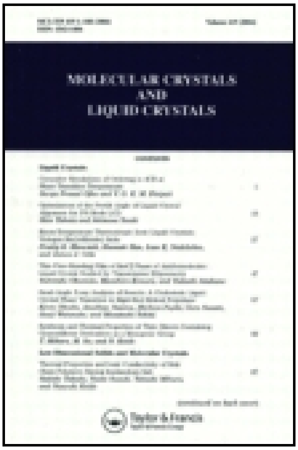

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Recent Achievements in Structure Ordering and Control of Properties of Para-Aramide Fibres

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Recent Achievements in Structure Ordering and Control of Properties of Para-Aramide Fibres

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The family of commercially produced high-strength, high-modulus fibres and yarns for the manufacture of technical textiles and construction composites, based on aromatic para-polyamides – poly-para-phenylene-terephphtalamide (Kevlar, Twaron), copolymers (Terlon, Technora), poly-para-heteroarylenes (SVM, Armos), was discussed and compared in the paper. The necessity of drawing such a comparison resulted from the fact that although there were papers on individual para-aramide fibres, but no comparative analysis of their structure and properties was performed yet. Therefore the main para-aramide fibres, their structure and its optimisation, their properties and ways of controlling these properties were reviewed in the paper. While discussing the main features of para-aramide fibres the following indices were taken into account: optimal molecular polarity and rigidity, energy of interatomic and intermolecular interactions, 3-D regularity, axial orientation, equal length of molecular chains in amorphous regions, etc.

A special attention was paid to Armos® fibres manufactured by J.S. "Tverkhimvolokno" Company because they have several advantages over other para-aramide fibres as concerns mechanical and thermal properties. Currently J.-S. "Tverkhimvolokno" Company manufactures Armos® yarns and roving with tenacity higher than 4.5 – 5.0 GPa and elasticity modulus over 145 GPa.

Keywords: para-amide fibres; Armos fibre; mechanical properties; thermal characteristics; realisation coefficient; anisotropy

INTRODUCTION

Aromatic para-aramide fibres are a new important step in the field of technical application of fibres and yarns. Their tenacity approaches 3–5.5 GPa, i.e. 3–5 times higher than traditional technical yarns [1–6]. There are two main groups of modern para-aramide fibres:

- high-modulus type (deformation modulus of which is in the range of 130–170 GPa) for the use in high-strength, high-rigidity textiles and hard construction composites;
- high-strength type (deformation modulus in the range of 60–90 GPa) for the use in high-strength, moderate-rigidity textiles and elastic composites, mainly tyres and rubber technical goods.

Fibres (yarns) belonging to the first-high modulus group, including new Russian fibre Armos®, are discussed in this paper.

There are five main types of para-aramide fibres based on different polymers:

- Kevlar® – based on poly-para-phenyleneterephthalamide (USA, Du Pont de Nemours);
- Twaron®) – based on poly-para-phenyleneterephthalamide (Holland, Akzo Nobel);
- Terlon® – based on copolymers similar to poly-para-phenyleneterephthalamide (Russia, "VNIIPolymervolokno");
- CBM® (formerly Vnivlon®) – based on para-aromatic heterocyclic polyamide (Russia, "VNIIPolymervolokno"; J.-S. Co "St-Pb NIIKhimvolokno" ", J.-S. Co "Kamenskkhimvolokno");
- Armos® – based on para-aromatic heterocyclic copolyamide (Russia, "VNIIPolymervolokno"; J.-S. Co "Tverkhimvolokno").

The highest mechanical properties among the above para-aramide fibres has Armos®.

PRINCIPLES OF CONTROLLING PRODUCTION AND PROPERTIES OF PARA-ARAMIDE FIBRES

The main ultra-high strength and deformation modulus fibres are based on para-polyamides, polyheteroarylenes and related copolymers. Para-aramide fibre production principles differ from those of conventional man-made fibres and discussed in literature [3, 5, 7, 8]. The fibre-forming ability and the achievement of high mechanical properties are based on the ability of rigid-chain linear polymers to transform into liquid-crystalline state. This fact results in self-ordering effects even in the case of small preliminary orientation both at the stage of fibre spinning and following thermal treatment.

