# THERMAL PROPERTIES OF FIBRES FROM A NEW POLYMER OF THE POLYIMIDEAMIDE GROUP

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## Abstract

The paper presents the thermal properties of fibres made of a modified polyimideamide. The effects of as-spun draw ratio and deformation during the fibre drawing stage on the structure, thermal properties, moisture absorption and tenacity of the obtained fibres have been determined. Based on the findings obtained by the DTA and DSC methods, it has been found that the modification of the polymer under investigation causes its glass transition temperature to decrease through the increase of molecular mobility. At the same time, the heat-resistant fibres with the amorphous oriented structure are characterized by a tenacity of 16 cN/tex, good absorption properties and increased porosity.

The thermal stability indices of the examined fibres have been determined on the basis of thermogravimetric curves obtained both under air and inert gas.

## Introduction

Polyimideamide (PIA) fibres known under the trade name Kermel combine properties such as thermal resistance and non-flammability with quite good moisture absorption properties and processability by the main textile technologies.

Their major applications include clothing goods, decorative woven fabrics and upholstery knitted fabrics to be used in areas with fire hazard due to a direct flame contact. An important advantage of PIA fibres is that during burning they emit very low volumes of smoke, even one to two orders of magnitude lower that those of natural or other synthetic fibres [1]. There are also no toxic products of thermal decomposition and combustion, while the most hazardous gases such as CO and HCN appear in trace amounts, considerably lower than those in the case of cotton and wool.

The synthesis of PIA is environment-friendly and the only by-product of the polycondensation of trimellitic anhydride and aromatic diisocyanate is carbon diox-

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ide being readily removable from the reaction system. The process carried out in polar solvents, mostly in N-methylpyrrolidone, results in the formation of a spinning solution, which is suitable for direct fibre spinning, mainly by the wet process [2]. Such properties are also shown by the product of our synthesis carried out with the use of an additional monomer [3, 4].

The incorporation of a flexible segment such as $-NH-C_6H_4-CH_2-C_6H_4-NH-$ derived from 4,4'-diamine diphenylene methane into the macromolecular chain brings about an increase in the fibre deformability during the plasticization drawing. Due to the processing of the spinning solution in a typical spinning machine designed for the wet process and mechanical properties of fibres it was necessary to select the intrinsic viscosity of the polymer and the dynamic viscosity of solutions [5]. The selection of spinning conditions made it possible to prepare fibres with an increased porosity and good moisture absorption properties, with their tenacity being at a level providing their good textile processing [6].

The aim of the present study was to examine the thermal properties of modified polyimideamide fibres with various deformation degrees during drawing and different porous structures.

## Object of studies

The object of studies was modified polyimideamide fibres spun under variable conditions of the as-spun draw ratio. The values of deformation in the single-stage plasticizing drawing were close to unity. These fibres are marked with symbols A–F.

An additional fibre sample was included in the examinations, marked as F, which was prepared during the selection of spinning conditions with the use of two-stage drawing. The second drawing stage took place in a superheated steam.

## Characteristics of the spinning solution

Fibres were spun from the post-reaction solution of the modified polyimideamide in N-methylpyrrolidone with an apparent dynamic viscosity of 35.7 Pas. The intrinsic viscosity of the fibre-forming polymer determined in the same solvent at a temperature of 25°C was 1.55 dL g$^{-1}$ and the polymer content in the spinning solution was about 19%. The rheological parameters determined according to the procedure given in [5] were as follows: $n$=0.9783; $K$=32.83.

## Fibre spinning

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 with a diameter of 0.08 mm.

The solidification process was carried out in a bath containing an aqueous solution of the solvent at a low temperature. The single-stage drawing process was performed in a plasticizing bath at elevated temperature. Then, the solvent was washed-off and the resultant fibres were dried under isometric conditions.

## 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 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 [7].

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.

Fibre thermal shrinkage was determined on the basis of the change in the fibre bundle length heated in air at 240°C for 5 h.

Fibre hypermolecular structure was measured by means of the wide-angle X-ray diffraction (WAXS). Selected samples (A, E and F) were measured with the use of a HZG4 diffractometer, using CuK$_\alpha$ and the following conditions: an acceleration voltage of 30 kV and an anode current intensity of 20 mA. The beam chromatization was obtained by using Roos filters and a pulse analyzer. A scintillation counter was used as a detector.

X-ray diffractograms were taken within the diffraction angle range (2θ) from 4 to 40° by the step method using a step of 0.1 degree and a pulse counting time of 10 s.

WAXS measurements of sample A heated in a derivatograph oven up to 330°C were carried out with the use of an URD-6 diffractometer with a detector-scintillation counter, using CuK$_\alpha$ radiation and a nickel filter under the following conditions: the acceleration voltage 40 kV, anode current intensity 30 mA. The X-ray diffractogram for this sample was made within the diffraction angle range from 5 to 36°, using a step of 0.1 degree and a pulse counting time of 10 s.

