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THERMAL CHARACTERISTICS OF HIGH-STRENGTH AND THERMOSTABLE AROMATIC FIBRES

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The thermal characteristics of ten kinds of para-aramid, meta-aramid, polyoxadiazole, and polyimide fibres were investigated by dynamic thermogravimetric analysis, differential scanning calorimetry, and thermomechanical analysis. It was shown that thermooxidative degradation of these fibres begins at 400-450°C and is intensified at higher temperatures. These fibres are characterized by dimensional stability up to the temperature of onset of thermooxidative processes (up to 400-450°C) except for meta-aramid fibres, which exhibit approximately 5% shrinkage at high temperatures. With respect to thermal stability, the fibres are in the following order: polyimide > heterocyclic para-aramid and polyoxadiazole > carbocyclic para-aramid > meta-aramid.

Of the fibres and fibre materials with extreme characteristics, aromatic ultrastrong and thermostable fibres and thread are the leader; world production is estimated at 70,000 tons a year and continues to increase. The materials made from these fibres are designed for prolonged use at high loads and/or temperatures: in designs for transportation (especially aircraft), high-revolution rotors, articles for occupational protection, rescue agents in transportation or in dangerous plants, and for many other purposes. In addition to high mechanical and thermal characteristics, these materials and articles should also satisfy other special requirements: preservation of size and shape, high insulating indexes, resistance to open flames, etc.

In many countries, including in Russia, aromatic fibres and thread have been developed whose use is determined by their elevated functional performance properties:

- high-strength and high-modulus heterocyclic para-aramid fibres based on polyamidobenzimidazole SVM (PABI) and carboheterocyclic copolymers Armos (CpPABI-1) and Rusar (CpPABI-2), which have the highest mechanical properties and simultaneously elevated thermal stability and resistance to open flame;
- high-strength and high-modulus thermostable para-aramid fibres based on poly-(*p*-phenylene terephthlamide): Twaron (PPTA-1), Kevlar (PPTA-2), and Terlon (CpPPTA) — the last one based on a copolymer close to PPTA with a 10-15% content of a second aromatic comonomer;
- carbocyclic thermostable fibres based on *m*-phenylene isophthalamide: Fenilon, Nomex and Conex (PMPIPA) which have the deformability necessary for textiles;
- polyoxadiazole fibres Arselon (POD) and Arselon-C (POC-C) — light-stabilized, with elevated thermal stability;
- polyimide fibre Arimid PM (PI-PM) and Kapton with elevated thermal stability and resistance to open flame, and high-temperature dielectric characteristics.

To optimize the use of these fibres and fibre materials, it is extremely important to compare and comparatively analyze their functional characteristics in prolonged exposure to high temperatures. Such data are reported in the literature only for the strength indexes, estimated at 20°C and 250 or 300°C [1-7]. The strength and the change in the strength in thermal aging and individual thermal characteristics of several types of aromatic fibres are compared in some studies [8-14]. However, the

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TABLE 1. Objects Investigated — Aromatic Fibres

Sample number	Polymer	Abbreviation
1	Polyamidobenzimidazole	PABI
2	Polyamidobenzimidazole (copolymer -1)	CpPABI-1
3	Polyamidobenzimidazole (copolymer -2)	CpPABI-2
4	Poly(*p*-phenylene terephthalamide)	PPTA-1
5	Poly(*p*-phenylene terephthalamide)	PPTA-2
6	Poly(*p*-phenylene terephthalamide) (copolymer)	CpPPTA
7	Poly(*m*-phenylene) isophthalamide	PMPIPA
8	Polyoxadiazole	POD
9	Polyoxadiazole (light-stabilized)	POD-C
10	Polyimide	PI-PM

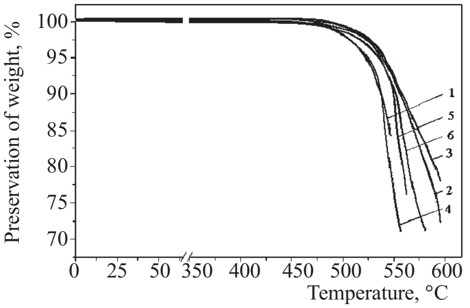

Fig.1

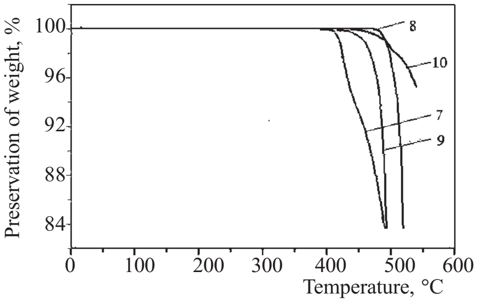

Fig.2

Fig. 1. Experimental TGA curves of para-aramid fibres. The numbers of the curves correspond to the numbers of the samples in Table 1.