All para-polyamides are infusible, therefore these polymers are dissolved in nucleophilic solvents – 100 % sulphuric acid or amide solvents with addition of lyophilic salts (in particular dimethylacetamide with the addition of lithium chloride). The fibres are spun by wet-spinning method (often through air layer). Solvent residue is washed out from the fibres formed and the latter are dried. All the operations mentioned above proceed step-by-step in a continuous process. The next stage is thermal treatment which leads to spontaneous orientation of the fibres. Some stretching is applied in order to increase the deformation modulus.

The properties of the fibres are determined, to a large extent, by the composition of raw material polymers or copolymers. It should be taken into consideration that the transition from poly-para-phenyleneterephthalamide to less regular polymers and copolymers results in a decrease in structuring of spinning solutions and promotes the formation of oriented structure of fibres during spinning and thermal treatment and therefore increases mechanical properties.

The state of 3-D order is thermodynamically more favourable for homo-polymers but this principle is in conflict with kinetic peculiarities of the formation of maximal highly-ordered structure of the fibres. This has brought about a necessity of creating new copolymers with controlled molecular rigidity and, in consequence, of developing new fibre-forming technologies suitable for this purpose. In this way the highest mechanical property indices of Armos® fibres were developed. Notice that the heterocyclic copolymer solution is in a non-isotropic state, but it transforms into a liquid-crystalline state in the fibre-forming process. At the same time new technological methods were developed and manufacturing equipment was upgraded.

STRUCTURAL PECULIARITIES OF PARA-ARAMIDE FIBRES

Para-aramide fibre structure on all three levels (molecular, supramolecular and microlevel) principally differs from the structure of conventional fibres based on flexible and semi-rigid polymers [3-5, 9-12]. The main structural peculiarities are shown in Table 1. Para-polyamides are characterised by molecular chain rigidity (statistical segment exceeds 20 - 50 nm) and by the presence of a large number of polar groups.

TABLE 1. Peculiarities of the structure of para-aramide fibres

Structural levels	Terlon®	SVM	Armos®
Molecular level	PphTA – copolymer statistical segment 30–50 nm Polar group: -CONH-	Heterocyclic para-aramide. Statistical segment 20–40 nm. Polar group: -CONH-; =N-	Heterocyclic para-aramide copolymer. Statist. segment 20–40nm Polar group: -CONH-; =N-
Supramolecu-lar level	Fibrillar; Extended chain 3-D crystalline order; Highly oriented; Stress-holding molecular chain contribution 0.5 – 0.7	Fibrillar; Extended chain 1-D crystalline order; Highly oriented; Stress-holding molecular chain contribution 0.5 – 0.7	Fibrillar; Extended chain 1-D crystalline order; Highly oriented; Stress-holding molecular chain contribution 0.5 – 0.7
Microlevel (fibre)	Cross-section: homogeneous; round	Cross-section: homogeneous; round	Cross-section: homogeneous; round

The supramolecular fibrillar structure of para-aramide fibres is characterised by a high orientation and the presence of ordered extended-chain regions. In this respect it differs from conventional fibres based on flexible or semi-rigid polymers which are characterised by folded supramolecular structures. The result of these peculiarities is a high contribution of stress-holding chains, their small length difference and therefore high level of mechanical properties. The structure of poly-*para*-phenyleneterephthalamide fibres is typical of amorphous-crystalline substances, but in the case of heterocyclic para-aramide fibres SVM and Armos, the 3-D order is low or it is closer to 1-D order. The fibrillar model with parallel differently ordered regions (amorphous and crystalline or quasi-crystalline) can be applied to para-aramide fibres.

Structure energy indices on molecular and supramolecular levels are characterised by high interatomic (in chains) and intermolecular interaction energies. The presence of a large number of polar groups and the rigidity of molecular chains result in a high glass transition temperature. At the same time, fully aromatic structure of elementary link leads to a high thermal stability of the fibres.

All para-aramide fibres are characterised by a high macrostructure homogeneity – minimal difference of layered structure (kernel and core) and small defectiveness. This is the another reason for their high mechanical properties. All structural peculiarities mentioned above point to a high stability of para-aramide fibres both under stretching mechanical stresses and in a wide temperature range. It is necessary to add that the high structural heterodynamics leads to a high anisotropy of mechanical and physical properties and also to capability of axial fibrillisation.

