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THERMAL PROPERTIES AND FLAMMABILITY OF FIBRES MADE FROM POLYIMIDOAMIDE NANOCOMPOSITE

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The effects of basic fibre-forming parameters on the thermal properties and flammability of fibres from polyimidoamide (PIA) nanocomposite have examined. The comparative analysis of the properties of fibres from modified PIA and PIA nanocomposite has been conducted.

The multi-functional fibres prepared from PIA nanocomposite show increased porosity and sorption properties as well as a high thermal stability and reduced flammability in comparison with fibres without MMT.

Keywords: *fibre properties, flammability, nanocomposites, polyimidoamide, thermal stability*

Introduction

The use of nanotechnology in making chemical fibres makes it possible to produce fibres with new properties without parallel in conventional fibre-forming polymers.

Montmorillonite-containing nanocomposites are characterised mainly by increased strength properties [1], decreased permeability of vapours and gases, higher crystallization rate [2], increased thermal stability and decreased flammability [3]. The intensification of these features is also desirable in the case of polyimidoamide (PIA) fibres, which show good thermal properties due to the chemical composition of the fibre-forming polymer [4, 5]. These properties have been maintained despite the polymer modification that we used to incorporate into the macromolecular chain flexible segments derived from diaminodiphenylmethane or diaminodiphenyloxide [6, 7]. The modified polymer has been used under selected spinning condition to produce multi-functional PIA fibres with combined properties of high thermal resistance and increased porosity and moisture absorption with the fibre tenacity being at a level of 15-16cN/tex [8–10].

Increased sorption properties are of importance considering the comfort of using protective clothing under so-called first-contact-with-flame conditions. However, the increase in fibre porosity that provides these properties may adversely affect the behaviour of fabrics being in contact with flame. This effect should be compensated by the action of montmorillonite (MMT), which is a natural clay characterized by a laminar structure in which the negative charge of layers is compensated by interlayer cations (e.g. Na^+, Ca^{2+}) [11–14], dispersed in the fibre-forming polymer. This is possible since the formation of carbonised polymer layers on the surface of MMT packages constitutes a barrier that cuts off the oxygen access and reduces the oxidation of gaseous decomposition products [15].

In this connection there arose an idea to incorporate MMT into the modified PIA by us, with diaminodiphenylmethane once its synthesis was completed. The resultant spinning solution was used to spin fibres whose fibre-spinning polymer consisted of PIA nanocomposite.

The aim of the present study was to assess the effect of spinning conditions on the thermal properties of PIA nanocomposite fibres as well as the effect of MMT dispersed in the polymer on the flammability of fibres. The obtained fibres (samples with symbols M_1–M_5) spun with various values of as-spun draw out ratio were used to assess the effect of spinning conditions on thermal properties of PIA nanocomposite fibres.

The effect of MMT incorporated into PIA was analysed by comparing the:

- the structure and properties of fibres made from PIA modified with diaminodiphenylmethane (W_1) spun under optimal conditions with the properties of fibres from PIA nanocomposite made under the same conditions (W_2),
- the structure and properties of both types of fibres spun under optimal conditions for the given type of polymer (W_1-fibres from modified PIA, M_1 and M_2-fibres from PIA nanocomposite).

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In the case of PIA nanocomposite fibres, the optimal conditions selected allowed us to prepare alternatively either fibres with higher strength or fibres with increased sorption properties.

Experimental

Materials

The object of study were fibres from PIA nanocomposite with symbols M_1–M_5 spun with variable values of as-spun draw out ratio from –20 to 50% and corresponding deformations during the drawing stage. Fibres from PIA modified with diaminodiphenylmethane (W_1) and fibres from PIA nanocomposite spun under the same conditions (W_2) were used for comparison.

Photographs taken by means of a scanning microscope confirm the presence of dispersed montmorillonite (MMT) in the fibre-forming polymer [17].

Characteristics of spinning solution and montmorillonite

Fibres were spun from post-reaction solutions of PIA modified with diaminodiphenylmethane in N-methylpyrrolidone prepared in accordance with the conditions given in paper [16]. The solidification process was carried out in a bath containing an aqueous solution of the solvent (above 55%) at a low temperature, about 15–18°C. The drawing process was performed in a single stage, in a plasticising bath containing the same content of solvent as that in the coagulation bath, at an elevated temperature up to 65–70°C. Finally, solvent was rinsed off, and the resultant fibres were dried under isothermal conditions at 80–120°C. MMT in the form of a suspension in solvent in a quantity of 3% in relation to the polymer was added when the synthesis stage was completed. The analysis of the effect of MMT on the rheological properties of spinning solutions is given in [17].

