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Multifunctional Thermostable Fibres from Modified Polyimidoamide

Abstract

The modification of fibre-forming polymers and the ability to select spinning conditions has made it possible to obtain multifunctional polyimidoamide fibres with high thermal stability, very good electro-insulating properties and a tenacity suitable for their textile processing. Alternatively, fibres with increased porosity can be used to make heat-resistant filtration materials, while fibres with improved strength properties are suitable for thermo- and electro-insulating materials.

Key words: *polyimidoamide, thermostable fibres, multifunctional fibres, modification, spinning conditions, electro-insulating properties, tenacity, porosity, filtration materials.*

■ Introduction

Fibres designed for the manufacture of textile and technical fabric for special applications are now required to possess multifunctional characteristics.

Among heat-resistant and flame-retardant fibres, polyimidoamide fibres are the most universally encountered. They are not inferior to polyimide and aramide fibres as far as thermal properties are concerned, and at the same time demonstrate more advantageous characteristics in terms of textile processing [1-3]. They can be used to make textiles of so-called first contact with flame, as well as technical fabrics to replace the carcinogenic asbestos which has been withdrawn from use in many fields (insulation and filtration materials).

Another important advantage of these fibres is that during their contact with flame they issue hardly any smoke or toxic decomposition products [1]. The synthesis of their fibre-forming polymer is environmentally friendly and can be performed at a relatively low temperature, while the post-reaction polymer solution can be used directly to spin fibres by the wet process [2, 4]. Moreover, polyimidoamide fibres can be advantageously modified to assume multifunctional qualities by modifying the polymer itself, or by suitable selection of fibre spinning conditions.

The addition of diamine segments to the macromolecular chain, resulting in an increased susceptibility to deformation (during the plasticising drawing stage), has made it possible to obtain fibres with a tenacity of 15 cN/tex [4], i.e. at a level suitable for their textile processing. On the other hand, appropriate selection of fibre spinning conditions resulted in a considerable increase in the porosity and sorption of these fibres [5,6].

The fibres made of the modified polyimidoamide (PIA) are characterised by an unusual combination of features such as high thermal stability, nonflammability resulting from the chemical structure of polymer, and improved sorption properties [7,8]. Owing to the latter properties, clothes made of these fibres show good comfort of use, and they should therefore be used as protective clothing against so-called first contact with flame.

On the other hand, in the case of fibres designed for technical applications, improved sorption properties are not necessary. Other features are preferable, such as electro-insulating properties or developed internal surface and increased porosity in the case of filtration materials (for the filtration of hot liquids and gases). At the same time, such fibres should show a high thermal stability.

According to literature data, the replacement of $-CH_2$ group between benzene rings in the modified macromolecule of PIA with an oxygen atom derived from diaminodiphenylether should increase the fibre thermal stability [2]. Consequently, the drop in tenacity after prolonged heating of the fibres at a temperature over 250°C should be considerably lower. The formula of the modified fibre-forming polyimidoamide is presented in Figure 1.

The maximisation of strength properties by a proper selection of fibre spinning should result in multifunctional fibres designed mainly for technical applications. We aim to obtain two types of PIA fibres with a fine-porous structure, as well as:
■ increased tenacity with decreased sorption properties at the same time,
■ increased total pore volume and internal surface retaining a suitable tenacity for filtration materials.
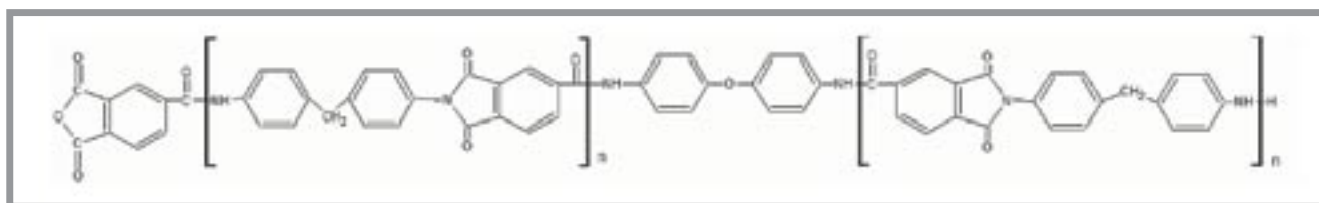

