PRODUCTION AND APPLICATION OF CHEMICAL FIBERS WITH SPECIAL PROPERTIES FOR MANUFACTURING COMPOSITE MATERIALS AND GOODS OF DIFFERENT USAGE

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The development of modern technologies demands the creation of new nonmetallic, fibrous materials with specific properties. In Fig. 1 you can see the selection of fibers and materials developed by NII "Chimvolokno", St. Petersburg, which we can conventionally divide into two groups:

Heat-resistant fibers	Refractory fibers
Fire-resistant fibers	Chemoresistant and antifriction fibers
Thermotropic fibers	Fibers on the basis of polyvinyl alcohol
Fibers for medical application	Microfiltering films
Textile structures	Paperlike and nonwoven materials

Composite materials

Figure 1. Fibers and materials developed by St. Petersburg NII "Chimvolokno" in cooperation with allied companies.

In cooperation with NPO "Chimvolokno" MYTITSHI we developed and started producing heat-resistant high-strength fibers on the base of polyhetarearilin and aromatic polyimides (SVM and terlon); heat-resistant fibers on the base of polyemede (aramid); fire-retardant fibers (togilen); chemoresistant and antifriction fibers on the basis of homo and copolymers of polytetrafluoroethylene (polyfen and ftorin); water soluble, acetylated and high-modulus fibers from polyvinyl alcohol (vylen). Separate reports will deal with textile structures and thermotropic fibers, as well as with medical fibers. The author of this report will discuss in detail one of the groups of refractory fibers—carbon fibers (CF) and about the corresponding paperlike nonwoven materials. Also, composite materials (CM) and their base, which is the subject of the author's research since 1968, will be discussed.

Due to certain circumstances and the economic situation in Russia, the major part of CF is produced on the base of fibers from polyacrylonitrile and hydrocellulose fibers (viscose). CF from pitch are produced on an experimental scale. The concept of carbon fibers (CF) is very broad. This large group of materials can be divided into several subgroups, such as:

1. Fibers for construction application
2. Heat-resistant
3. Materials with controlled electrophysical properties
4. Materials with controlled physical/chemical properties (i.e., sorbents, accelerators, filters, antifriction materials, etc.)

According to the level of physical and mechanical characteristics, (strength and Young's Modulus), CF are very often subdivided into high-modular, high-strength, medium-modular and soft/low modular CF. The latter, if they are produced using modern technology, cannot be considered as low-quality fibers because CF are characterized by complex properties, not by one or two characteristics. An attempt to receive CF with maximum Young's Modulus (E) and strength, which is clear from the point of view of structural materials, resulted in the worsening of other characteristics, such as increase of crispness, decrease of flexibility, and reduction of relative elongation. This gives a negative effect when CF are applied, for example, as electroconductive fillers of plastic materials, rubbers, papers, films, artificial leather, etc. In Fig. 2 you can see the graphical dependence $lge = f(E)$ for CF produced in different countries. As follows from Fig. 2, value $\mathcal{E}$ decreases almost linearly with the increase of value "E"; down to $E = 400$–500. Any attempt to select some special property and, on this base, to rate CF as "better" or "worse" fibers will suffer a setback because the change of one property is connected with the alteration of several others.

Depending on the practical problem, the type of CM or any other material which found it necessary to use CF, we should decide on which class of CF to use. Economics is very important here. High-modular and high-strength CF (HCF) are 6–7 times more expensive than soft CF with controlled electrophysical properties. At the same time, costs of soft CF with branched pore structure, i.e., fibrous adsorbers, are as high as HCF. The cost of medium-modular CF and HCF, used for thermal protection, development of antifriction materials and others, has intermediate value.

From the chemical composition point of view, all of the industrial CF can be subdivided into carbon and graphite-like fibers. Carbon polymer is the base of the first CF which can receive thermal treatment up to 800–900°C, where, as graphitolile polymer, is the base of the second fibers received in the process of thermal treatment within the range of the temperature 1500–2500°C.

During the last 25 years, scores of CF and HCF of all the above mentioned types were developed in Russia by the Institute NII "Chimvolokno", NII "Graphite" and NPO "Chimvolokno." Table 1 gives the main CF, which are used for reinforcement of CM. Here we can also see the properties of CM received on their base. If the strength of industrially produced HCF is at the level of 350–400 kg/mm^2, then at the pilot installations where we receive HCF, the strength is 50% higher. At NII "Chimvolokno" we developed the assortment of medium-molecular (MMCF) and soft (SCF) carbon fibers on the base of the industrial fiber "Nitron", from the copolymerization of acrylonitrile with methylacrilate, itaconic acid and industrial viscose fibers produced in two. We also received carbon staple fibers with the length of 50–60 mm on cutting machines. The properties of these fibers are listed in Table 2.

