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NEW TEXTILE COMPOSITE MATERIALS DEVELOPMENT, PRODUCTION, APPLICATION

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P. 14

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The history of the Research Institute and Chemical Fibers/Composite Materials Works, *Khimvolokno* RI in St. Petersburg, goes back to the eighteenth century. In 1717, by Peter the Great's edict, the "Gunpowder Manufactory" was erected on the Okhta River on the outskirts of St. Petersburg, and later it became a huge gunpowder works closed down soon after World War I.

In 1930 the chemical (viscose) fibers works, the first in Russia, was erected on the territory of the former gunpowder works.

The branch of the Artificial Fibers Institute was established in 1948, and in 1968 the works was reconstructed into a pilot industrial enterprise intended to produce new fibers.

In 1985 the organization achieved a new status and became independent: the "Research Institute and Chemical Fibers/Composite Materials Works" (*Khimvolokno* RI) in St. Petersburg.

At present the Institute and Works constitute a unified complex engaged in the creation of new types of chemical fibers, textile and composite materials:

- laboratory research in synthesis of new polymers and production of fibers based on them
- creation of pilot plants which enable development of new fibers technologies
- pilot industrial production of the developed fibers
- manufacture of textile materials and products based on new fibers
- manufacture of polymer-polymer composites and some types of products based on such composites
- reclaiming of chemicals, gas emission cleaning, and sewage treatment
- twisting of fiber structure and properties, textile and composite materials
- economy, economic trends, and marketing in the field of the developed materials and products

In Russia, the *Khimvolokno* RI is the leader in the development and manufacture of fibrous and composite materials having special properties, including the types of materials (1–4) that follow:

- high-strength and high-modulus fibers made of poly-para-aramides and poly-para-arylates (para-polyesters)
- heat-resistant fibers made of polyimides, polybenzimidazoles

- fluorocarbon polymer fibers
- carbon fibers based on viscose and polyacrylonitrile precursors
- various types of polyvinyl alcohol fibers
- porous and reinforced films for ultrafiltration
- single-component and multicomponent (combined) textile fabrics of all types based on the above-mentioned and other fibers: braids, ribbons, fabrics, knitted fabric, nonwoven fabrics, cords, ropes, etc.
- polymer-polymer composites and products: constructional, heat-shielding, chemoresistant, antifriction, electrical and radio engineering products, etc.

New types of fibers, filaments, and combined textile and composite materials based on them have been adequately described in the literature (3–12). Many developments by *Khimvolokno* RI in St. Petersburg are basically new and original both for Russian and world-wide practice.

In what follows, the main data are presented for some types of fibers, textile structures and composite materials manufactured on their basis. Developments in carbon fibers and fibrous carbon materials for engineering and medical applications are also discussed by Prof. R. M. Levit and Prof. L. I. Fridman in their papers.

SUPER-HIGH-STRENGTH, SUPER-HIGH-MODULUS FIBERS, FILAMENTS, AND MATERIALS MANUFACTURED ON THEIR BASIS

New types of super-high-strength and super-high-modulus organic fibers and filaments, and textile and composite materials based on them are available in a wide range of products. They play an important role in the manufacture of products for engineering, sports, medical and other applications: ropes, cables, ribbons, reinforced fabrics, nonwovens, fabricated rubber products, composites, etc.

The main types of fibers and filaments for such applications are as follows (3–5, 9–11):

- polyvinyl alcohol types for MVM and MVP vinol
- para-aramid types for SVM and terlon

Although the fibers and filaments are available in a wide range of linear densities, the main filaments of 29.4 tex and 58.8 tex have the following properties:

Characteristics	MVM vinol	SVM	Terlon
Strength, GPa	1.2–1.6	4.2–4.5	3–3.3
Modulus of elasticity, GPa	25–35	120–130	125–140
Elongation, %	5–6	3–3.5	2–3

Should the need arise, the thinner filaments of 14.2 tex are manufactured and the braids with linear density 1000 tex are produced by splicing filaments of 58.8 tex.

Since the above-mentioned filaments feature high rigidity, the corresponding conditions have been developed for processing them, allowing the maintenance of their structure and properties to remain almost unchanged, i.e., to ensure efficient use of 90% or more of their rated strength (1–4, 13–15).

The super-high-strength ropes are manufactured from the terlon and SVM filaments and braids on cord-braiding machines. The rope core is composed of parallel super-high-strength filaments and is braided with polyfen, vinol, arimid and SVM filaments. Those may be illustrated by referring to the properties of the 6 mm and 10 mm diameter ropes.

rope dia, mm	6	10
rope mass, g/m	22	66
breaking load, GPa	17–30	70–95
elongation, %	4–5	4–5

The strength of SVM ropes is 2–5 times that of polyamide and polyester ropes. The annual loss of rope strength due to sea water or oil products does not exceed 25–35%.