Figure 1. *Formula of the modified fibre-forming polyimidoamide.*

The aim of the present study was to assess the effects of as-spun draw ratio and related deformation during fibre drawing on the structure and properties of fibres made of a modified polyimidoamide material. The findings will be used to select fibre-forming conditions for the two above-mentioned types of fibres by using a computer-aided experiment designing system [11].

■ Experimental

Characteristics of the spinning solution

Fibres were formed from the post-reaction solution of modified polyimidoamide prepared according to the conditions given in [4].

The spinning solution was a 22.56% polymer solution with an intrinsic viscosity of $\eta=1.33$ dcl/g in N-methylpyrrolidone. Its rheological parameters determined from its flow curves amounted to n=0.99, k=38.61, where (n) and (k) are the rheological parameters in Ostwald de Wael's model [10].

The value of the rheological parameter (n) and the character of flow curves are the same as those found previously [9], which indicates that the spinning solutions used are non-Newtonian fluids, rarefied by shearing, without flow limit, quite similar to Newtonian fluids.

Fibre spinning

Fibres were spun from solution in 5% N-methylpyrrolidone by the wet process using a laboratory spinning machine, whose construction made it possible to stabilise technological parameters at a required level under continuous control. Spinnerets with 500 orifices of a diameter of 0.08 mm were used.

The solidification process was carried out in a bath containing an aqueous solution of the solvent (above 50%) at a low temperature, about 10-20°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 60-80°C. Finally, the solvent was rinsed off, and the resultant fibres were dried under isothermal conditions at 80-120°C. Detailed process parameters are protected by know-how property.

Measuring methods

Fibre porosity was measured by means of a Carlo-Erba mercury porosimeter,

which was linked to a computer system to register the numerical values of the parameters measured. The values measured included the total pore volume, the total internal surface, the volume of capillary group with a defined radius and 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% relative air humidity was determined by the desiccator method according to Polish Standard PN-71/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 10,000 m/s². *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 performed by means of a derivatograph and differential scanning calorimetry (DSC), using a Paulik-Erdey system derivatograph and a Nitzsch DSC204 microcalorimeter. The derivatographic analysis was carried out in air, using weighed portions of 40 mg and a heating rate of 7.9°C/min within the temperature range from 20 to 800°C. In the microcalorimetry, the measurements were carried out in inert gas, using weighed portions of about 3.0 mg and a heating rate of 10°C/min within the temperature range from 30 to 550°C.

The specific density of fibres was determined by the floatation method in a gradient column. The linear gradient of density in the column was obtained with the use of two liquids with different densities, carbon tetrachloride and toluene. The conditioning time of fibre samples in the gradient column was 48 h at the conditioning temperature of 25°C. The fibre density was calculated as an average value of 5 independent measurements.

The optical birefringence of fibres was measured by the interference method by means of a BIOLAR PI microscope, using the interference technique of striated field in a variant of birefringent prisms. Based on the experimentally determined values of optical birefringence (Δn) and density (d), a conventional index of fibre molecular orientation was calculated from the following relationship:

$$F_{conv} = \Delta n/d$$

while nevertheless not considering the birefringence coefficient and density of PIA with ideal crystallinity and molecular orientation which appears in Hermans' equation.

