TECHNICAL SCIENCES

CARBON FIBER. OVERVIEW

Nurmukhametova A.
Candidate of technical sciences, process engineer Limited Liability Company «Alabuga-Volokno», Umatex Group. State Corporation «Rosatom». Territory of the SEZ "Alabuga", Sh-2, construction 11/9. Yelabuga district, 423601. Tatarstan Republic. Russia.
Zenitova L.
Doctor of technical sciences, head of the department of synthetic rubber technology Kazan National Research Technological University. K. Marx St., 68. Kazan, 420015. Tatarstan Republic. Russia
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Abstract
The main methods for producing a polyacrylonitrile precursor, methods for producing carbon fiber, its properties, and applications are presented. Patent research in the field of polyacrylonitrile precursor and carbon fiber. Technological problems in the subject area are identified, namely the development of technologies and equipment for producing high-strength carbon fiber, the development of technologies and equipment to reduce the cost of carbon fiber production, the development of technologies for improving the quality of carbon fiber-based composites, and the main ways to solve them are given.

Ways to solve them are developing a technology for producing a polyacrylonitrile precursor for producing high-strength carbon fibers by the wet spinning method, developing a "dry-wet" method for producing polyacrylonitrile, developing high-performance equipment for producing technical polyacrylonitrile precursor in the form of bundles, developing technologies and equipment for efficient regeneration and utilization waste, heat and emissions from the production of carbon fibers, the development of new compositions of precursors and the transition to materials with a higher linear density, optimization of the structure of carbon fiber reinforced plastic to increase strength, the development of technologies and the creation of production of modern types of binders, including the addition of nanoparticles.

The main methods for modifying the surface of a carbon fiber that are currently existing are considered.

Keywords: polyacrylonitrile precursor, carbon fiber, modification.

Content

Introduction

Polyacrylonitrile fibers and filaments (PAN) are currently the most common type of commercially developed carbon-chain synthetic fibers. This is due to the special properties of PAN-fiber: low coefficient of thermal conductivity, fluffiness, volume, which make PAN-fiber almost equivalent substitutes for wool. In addition, this polymer under certain conditions has the ability to cyclize, which determines the range of production of PAN, as a technical flagellum used as a raw material for carbon fibers.

The term "polyacrylonitrile fiber" is usually used in relation to fibers containing at least 85% of Acrylonitrile (AN) links. The term "modacrylic fiber"is used in relation to fibers, the proportion of AN in which is from 35% to 85%. Modacrylic fibers contain a significant amount of halogen-derived monomers and are used in cases where it is necessary to increase the fire resistance of the material.

The technological process of obtaining PAN includes the following main stages:

- synthesis of polyacrylonitrile, obtaining a spinning solution and preparing it for molding – this is carried out in the chemical production shop;
- formation and orientation the stretching and finishing of a fiber or filament – spinning and finishing shop;
- solvent regeneration – plant regeneration of solvent.

1.1. Getting PAN fibers

In the world, there are a number of companies engaged in the production and sale of poly-Acrylonitrile (PAN) precursor for companies that produce carbon fiber (CF). However, the largest players in the hydrocarbon supply market have their own production sites for PAN precursor.

Industrial technologies for the production of PAN precursor are divided into three main technological solutions:

- type of polymerization;
- solvent used in the technology;
- molding method.

Two types of polymerization are used in industry: suspension (Toray-Zoltek, Toho Tenax, Mitsubishi Rayon, SGL, Hexcel, etc.) and solution (Toray, Cytec, Hyosung, Bluestar, etc.). During solution and suspension

polymerization, both continuous and periodic operation modes can be used. Both types of polymerization have both advantages and disadvantages. The main advantage of solution polymerization is the absence of additional stages associated with the separation, washing, drying and dissolution of the polymer. The disadvantages include the: the high viscosity of the solution obtained during polymerization, which leads to the need to solve problems with the removal of heat from the reaction mass; the presence of impurities in the spinning solution, which were contained in the components of the reaction mass, which leads to the need for finer filtration of high-viscosity solutions. The advantages of suspension polymerization are: high conversion of the copolymerization process; the ability to store the dry polymer for a long time without loss of quality characteristics; impurities contained in the reaction mass are separated from the polymer along with the liquid phase. The disadvantages of suspension polymerization include: the need for additional stages associated with the separation, washing, drying and dissolution of the polymer; the complexity of implementing the process of dissolving the polymer without the formation of gel particles.

Both organic and inorganic solvents are used in industry. Organic solvent:

- dimethylsulfoxide (Toray, Cytec, Hyosung);
- dimethylformamide (Toray-Zoltek, Formosa Plastics, EPG);
- dimethylacetamide (Mitsubishi Rayon, SGL, Dow Aksa).

Inorganic solvents:

- aqueous solution of sodium rhodanide (Hexcel, Bluestar);
- a solution of zinc chloride (Toho Tenax).

It should be noted that, despite the possibility of using various types of polymerization and solvents, which leads to a fairly large number of combinations, this primarily affects the specific operating modes of the equipment, and not the principal possibility of obtaining the qualitative characteristics of the PAN precursor. That is, using any type of polymerization or solvent, it is possible to produce a high-quality PAN precursor that provides high-strength CF.

Two technological approaches can be used for forming a PAN precursor: wet and dry-wet molding. Wet molding is most widely used in the production of PAN precursors for CF, due to the simpler implementation of the technological process and the possibility of forming fibers of various denominations. Dry-wet molding is implemented in a small number of production facilities due to the complexity of the implementation of this technological process. However, dry-wet molding allows the production of precursors with lower operating costs than wet molding. CF produced from a precursor obtained by the dry-wet method has higher strength characteristics. The disadvantage of dry-wet molding, in addition to the complexity of the technological process, is also the production of a PAN precursor with a nominal value of no more than 6K (6 000 filaments).

The main raw material for the production of high-strength high-modulus CF is polyacrylonitrile (PAN) fiber [1-3]. Its advantages are high carbon yield (about 40-50 % of the polymer mass) [4] and pre-cycled macromolecules, which are pre-material, located parallel to each other and the fiber axis. Stretching during heat treatment and the formation of intermolecular bonds helps to preserve the orientation of macromolecules. This further facilitates the formation of an organized form of carbon and simplifies the technological process of obtaining carbon, especially high-strength fiber [5]. The production of CF with high strength is also inherent in the features of the chemical composition and supramolecular structure of the source fiber [3, 6].

The cost of PAN fibers in the world in 2007 varied in the range of 2300-2850 dollars/t [7]. According to sources [8, 9], the global production of PAN fibers in 2007 was about 2400 thousand tons. Then there was a slight decline and in 2012-2013 the volume of production of PAN fibers did not exceed 2000 thousand tons per year [10, 11]. In Russia, this indicator was significantly lower – 0.4 thousand tons, while consumption was 8 thousand tons [12], which is due to lagging behind the world level in all indicators: volumes, assortment, fiber quality, industry structure, innovation, and so on [13]. Currently, there are two industrial enterprises in the Russian Federation that produce PAN precursor: *LLC "Composite fiber"* (on the territory of *"Saratovorgsintez"*) and *JSC "VNIISV"*, Tver. *LLC "Composite Fiber"* produces a PAN precursor with a nominal value of 1-48K using solution polymerization and wet molding, using an aqueous solution of sodium rhodanide as a solvent. *JSC "VNIISV"* specializes in the production of a PAN precursor of thin denominations (33.3 Tex – 0.3 K and 50 Tex – 0.45 K) using a technology that involves the use of suspension polymerization and organic solvent for molding.