MMT used consisted of a commercial Nanomer PGW of Nanocor (USA). The type of modifier used to change hydrophilic properties of MMT into organophilic properties is a manufacturer's secret. The dimensions of packages determined with the use of a scanning microscope are 800×500 nm. The interlayer distances determined on the basis of the position of the first peak in diffractograms obtained by the WAXS method are equal to 2.3 nm.

The characteristics of polymer and spinning solution are given in Table 1.

Fibre formation

Fibres were spun by the wet process from the PIA solution in N-methylpyrrolidone, using a spinning machine whose construction allowed one to stabilize the technological parameters at a required level under a continuous control. The spinnerets used had 500 orifices (for spinning solution PIA nanocomposite W_2) or 240 orifices (for spinning solution PIA nanocomposite M) with a diameter of 0.08 mm.

Measuring and testing methods

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 determination included: the total pore volume, total internal surface. 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-81/P-04635.

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 tex.

The thermal analysis of fibres was carried out by means of a derivatograph, differential scanning calorimetry (DSC) and thermogravimetry (TG), using a Paulik–Paulik–Erdey system derivatograph, a DSC–204 microcalorimeter and a TG–209 thermobalance of Netzsch. The derivatographic analysis was carried out in air using weighed portions of 40 mg at a

Table 1 Characteristics of polymer and spinning solutions of PIA nanocomposite and modified PIA

Polymer type	Concentration of spinning solution/%	Intrinsic viscosity/dL g^{-1}	Apparent dynamic viscosity/Pa s	Rheological parameters of spinning solution	
				n	k
M	19.78	1.63	30.95	0.99	29.58
W_2	19.78	1.80	33.33	0.96	34.36
W_1	19.20	1.20	21.43	0.98	35.76

M – spinning solution of PIA nanocomposite used to spin fibres with symbols M_1 – M_5, W_2 – spinning solution of PIA nanocomposite used to spin fibres with symbol W_2, W_1 – spinning solution of modified PIA used to spin fibres with symbol W_1

heating rate of 7.9°C min^{-1} within the temperature range from 20 to 800°C. In the case of microcalorimetry and thermogavimetry, 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 550°C.

Results and discussion

The structure formed during solidification determines the polymer deformability during drawing and preparation of fibres with specified properties.

In the case of PIA with a rigid macromolecular structure containing additionally MMT, the strength properties depend not only on the extent of deformation during drawing, but also on the orientation of structural elements taking place in still liquid stream as a result of the action of longitudinal rate gradient [18]. Its value depends on the as-spun draw out ratio. The latter was changed within a wide range from negative to positive values (–20 to 50%).

Aiming at the formation of a fine-porous structure that facilitates the preparation of fibres with increased strength properties, the solidification process was carried out under mild conditions in a bath with an increased solvent content up to 55% at low temperatures 15–18°C. A detailed analysis of the porous structure formed under these conditions and sorption properties of fibres from PIA nanocomposite are given in paper [18].

The highest values of moisture absorption at 100% RH and retention are shown by the fibres formed with the negative value of as-spun draw out ratio –5% and at the extremely positive value of this ratio 50% (Table 2). The moisture absorption at 65% RH varies within a narrow range from 5.3 to 5.6%. Generally, the character of changes in the sorption properties *vs*. both process parameters is similar to the changes in the total pore volume, but within the range of positive values of as-spun draw out ratio the increase in the total pore volume is considerably smaller as compared to the increase in sorption properties. With the downward trend of changes in the internal surface, being particularly clear within the range of positive values of as-spun draw out ratio, the sorption properties of fibres depend not only on the total pore volume and internal surface, but also to a considerable extent on the character of the formed porous structure. The moisture absorption at 100% RH depends on the percentage contents of capillaries with dimensions capable of absorbing moisture through capillary condensation, while the value of retention is connected with the content of large pores and those from the end range of medium pores [19].

The changes in the tenacity of PIA nanocomposite fibres *vs*. both process parameters show an extreme course, with higher values of this parameter by 1 cN/tex being observed in fibres spun with positive values of as-spun draw out ratio. On the other hand, the tenacity of fibres from modified PIA containing no MMT show higher values when negative values of as-spun draw ratio were used [8].