In connexion with the generally accepted criterion of electro-insulating power (for materials excluding fibrous structures), we decided to assess the specific resistance of a PIA monofilament. Under the conditions of fibre use exposed to static charge accumulation, the *electric surface conductivity* of fibres is of great importance in static charge decay as the charges are mostly dissipated in the form of surface leakage current. Therefore, the fibre's capability to decay static electricity was estimated in this paper on the basis of electric surface resistivity. Thus. the electric surface resistivity of fibres was measured in a screened standard measuring system with the use of rigid strip electrodes [12,13], which measured the conduction current in an electrostatic field with an intensity of 2.0 kV/cm. The conduction current intensity was determined from the absorption current corrected by the depolarisation current (measurement duration 1 min). A Keythle 610 C electrometer and a Statron stabilised power supply unit type 4218 were used.

The fibres were initially dried and then conditioned under measuring conditions for 24 h. Conditioning and measuring were performed under isothermal conditions (t=25°C) at relative humidity values of 25% and 65% in a Feutron 3001-01 conditioning chamber.

■ Results and Discussion

In the method of fibre spinning by the wet process, the properties of fibres depend on their structure formed during solidification and its susceptibility to deformation during the plasticising drawing. One of the basic parameters is the as-spun draw ratio. Its value was changed within the range from -64% to +33.4%. The fibre deformation during drawing ranged from 101.28 to 163.4%, being close to the possible maximum values for the given value of as-spun draw ratio.

The change in the as-spun draw ratio towards positive values is followed by a slight increase in the absorption of moisture at 100% RH (Figure 2) up to 10%, while the moisture absorption at 65%
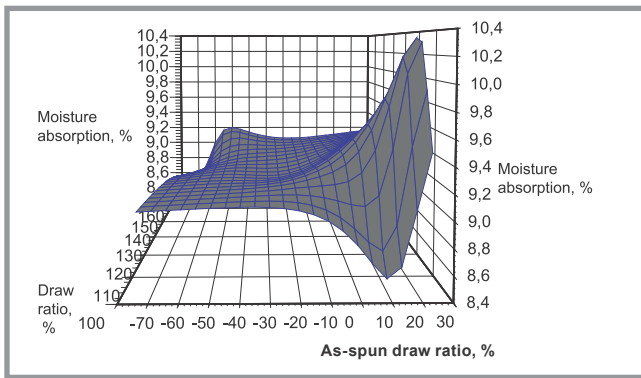
Figure 2. *Dependence of moisture absorption at 100% RH on the as-spun draw ratio and total draw ratio.*
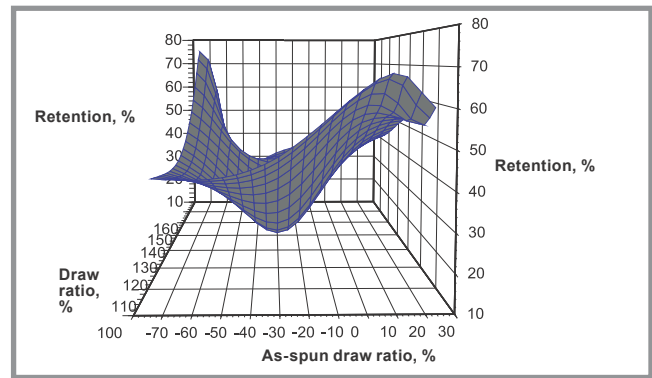

Figure 3. *Dependence of retention on the as-spun draw ratio and total draw ratio.*

RH amounts to 5.1-5.5%. A different, extreme course is shown by the water retention as a function of the examined parameters (Figure 3). Unexpected agreement between this relationship and the changes of density (Figure 4) is probably associated with the penetration of the immersion liquid (during density measurements) mainly into medium and large pores which are also responsible for the retention value. The changes in density correspond to the previously found dependence of the total pore volume on the as-spun draw ratio and the total draw ratio [5]. However, the sorption properties of fibres also depend on the type of porous structure being formed.

As the distribution of pores versus their radius has the same character as in previous studies, one can suppose that the high values of retention obtained for the extremely negative and positive values of as-spun draw ratio are connected with the dominating amount of medium pores in the structure formed (Figure 5). This is shown by the high maximum of the pore distribution curve.