Polyacrylonitrile is a white, hard-to-crystallize linear, carbon-chain polymer [14-16]. The presence of nitrile groups provides a relatively strong intermolecular interaction, which is expressed in a sufficiently high glass transition temperature of PAN (about 120 ºC) [14].

The main stage of obtaining PAN fibers is molding, the task of which is to give the polymer a physical structure that would provide the required physical and mechanical properties of the fiber. The polymer structure begins to be created even in the spinning solution. When the solution flows through the holes of the die, the polymer structure undergoes significant changes, which partially remain fixed in the fiber. One of the main points of fiber forming is the polymer planting out of the solution. In this case, there are several interrelated processes. Freshly planted fiber (thread) from the solution is subjected to orientation pulling, washing from the solvent, drying, heat treatment and finishing with various preparations [14, 17, 18]. In all these operations, the polymer structure changes, and therefore all of them affect the properties of the finished fiber to some extent.

When forming PAN fibers from solutions, dry, dry-wet and wet methods of obtaining fibers can be used [19]. The wet method of forming PAN fibers is the most common in the industry. In this case, it is possible to use dies with a large number of holes (more than 100,000). During the flow of the spinning solution through the capillaries of the die, a significant change in the structure of the dissolved polymer occurs. In addition to the properties of the PAN and the solvent, the solution flow conditions play a crucial role in changing the structure of

the polymer in the capillary: the size of the capillary, the speed of pushing the solution, the duration of the solution in the capillary, and, of course, temperature conditions. In addition, conditions at the entrance and exit of the solution from the capillary also have a significant impact.

The trickle of the spinning solution when it flows out of the hole of the die into the precipitation bath expands significantly. Simultaneously with the expansion on the surface of the liquid stream, the polymer begins to be planted. In accordance with the law of phase equilibrium, the spinning jet turns into a gel-like state. Under the action of water as a precipitator, the spinning stream as a system passes into a non-equilibrium state and splits into two phases: the first phase with a high concentration of polymer is a dense frame that determines the mechanical properties of the gel thread; the second (liquid) phase is distributed as microparticles inside the gel frame. The resulting gel thread goes through the stages of washing, drawing and drying. Extraction is necessary to increase the degree of orientation of macromolecules in the fiber, which contributes to the further formation of graphite planes in the CF.

The properties of CF depend to a large extent on the defect and textile form of the PAN fiber [20-25]. The textile form of PAN is determined by the purpose and method of obtaining CF. It also, to a greater extent, determines the cost of production and the cost of hydrocarbons. PAN fibers used in the production of UV differ from commercial fibers used in the textile industry in their chemical composition, type, content of comonomers, and physical and mechanical characteristics [15]. Special PAN fibers contain carboxylic acids, vinyl bromide, acrylic, methacrylic and itacanic acids as comonomers. Comonomers act as catalysts for processes occurring during the production of hydrocarbons, so special types of comonomers are selected. Special PAN fibers, which are usually used for the production of CF, have a round cross-section shape, a diameter of up to 15 microns, a cross-section area of up to 180 microns^2 and a low linear density of up to 0.17 tex.

Among the large number of defects inherent in PAN fibers, the porosity and unevenness in the diameter of elementary filaments (filaments) are the most strongly affecting the quality of CF [3]. Since the structure of the CF retains the structure features of the original PAN fiber, the porosity is also preserved, causing uneven internal stresses of the CF, which leads to an increase in its fragility and a decrease in strength [5, 15, 26], thereby reducing the quality of the product. The pores also serve as the nuclei or centers of the beginning of thermolysis of the PAN fiber. If they are present, the thermal stability of the PAN fiber decreases, that is, the value of the temperature of thermal decomposition of the polymer decreases. Unevenness of filaments in diameter is usually characterized by the coefficient of variation of the linear density of filaments Kν. At its high value, PAN bundles contain a large number of filaments with a diameter of 18-20 microns and a linear density of 0.3 tex, which are difficult to process using a technology designed for the use of filaments with a lower linear density [23, 24].

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- type of polymerization;
- solvent used in the technology;
- molding method.

Currently, there are two industrial enterprises in the Russian Federation that produce PAN precursor: *LLC "Composite Fiber"* and *OJSC "VNIISV"*.

1.2. Review of scientific and technical information and patent literature on PAN-precursor

In the RF patent 2549075 [27] "Method for separating a polymer from a solution when forming a PAN-recurser to produce carbon fibers", the invention relates to the technology for producing fibers from polymers based on polyacrylonitrile-polyacrylonitrile and copolymers of acrylonitrile (AN), namely, to the stage of separating a polymer from a solution, and can be used in the production of materials for the textile industry and precursors for obtaining high-strength carbon fiber of new quality, used in various fields of technology. Method for isolation of a polymer based on polyacrylonitrile from 15-22 vol.% of the solution when forming a PAN-precursor to produce carbon fibers involves the actual separation of the polymer from its solution without the use of precipitators and subsequent removal of the solvent by blowing the fiber with a jet of air. Separation of the polymer from the solution is carried out under the influence of mechanical stresses at a temperature below the boiling point of the solvent by 150 ºC, with 8-12-fold extraction until the newly formed fiber is obtained, with a residual solvent content of no more than 1%. It provides a significant acceleration of fiber formation, a sharp simplification and acceleration of the polymer separation process, eliminating the need for multi-stage fiber extraction, simplifying the process of solvent regeneration.

In the RF patent 2541473 [28] "Method for obtaining a copolymer solution based on acrylonitrile in *n*-methylmorpholine-*n*-oxide", the invention describes a method for obtaining a copolymer solution based on acrylonitrile suitable for producing polyacrylonitrile fibers – precursors of carbon fibers. The method for obtaining a copolymer solution consists in conducting a solid-phase mixing of an acrylonitrile-based copolymer with a comonomer content of no more than 8% by weight with *N*-methylmorpholine-*N*-oxide hydrate containing 5-13.3% by weight of water, at room temperature until the mixture is completely homogenized. Then the resulting mixture is heated to a temperature of 80-135 ºC. A copolymer based on acrylonitrile is taken in an amount of 20-50 wt.%, the rest is *N*-methylmorpholine-*N*-oxide hydrate. The invention makes it possible to increase the concentration of the PAN solution when preparing it in an environmentally friendly way.

In the RF patent 2702642 [29] "Non-woven heat-insulating fire-resistant arc-resistant material", the invention concerns the field of special-purpose textile materials and non-woven heat-insulating arc-resistant material. Non-woven material is made in the form of an isotropic structure – a solid porous medium formed from a mixture of fibers, one of which is oxidized polyacrylonitrile fibers from precursors for carbon fiber. The claimed solution can be used for thermal insulation of products, objects, buildings, structures, structures, composite products to protect against the effects of high and low temperatures, as well as thermal risks of an

electric arc. The invention provides an increase in the fire resistance of the material when exposed to an open flame and the arc resistance of the material – the thermal risks of an electric arc.