From the comparison of the structures and sorption properties of both types of PIA fibres (W_1, W_2) spun under optimal conditions for the polymer with no intercalated MMT (W_1) it follows that its presence is accompanied with the increase in sorption properties, especially retention. At the same time, the fibres from PIA nanocomposite (W_2) show lower tenacity by 5 cN/tex. This is connected with the fact that in the case of PIA nanocomposite fibres it has turned out to be beneficial to use positive as-spun draw out ratios due to the possible deformation of the still liquid stream. The dispersed layers of intercalated MMT in the fibre-forming polymer can be easier ordered under such conditions along the axis of the solidifying stream. With the positive values of as-spun draw out ratio (25 or 50%) it is possible to obtain alternatively either higher fibre strength or higher sorption properties (M_2, M_1). The higher sorption properties of fibres from PIA nanocomposite in comparison with those of the fibres with no MMT are connected with higher total pore volume and internal surface (increased almost twice).

With a similar character of the distribution of pores *vs*. their radius [8, 18] the high values of retention of PIA nanocomposite fibres are connected with the presence of considerably higher total contents of medium and large pores amounting to 67.08 and 59.09% for samples M_1 and M_2, respectively.

From the thermal analysis it follows that the examined PIA nanocomposite fibres contain 5–5.5% of absorbed water, which correlates with the values of moisture absorption at 65% RH (Tables 2 and 3). A clear endothermic peak at T=61.4°C connected with the evaporation of water is observed in the DSC curve (Fig. 1). The fibres contain also some slight amount of sparingly removable solvent: N-methylpyrrolidone.

The glass transition temperature (T_g) of PIA nanocomposite fibres found from the DTA curve is

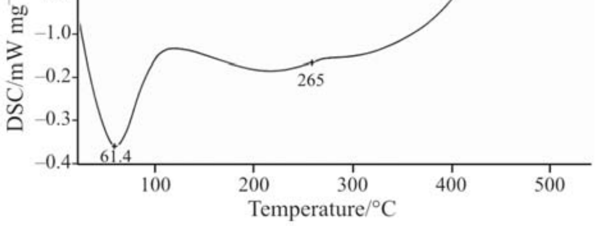

Fig. 1 DSC curve of fibres from (PIA) nanocomposite (M_5)

Table 2 Structural parameters and properties of fibres from PIA nanocomposite and modified PIA

Sample	As-spun draw ratio/%	Total draw ratio/%	Total pore volume/cm^3 g^{-1}	Internal surface/m^2 g^{-1}	Moisture absorption at 65 RH/%	Moisture absorption at 100 RH/%	Water retention/%	Tenacity/ cN tex^{-1}	Elongation/%
M_1	50	96.10	0.59	59.75	5.60	12.2	72.0	11.36	8.20
M_2	25	123.60	0.42	53.91	5.30	11.1	70.0	12.44	7.90
M_3	10	110.10	0.48	76.94	5.60	11.3	65.4	11.89	8.50
M_4	–5	108.60	0.75	80.68	5.60	12.0	72.9	10.67	7.20
M_5	–20	114.60	0.63	78.92	5.20	10.4	70.0	11.55	12.80
W_2	–20	127.00	0.44	55.53	6.20	13.3	76.2	10.77	15.50
W_1	–20.3	128.30	0.29	32.26	4.50	11.0	58.5	15.00	15.90

M_1–M_5 – fibres from PIA nanocomposite, W_2 – fibres from PIA nanocomposite, W_1 – fibres from modified PIA

Table 3 Thermal properties of fibres from PIA nanocomposite and modified PIA

Symbol of sample	Z_z/%	Z_R/%	T_g/°C	T_5/°C	T_{50}/°C	T_R/°C	T_{Rmax}/°C
M_1	5.5	2.5	290	380	500	350	495
M_2	5.5	2.5	280	370	500	340	495
M_3	5.0	2.5	285	380	500	350	500
M_4	5.0	3.5	290	385	500	350	510
M_5	5.0	3.7	285	410	510	370	515
W_2	5.5	1.25	290	410	510	380	520
W_1	2.5	3.75	310	410	520	370	515

Z_z – adsorbed water content, Z_R – solvent content, T_g – glass transition temperature, T_5, T_{50} – thermal stability indicators, T_R – temperature of initial polymer decomposition, T_{Rmax} – temperature of polymer decomposition maximum rate

280–290°C, while that determined by the DSC method is lower by about 25°C (Figs 1 and 2, Table 3). Taking into account the fact that T_g of fibres without MMT determined from DSC and DTA curves ranges from 280 to 286°C [6] one should believe that the addition of 3% MMT does not exerts any significant influence on the temperature of this phase transition.