Particularly interesting is the Armos® fibre which is a heterocyclic para-copolyamide. Its elementary links involve very polar groups – peptide and tertiary nitrogen atoms. The structure of this copolymer is characterised by a poorer regularity and smaller rigidity in comparison with poly-*para*-phenyleneterephthalamide. This heterocyclic copolymer cannot form liquid-crystalline domains in solution. Therefore there is a possibility of controlling the structure-building towards maximal orientation order during fibre-forming and thermal treatment processes. Conformations of extended chains with irregular elementary link positions form 1-D order regularity with the possibility of axial movements. This fact facilitates structural transformations of fibres during thermal treatment and leads to a better axial order in supramolecular structure. Less regular molecular chain structure results in a higher contribution of stress-holding molecular chains and thus to maximal level of mechanical properties of Armos® fibre among all para-aramide fibres.

MECHANICAL PROPERTIES OF PARA-ARAMIDE FIBRES

A wide variety of mechanical properties of para-aramide fibres was investigated; some of the results are given in Table 2 [1–6, 9].

TABLE 2. Main mechanical properties of high-modulus para-aramide fibres

Index	Kind of fibre (yarn)		
	Kevlar, Twaron, Terlon	SVM	Armos
Density, g/cm^3	1.44	1.43	1.43
Elasticity modulus, GPa	130–170	135–150	140–160
Tenacity, GPa	3.3–3.8	4.2–4.5	4.5–5.5
Elongation at break, %	2.5–3.0	3.0–3.5	3.5–4.0
Standard humidity, %	2.0–3.0	3.5–4.0	3.0–3.5

An objective comparison is difficult because there are clear differences in data on mechanical properties of the same para-aramide fibres reported in the literature. They result of from differences in testing methods and insufficient information.

Modern Armos® fibres and yarns have a number of advantages in comparison with other para-aramide fibres mentioned above. There is a possibility to increase tenacity of this fibre to more than 5.5 GPa.

Stress-strain plot of para-aramide fibres is not far from being linear. Tenacity of para-aramide fibres depends on moisture content as a result of two factors: intermolecular interactions become stronger due to formation of hydrogen bridges in the presence of water molecules and plasticization effect appears. These two factors lead to an increase in tenacity to a certain extent, when moisture content rises. However, if moisture content continues to increase, a reduction in tenacity occurs to the level of 90 - 95 % compared to tenacity of dry fibres.

Degree of the realisation of mechanical properties by para-aramide fibres

The extent of the realisation of mechanical properties (E and σ) by para-aramide real fibres compared to theoretical and limited attainable properties directly depends on structural order level and the presence of defects [10-12]. The theoretical and limited attainable indices, which are estimated for ideal ordered structure of extended chain polymer crystals, are as follows: theoretical (E_{TH}) and limited attainable (E_{LIM}) elasticity modulus and theoretical (σ_{TH}) or, more correctly, limited attainable strength (σ_{LIM}). These indices are shown in Table 3.

TABLE 3. Calculated limited obtainable mechanical properties for two regular para-aramides

Polymeric crystals	$E_{TH} \approx E_{LIM}$ GPa	σ_{TH} , GPa	σ_{LIM} , GPA
Poly-para-phenylene-terephthalamide	235	30	24
Heterocyclic para-polyamide	230	24	18

The realisation coefficient K_E depends on number of stress-holding polymeric chains in fibre cross-section, i.e. on fibre structure perfection on all three levels.

At the same time, the second realisation coefficient K_σ depends both on the general structural order and the presence of defects on all the structural levels mentioned above. These realisation coefficients of mechanical properties are presented in Table 4. It results from Table 4 that the structural order level is high for all para-aramide fibres and shows a limited reserve of increase. At the same time the presence of structural defects is the general reason for the tenacity limit. This means that there is a reserve of increase in mechanical properties.

TABLE 4. Results of calculations of realisation coefficients

Fibres	E, GPa	$K_E = E / E_{\Pi P}$	σ*, GPa	$K_\sigma = \sigma / \sigma_{\Pi P}$
Kevlar, Twaron, Terlon	140–170	0.6–0.72	3.5–3.8	0.15–0.16
SVM	140–150	0.61–0.65	4.2–4.5	0.23–0.25
Armos	140–160	0.61–0.70	5.0–5.5	0.28–0.31

The realisation degree of mechanical properties not only indicates structural order level of fibres but it makes also an integral characteristics of technological process level and shows further reserve for upgrading their perfection level.

Anisotropy of mechanical properties

High level of orientation, structural and energy anisotropy of para-aramide fibres lead to high anisotropy of mechanical properties [9]. The results of mechanical anisotropy determinations are presented in Table 5.