In the RF patent 2497587 [30] "Method for obtaining a membrane catalyst and a method for dehydrogenating hydrocarbons using the resulting catalyst", the invention relates to the creation and use of catalysts for dehydrogenating hydrocarbons, which is a porous substrate made of stainless steel, Nickel or copper, on one side of which a layer of pyrolyzed infrared polyacrylonitrile (IK-PAN) is applied, and on the other side – a layer containing nanoparticles of Pt-Ru, Pt-Re, Pt-Rh or Pd alloys-ru distributed in the IK-PAN film. The method for producing a catalyst includes applying a layer of PAN to the substrate from its solution in an organic solvent, drying, and irradiating it with IK light. Applying a precursor to the other side of the substrate – a joint solution of PAN and Pt or Pd compounds with Ru or Re, or Rh in the ratio Pt(Pd): Ru(Re,Rh)=(7-10): 1 with the introduction of a fine carbonaceous material into the solution. Step-by-step irradiation with IK-light occurs at a certain intensity at each stage, and then cooling. The method of dehydrogenation of hydrocarbons is carried out in an installation with a flow-through membrane reactor, where the resulting catalyst divides the installation into a dehydrogenation zone and a zone into which hydrogen selectively diffuses. The technical result is an increase in the performance and stability of the catalyst and the efficiency of dehydrogenation.

In the RF patent 2647861 [31] "Polyacrylonitrile (PAN) polymers with a low polydispersity index (IPD) and carbon fibers obtained from them", the invention relates to a method for producing a polyacrylonitrile polymer with a narrow molecular mass distribution and to a method for producing UV from a PAN polymer. The method for producing a polyacrylonitrile polymer consists in combining an acrylonitrile monomer with a solvent with at least one comonomer and a thiocarbonylthiosociation. The resulting solution is heated to a temperature of 40°C to 85°C. Then an initiator is added to the solution to regulate the polymerization reaction. Polymerization is regulated by controlled/live radical polymerization, in which the thiocarbonylthiocomposite acts as a chain transfer agent with reversible attachment-fragmentation (RAFT). The comonomer is selected from a group consisting of vinyl acids, vinyl esters, and vinyl derivatives. The initiator is an azo compound or organic peroxide. The method for producing carbon fiber consists in first obtaining a solution of the above polymer. Next, the molding is carried out by wet molding or molding with an air gap to form a precursor of polyacrylonitrile fiber, which is coagulated in a coagulation bath. Next, pull the precursor fiber from the coagulation bath by the rollers through the washing bath to remove excess of coagulant. Then the fiber precursor is stretched in hot water baths to give molecular orientation in the fibers. After that, the elongated fiber precursors are dried. Then, the fiber precursor is oxidized under voltage in one or more furnaces, which are fed with heated air. Next, the oxidized fiber precursor is carbonized in one or more furnaces that have an inert, oxygen-free atmosphere. The invention makes it possible to obtain a polyacrylonitrile polymer that has a low polydispersity index of 2 or less and a molecular weight in the range from 60 kg/mol to 500 kg/mol, and to obtain carbon fibers with improved mechanical properties, a constant cross-section and small microdefects.

In the patent CN 206457564 [32] "PAN precursor coagulating bath corridor degree of depth gradual change formula adjusting device", the utility model is a device for regulating the gradual change in the depth of the coagulating bath of the PAN precursor.

The patent CN 106480515 [33] "Filtering device for PAN-based carbon fiber precursor spinning" reveals a filter device for forming the source carbon fiber based on PAN precursor, refers to the filter device and eliminates the disadvantage of clogging the holes of the die, which makes it unsuitable for forming carbon fibers. The filter device contains a filter mesh element that is made in the form of a bamboo joint, consisting of four filter meshes, the total diameter of the filter meshes is reduced from the inside out, and the filter mesh on the innermost layer performs the function of support. The filter element is simple in design, has a good filtering capacity and effectively reduces blockage of die holes, increasing productivity and reducing production costs.

In patent CN 104231158 [34] "Preparation method of PAN precursor for carbon fiber", the invention offers a method for producing a precursor of polyacrylonitrile (PAN) for CF. In accordance with this method, the PAN polymer is first obtained using the water-phase polymerization technology. In particular, the co-polymerization reaction using ammonium sulfate-sodium bisulfite-iron sulfate used as the initiating system, vinyl acetate used as the second comonomer, vinyl carboxylic acid compound used as the third comonomer, sulfuric acid used as a pH modifier, and acrylonitrile is carried out in the aqueous phase with its pH value of 2-5; after the reaction, an alkalizing treatment is performed in the reaction system using ammonia water; separation, washing and drying is carried out sequentially to obtain a PAN-polymer powder; the PAN-polymer powder is dissolved in a polar organic solvent to produce a spinning solution; the PAN precursor is obtained using wet spinning technology. The method has advantages-low cost and high production efficiency. The resulting PAN-precursor has a good structure and can meet the requirements of industrial production of UV. This method is useful for improving the performance of carbon fiber and reducing production costs.

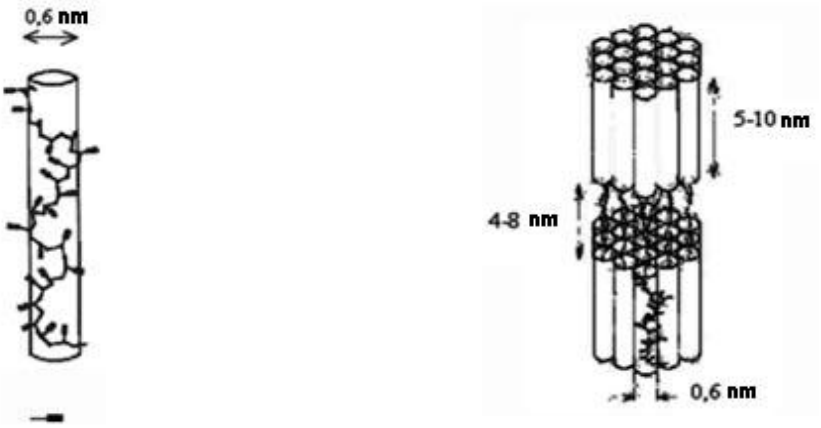
The patent KR101161094 [35] "The method for preparing the dope of PAN precursor for carbon fiber" offers a method for producing a precursor based on polyacrylonitrile for CF to increase the yield of unreacted monomers and reduce the cost of production. A method for producing a polyacrylonitrile-based precursor for UV includes: a stage for feeding the spinning solution to a thin film evaporation device with an evaporative spray for applying the spinning solution to the inner wall of the discoloration device; a stage for heating the applied spinning solution for evaporation; and a stage for collecting the evaporated solvent and unreacted monomers.