In the DTA curves of PIA nanocomposite fibres within the temperature range from 360 to 450°C appears an endothermic transition connected with the beginning of polymer macromolecule fragmentation, which is accompanied by the emission of volatile products of thermal decomposition (Fig. 2). This transition is associated with a considerable mass decrement amounting to 26% after its termination. It is not noticeable in DTA curves of fibres marked with symbols W_2 and M_5 formed with the negative value of as-spun draw out ratio –20%, being optimal for fibres without MMT (Fig. 3). However, within the mentioned temperature range the fibre-forming polymer is also thermally decomposed, which results in mass decrements of 16 and 28% for fibres with lower and higher total pore volumes and internal surfaces, respectively (Table 2). In our opinion, this is a symptom of the presence of oxygen in the air that fills the pore system in fibres.

At 450°C in DTA curves of all fibres, one can observe the beginning of a high exothermic peak with its maximum at range temperature 495–520°C connected with the destruction of the fibre-forming polymer. The mass decrement after this process corresponds to the residue amounting to 5% of the initial sample mass. It is slightly higher for the fibres containing MMT that is partly decomposed when heated within the temperature range under investigation

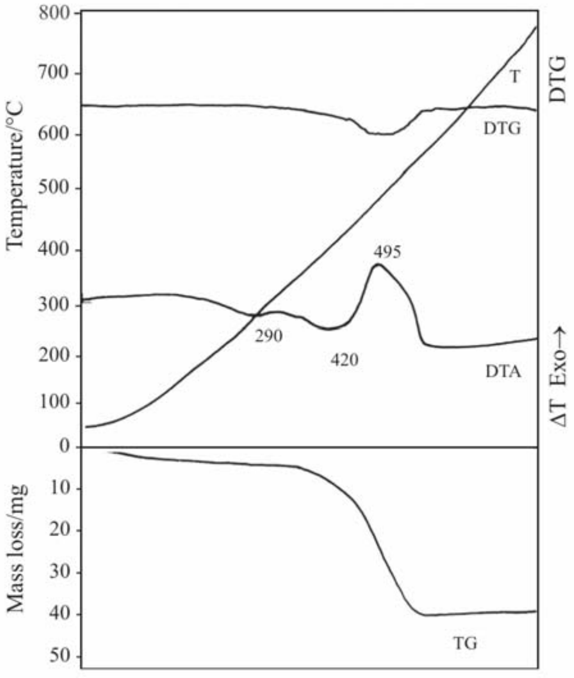

Fig. 2 TG, DTG, DTA and *T* curves of fibres from (PIA) nanocomposite (M_1)

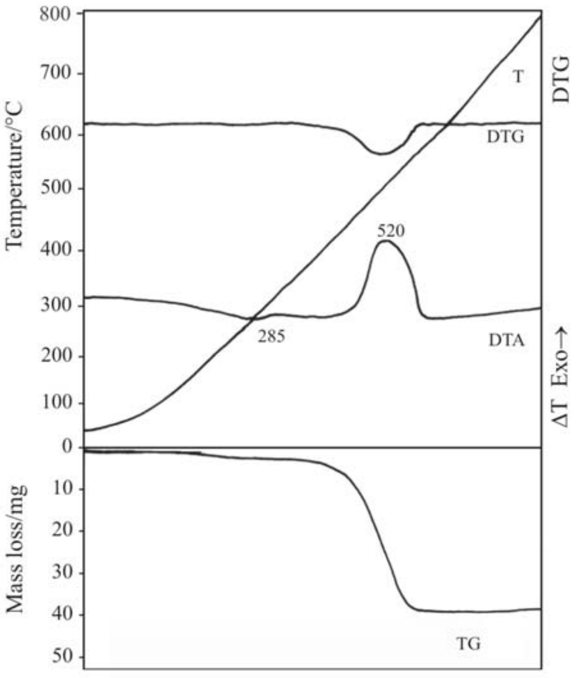

Fig. 3 TG, DTG, DTA and *T* curves of fibres from (PIA) nanocomposite (W_2)