The research work which preceded the development of the technology of middle-modulus and soft CF with controlled electrophysical and physical properties enabled us to draw a deep analogy between CF, coals, and cokes, taking into account specific characters of the oriented structure of original polymeric fibers—the raw material for CF synthesis. Namely, this analogy explains practically the equal level of electrical characteristics for one and the same temperature-time conditions of treatment. At the same time, the specific character of oriented structure of source, (raw and CF), provides physical and mechanical characteristics which are by an order of 1–2 times greater than corresponding characteristics of cokes. Depending on the thermal treatment temperature (TTT) there is a basic difference between the changes of mechanical and electrical properties of carbonized source fibers (polymers). This is because the mechanical properties are greatly affected, with the other conditions being equal, by supermolecular structure of the substance, while the electrical properties depend on chemical structural changes. Thus while using CF and SCF as electroconductive CM filler, it is not necessary to increase the cost of the technological process using high-oriented fibers or to subject the processed fiber to high elongation or mechanical tension both at the stage of its prior treatment and during carbonization or graphitization.

Middle (MMF) and soft (SMF) fibers are carbon fibers of wide application, and they are used in numerous technological fields with great economic effect (Fig. 3). Machine-cut CF are widely used as an effective antistatic additive to synthetic materials (i.e., papers, plastic material, artificial leather, rubber, etc.). In contrast to the majority of organic and nonorganic antistatics, these agents are not washed out by liquids, they do not migrate to the surface, nor do they attenuate materials; but in certain cases they reinforce and give constant antistatic properties to synthetic materials.

Adding 1.5% Uglen fiber, 5 mm cut, to PVC composition while manufacturing artificial leather decreases its electrical resistance R_0 from 10^{10} to 10^4–10^6 ohm. In this case CF used as electroconductive filler are much more effective than carbon black and graphite, because similar to the last, they have electronic hole conductivity (different CF types spread over a large area from semiconductors to conductors) and already, in case of a small filling, create a semiconductive or conductive network. This is because soft CF with their relatively high flexibility and slight brittleness are hardly affected when they are injected into CM by means of mixing with the other ingredients.

For the same reason, SCF having CF with specified properties are considered to be excellent conductive fillers for manufacturing electroconductive papers and paper-like composite materials (Fig. 4). They substitute for black carbon graphite and other active fillers. Carbon fibrous papers are used for electromodelling, shielding of underground electrical cables and transformer inputs, and most of all for obtaining heat-producing layers of low-temperature nonmetallic composite electrical heating elements (HE). At present, industry produces electroconductive carbon-fibrous papers with $R_0 = 8 + 10^4$ ohm, similar to CF-cellulose and CF synthetic fibers. On the base of carbon-fibrous papers, non-metallic, electrical, rigid, and flexible composite heating elements are produced for voltages of 6–22ov and operating temperatures up to 80–200°C. Rigid sheet HE of the laminated plastic type (sleterm) or the glass-textolite type (glasterm), are flexible on a carbon-fibrous paper base, duplicated by film or rubber layers and used for heating of different areas; especially for travelling covered vans and houses, the operator cabins of road-building machines, tower cranes, green-houses, farms, the thermostating of equipment, etc.

Carbon and graphitized braids and laces were developed as HE, providing temperatures up to 250°C. Original and high productive equipment was used for their manufacture, for example, ovens used for the direct treatment of CF by high-temperature currents.

The above-mentioned fibers and the developed nonwoven materials (thick felts of lycron type) are used with great economic effect as electrodes or components of composite electrodes for

- electrochemical extraction of gold and other precious metals from diluted solutions
- adjustment of the moisture content of soil in agriculture
- electrothermic production of carbide, calcium and white phosphor
- medical purposes
- electrochemical deactivation of metallic surfaces from radioisotopes

On SCF and MCF base with controlled electrophysical properties, a large assortment of radiotechnical CM was received: screening CM absorbing waves with increased acoustic characteristics for loudspeakers, CM for "locating" stormclouds, and others.

Highly effective composite antifriction materials were developed for sliding bearings and stuffing box sealings on MCF and SCF base combined with thermoplastic and reactoplastic.

We have developed a number of heat insulating CM on the same base of CF. In fact, the strength of these materials is not worse, but in certain cases even better than the strength of CM, including the more expensive HMCF. In relation to this research, work was conducted on obtaining construction sheet CM on the base of combinations of high modular and soft CF, in particular, ribbon LU-P and thin carbon felt lycron. Positive results were obtained in the case of combined carbon plastic when the bending stress limit per active layer is considerably higher.

It is rather promising to use binders containing SCF and HMCF in the process of developing composite carbon plastics.

Table 1. Carbon Fibers (CF) Carbon Fibrous Materials (CFM) Composite Materials (CM).