Fig. 2. Experimental TGA curves of polyoxazole, meta-aramid, and polyimide fibres. The numbers of the curves correspond to the numbers of the samples in Table 1.

attempts to compare the few data from different investigators were very approximate due to methodological differences and indeterminacy of sample selection. We found no published comparative studies of thermooxidative degradation of different kinds of aromatic fibres/thread. A change in dimensions (spontaneous elongation or shrinkage) for the individual kinds of fibres made of aromatic polymers was only noted in [15].

There are thus only data on the dependence of the properties of aromatic figures/thread on the temperature for isolated types, and they were determined by different investigators with different methods and without sufficiently complete characterization of the initial samples. Due to the above, comparative studies of thermooxidative degradation and dimensional stability (elongation or shrinkage) of these fibres/thread were conducted to assess their behavior in conditions close to performance conditions and to refine some of the previously obtained data [16, 17].

The studies were conducted on samples of the fibres listed in Table 1 using a Stentor Redcroft instrument in heating in dynamic conditions.

Thermooxidative degradation was investigated by dynamic thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The determinations were performed in air medium at temperatures under 600°C. The samples weighed 5-10 mg and aluminum oxide was used as the standard. The measurements were performed at a temperature elevation rate of 20 and 10 deg/min. The difference in the temperatures of the sample and standard was fixed in the measurements and conversion per unit of heat flux (mcal/sec) was performed.

The change in the dimensions of the fibres with an increase in the temperature was determined by thermomechanical analysis (TMA) in linear heating from room temperature to 600°C at a rate of 10 deg/min. The straightening constant load was 0.1 cN/tex.

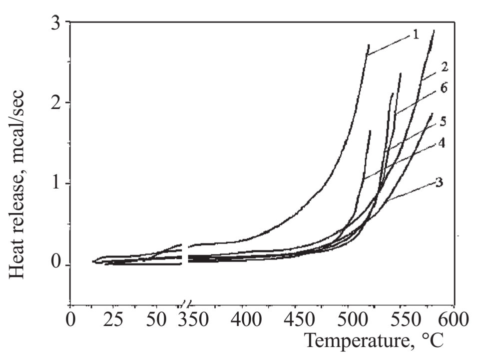

Fig.3

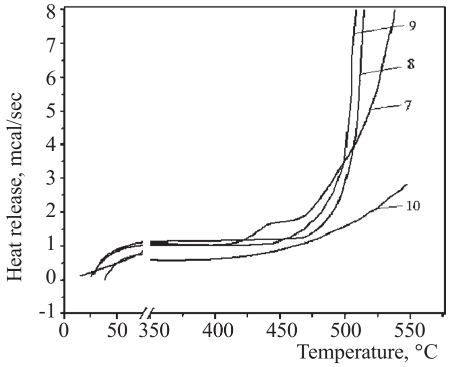

Fig.4

Fig. 3. Experimental DSC curves of para-aramid fibres. The numbers of the curves correspond to the numbers of the samples in Table 1.

Fig. 4. Experimental DSC curves of polyoxazole, meta-aramid, and polyimide fibres. The numbers of the curves correspond to the numbers of the samples in Table 1.