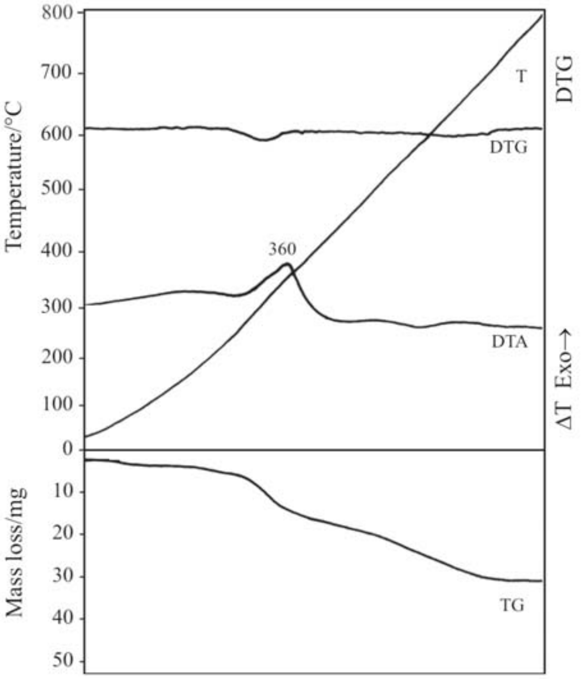

Fig. 4 TG, DTG, DTA and *T* curves of montmorillonite

(Fig. 4). The first stage of this decomposition takes place within the temperature range from 265 to 430°C and is seen in the DTA curve as an exothermic transition at 360°C. The total mass decrement of the examined nanoaddition is 32.2%. It may be connected with the modifier used by its manufacturer (Nanocor, USA) to change the properties of MMT from hydrophilic to organophilic.

The thermal stability determined by indicators T_5 and T_{50} (Table 3) depends to a slight extent on the spinning conditions of PIA nanocomposite fibres, nevertheless the higher values of the indicators are shown by fibres formed with negative values of as-spun draw out ratio. If the thermal stability T_5 of the fibres from PIA nanocomposite is comparable with T_5 of fibres without MMT, contrary to expectation the incorporation of nanoaddition into the fibre-forming polymer has failed to increase T_{50} of the fibres. This may be due to the higher porosity of the fibres from PIA nanocomposite, especially their internal surface that is twice as high (Table 2).

The above parameters exert a considerable effect on the flammability of fabrics made from the fibres under investigation. Flammability tests were carried out with woven fabrics made from fibres without MMT (W_1) and PIA nanocomposite fibres spun under optimal conditions for the given type of polymer (W_2 and M_2). Additionally a sample of fabric from PIA nanocomposite fibres showing a similar porosity and considerably higher internal surface was tested (M_3).

Woven fabrics made from PIA nanocomposite fibres showing the total pore volume at a level of 0.42–0.44 cm^3 g^{-1} and internal surface of about 54–55 m^2 g^{-1} are not subject to ignition being in contact with flame during 8 s, which allows one to consider them to be flame-retardant. The fabric sample from fibres containing no MMT does not meet this requirement. This indicates that MMT facilitates the carbonisation process of the MMT-containing polymer, while the created charred layer is a barrier that inhibits the propagation of flame. This effect, in the case of the fabric made from PIA nanocomposite with a high internal surface, is however considerably reduced due to the presence of air in the pore system. Thus, one should believe that besides MMT present in the polymer a considerable effect on fabric flammability is exerted also by the structural parameters of fibres, total pore volume and especially their internal surface.

Conclusions

- The porous structure, sorption properties and strength of fibres made from PIA nanocomposite depend on the value of as-spun draw out ratio and deformation during the drawing stage. Both process parameters affect the fibre thermal properties to much lesser extent.
- The incorporation of intercalated MMT into the modified PIA results in a beneficial increase in fibre porosity and internal surface and consequently in increased sorption properties, especially retention of the fibres made from PIA nanocomposite in comparison to fibres without the nanoaddition, which improves the comfort of using clothes made from these fibres.
- A slight decrease in the thermal stability of PIA nanocomposite fibres, determined by indicator T_{50}, is connected with their higher porosity and internal surface in comparison with fibres made from modified PIA.
- The dominating effect over the increased air content in the pore system in fibres made from PIA nanocomposite consists in creating a barrier by the dispersed MMT in the polymer. This produces a desired effect of reduced flammability of woven fabrics made from PIA nanocomposite fibres that meet the requirement of a limited internal surface to a level of 54 m^2 g^{-1}.
- The multi-functional fibres prepared from PIA nanocomposite show increased porosity and sorption properties as well as a high thermal stability and reduced flammability.

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