The article [36] "Polyacrylonitrile fibers and carbon fibers based on them as nanostructured materials" shows

that the vast majority of carbon fibers are obtained by heat treatment of polymer fibers, primarily based on polyacrylonitrile. The process of converting PAN-fibers to carbon occurs in a solid, and therefore the original structure of the PAN-fiber largely determines the structure features and basic properties of carbon fibers. This review examines the features of the formation of nanoscale elements of the structure of PAN-fibers and carbon fibers based on them, as well as the influence of these elements of the structure on the formation of the strength and modulus of elasticity of hydrocarbons.

The nanoscale structure of PAN fibers is laid at the stage of polymer production – the PAN macromolecules growing during polymerization, due to the repulsive interaction of electronegative nitrogen atoms of nitrile groups, have a spiral shape and become rigid (Fig. 1a). The diameter of such a spiral is about 0.6 nm, and the length is about several hundred nanometers. Macromolecules in the PAN fiber are combined into elongated primary supramolecular formations – microfibrils (Fig. 1b). The average cross-section size of microfibrils does not exceed 15 nm.

Inside the microfibrils, defective crystals (crystallites) with a length of 5-10 nm and amorphous layers between them with a length of 4-8 nm alternate sequentially along their axis. All these elements of the structure have specific nanoscale dimensions.



a) *b)*

Fig. 1. *Spatial model of the molecule (a) and fibrils (b) PAN*

A number of methods of polymerization are used in the production of PAN fibers, the main of which are suspension and solution. Already at the polymerization stage, due to the developed surface of macromolecules, they are combined into microfibrils, which have high strength and can be partially preserved even when the polymer is dissolved in a good solvent.

Therefore, it is extremely important to carry out polymerization while simultaneously obtaining a polymer solution suitable for further shaping the fiber. In this case, the solution contains a minimum number of non-soluble microfibrils, the ingress of which into the PAN fiber makes it difficult to Orient its structure, and then during conversion to carbon fiber leads to a decrease in its strength characteristics.

PAN-fiber is usually formed from a spinning solution by a wet method into a liquid precipitation bath. The schematic diagram of forming a PAN-fiber is shown in Fig. 2.

In the article [37] "Investigating the spinnability in the Dry-Jet Wet Spinning of PAN Precursor Fiber", the spinability of a spinning solution was investigated using DMSO as a solvent for dry-wet spinning of PAN-precursor fiber. Among the many variables responsible for spinability, coagulation conditions, air gap length, non-solvent content during spinning, and spinning temperature were considered and investigated as key factors. However, unlike wet spinning, spinning in the dry-wet spinning process was influenced by coagulating conditions, probably due to the existence of an air gap. However, the spinability worsened when the air gap was greater than 30 mm. The quality of the spinning solution deteriorated with an increase in the water content in it. Spinability improves when the spinning temperature is maintained between 60 and 72 ^{o}C and once the temperature is lowered below 72 ^{o}C. The results of the experiment indicate that all factors must be comprehensively considered to ensure good spinability in the dry-wet spinning process.

In the article [38] "Thermal Stabilization study of polyacrylonitrile fiber obtained by extrusion", the authors showed that the low cost and environmental friendliness of the polyacrylonitrile polymer extrusion process was achieved using 1,2,3-propantriol (glycerol) as a plasticizer. In this paper, the object of research was the characteristic of fibers.

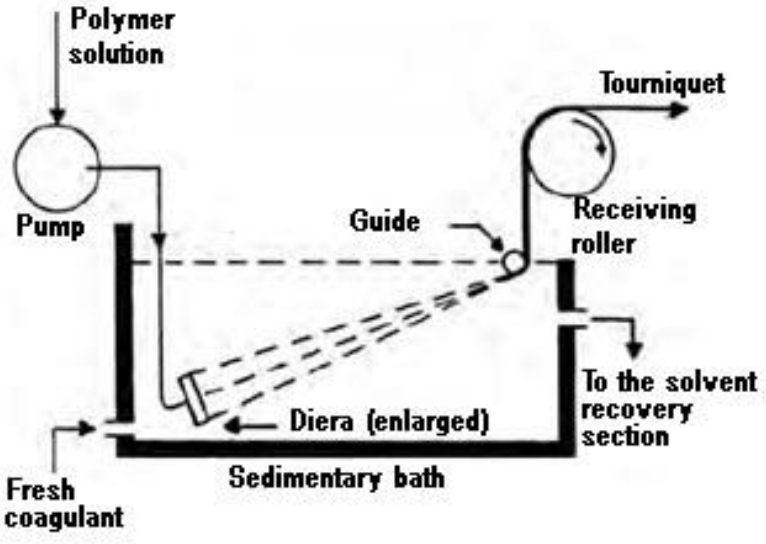


Fig. 2. *Schematic diagram of the PAN fiber forming process*

PAN fibers were subjected to heat treatment in the range from 200 to 300 ºC, which is the temperature range associated with the stabilization/oxidation stage. This is the limiting step in carbon fiber recycling. The fibers were characterized using infrared spectroscopy, thermal analysis, and microscopy. The thermogravimetric method of analysis showed that the decomposition of extruded PAN fibers between 250 and 350 ºC corresponds to a weight loss of 9% before the analysis of samples in an oxidizing atmosphere and 18% when the samples were analyzed in an inert atmosphere. The DSC method showed that exothermic reactions on extruded PAN fibers during air oxidation were broader and cyclization started at a lower temperature compared to tests in an inert atmosphere. In addition, FT-IR analysis correlated with thermal analysis and showed that the stabilization/oxidation process of extruded PAN fiber is consistent with other works that used PAN fibers obtained by other spinning methods.

In the article [39], the influence of filler activity and structural parameters of a composite fiber material obtained by introducing a sorption-active filler of various granulometric composition inside and on the surface of a polymer fiber during aerodynamic molding from a polymer solution on its physical, chemical and physical-mechanical properties is studied.

The author Nebratenko M.Y. and others in the article "Organic solvents and properties of spinning solutions" [40] reflected the main aspects of the choice of solvents in the creation of filter materials FP (Filter of Petryanov®). The results of the study describing the solvent as an effective tool [41, 42] that allows combining polymers through solutions and obtaining spinning solutions used in the EFV process (the process of electroforming fibrous materials) are presented.

In the article [43] "A review of heat treatment on polyacrylonitrile fiber", the development of carbon fiber from polyacrylonitrile-based fiber usually undergoes three processes, namely stabilization, carbonation, and graphitization under controlled conditions. The PAN fiber is first stretched and simultaneously oxidized in the temperature range of 200-300 ºC. This treatment converts a thermoplastic PAN into a non-plastic cyclic or ladder polymer. After the fiber is oxidized, the carbonation process takes place at about 1000 ºC in an inert atmosphere, which is usually nitrogen. Then, to improve the ordering and orientation of the crystallites in the direction of the fiber axis, the fiber should be heated to 1500-3000 ºC until the polymer content is 92-100%.

The high-temperature process usually results in higher-modulus fibers that remove impurities in the chain as volatile byproducts. During heat treatment, the fiber shrinks in diameter, changes to a larger structure, and increases strength by removing the initial nitrogen content in the PAN precursor and the timing of nitrogen delivery. After this pyrolysis process, under more controlled conditions, the fiber strength can reach up to 400 GPa.

