures. These processes are observed in the thermogravimetric curves as further slow mass losses. The highest mass loss, amounting to 30%, in this process, besides the fibres with no nanoadditive, is shown by the nanohydroxyapatite containing fibres. This is consistent with the character of thermal changes in hydroxyapatite (Fig. 4).

Within the temperature range 450–630°C all the DTA curves of the examined fibres show a broad exothermic peak connected with the oxidation of the previously formed carbon structures. The oxidation process results in a violent mass loss of the examined samples, reaching even 100% in the case of fibres with no nanoadditive. The highest mass residue after this process, amounting to 7.5%, is shown by the MMT-containing fibres formed with negative values of as-spun draw out ratio (Table 2). Comparably high residue at a level of 6.25% is shown by fibres containing nanosilica (PAN S2).

Different mass losses are connected with the destruction degree of nanoadditive that is dependent of its type (Fig. 4).

The thermal stability of the fibres under discussion was assessed on the basis of indicators T_5 and T_{50} [23, 24]. The performed examinations have shown that the presence of a nanoadditive in the fibre-forming polymer causes a slight increase in the thermal stability of fibres, determined with indicators T_5 and T_{50} . This is consistent with the literature reports concerning other fibre-forming polymers [25]. Anyway, the MMT-containing fibres show the highest thermal stability (Table 2). However the thermal stability indicators of the fibres containing nanosilica (PAN S1 and PAN S2) are lower in comparison to those of samples PAN M1 and PAN H1.

In the case of all the types of fibres, the porous structure of fibres exerts some influence on their thermal stability. For fibres spun with negative values of as-spun draw out ratio, i.e. those with a lower total

pore volume the thermal stability is higher by 5% from that of fibres spun with positive values of as-spun draw out ratio (Table 1). The lower thermal stability of the fibres with higher total pore volume results from the presence of higher quantity of oxygen in the pore system that activates the fragmentation of the fibre-forming polymer at elevated temperature.

Conclusions

- The thermal stability of nanoadditive-containing PAN fibres depends both on the type of the incorporated nanoadditive and the porous structure created during fibre formation. The highest thermal stability is shown by the MMT-containing fibres spun with negative values of as-spun draw out ratio.
- The incorporation of nanoadditive into the fibre-forming polymer of precursor PAN fibres causes changes in the temperatures of characteristic thermal transitions, which indicates the necessity of proper selection of the carbonisation parameters.

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References

- 1 R. A. Sousa, R. L. Reis, A. M. Cunha and M. J. Bevis, *Compos. Sci. Technol.*, 63 (2003) 389.
- 2 R. R. M. Bos, F. R. Rozema, G. Boering, A. J. Nijenhuis, A. J. Pennings, A. B. Verwey, P. Nieuwenhuis and H. W. B. Jansen, *Biomaterials*, 12 (1991) 33.
- 3 S. Gogolewski, *Int. J. Care Injured*, 31 (2000) 28.
- 4 C. Morrison, R. Macnair, C. MacDonald, A. Wykman, I. Goldie and M. H. Grant, *Biomaterials*, 16 (1995) 987.
- 5 S. Błażewicz, J. Chłopek, A. Litak, C. Wajler and E. Staszko, *Biomaterials*, 18 (1997) 437.
- 6 A. C. Campbell and P. S. Rae, *Ann. R. Coll. Surg. Engl.*, 77 (1995) 349.
- 7 A. Górecki, W. Kuś, S. Błażewicz and A. Powroźnik, *Chir. Narz. Ruchu Ortop. Pol.*, LV 2 (1990) 131.
- 8 S. P. Papkow, *Chim. Wołok.*, 4 (1981) 13.
- 9 T. Mikołajczyk, I. Krucińska and K. Kamecka-Jędrzejczak, *Textile Res. J.*, 59 (1989) 557.
- 10 T. Mikołajczyk and I. Krucińska, *Fibres and Textiles in Eastern Europe*, 3 (1995) 44.
- 11 T. Peltola, M. Jokinen, S. Veittola, H. Rahiala and A. Yli-Urpo, *Biomaterials*, 22 (2001) 589.
- 12 M. Kubranova, E. Jona, E. Rudinska, K. Nemcekova, D. Ondrusova and M. Pajtasova, *J. Therm. Anal. Cal.*, 74 (2003) 251.
- 13 Z. Yermiyahu, A. Landau, A. Zaban, I. Lapidés and S. Yariv, *J. Therm. Anal. Cal.*, 72 (2003) 431.
- 14 J. Heikkilä, J. A. Aho, A. Yli-Urpo, O. H. Andersson, H. J. Aho and R. P. Happonen, *Acta Orthop. Scand.*, 64 (1993) 678.
- 15 S. Błażewicz, M. Błażewicz, J. Chłopek, E. Pamuła, C. Wajler, T. Mikołajczyk, M. Boguń, A. Powroźnik, A. Kurzak and B. Stawińska, *Polish Patent*, No P-377-921 (2005).
- 16 G. Janowska and T. Mikołajczyk, *J. Therm. Anal. Cal.*, 71 (2003) 549.
- 17 G. Janowska, T. Mikołajczyk, D. Wołowska-Czapnik and M. Boguń, *J. Therm. Anal. Cal.*, 79 (2005) 1.
- 18 G. Janowska, T. Mikołajczyk and M. Olejnik, *J. Therm. Anal. Cal.*, OnlineFirst, DOI: 10.1007/s10973-005-7429-6.
- 19 I. A. Pastre, I. do Nascimento Oliveira, A. B. S. Moitinho, G. R. de Souza, E. Y. Ionashiro and F. L. Fertonani, *J. Therm. Anal. Cal.*, 75 (2004) 661.
- 20 V. L. P. Soares, R. S. V. Nascimento, V. J. Menezes and L. Batista, *J. Therm. Anal. Cal.*, 75 (2004) 671.
- 21 I. Kiricsi, *J. Therm. Anal. Cal.*, 79 (2005) 533.
- 22 Y. Xi, W. Martens and R. L. Frost, *J. Therm. Anal. Cal.*, 81 (2005) 91.
- 23 G. Janowska and T. Mikołajczyk, *J. Therm. Anal. Cal.*, 63 (2001) 815.
- 24 G. Janowska, *J. Thermal Anal.*, 53 (1998) 309.
- 25 M. Kacperski, *Polimery*, 2 (2003) 85.

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