Generally, the fibres made of modified PIA can be included among fibres with increased sorption properties, but the level of these indicators, especially the mois-

ture absorption at 100% RH, is lower than that of the previously obtained fibres.

The density of PIA fibres at a level of 1.300-1.334 g/cm^3 is high, and comparable with the density of aramide fibres.

The changes in fibre tenacity (Figure 6) and orientation coefficient (Figure 7) versus as-spun draw ratio and total draw ratio show a similarly extreme course, maintaining a general trend towards lower values while the as-spun draw ratio changes towards positive values. The highest tenacity (17.7 cN/tex) with a high orientation of 8.0 x 10-2 is shown by the fibres spun at negative values of the as-spun draw ratio, -25% and -30%.

The fibres made of modified PIA show optical anisotropy under conditions of polarised light. The anisotropic state of polymer indicates that the macromolecules of modified PIA are ordered along their axis during the deformation processes. We observed a low differentiation of the conventional index of general orientation as a function of the as-spun draw ratio and deformation during fibre drawing, which may be due to the limited susceptibility of rigid PIA macromolecules to being ordered along the axis. The degree of optical anisotropy

of the fibres is considerable, despite the quite low draw ratios used during fibre spinning. This is indicated by the values of optical birefringence coefficients ranging from 0.08 to 0.11 (depending on the spinning conditions). The high values of directional refractive indices of polarised light are noteworthy (in parallel to the fibre axis they range from 1.730 to 1.755, and perpendicular to the fibre axis, from 1.633 to 1.645). This may be due to the strong polarisability of phenyl rings present in the PIA macromolecule. The high values of the directional refractive indices are accompanied by a high chromatic dispersion of the indices as shown by the overcolouring of interferential striae in the microscopic images of the fibres.

Based on the measurements of surface resistivity of PIA fibres performed at 25% and 65% RH (Table 1), we can state that these values are considerably higher than the criterion of insulating power accepted at a level of 1.0×10^{10} Ω [14]. Thus, one can assume that these fibres will show excellent electro-insulating properties under exploitation conditions with different values of humidity. The resistivity values at 65% RH are lower by about two orders of magnitude than those at 25% RH; this is due to the fact that the moisture content of the fibres is 5% under standard conditions. However, this has no significant influence on the electro-insulating power of these fibres. It may be expected that in PIA fibres a low leakage current is generated, connected with the presence of a water layer adsorbed onto the fibre surface, which contains dissolved ionic impurities. The surface leakage conductance will depend on the hydrophobicity of PIA surface and the mechanism of water combination.
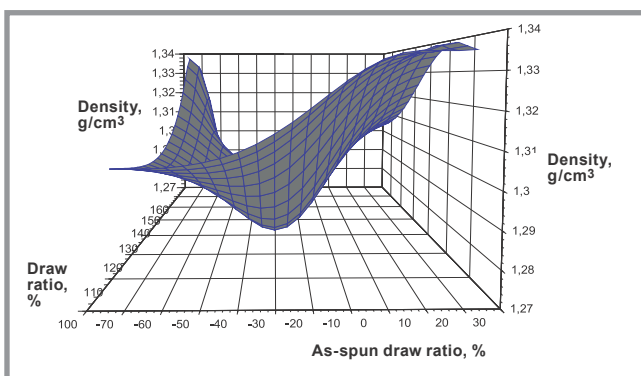
Regardless of their spinning conditions,

Figure 4. *Dependence of fibre density on the as-spun draw ratio and total draw ratio.*

Table 1. *Electrical resistivity of fibres from modified polyimidoamide (E=2.0 kV/cm).*