In the article [44] "Investigation of the influence of parameters of pan-flagellum modification by applying compositions on its properties", the mechanical and adhesive properties of modified polyacrylonitrile technical flagellum by applying compositions are studied. The analysis of the data shows an increase in the strength characteristics of the modified fibers in comparison with the original PAN-flagellum. Optimal parameters of fiber modification are determined.

In the article [45] "The effect of flow rate, concentration, and voltage on diameter of pan precursor fiber by electrospinning technique", the PAN precursor fiber obtained by electroforming is processed at various parameters, including the applied voltage, flow rate, and polymer concentration, which affect the diameter of electroformed PAN nanofibers. The results show that the fiber diameter increases with increasing flow rate and concentration, and decreases with increasing applied stress. Of particular interest, it has been demonstrated that fiber morphology and granule concentration can be controlled by controlling the applied stress. In this article, the physical properties of the PAN-precursor fiber were investigated by scanning electron microscopy and thermogravimetric analysis. The main contribution in this study was to determine the conditions for controlled production of fibers that are smooth and have diameters ranging from 588 to 800 nm.

The article [46] "Formation Mechanism of Skin-Core Chemical Structure within Stabilized Polyacrylonitrile Monofilaments" states that despite the fact that it has been half a century since polyacrylonitrile-based carbon fibers were first developed, the exact mechanism for the formation of the skin-core structure of PAN-based carbon fibers, especially stabilized PAN fibers, is still not well understood from the point of view of chemical structure. To solve this problem, it was necessary to apply a powerful tool with nanoscale resolution, called photo-induced force microscopy, to map the chemical.

The method allowed us to determine the distribution of groups in the cross-section of the stabilized PAN fibers and to identify the mechanism of evolution of the "shell-core" structure throughout the stabilization process. The results showed that the formation of the "shell-core" structure of the stabilized PAN fiber is caused by complex and overlapping chemical reactions caused by the oxygen gradient along the radial direction and the formation of a dense crystal layer at the interface between the shell and the core of the core. In conclusion, the crystal layer was destroyed, and the monofilaments tended to be homogeneous with further oxidation.

In the article [47] "Formation of Surface Morphology in Polyacrylonitrile (PAN) Fibers during Wet-Spinning", the authors investigated the effect of the concentration of dimethylsulfoxide (DMSO) in a coagulation bath, the degree of extraction and the speed of extrusion on the surface roughness of polyacrylonitrile fibers obtained by wet molding and dry-wet molding. The surface roughness was much higher for PAN fibers obtained wet than dry-wet. The fiber surface roughness increased linearly with increasing DMSO concentration in the coagulation bath. Higher roughness was observed at higher drawing coefficients during molding. The surface roughness of the PAN fibers first decreased, and then increased with a further increase in the extrusion speed to 90 m/h. A mechanism for forming the surface morphology of PAN fibers is proposed, based on the deformation of the soft shells of individual fibers during solidification of the PAN/DMSO solution caused by stress perpendicular to the fiber axis. Stress occurs as a result of the recovery of aligned PAN macromolecules due to a shift in the die during extrusion.

The work on obtaining a PAN precursor is aimed at obtaining a PAN precursor with a narrow molecular mass distribution, further obtaining carbon fiber, improving the hardware design, the use of solvents and methods for their research.

2.1. Carbon fiber. Properties, purpose and applications of carbon fiber plastics.

Carbon atoms can form various allotropic modifications (diamond, graphite, and so on). From a wide range of forms of carbon, a special role is played by carbon fibers (table 1), which are used in the production of polymer composite materials – carbon fiber.

Table 1.

Comparison of carbon fiber types

Name	Type of carbon fiber			
	on the basis of PAN fiber	on the basis of viscose fiber	on the basis of peking fiber	fiber from gas phase
Strength, GPa	1.8-7.0	0.35-0.70	1.4-4.0	1.0-4.0
Modulus of elasticity, GPa	200-600	20-60	140-930	200-300
Price, $/kg	40	20	300	no data
Consumption market volume	***[1]	*	*	**
Proven technology	***	**	-	-
Fiber output from raw materials	***	*	**	-
Availability of raw materials and production in Russia	***	*	-	-
Biocompatibility	-	*	-	-

[1] – sign * – presence of a sign, *** – high, ** – medium, * – low, - – indicator is missing.

According to the results of the study [183], there is the widest market for carbon fibers based on PAN – from mass to special applications. Experts consider it appropriate to use carbon fibers based on viscose in medicine, as well as in those areas where the use of this type of CF is established by law.

Pitch-based fibers have a fairly limited use, mainly of a special nature (in particular, it is possible to combine PAN-based fibers and pitch in the production of gas centrifuges).

The technology for producing carbon fibers from the gas phase is currently under development, so there are no such fibers on the market. However, the study showed that UV from the gas phase has prospects for wide application, which is explained by its expected low price with relatively high characteristics.

According to the results of the study [182], there is the widest market for carbon fibers based on PAN – from mass to special applications.

The study identified seven main areas of application of CF:

- aerospace industry;
- building activity;
- energy;
- industry;
- sports and leisure;
- oil and gas production and transportation;
- medicine.

According to the results of the study revealed that it is reasonable to extend the use of hydrocarbons in industry to manufacture equipment with high performance, in particular in the automotive industry (for example, to

significantly reduce the weight of the car), shipbuilding (mainly to skins).

The results of the study [183] indicate that the use of CF is appropriate for the production of medical products (medical napkins, wheelchairs), goods for sports and leisure.

The results of the study [183] indicate that a significant increase in the volume of hydrocarbon production and improvement of its quality requires a set of measures aimed at solving key technological problems.

The main efforts should be focused on increasing the strength of CF, reducing the cost of their production and improving the quality of CF -based composites. The list of key technological tasks [183] is presented in table 2.

Table 2.

Technological tasks for the subject area

Sr. No.	Task	Way of solution
1	Technology development and equipment for receivings of high-strength UV	1. Development of a PAN-precursor production technology for obtaining high-strength hydrocarbons by wet molding. 2. Working out the "dry-wet" method of obtaining PAN. 3. Development of technologies for reducing defects and impurities of PAN-fibers and UV. 4. Development of technological modes of thermal oxidation and carbonation of PAN-threads and bundles. 5. Development of high-performance equipment for obtaining high-strength UV in the form of bundles.
2	Development of technologies and equipment for reducing cost of production of hydrocarbons	1. Development of high-performance equipment for obtaining technical PAN-precursor in the form of bundles 2. Reducing the specific rate of raw material consumption. 3. Creation of equipment for the production of PAN-harness and UV based on textile PAN-harness. 4. Development of technologies and equipment for efficient recovery and utilization of waste, heat and emissions generated during the production of hydrocarbons. 5. The development of new formulations of precursors and the transition to the material a greater linear density.
3	Development of technologies for improving the quality of composites on the basis of UV	1. Optimization of the carbon fiber structure in order to increase the strength. 2. Development of technologies and creation of production of modern types of binders, including those with the addition of nanoparticles. 3. Development of surface treatment technologies and optimization of the compositions of oiling agents used in the production of hydrocarbons.