Nonwoven fabrics are manufactured from SVM fibers having the above properties as well as from all types of fibrous waste after being cut. Nonwoven fabrics are manufactured on the plants including the 4–11-Ш card machine, the ПШ carding converter, and the ИМ -1800 M needle-punching machine or the ВП -180 sew-knit machine. The two types of nonwoven fabrics designed and produced are as follows:

- needle-punch MIP
- sew-knit MVP

The principal consumer characteristics of the fabrics are as follows:

Characteristics	MIP	MVP
Surface density, g/m^2,		150–200
Punching density, 1/cm^2	1	–
Knitting density per 100 mm (horizontal-vertical)		40/36 knitted fabric

Because of fibrillation of fibers in carding, the resulting web is well formed and production of nonwoven fabrics presents no problem.

When epoxide and epoxyphenol binders are used, both types of nonwoven fabrics allow production of constructional fabric-based laminates possessing high mechanical properties.

Fiber content, %	50–75
Density, g/cm^3	1.25–1.3
Strength, MPa:	450–480
Tensile strength	450–480
Bending strength	470–520
Shear strength	110–120

Super-high-modulus filament-based fabrics play an important role in the manufacture of constructional composite materials. High rigidity of the filaments calls for development of special conditions to prepare them for weaving as well as for development of the weaving process itself. In this case, the following factors are important: reduction of an excessive bend radius of filament-guiding parts, reduction of filament friction, reduction of filament tension, and a change in the loom set-up scheme to reduce dynamic forces in the filaments. Weaving is performed on shuttle and shuttleless looms at reduced speeds. The fabrics produced have the characteristics shown in Table 1.

Braids, fabrics and nonwoven materials of super-high-modulus fibers and filaments form the basis for production of various types of composite materials, where epoxide and epoxy-phenol binders are used, by employing molding methods. The properties of these materials are given in Table 2 for illustration only.

HEAT-RESISTANT AND NONFLAMMABLE FIBERS, FILAMENTS AND TEXTILE FABRICS

Among the high-heat-resistant and nonflammable fibers and filaments designed and produced by *Khimvolokno* RI in St. Petersburg, there are two main types:

- polyamide: Arimid, Arimid T
- polyamidobenzimidazole: Togilen

Their principal characteristics are as follows:

Characteristics	Arimid, filament,	Togilen, filament,	Togilen, fiber,
Linear density, tex	11–100	11–200	0.12–0.44
Strength, cN/tex	40–60	40–60	30–50
Elongation, %	6–12	10–15	20–25
Strength retention at 300°C	55–65	60–70	60–70
Strength retention after heating at 300°C, 100 h, %	60–80	80–95	80–95
Oxygen index	42–45	43–46	43–46
Moisture content (at 65% relative humidity), %	2–3	13–15	13–15

Fibers and filaments, arimid and togilen, are classed as heat-resistant and nonflammable materials. It should be noted that arimid has low hygroscopicity and high dielectric properties, whereas togilen is the most hygroscopic material of all the filaments of a similar class (1, 2, 4, 9, 11).

Woven Fabrics Based on Arimid and Arimid T. Filaments.

These filaments are readily processed into knitted fabrics using standard facilities. In most cases, textile fabrics consist only of arimid filaments, though occasionally these are combined with polyfen ftorin filaments. The characteristics of two types of fabric are given in Table 3 for illustration only.

The applications are largely governed by thermal characteristics, nonflammability, low hygroscopicity and high dielectric properties. These are

- high-temperature electrical insulation (filaments, ribbons, fabrics)
- protective clothing for firemen, welders, etc.
- decorative finishing material, curtains, fabrics for aircrafts, ships, automobile and railway transport, and welfare rooms.

It should be noted that intensive yellow colouring places definite restrictions on their application as decorative finishing materials.