Assortment	Make of material	Filament diameter d μ	WI,/Unit Length tex	Density g/cm^3	CF and CFM Properties: σ GPa	CF and CFM Properties: E GPa	CF and CFM Properties: $\mathcal{E}$ %	CM Properties: σ_x^+ GPa	CM Properties: E_x^+ GPa	CM Properties: σ_x^- GPa	CM Properties: σ_{bend} GPa	CM Properties: E_{bend} GPa	CM Properties: τ_{shear} MPa
	VMN-3	7		1.6	1.2–1.5	200–250	0.6–0.8						
	VMN-4	6		1.7	2.0–2.2	200–270	0.6–0.8						
	VMN-RK	6		1.6	2.0–2.5	300–350	0.6–0.8						
	VMN-S	6		1.9	1.5-	400	0.6–0.8						
	Liral-N			1.6	1.5	70	1.5						
	Granit-P		410	1.8	3.5–4.0	320–400		1.4	110	1.0			
	VEN-210	10		1.9	1.5	340	0.6–0.8						
Yarn, Roving Fiber	UKN-5000		400	1.75	3.0–3.5	180–220	1.5	1.5	130				
	UKN-P5000		400	1.75	3.5	210–230	1.5	1.7		1.2	2.0	140	80
	UKN-5000M		4[illegible]	1.75	4.0–4.5	240							
	UKN-300		450	1.75	3.0	200–220	0.8–1.0						
	UKN-400		125–410	1.75	4.0–4.5	220–250		1.9	140	1.3			
	Kulon-M			1.95	3.0	600							
	Kulon-N24			1.75	2.5–3.0	380–400	0.6–0.8						
	Uglen-9	9	12000	1.6	0.5	20–25	1.8–2.5	0.2		0.3	0.3		30
	Evlon	13	32000	1.7	1.5–2.0	80–100	1.5–2.0	0.5		0.3	0.5		27
	FFE	12	30000	1.8	1.1–1.5	120–180	1.3–1.6						
		Thickness mm	Width mm										
	LU-3	0.1–0.2	90–250	1.75	2.5–3.0	250–300	0.8						
	LU-4	0.1–0.2	90–250	1.75	3.0–3.5	300–350	0.8						
	LU-P	0.1–0.2	250	1.75	2.9–3.0	265	0.8–1.0	0.8	140	0.6	1.25	125	60
Band (Ribbons)	LU-24P			1.8	2.5–3.0	320–350	0.8	1.3	240	1.0			
	Eluz-P	0.17	250	1.75	3.0–3.2	235		1.0	130	1.0	1.3	110	70
	Kulon	0.2–2.2	90–250	1.95	2.5	450-500	0.5–0.6						
	Kulon-P	0.2	90	2.0	2.5–3.0	450–550		1.2	265	1.0			
	UOL-300K		300		3.0–3.5	180–220	1.5	1.5	130	1.2			
	UralTz 3/2	1.7	200		1.0–1.2	30–50		0.15	35				
	Ural-15			1.6	1.5–1.7	70-80	1.5–2.0						
	Ural-25			1.75	1.7–2.0	150–200	1.0						
	Ural-LO	0.3			1.5–2.0	50–80							
	UUT-2	0.5–0.6	600	1.6	0.8–1.2	20–25	1.2–2.4						
	UTM-8	0.5–0.9	600	1.6	0.5–0.8	50–60							
	TMP-4	0.6	600	1.6	0.6–0.8	5–10							
Cloth	PTU-3/2	2.0–2.2	600	1.6	1.2	5–10							
	UT-900	2.5	900		3.0–5.0	180–220	1.5	0.7	65				
	Ural-T	0.5	500		1.0–1.3	30–50	0.9–1.1	0.2	50				
	Ural-TM/4	1.8	500		1.3			0.15	35				

Table 2. Properties of widely used CF

CF	d, μ	σ, GPa	E GPa	$\mathcal{E}$ %	δv 10^4, $\Omega \cdot m$	TCR 1/gr:10^3	d μ/grad
Uglen	7–10	0.4–0.6	19.5–24.5	1.8–2.5	4.3	−2.0	22.1
Gralen	6–9	0.3–0.5	29–39	1.3–1.7	1.9	−0.6	26.1
Evlon	12–14	1.5–2.0	78–98	1.5–2.0	2.1	−0.9	–
FFE	11-13	1.0–1.5	118–147	1.3–1.6	1.0	−0.4	–