UV in industrial production is obtained by thermal degradation in an inert environment or vacuum of organic fibers, fibers of oil and coal pitches, phenolic resins and other carbon-containing substances. CF is obtained only from fibrous polymers that do not melt during heat treatment, providing a high yield of carbon and the required mechanical properties [20, 48].

Thus, according to Markets&Markets, global consumption of carbon fiber is expected to grow rapidly in the next decade: from $3.5 billion in 2018 to $8 billion in 2026 (Fig. 3).

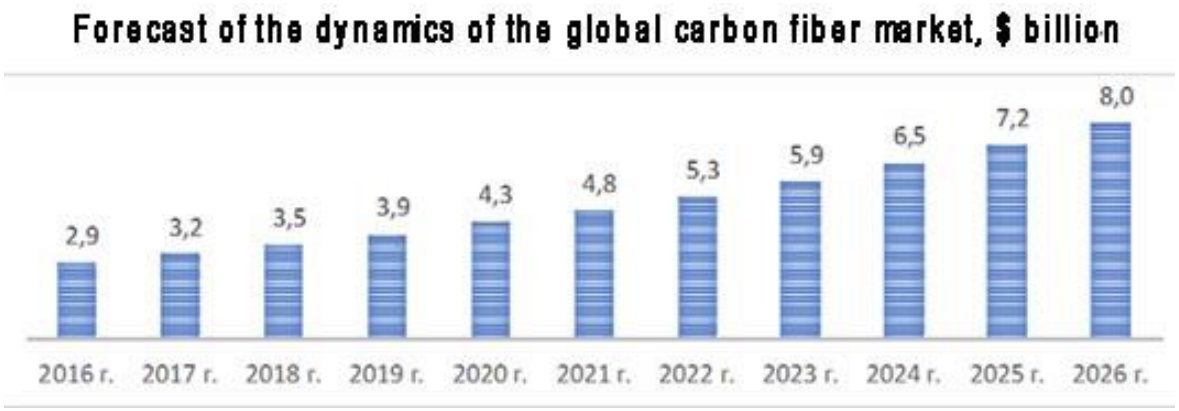


Fig. 3. *Forecast of global hydrocarbon market dynamics, $ billion*

The key drivers of growth will be digital, high-tech industries. Separately, it is necessary to highlight bionics (biomechanics) – the production of new-generation prostheses controlled by the "power of thought", due to the reading and processing of nerve impulses. The advantage of carbon here is not only its lightness, but also a very high biocompatibility.

CF production is a complex and high-tech process. As a result, the main export volumes of this material, as well as other similar technology products made of graphite, are supplied by companies of industrially developed countries – the United States, Germany, and Japan.

Important examples here are Vietnam and Romania, which over the past 10 years have managed to create a significant potential for exporting hydrocarbons.

Against the background of the leading players, Russia is successfully increasing the export of hydrocarbons, but the total volume is still inferior to a number of countries, including Belarus. The development of this industry can not only strengthen high-tech exports, but also stimulate the development of domestic production of modern, high-tech and competitive products that use carbon plastics in their construction (table 3).

Table 3.

Dynamics of production of carbon materials

Dynamics of production of carbon materials, including carbon fiber, heading 681510, thousand US dollars

No.	Exporters	2007	2018	Growth dynamics, times
1	USA	691 334	1 259 652	1,8
2	Germany	407 422	1 064 122	2,6
3	Japan	599 212	782 326	1,3
4	France	311 750	506 780	1,6
5	Great Britain	330 789	454 969	1,4
6	Spain	35 668	200 511	5,6
7	South Korea	65 593	198 324	3,0
8	Hungary	111 718	146 099	1,3
9	Mexico	15 939	124 897	7,8
10	Holland	18 114	121 102	6,7
11	Czech Republic	27 395	104 932	3,8
12	Poland	10 383	82 704	8,0
13	Italy	41 258	81 638	2,0
14	China	2 111	55 082	26,1
	...			
22	Vietnam	41	26 670	650,5
23	Romania	25	22 750	910,0
24	Belarus	9 633	22 560	2,3
	...			
28	Russia	6 601	17 868	2,7

The process of large-scale fiber production includes high-temperature processing (carbonization and graphitization) of organic fibers [3]. Carbonation is carried out in the temperature range of 900-2000 ºC (carbon content 80-99%), and graphitization is carried out at temperatures up to 3000 ºC (the carbon content is higher than 99 %). To obtain higher-quality carbonation and graphitization, the fibers are simultaneously pulled out of the die, which improves the structure and improves their mechanical properties [20, 48-51].

The uniqueness of composite materials is that it is possible to design the material in advance in such a way as to give the product from it the properties necessary for a specific application [52-54].

According to [20, 54-56], one of the unique properties of KM is the ability to redistribute the impact energy, as a result, the composite element is deformed, quenching the applied impact force.

With this set of properties, they can be used in almost all industries. For example, modern rocket and space technology is characterized by intensive use of new materials, technologies and advanced structures based on them.

Head fairings, stage fairings, instrument frames and air ducts of launch vehicles; shells, pipes, and power profiles for space telescopes and satellites; thermal panels of spacecraft thermal control systems; heat-protective coatings for spacecraft, and so on are made from composite materials based on CF [54, 57].

The world's aircraft industry is currently actively transitioning from metals to composite materials containing CF as reinforcing elements. Savings on operating costs are formed due to lower fuel costs and less need for material and technical maintenance, which is necessary when using metals due to their fatigue and corrosion [58].

Composite materials (KM), in addition to their high strength characteristics, have high corrosion resistance and hydrophobicity, which determines their use in shipbuilding. The use of composites also reduces the weight of structures, resulting in reduced fuel consumption and increased maneuverability of vessels [59-61].

Composites are widely used in the production of parts and assemblies in the automotive and agricultural engineering industries. The main advantages of composites for these industries: corrosion resistance, increased resistance to damage, sound absorption, and economy. Thanks to the use of lightweight composites, the total weight of automotive and agricultural machinery is reduced, which means that fuel is saved during its operation [62].

In civil construction, KM based on CF are used as reinforcing elements of construction materials for various purposes, ready-made products for the improvement of territories adjacent to buildings and structures, as well as in the housing and communal sphere. The use of KM reduces the overall cost of construction and subsequent operation, increases productivity, reduces the weight of structures and products, resistance to corrosion and their durability, and also solves the problem of wear and tear of pipeline systems [63]. For example, these MK are used to make: connecting elements for three-layer enclosing structures, rebar for concrete reinforcement, profiles for Windows, external pipeline systems for water supply and sewerage, playgrounds, swimming pools, fountains, benches, and so on.