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 60 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 and thermogravimetry, the measurements were per-

formed both in air and 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 properties of fibres spun from solution by the wet process depend on the course of fibre solidification and its structure being formed during this stage. Under constant parameters of concentration and temperature of the coagulation bath, the fibre deformability during the plasticizing drawing is affected by the as-spun draw ratio. This draw ratio was changed from negative to positive values within the range from –30 to +50%. During the drawing stage, the deformation used for each as-spun draw ratio was close to the maximum value.

The detailed analysis of changes in the moisture absorption and tenacity of fibres spun under these conditions in association with the formed fibre porous structure and porosity is given in [6].

The increase in the fibre deformability during drawing and the possibility of getting higher values of draw ratio and consequently higher fibre tenacity are connected with the change in the as-spun draw ratio from positive to negative values (Table 1).

This is however accompanied by the trend towards the deterioration of moisture absorption of the fibres. The character of these changes with the extreme total pore volume and internal surface *vs.* the as-spun draw ratio and the total draw ratio is associated to a large extent with the type of the porous structure formed [6].

The high moisture absorption and in particular the high water retention, as for this type of polymer, are associated with the dominating content of medium pores with dimensions from 15 to 150 nm of their upper range, with the fine-porous character of the structure being maintained. The water retention value is determined by the pores being large enough to be able to absorb water and small enough to retain water after its mechanical removal. The moisture absorption at 100% RH at a level reaching 15% is connected with considerable contents of small pores from 4 to 15 nm. These pores must be small enough to be able to absorb moisture on the capillary condensation bases.

Generally, the fibres spun from the new polyimideamide material due to the order of magnitude of the total pore volume and internal surface can be classified as fibres with an increased porosity. The character of the internal porous structure can be determined as fine porous with the quantitative advantage of medium-sized pores. With such a type of structure are connected particularly high, as for this polymer, values of water retention and high values of moisture absorption at 100% RH amounting to 40–76 and 11–14.5%, respectively. They are about twice as high as those of Kermel fibres.

The values of thermal shrinkage depend on the internal stresses created in fibres during the drawing stage. They vary within a narrow range of about 1%. The highest shrinkage value of about 8.1% is shown by the fibres formed with the negative value of the as-spun draw ratio –15% for which the drawing process was carried out with the highest deformation.

**Table 1** Properties of polyimideamide fibres spun with variable values of the as-spun draw ratio and the total draw ratio

| Symbol of sample | As-spun draw ratio/% | Total draw ratio/% | Moisture absorption/% | | Water retention/ % | Tenacity/ cN tex$^{-1}$ | Shrinkage at 240°C | Total pore volume/ cm$^3$ g$^{-1}$ | Total internal surface/ m$^2$ g$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | at 65% *RH* | at 100% *RH* | | | | | |
| A | 53.0 | 100.4 | 5.4 | 14.5 | 76.8 | 12.66 | 7.7 | 0.426 | 32.862 |
| B | 15.1 | 111.5 | 4.5 | 12.8 | 63.2 | 13.09 | 7.4 | 0.502 | 74.386 |
| C | 0.5 | 118.4 | 4.7 | 12.0 | 62.2 | 14.50 | 7.5 | 0.202 | 23.489 |
| D | −15.2 | 129.4 | 4.5 | 11.3 | 39.1 | 15.10 | 8.1 | 0.239 | 34.904 |
| E | −30.0 | 122.7 | 5.6 | 12.8 | 62.1 | 15.70 | 7.1 | 0.299 | 28.150 |
| F | −20.3 | 154.5 | 4.3 | 11.0 | 55.4 | 16.40 | 8.8 | – | – |
| Kermel yarn | | | 3.1 | 7.6 | 21.6 | 13.20 | 0.8 | – | – |
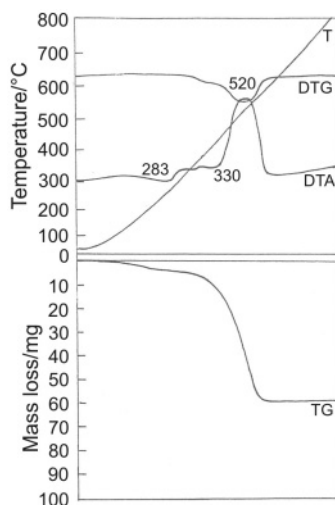
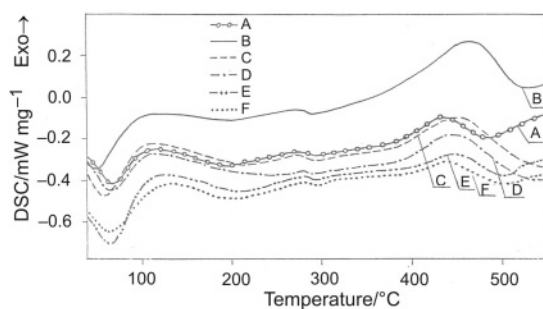**Fig. 1** Thermal curves of sample A in air atmosphere