Sample	As-spun draw ratio, %	Draw ratio, %	Surface resistivity ρ_s, Ω m/m	
			RH=25%, t=25°C	RH=65%, t=25°C
S-2	-64.06	163.40	>1.0×10^{17}	1.0×10^{15} - 3.1×10^{15}
S-4	-40.00	165.75	>1.0×10^{17}	$1.5 \times 10^{16} \pm 0.5 \times 10^{16}$
S-3	-20.00	132.75	>1.0×10^{17}	$4.0 \times 10^{15} \pm 1.2 \times 10^{15}$
S-5	20.00	101.28	>1.0×10^{17}	2.7×10^{14} - 1.3×10^{15}
S-1	33.42	109.62	>1.0×10^{17}	4.0×10^{14} - 9.4×10^{15}
S-10	-30.00	190.00	>1.0×10^{17}	5.5×10^{14} - 3.0×10^{15}

Table 2. *Results of thermal analysis (T_{Ro} - temperature of initial decomposition of the fibre-forming polymer; T_{Ri} - temperature of intensive decomposition of the fibre-forming polymer; T_5 and T_{50} - temperatures of 5% and 50% of mass loss of the fibre-forming polymer respectively; dm/dt - maximum rate of thermal decomposition).*

Sample	As-spun draw ratio, %	Draw ratio, %	T_{Ro}, °C	T_{Ri}, °C	T_5, °C	T_{50}, °C	dm/dt, mm
S -2	- 64.06	163.40	370	490	420	530	13
S -4	- 40.00	165.75	380	480	420	520	14
S -3	- 20.00	132.75	380	480	415	530	14
S -5	+ 20.00	101.28	380	460	430	510	15
S -1	+ 33.42	109.62	365	470	410	515	10
S -10	- 30.00	190.00	370	485	420	520	12

PIA fibres are subject to similar thermal changes (Figure 8, Table 2). A slight weight loss within the temperature range of 50-100°C amounting to 2.5% is due to the moisture content in the fibres as clearly shown in DSC curves (Figure 9). The second stage of weight loss is connected with slow evaporation of the residual hard-to-remove solvent in an amount of about 3.7%. At 365-370°C the thermal decomposition of the fibres starts and proceeds slowly up to the temperature of 440°C, at which a violent polymer destruction takes place as shown by the two overlapping thermal changes recorded in DTA curves at 520 and 560°C (Figure 8). From the DTG curves, it follows that the destruction rates of the examined fibres are comparable and independent of their spinning conditions. The low decomposition rate is consistent with the high

oxygen index of PIA fibres (LOI=32) [2]. The polymer decomposition residue is about 2.5%.

The indices of thermal stability T_5, determined on the basis of TG curves, are high, and higher by about 10-15°C than those of modified PIA fibres containing the -CH_2 group instead of oxygen in the macromolecular chains between benzene rings. Slightly higher stabilities are shown by the fibres obtained with higher draw ratio values; these fibres are also characterised by higher values of density, orientation coefficient and tenacity. On the other hand, the presence of oxygen atoms in the macromolecular chain has no effect on the glass transition temperature, $T_g \approx 283$°C (Figure 9).

The use of a computer-aided experiment designing system made it possible to

select, in accordance with the accepted assumptions, spinning conditions for two types of PIA fibres differing in their properties. The use of milder conditions of solidification and selecting the deformation with the aim of obtaining higher mechanical properties resulted in fibres with a fine-porous structure and increased tenacity up to 17.6 cN/tex, while at the same time possessing decreased sorption properties (moisture absorption at 100% RH: 8% and retention 21.4%). The total volume of pores amounts to 0.2 cm^3/g, and the internal surface is equal to 30.35 m^2/g (sample S-10). On the other hand, a considerably higher porosity at a level of 0.9 cm^3/g and internal surface of 58.4 m^2/g can be obtained during fibre solidification in a bath with a lower solvent content (sample S-5); this type of fibre is suitable for filtration materials (for hot liquids and gases). The increased porosity and the type of formed porous structure are connected with better sorption properties of these fibres in comparison with the fibres of the first type. In particular this concerns the water retention, amounting to 68.8%. At the same time, their tenacity is lower and amounts to 12.5 cN/tex.