CF is produced from polyacrylonitrile fibers, liquid crystal pitches and conventional pitches. According to [64, 65], first of all, the initial fibers are made, which are then heated in the air to 200-300 ºC. This treatment for polyacrylonitrile fibers is called pretreatment or treatment for fire resistance, and for pitch fibers – treatment for non-fusibility. During processing, the oxidation of hydrocarbons occurs. These oxidized fibers are then subjected to high-temperature heating. The heating process, depending on the mode, can lead to carbonation or graphitization of the fiber structure. At the final stage of the process, the surface of carbonized or graphitized fibers is processed, after which the surface is appreted or shliht [20, 48, 66, 67] (Fig. 4).

Processing in the air environment gives CF fire resistance due to partial oxidation, intermolecular crosslinking and others. This increases the resistance of the fibers to melting when heated and retains an undesirable large removal of carbon atoms. During carbonation, gasification and removal of organic polymer atoms, with the exception of carbon atoms, occurs as the temperature increases. The resulting hydrocarbons consist of fragments of polycyclic aromatic molecules with a flat hexagonal honeycomb structure. During graphitization, aromatic fragments accumulate. This increases the elastic modulus and electrical conductivity of the fibers [20, 48, 49, 68].

At the carbonation stage, these fibers are processed in a nitrogen medium at a temperature of 1000 - 1500 ºC. Based on the work [20, 48, 49, 69], the heating temperature for producing CF with high elastic-strength characteristics is 1200-1400 ºC. High-modulus CF is produced at a higher temperature-about 2500 ºC. During pretreatment, the PAN fibers are oxidized and acquire a ladder structure. This structure occurs due to intramolecular condensation during carbonation; a polycyclic aromatic chemical compound is formed. As the temperature increases, the proportion of cyclic structures also increases. In fibers, after all stages of heat treatment, the molecules or aromatic fragments are arranged so that the main axes of the molecules or cyclic structures are parallel to the axis of the fibers. When heated, the tension of the fibers is created, so that their degree of orientation does not decrease. As the tension of the PAN fibers increases during this pretreatment their modulus of elasticity increases and the modulus of elasticity of carbon fibers increases accordingly [20, 62, 63, 70].

The elastic modulus of the CF increases with increasing heating temperature (Fig. 5). According to [49, 50, 71], the tensile strength increases with increasing heating temperature during carbonation and decreases during graphitization (Fig. 6).

Improvement of the elastic modulus at the carbonation stage is associated with an increase in the aromatic fragments that form UV, with the process of cross-linking these fragments, an increase in the degree of orientation, complexity of the fiber texture, and other factors [98, 72, 73]. The decrease in the elastic modulus with a further increase in temperature is due to porosity

associated with the release of gases during the reaction of inorganic impurity particles with carbon. Fig. 12 shows the dependence of the tensile strength on the heating temperature for UV obtained from conventional PAN fibers, in comparison with carbon fibers based on PAN fibers obtained by spinning in high-purity conditions from a spinning solution, from which impurity particles are removed by special filtration [20, 48, 74, 75]. From the data shown in Fig. 7, it can be concluded that impurity particles strongly affect the tensile strength of hydrocarbons. Using PAN fibers that do not contain impurity particles and whose surface is not contaminated, you can increase the strength of carbon fibers. Thus, the tensile strength of CF is largely determined by the presence of defects, and therefore, at all stages of their production (obtaining the initial pan fibers, heat treatment, surface treatment, and so on), the possibility of formation of inorganic impurity inclusions, the appearance and development of pores and other defects should be prevented [48].

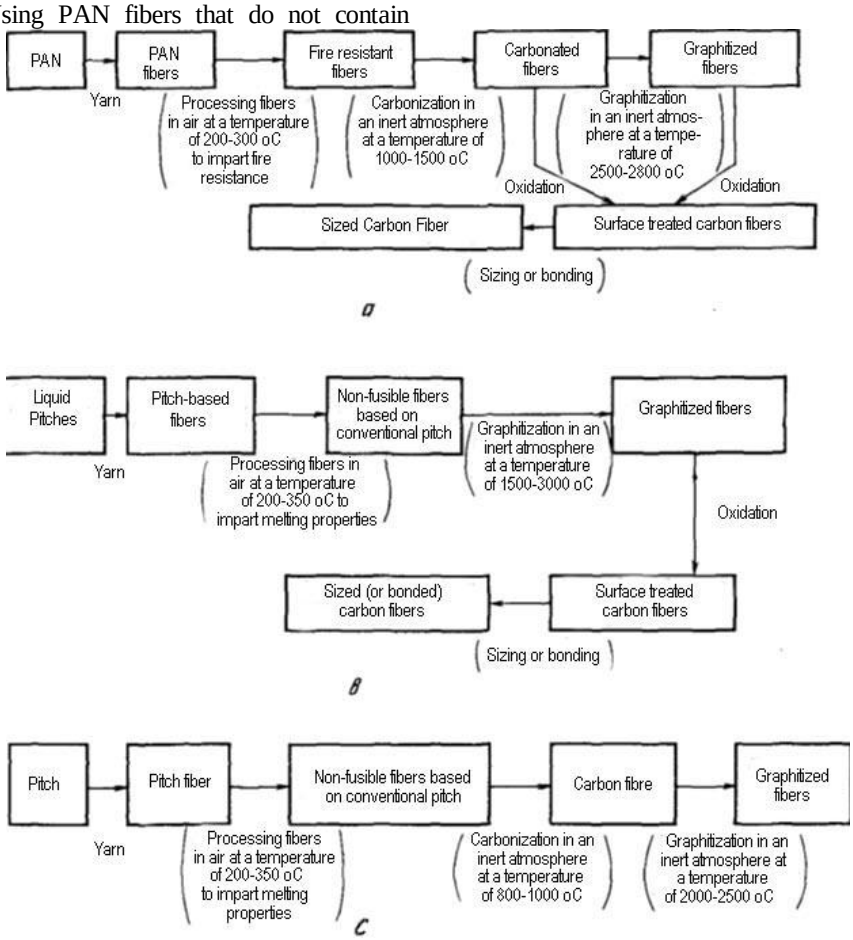


Fig. 4. *Stages of production of carbon fibers based on PAN (a), liquid crystal (b) and conventional (c) pitches. According to [48].*

Table 4 shows the characteristics of CF [48, 49]. They have a low density value and a high tensile strength and modulus of elasticity. A characteristic feature of UV is their high specific tensile strength. This is what makes it possible to successfully use CF for reinforcing structural materials [50, 76]. CF also have a relatively high electrical conductivity (0.0015-0.0015 Ohms·cm) and a negative coefficient of thermal expansion (along the fibers) (- 0.7-1.2 × 10^{-6} K^{-1}). CF is not resistant to oxidation in the air. They have a high chemical resistance to acids and alkalis. In addition, they have a very high heat resistance [57, 77-79].