**Fig. 2** DSC curves of fibres in inert atmosphere

The character of thermal changes in the fibres under investigation is similar (Figs 1 and 4). From the thermogravimetric curves it follows that within the temperature range 50–260°C the low-molecular-mass substances (about 8.3%) are evaporated independently of the fibre formation conditions and the formed structure. As is seen from DSC curves, within the mentioned temperature range, two endothermic peaks are observed, one of which is connected with the presence of water, while the other one with N-methylpyrrolidone (Fig. 2). Their presence results from quite a high moisture absorption amounting to 5–6% and low amounts of residual sparingly removable solvent, which is the component of the solidification and plasticizing baths. It should be mentioned that Kermel fibres also contain water about 4.5%, but no solvent content was found in them (Figs 3 and 7). At 280–285°C in the DTA curves and at 283–286°C in the DSC curves, the glass transition temperature, $T_g$, of the modified polyimideamide fibres can be observed (Figs 2 and 4). It is lower by about 20°C than that of Kermel fibres, thus the incorporation of mentioned segments derived from
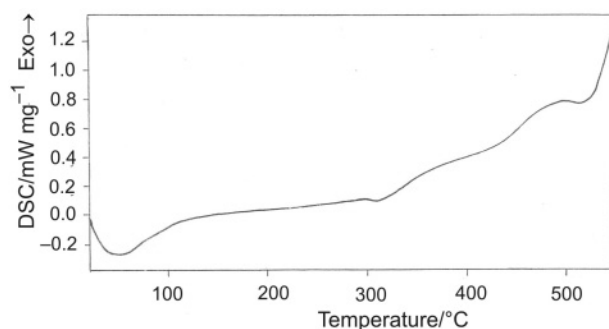
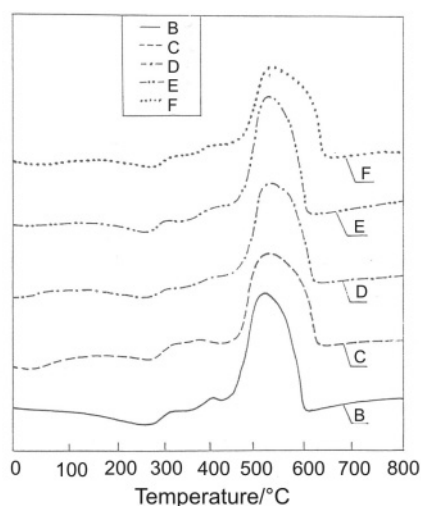**Fig. 3** DSC curve of Kermel fibres in inert atmosphere



**Fig. 4** DTA curves of fibres in air atmosphere

4,4'-diamine diphenylene methane into the macromolecule has brought about a clear increase in the flexibility of the polymer chain (Figs 2 and 3).

DTA curves show that a slight exothermic change begins at a temperature of about 330°C (Fig. 4). The temperature of the beginning of this changes as well as the maximum of its rate increase with increasing the total draw ratio of the fibres under investigations. The highest temperature of this transition is shown by fibres with symbol f for which the drawing process was performed in two stages and the obtained value of the total draw ratio was 154.5%. In the DSC curves obtained under inert gas this transition begins at a temperature of about 360°C. In our opinion, this is a symptom of formation of ordered structures known as substructures, which cannot be however considered to be typical crystalline structures. This hypothesis has been confirmed by the X-ray measurements performed by the WAXS method for selected fibre samples heated up to 330°C in the thermal analyzer oven. Figure 5 shows an exemplary diffractogram of sample A. There is seen a single broader maximum indicating the already mentioned order of structural elements. In the face of this fact, the angle position of the observed maximum was found and
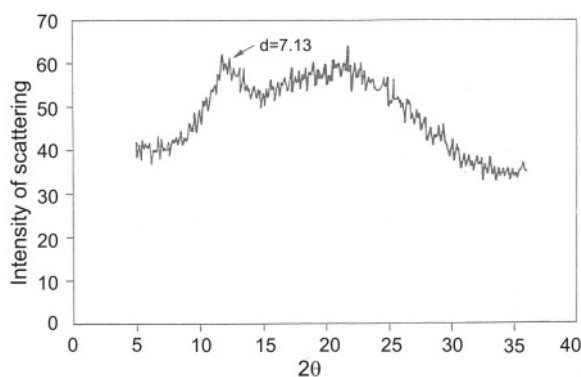
**Fig. 5** Diffractogram of sample A heated in the thermal analyzer oven to temperature of 330°C
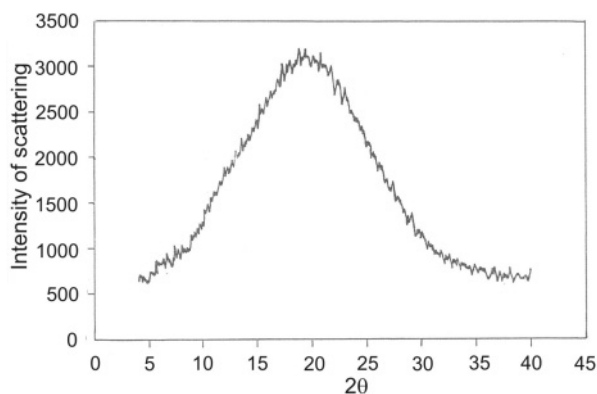