TABLE 5. Anisotropy of mechanical properties of para-aramide fibres

Fibres	Elasticity modulus, GPa		Tenacity, GPa	
	Axial	Transverse	Axial	Transverse
Terlon	150–160	3.5–5.5	3.3–3.8	0.025–0.055*
SVM	140–150	4.0–6.0	4.0–4.5	0.035–0.055*

Elasticity modulus across fibre axis was determined by two methods: fibre compression and calculation based on one-dimensional composite data. Tenacity across fibre axis was determined by stretching of epoxide film including a single fibre.

Direct investigation across fibre axis of such fibres as Kevlar, Twaron and Armos was not carried out, but the relevant indices will be roughly the same.

THERMAL CHARACTERISTICS OF PARA-ARAMIDE FIBRES

All para-aramide fibres are characterised by high glass transition temperatures, high thermal and thermal-oxidative resistance. These fibres have high ignition and self-ignition temperatures as well as oxygen indices [2-5, 13, 14]. The main thermal characteristics are presented in Table 6.

TABLE 6. Thermal characteristics para-aramide fibres

Indices	Kind of fibre (yarn)	
	Terlon, Kevlar, Twaron	SVM, Armos
Glass transition temperature, ^{0}C	345–360	270–280
Exploitation temperature (limited), ^{0}C	250–270	300–330
Destruction temperature, ^{0}C	450–550	550–600
Ignition temperature, ^{0}C	450–500	500–600
Self-ignition temperature, ^{0}C	500–600	550–650
Oxygen index, %	27–30	37–43

It results from the above data that thermal characteristics of Armos heterocyclic fibres are similar to SVM fibres, but these fibres show higher resistance to thermal oxidation and open fire than other para-aramide fibres based on poly-para-phenyleneterephthalamide and related copolymers (Kevlar, Twaron, Terlon).

THE ASSORTMENT AND PROPERTIES OF ARMOS® YARNS

Armos® yarns are produced by J.-S."TVERKHIMVOLOKNO" Co. Yarns of linear density of 29.4; 58.8 and 100 tex are the main assortment. Moreover, there are bands or roving of 600 tex or 1000 tex manufactured by slubbing of 100 tex yarns. The technical indices for the yarns (type A) are shown in Table 7.

TABLE 7. Indices of mechanical properties of Armos® yarns according to technical specification (guaranteed)

Index	Yarn 58.8 tex	Yarn 100 tex	Roving 600 tex
Load at break, N (kg)	no less than 116 (11.8)	no less than 206 (21)	no less than 221 (225)
Elongation at break, %	no less than 4	no less than 4	–
Breaking stress by microplastic method, MPa (kg/mm^2)	no less than 4412 (450)	no less than 4412 (450)	no less than 4905 (500)
Dynamic elastic modulus, GPa (kg/mm^2)	142.2 (14500)	142.2 (14500)	142.2 (14500)
Yarn twist, twist/m	50±15	50±15	35±15

All indices were measured by standard methods. Testing of the yarns was performed according to the Russian State Standard No. 6611 at clamp length of 500 mm, microplastic tests were carried out according to the Russian Standard No. 28007 at clamp-length of 100 mm. Dynamic elastic modulus was determined by pulse methods described by the Russian Standard No. 28007 at clamp-length of 100 mm. Moisture content of the yarns was 3.5 % in standardised conditions.

Indices of real mechanical properties of Armos® yarns are higher than guaranteed by technical specification. Results of research conducted recently show that there is a possibility of further increase in mechanical properties.

CONCLUSIONS

The creation of para-aramide fibres was an important step in the development of new fibres and yarns for the manufacture of high-performance technical textiles and composites. Their production principles, structure, properties and application areas were discussed in this paper. Research work on the development of fibres of even higher values of their properties were discussed.

New fibre Armos®, which is distinguished by higher indices of maximal mechanical and thermal properties than other para-aramide fibres, was created by using advanced manufacturing methods. Structure and properties of this fibre and its comparison with other high-performance fibres were presented in this paper.

At present J.-S. "Tverkhimvolokno" Company manufactures Armos® fibres (yarns) with the strength of 4.5–5 GPa and higher and deformation modulus exceeding 145 GPa. This fibre is characterised by a high thermal resistance in exploitation conditions (up to 300–330 ^{0}C) and is flame resistant (oxygen index about 37–43 %).

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