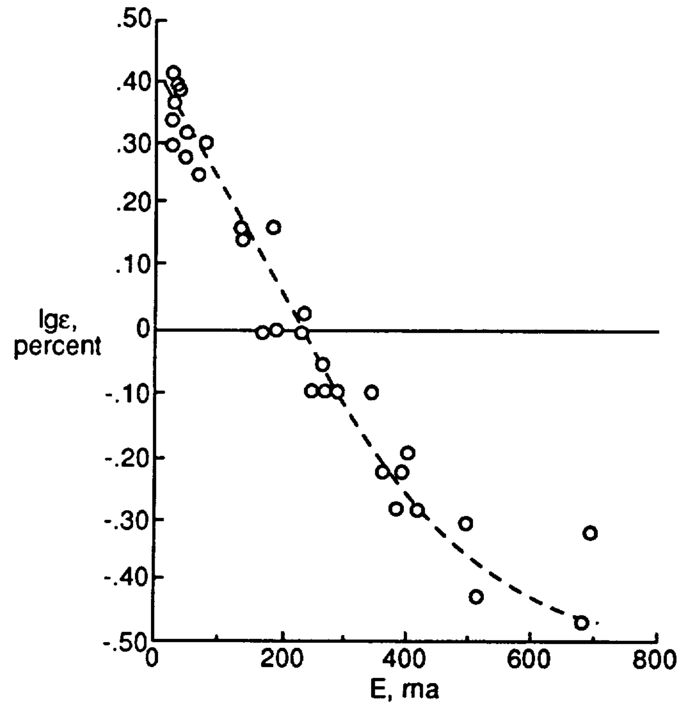

Figure 2. Dependence of the value of relative elongation ($\mathcal{E}$) of carbon fibers on the modulus of elasticity (E).

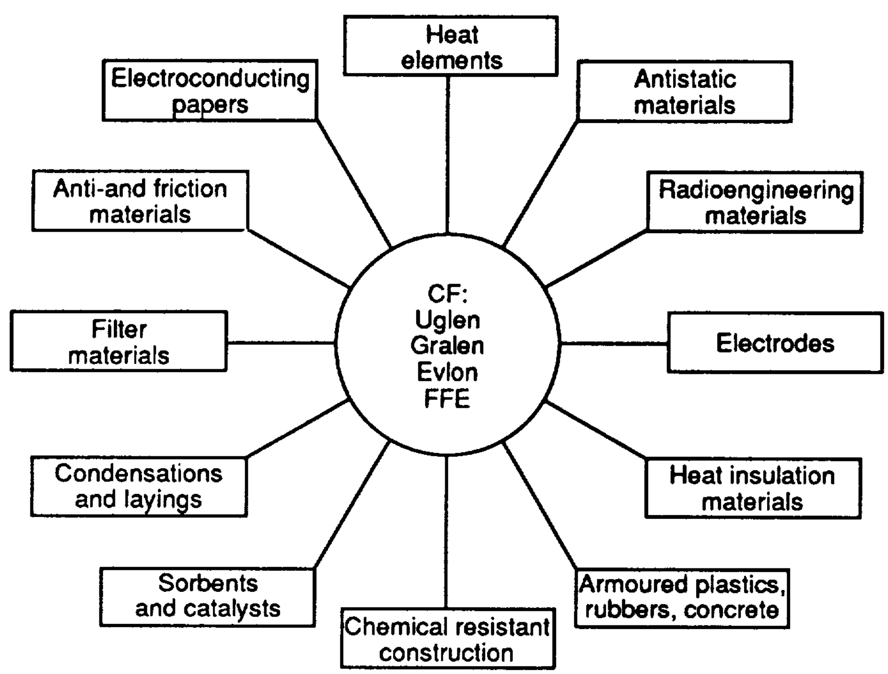

Figure 3. Field of application of soft and middle-modular CF.

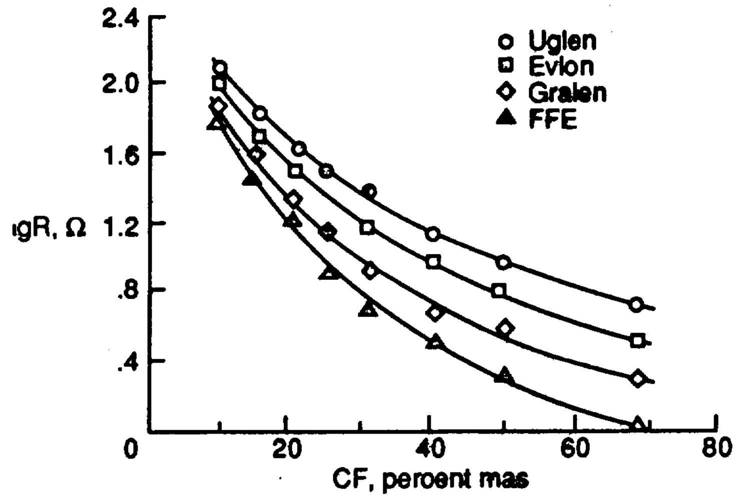

Figure 4. Variation of electrical conductivity of carbon fibrous paper (CF-cellulose) in relation to CF contents. 1-urglen; 2-evlon; 3-gralen; 4-FFE.