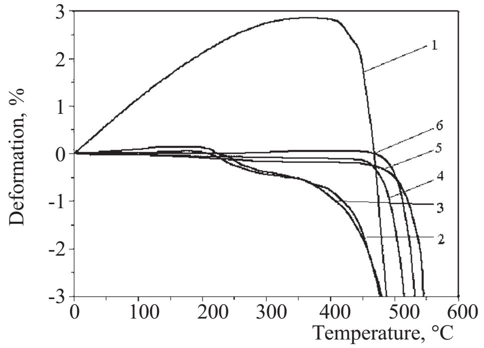

Fig.5

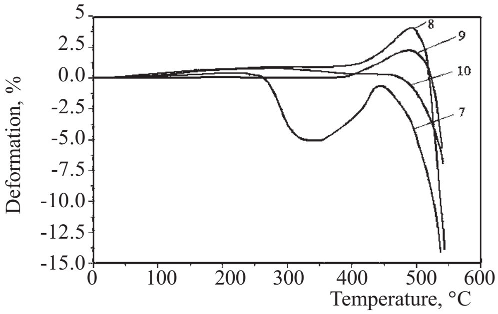

Fig.6

Fig. 5. Experimental TMA curves of para-aramid fibres. The numbers of the curves correspond to the numbers of the samples in Table 2.

Fig. 6. Experimental TMA curves of polyoxazole, polyimide, and meta-aramid fibres. The numbers of the curves correspond to the numbers of the samples in Table 2.

TGA and DSC studies of thermooxidation. The general shape of typical TGA and DSC experimental curves of the investigated fibres is shown in Figs. 1-4. The onset of weight loss is observed within the temperature limits of 425 to 480°C according to the TGA curves. Intensive decomposition begins at higher temperatures, 450-540°C. The onset of oxidation for these fibres is observed at 400-450°C according to the DSC curves. More intensive oxidation, clearly visible on the TGA and DSC curves, begins within the 470-520°C temperature limits.

Change in the linear dimensions of the fibres (spontaneous elongation or shrinkage). The experimental TMA curves are shown in Figs. 5 and 6.

Insignificant spontaneous elongation of para-aramid fibres (samples 1-6) was observed: up to 0.2% at 170°C for CpPABI-1 and CpPABI-2, up to 2.5% at temperatures up to 400°C for PABI. This was due to the known capacity of rigid-chain para-aromatic fibres for additional orientation in heat treatment [2, 5]. The shrinkage did not exceed 1% with an increase in the temperature, but it increased simultaneously with the occurrence of thermooxidation at 500-520°C, visible on the TGA and DSC curves.

A limited change in dimensions in a wide range of temperatures was characteristic of samples 7-10. Shrinkage occurred in the 250-440°C temperature region for PMPIPA meta-aramid fibres (sample 7), attaining 5%. At temperatures above 450-470°C,

TABLE 2. Characteristics of Thermal Degradation of Aromatic Fibres Based on TGA and DSC Data*

Sample number	Fibre	Temperature, °C				
		onset of weight loss (TGA)	onset of intensive decomposition (TGA)	4% weight loss (TGA)	onset of oxidation (DSC)	onset of intensive oxidation (DSC)
1	PABI	450	510	515	390	515
2	CpPABI-1	470	530	530	410	505
3	CpPABI-2	470	525	535	400	515
4	PPTA-1	475	530	515	405	480
5	PPTA-2	470	540	490	400	495
6	CpPPTA	430	525	525	390	500
7	PMPIPA	425	450	–	400	470
8	POD	485	505	–	470	510
9	POD-C	470	505	–	445	500
10	PI-PM**	> 480	> 520	540	460	> 500

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*Averaged values are reported.

**Due to the small slope of the curves, it is difficult to precisely establish the inflection site for PI-PM fibres.

TABLE 3. Results of Processing the TMA Curves

Sample number	Fibre	Max/min point		Point of inflection	
		temperature, °C	deformation, %	temperature, °C	deformation, %
1	PABI	–	–	400	+ 2.5
2	CpPABI-1	170	+0.16	460	– 1.32
3	CpPABI-2	170	+0.11	460	– 1.55
4	PPTA-1	–	–	425	– 0.05
5	PPTA-2	–	–	435	– 0.2
6	CpPPTA	–	–	420	+ 0.1
7	PMPIPA	347	–5	447	– 1.8
8	POD	495	+4	–	–
9	POD-C	480	+2	–	–
10	PI-PM	–	–	485	– 0.22

shrinkage of the fibres was significant due to thermooxidative processes, which was also demonstrated by TGA and DSC (see Figs. 1-4).