Table 1. Characteristics of Reinforcing Fabrics Based on High-Modulus Filaments

Filament	Weaver	Linear density of filaments, tex	Number of filaments per 10 cm	Thickness, mm	Surface density g/m^2	Strength of strip 25 mm wide, N	Elongation, %
MVM vinol	Basket 2/2	93.5/93.5	140/155	0.65	300	1450/1650	9/10
SVM	Linen	29.4/29.4	150/160	0.30	110	1600/1800	14/12
	Basket 2/2	29.4/29.4	300/250	0.35	180	2700/2400	11/9
	Sateen 8/3	29.4/29.4	255/235	0.40	160	2100/2600	12/9
Terlon	Linen	58.8/58.8	178/142	0.42	130	2500/2100	–

Table 2. Characteristics of Composites Based on Textile Fabrics Made From High-Modulus Filaments

Reinforcing Filler	Density g/cm^3	Strength, MPa		Modulus in tension GPa	Elongation at rupture
		tensile	bending		
Unidirectional braid, SVM	1.3–1.32	1500–2500	280–300	80–84	1.7–2.1
SVM fabric	1.28–1.32	500–750	–	32–40	2.5–4.0
Nonwoven fabric, SVM	1.27–1.30	210–300	–	14–17.5	–
Unidirectional braid, Terlon	1.30–1.32	1300–2000	280–300	90–100	1.5–2.0
Terlon fabric	1.28–1.32	400–600	–	35–42	2.0–3.0

Table 3. Characteristics of Fabrics Based on Heat-Resistant, Nonflammable Arimid Filaments

Characteristics	Types of fabric	
Weave	linen	crêpe
Linear density	29.4/29.4	29.4/29.4
Number of filaments (stitches) per 10 cm	230/240	248/275
Thickness, mm	0.25	0.32
Surface density, g/m^2	130	157
Strength of strip 25 mm wide, N	–	1500–1900
Elongation, %	–	15/13

Textile fabrics based on togilen fibers and filaments are readily manufactured using standard textile facilities. When combined with woolen or chemical fibers, the fibers are also readily processed. The assortment comprises various structures of knitted and nonwoven fabrics. The characteristics of (knitted) fabrics are given in Table 4 for illustration only. Their applications are largely governed by high thermal properties, nonflammability, and high hygroscopicity. These are

- protective clothing for firemen, metal-makers, welders, drivers, pilot, pilots, etc.
- decorative finishing materials, mats for aircraft, ships, automobile and railway transport, public buildings and rooms
- high-temperature filtering media
- thermal insulation, and some other products

It should be noted that in mass and as ready-made material, togilen can be coloured in bright hues.

Togilen fibers and filaments are distinguished for their unique properties among other types of heat-resistant and nonflammable fibers and materials based on them that are produced in other countries.

Table 4. Characteristics of (Knitted) Fabrics Based On Heat-Resistant, Nonflammable Togilen Filaments

Characteristics	Togilen	
	Fabric	Knitted fabric
Weave	twill 2/2	satin-stitch
Linear density	58.8/58.8	29.4
Number of filaments (stitches) per 10 cm	200/220	120/90
Thickness, mm	0.40	0.55
Surface density, g/m^2	240	–

FIBERS AND TEXTILE FABRICS BASED ON FLUOROCARBON POLYMERS

In Russia the *Khimvolokno* RI (St. Petersburg) is the leader in the development and manufacture of fibers and filaments based on fluorocarbon polymers. The two main types of fibers and filaments manufactured are as follows:

- polyfen (manufactured from polytetrafluoroethylene)
- ftorin (manufactured from a copolymer of tetrafluoroethylene with hexaftuoropropylene)

Table 5. Characteristics of Fabrics and Filaments Based on Fluorocarbon Polymers

Characteristics	Polyfen Complex filament	Ftorin		4MB Staple fiber
		Monofilament	Complex filament	
Linear density, tex	13–44	10–70 (0.13–0.5 mm)	4–20	3–5
Density, g/cm^3	2.2-2	2.15–2.16	2.15–2.16	2.15–2.16
Strength, MPa	250–820	150–180	170–210	130–180
Elongation at rupture,%	15–30	15–30	15–35	20–50
Permissible operating temperature, °C	up to +225	up to +200	up to +200	up to +200

The main characteristics are given in Table 5 for illustration only. Fibers and filaments of polyfen and ftorin types have unique properties: absolute chemical resistance, nonflammability, biological inertness, low friction coefficient, high dielectric characteristics, absolute nonhygroscopicity and nonwettability (1, 2, 4, 9, 11, 16, 17).

Antifriction Textile Fabrics Based on Polyfen Filaments.