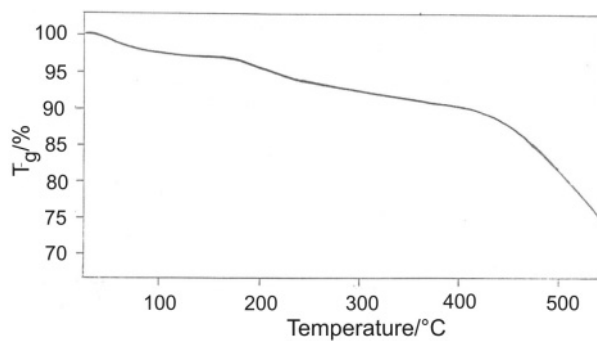**Fig. 6** Diffractogram of sample A



**Fig. 7** TG curve of sample A in inert atmosphere

the corresponding interplanar spacing, d, was calculated according to Bragg's law and shown in Fig. 5. The process of substructure formation is accompanied however by a slight mass loss which indicates the commencing fragmentation of the fibre-forming material macromolecules. On the other hand, the unheated samples show an ordered amorphous structure (Fig. 6).

The high exothermic peak recorded in the DTA curves at 520–530°C is associated with the thermal decomposition of the fibre-forming material resulting as in the case of Kermel fibres in the total mass loss of the sample. The thermal decomposition rate is independent of the obtained draw ratio or the formed porous structure.

**Table 2** Thermal stability indices of polyimideamide fibres formed under variable conditions of the as-spun draw ratio and the total draw ratio

| Sample | Thermal stability indices/°C | | | |
| | Air atmosphere | | Inert atmosphere | |
| | $T_5$ | $T_{50}$ | $T_5$ | $T_{50}$ |
| --- | --- | --- | --- | --- |
| A | 390 | 510 | 472 | x) |
| B | 395 | 510 | 472 | x) |
| C | 395 | 520 | 473 | x) |
| D | 405 | 520 | 475 | x) |
| E | 405 | 530 | 480 | x) |
| F | 410 | 535 | 483 | x) |
| Kermel | 395 | 520 | 473 | x) |

$T_5$ and $T_{50}$ - temperatures of 5 and 50% mass losses, respectively [9];
x) the samples heated up to 560°C do not show the 50% mass loss

The thermal stability indices found on the basis of the thermogravimetric curves, $T_5$ and $T_{50}$, are of course considerably higher in the atmosphere of inert gas than those in air (Figs 1 and 7). A slightly higher thermal stability is shown by the fibres obtained with higher values of the total draw ratio; they show also a higher tenacity, which results from a higher orientation of macromolecules in the direction of the fibre axis.

## Conclusions

1. The modification of polyimideamide and selection of fibre spinning conditions made it possible to prepare heat-resistant fibres with oriented amorphous structure showing good moisture absorption properties and increased porosity, with their tenacity being suitable for textile processing.
2. The incorporation of a flexible segment derived from diamine caused the glass transition temperature of the fibre-forming polymer to decrease and the resultant fibres to maintain a high thermal stability comparable to that of Kermel fibres.
3. The increase of polymer deformability makes it possible to prepare fibres with good strength and absorption properties as well as a high heat-resistance.
4. The values of as-spun draw ratio and deformation during the fibre drawing stage affect the thermal stability of fibres only to a slight extent.
5. When the fibre drawing process is carried out at considerably lower temperatures than the glass transition temperature of the polymer (regardless of the extent of defor-

mation), the resultant fibres will have an amorphous oriented structure and an increased porosity. The formation of a highly ordered structure takes place only if the drawing temperature is 330°C.

# References

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