The character of the porous structure formed of both types of fibres can be defined as fine-porous. The high maximum appearing in the pore distribution curve for sample S-5 (Figure 5) includes the initial range of medium-sized pores, and their total content is at a high level of about 36.4. However, a considerable amount of very large pores is a drawback of the formed structure, which is accompanied by lower strength properties of the second type of fibre.

Both types of fibres are characterised by a high temperature of initial decomposition, 370-380°C, and a high temperature of initial intensive decomposition, 460-485°C. The high thermal stability of these fibres is confirmed by coefficients T_5 and T_{50}, amounting to 420-430°C and 510-520°C respectively. The above features, together with good electro-insulating power (the surface resistivity at a level of 10^{15} Ω m/m), make these fibres suitable for thermo- and electro-insulating materials. When using PIA fibres for the manufacture of materials for liquid and technical gas filtration, one should take into account the hazard resulting from the possible static charge accumulation when the PIA filter comes in contact with the filtered media. How-
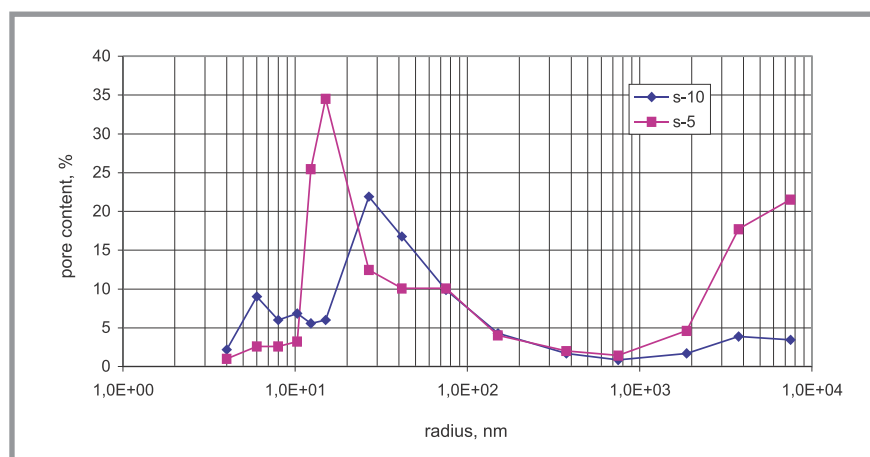

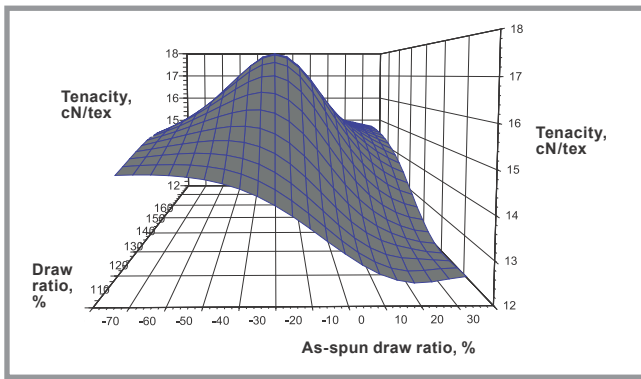**Figure 5.** *Dependence of pore percentage on pore radius for sample S-10.*

Figure 6. *Dependence of fibre tenacity on the as-spun draw ratio and total draw ratio.*
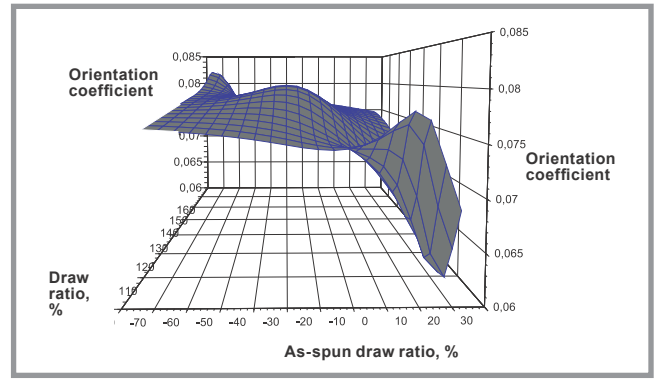