Antifriction polymer materials based on fluoroplastic, polyamides and some other polymers and extensively used in engineering, are essentially bonded in their application by the magnitude of unit pressure, friction wear and other indicators. Woven fabrics based on polyfen filaments made it possible to avoid these disadvantages. The designed fabrics, such as naftlen, aftlen, daclen, vsetal, etc., have an original structure with such an arrangement of mutually related filament systems that only polyfen filaments appear on the right side, thereby forming an antifriction layer. The inside of the fabrics is composed of the filaments of vinol, cotton yarn and other materials having a high friction coefficient. This side of the fabric can be bonded to any hard surface as may be required. The structure and surface of naftlen and aftlen fabrics are smooth, and those of daclen fabric are corrugated. The characteristics of these fabrics are given in Table 6.

Special features of the fabrics are high strength and low creep. They can be used in the friction units of machinery, lubricated and unlubricated, and can operate at moderate speeds and under high unit loads.

The above-mentioned fabrics offer the possibility of carrying large-sized cargoes and structures, whose mass amounts to hundreds and thousands of tons, such as bridge bays and structures, a large-sized apparatus, ships on building berths, etc.

Table 6. Characteristics of Antifriction Fabrics

Characteristics	Fabrics				
	Naftlen	Aftlen	Daclen	Vsetal	Ancotex
Weave	Combined two-layer			Combined multi-layer	
Right side and inside layers	Polyfen vinol	Polyfen cotton	Polyfen arimid	Polyfen vinol	Polyfen lavsan
Thickness, mm	2.5	0.5	1.0	1.4	5
Surface density g/m^2	1500	500 and lower	600 and lower	1300	2800
Surface	smooth	smooth	corrugated	corrugated	corrugated
Maximum unit load, MPa	600	600	600	1800	900
Friction coefficient	0.016	0.016	0.016	0.08-	0.012-
For steel	0.032	0.032	0.028	0.016	0.022

The composite antifriction material, ataalen, is produced by combining naftlen, daclen and other fabrics with the plates made of metal (aluminium alloys), glass-reinforced and organic plastics that are bonded together. This material is manufactured in the form of sheets and offers the possibility of carrying heavy large-sized structures and cargoes up to 100–150 thousand tons.

All of the above materials have no match among the antifriction materials used in various fields of engineering where high unit loads and average speed of movement are employed.

Chemoresistant textile fabrics based on polyfen and ftorin fibers and filaments include a variety of filtering, protective and nonwoven fabrics designed for filtering corrosive liquids and gases. Unique chemoresistance allows these fully fluorinated fibers and filaments to be used in the manufacture of nitric, phosphoric and sulphuric acids, chemical agents, fertilizers, etc.

Fabrics are largely used to filter corrosive liquids, while nonwoven materials are preferred in filtration of gases. Gauzes and nonwoven materials based on ftorin monofilaments are most efficiently used to form the layers for trapping splashes of concentrated process gases.

Another important application of polyfen filament-based fabrics is reinforcement of fluorocarbon polymer films employed as ion-exchange membrances for electrolysis (of sodium chloride solutions in the manufacture of caustic soda and chlorine) and reinforced ultrafiltration films (described below).

The fabrics manufactured from polyfen and ftorin filaments may not be wetted with molten metal and are used in the manufacture of working clothes and protective means for nuclear reactors and similar plants where liquid metal heat-transfer agents are employed.

Polyfen and ftorin fibers and filaments are also used in the manufacture of packing cords and glands for rotary shafts in chemical equipment (reactors, pumps), and gaskets for various devices such as gate valves, etc. In these cases, braided cords of square, rectangular and round cross sections are manufactured by combining fluorine filaments with carbon, asbestos and other filaments. High chemoresistance, heat resistance and a low friction coefficient ensure long service life for them.

DEVELOPMENTS OF NEW TYPES OF TEXTILE COMBINED AND COMPOSITE MATERIALS

Based on a wide range of new types of fibers, pilot and industrial plants and shops for the manufacture of textile combined and composite materials are available at the institute; it develops new types of fibers to order for organizations and firms both in Russia and other countries (1–4, 18, 19).

Yarn and woven fabrics based on para-aramid high-modulus fibers.

In some types of industrial woven fabrics, the employment of the yarn based on para-aramid fibers, both in pure form and in combination with other fibers, such as wool, is an absolute necessity. The SVM fibers used for this purpose have the following characteristics:

linear density, tex	3.5–4.2
modulus of elasticity, GPa	100–120
elongation, %	3–33
cutting length, mm	65
oil content, %	1–2

The yarn is manufactured by a spinning apparatus system that is similar to the one employed to produce woolen yarn and comprises the main equipment that follows: *Befama* two-web machine, ПБ-114-Ш ring-spinning machine.

A special feature of SVM fibers is their partial fibrillation in combing, which ensures the adequate binding of the web and roving.