The data on thermooxidative degradation are compared for the fibre samples investigated in Table 2. The following parameters were assessed for evaluating the thermal characteristics of the fibres based on the TGA and DSC results, as in many studies [16-19]:

- onset of weight loss according to TGA (point of deviation of the curve from tangent to straight/horizontal segment);
- 4% weight loss according to TGA;
- onset of intensive decomposition according to TGA (point of intersection of the tangent to segments of the curve before and after the inflection);
- onset of oxidation according to DSC (point of deviation of the curve from tangent to horizontal/linear segment);
- onset of intensive oxidation according to DSC (point of intersection of tangent to segments of the curve before and after the inflection).

Judging by the results of the TGA and DSC studies within the temperature limits up to 400-450°C (see Figs. 1-4), thermooxidation in air did not take place in aromatic fibres. Only when these values were attained and above 450°C did thermooxidation become significant. These temperatures almost coincide with the TMA data (Figs. 5 and 6), confirming the possible temperature limits of use of articles made from these fibres. As the data in Figs. 1-4 show, polyimide fibres are degraded to the smallest degree.

The data on preservation/alteration of the dimensions of the aromatic fibres are reported in Table 3. According to the TMA data, heterocyclic para-aramid fibres (CpPABI-1, CpPABI-2) insignificantly lengthen spontaneously by a maximum of 0.2% at temperatures up to 400°C. Carbocyclic fibres PPTA-1, PPTA-2, and CpPPTA are not subject to significant deformations up to 400-450°C and polyimide fibres do not significantly deform up to 450°C.

Comparison of the thermal characteristics of aromatic fibres. A comparison of the TGA and DSC studies of the thermal characteristics of para-aramid, meta-aramid, polyoxadiazole, and polyimide fibres shows their elevated thermooxidative stability up to 400-450°C. Pronounced thermal decomposition is only observed at temperatures above 450-500°C.

Comparative TMA studies show the high stability of the linear dimensions of the aromatic fibres when the temperature changes. The basic kinds of CpPABI para-aramid fibres, PPTA fibres, and polyoxadiazole and polyimide fibres are characterized by dimensional stability up to 400-450°C. Spontaneous elongation or shrinkage does not exceed 0.5-1%. Only PMPIPA meta-aramid fibres have limited shrinkage deformation — under 5%. A comparison of the TMA data with the results of the TGA and DSC studies showed that thermooxidative degradation is accompanied by an insignificant change in the linear dimensions of the fibres up to 450-500°C.

With respect to thermal stability, the fibres are in the following order: polyimide > heterocyclic para-aramid and polyoxadiazole > carbocyclic para-aramid > meta-aramid. The elevated thermal stability and dimensional stability of the aromatic fibres, especially the lack of shrinkage, are extremely important in using them in articles where shrinkage phenomena are unacceptable, particularly in agents for personal protection (special heat-protection clothing).

The examined kinds of polyimide and aramid fibres are not only thermostable but also difficult to burn (resistant to open flame). Of these fibres, polyimide and heterocyclic para-aramid fibres are most resistant to open flames: their oxygen index (OI) is 43-46%, the OI of PPTA and PMPIPA fibres is 28-29%, and the OI of polyoxadiazole fibres is 26-27% [3-5, 20, 21]. These data are extremely important for practical selection of the initial fibres/thread for use in different kinds of fibre materials and articles used in extreme conditions with lengthy or brief exposure to high temperatures.

In selecting the initial fibres/thread for highly thermostable fibre materials and articles, their availability and price are also important as they determine the cost of the finished items. With respect to the relative cost, the fibres are in the following order: polyoxadiazole < PMPIPA aramid < PPTA aramid < PABI and CpPABI aramid < polyimide.

For highly loaded textiles and composites, including those exposed to high temperatures, CpPABI and PPTA fibres are priority. However, the cost of the latter is approximately 1.5-2 times less than the cost of heterocyclic para-aramid fibres.

Polyoxadiazole and meta-aramid fibres/thread should be used for thermostable filter materials and heat-protection textiles. They can also be used in thermostable polymer composites, including friction compositions, which are not heavily loaded. Priority can frequently be given to the cheapest polyoxadiazole fibres/thread.

Polyimide fibres/thread have the highest thermal characteristics of all of the types investigated. They can be used in the most essential fibre materials and articles with maximum thermal stability and resistance to open flames, particularly in aircraft, ships, and other means of transportation, and in closed premises. However, their cost is high. The stability of the dielectric characteristics of these fibres/thread in exposure to high temperatures makes them irreplaceable for use in high-temperature thermal insulation.

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