Figure 7. *Dependence of conventional orientation coefficient on the as-spun draw ratio and total draw ratio.*
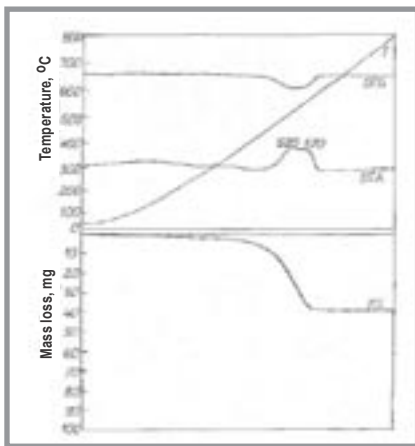

Figure 8. *Thermal curves of PIA (S-10) fibres.*

ever, the static electricity can be limited by an appropriate selection of the filter's technological parameters.

Thus, the fibres made of modified polyimidoamide can be considered multifunctional. They combine features such as high thermal stability, different porosity and sorption (depending on application) and very good electro-insulating properties, while showing at the same time a tenacity which makes them suitable for processing into linear and flat fabrics designed for technical applications.

■ Conclusions

■ By the modification of the fibre-forming polymer and selection of spinning conditions, multifunctional polyimodoamide fibres with different structures and sorption properties were obtained. These fibres are characterised by high thermal stability, very good electro-insulating properties and a suitable tenacity for their textile processing.
■ The extent of as-spun draw ratio and deformation during the fibre drawing process only slightly influences the fibre's thermal stability and the electro-insulating power. On the other hand, these parameters decide the porous structure, sorption properties and strength characteristics of the fibres.
■ The incorporation of oxygen atoms into the macromolecular chain, replacing the -CH$_2$ group between aromatic rings, brings about some improvement in the thermal properties of fibres with no change in their glass transition temperature.

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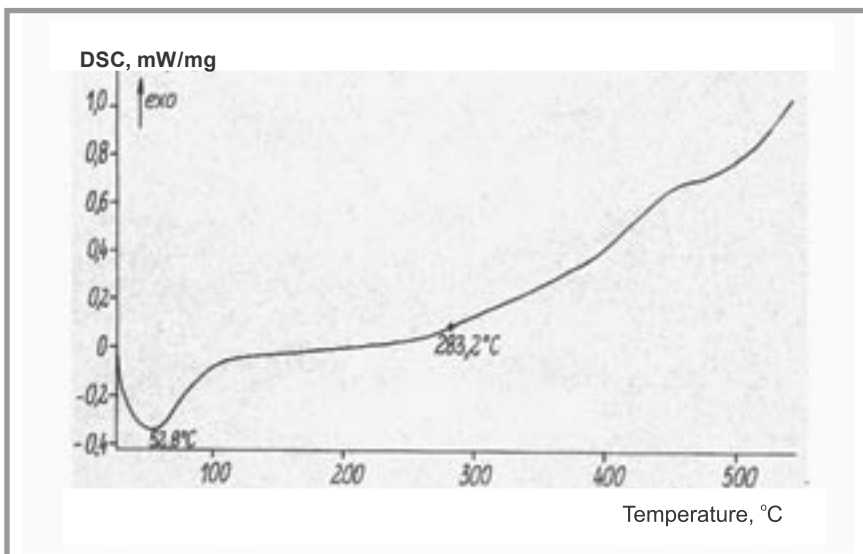14. *PN-92/E-05200 Protection Against Static Electricity Terminology.*

Figure 9. *DSC curves of PIA (S-10) fibres.*