The 100% SVM fibers yarn has the following characteristics:

Linear density, tex	150–170
Coefficient of variation for Linear density, %	6–6.5
Number of twists per 1 m	230–250
Relative strength, cN/tex	28–35
Elongation, %	3–3.2

At the same time, the institute has designed woolen yarn containing 10% of SVM fibers.

The yarn enables production of the fabrics and knitted goods used to manufacture protective means for people engaged in some forms of mechanical and chemical production. Moreover, the SVM yarn fabrics are used in the manufacture of composite materials and articles having substantially curved surfaces where the low-tonnage fabrics based on super-high-strength para-aramid filaments cannot be used. The terlon fiber-based yarn, whose properties are nearly the same as the SVM yarn, is used for the same purposes.

Carbon Filament-Based Fabrics.

The traditional method of producing carbon fibrous materials such as fabrics, nonwoven materials, ribbons, and knitted goods is to manufacture them from fibers and filaments of precursors (viscose or polyacrylonitrile) subsequently carbonized and graphitized. This method, however, has its own limitations:

- impossibility of obtaining dense structures because of an abrupt reduction in the size across the fibers carbonized, which results in an increase of through porosity

- impossibility of producing the combined woven fabrics which include, along with carbon fibers and filaments, some other types

In order to create new types of composite materials, the institute has designed the fabrics based on carbon fibrous filaments having the following properties:

Characteristics	Ural H	Types of filament		
		YKH-2500		YKH-5000
Linear density, tex		225		450
Fiber strength, GPa	1.3–1.5	2.5	–	2.7
Modulus of elasticity, GPa	150–170	200	–	240

In processing carbon filaments, a serious problem was presented by their brittleness, which made it necessary to development special conditions for the process of preparing them for weaving as well as for the weaving itself.

In forming packages and warp beams, the filaments were gently laid without excessive kinks, the threads were treated with oil, and the speed and tension of filaments were half and one-third as much as the traditional ones. The weaving was accomplished on СТБ-type shuttleless looms with modernized filament-guiding devices at reduced speeds.

The institute has designed the fabrics in which either warp filaments or weft filaments are of carbon type, and the second system filaments consists of any specified types of ordinary chemical fibers. Their special feature is the choice of such weaving conditions that the carbon filaments are laid without bending as if they are braided with ordinary chemical filaments.

When tested for bending, compression and tension, the structural composites based on the above-mentioned fabrics had indices 15–20% higher than those of the materials based on fabrics where ordinary webs of the same filaments were employed.

Hybrid woven fabrics and reinforcing semifinished items based on high-strength and high-modulus para-aramid and carbon filaments are produced by the methods of weaving and by placing one over another the layers of filaments or fabrics composed of alternate components. In this manner the fabrics are produced for the manufacture of reinforced structural thermosetting plastics with controlled mechanical properties, in particular, rigidity.

Reinforced ultrafiltration film membranes have been developed and are available in two main types:

- the type based on aliphatic polyimides and reinforced by polyimide filament gauze (FAM-PA):

- the type based on fluorocarbon polymers and reinforced by fluorocarbon fiber or fabrics.

The above two types of ultrafiltration materials are designed for fine treatment of liquids in the electronic industry, biotechnology, the medical equipment industry, and in the treatment of fuel and chemical agents, etc. The FAM-PA material is used to filter low-corrosive media.

The FKM-PTFE material is used to filter solutions of acids, alkalies, organic solvents and other highly corrosive media. The principal characteristics of these materials are given in Table 7.

Table 7. Principal Characteristics of Reinforced Ultrafiltration Film Membranes

Characteristics	FAM-PA	FKM-PTFE		
		0.2 type	0.5 type	1.0 type
Minimum size of retain particles, μm	3.0	0.2	0.5	1.0
Rate of water flow (at a pressure drop of 0.05 MPa), $cm^3/cm^2 \cdot s$	2.0	0.1	0.25	0.6
First bubble pressure, MPa	0.02	0.09	0.05	0.02

In conclusion, it should be noted that the *Khimvolokno* Research Institute in St. Petersburg attaches great importance to integration with institutes, works, and firms in Russia and other countries (CSFR, USA, Poland, Japan, Germany, Finland) that is accomplished by establishing two-sided contacts and with the assistance rendered by the Russian concern *Khimvolokno* and its organizations and International and Russian academies.

In St. Petersburg especially close relations were established within the scope of the Engineering Academy, the Institute of Light, and the Textile Industry (research developments in new types of fibers and woven fabrics), Machine-Building Production Association (development), and the Integrated Fine and Industrial Fabrics Works (production of woven fabrics).

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