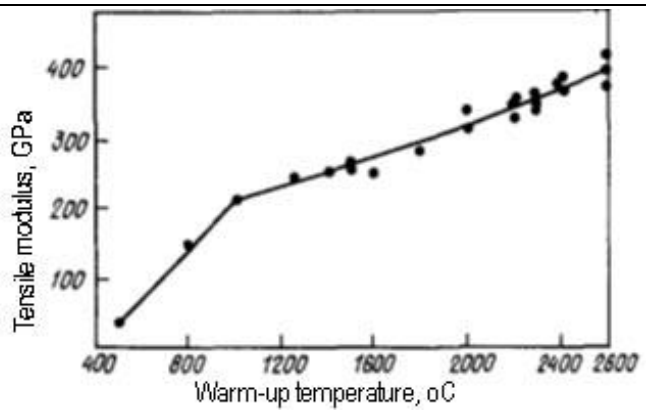


Fig. 5. *Dependence of the elastic modulus in tension carbon fibers based on PAN from the heating temperature [48]*

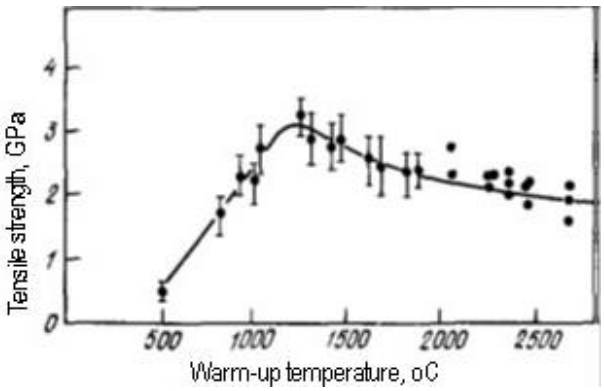


Fig. 6. *Dependence of the tensile strength of CF based on PAN on temperature warm-up (confidence interval calculated with a probability of 95%) [48]*

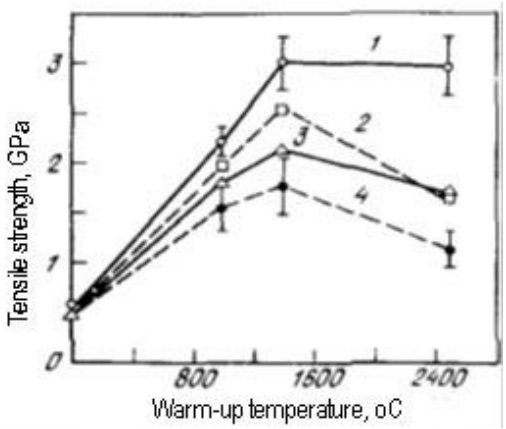


Fig. 7. *Influence of the heating temperature on the tensile strength of CF based on PAN fibers obtained under various spinning conditions from the melt [48].*
1 – Spinning from a filtered spinning solution in a particularly clean room;
2 – Spinning from unfiltered spinning solution in a particularly clean room;
3 – Spinning from a filtered spinning solution in a normal air environment;
4 – Spinning from unfiltered spinning solution in a normal air environment.

Table 4.

Characteristics of high-quality UV [48]

Characteristic	Pan-based fibers		
	High-strength	With high elongation	High-modularity
Fiber diameter, microns	7-8	6-7	6-7
Tensile modulus of elasticity, GPa	230-240	230-250	350-450
Tensile strength, GPa	2.0-5.0	4.0-4.5	2.0-2.5
Breaking elongation, %	1.3-1.4	1.7-1.8	0.5-0.6
Density, g/cm-3	1.74-1.78	1.74-1.78	1.78-1.84

The tensile modulus (Young's modulus) of high – quality high – strength CF (based on PAN) is 200-250 GPa, high-modulus type (based on PAN) is about 400 GPa, and CF based on liquid crystal pitches is 400-700 GPa [48-50, 57, 81].

As it was established by Dienfendorff R. and Tokorsky E. [81], high-quality CF consist of layers of aromatic hexagonal cells, the atomic planes of which are oriented parallel to the fiber axis. At a high heating temperature, these planes are long and highly oriented. In the cross-section of the CF, the atomic planes are arranged in disorder, and the structure is usually similar to the structure of the bulb, that is, it repeats the structure of the outer layer in volume (Fig. 8).

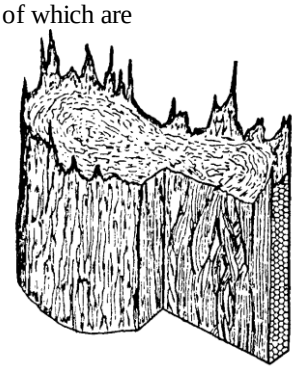


Fig. 8. Model of the structure of high-modulus UV based on PAN [48]

The elastic modulus of tension across the fibers (the modulus of stiffness when bending) decreases with the growth of the elastic modulus of tension along the fibers (Fig. 9). For CF based on PAN, it is higher than for fibers based on liquid crystal pitches [20, 48, 49, 83, 84].

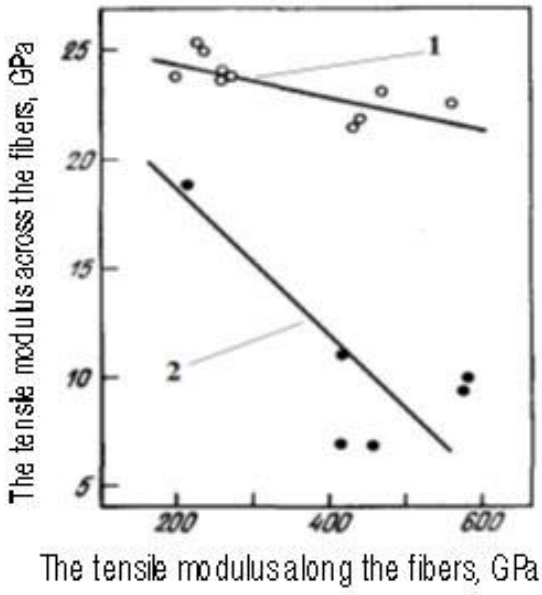


Fig. 9. Modulus of elasticity when stretched along and across the fibers.
1 – fibers based on PAN; 2-fibers based on liquid crystal pitches [48].

The tensile strength along the CF axis based on PAN is 2.0-5 GPa, high elongation fibers 4.5 GPa and high modulus fibers 2.0-2.5 GPa. High-temperature processing of fibers with high elongation allows you to obtain high-modulus fibers with a tensile strength of approximately 3 GPa. The strength of fibers based on liquid crystal pitches is usually equal to 2.0 GPa. The strength of carbon fibers

depends on their production conditions and microscopic defects [20, 48-50, 85-94].

Given the various hydrocarbons of PAN-based fibers, viscose fibers, pitch fibers and the fibers from the gas phase.

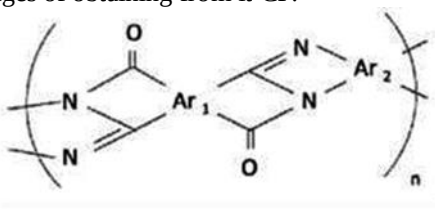
Three main tasks for the subject area are defined, namely, the development of technologies and equipment for obtaining high-strength CF, the development of technologies and equipment for reducing the cost of production of CF, and the development of technologies for improving the quality of composites based on CF.

2.2. Overview of scientific and technical information and carbon fiber patent literature

In the RF patent 2497587 [95] "The method of binding the fibrous pan material at the stages of obtaining carbon fiber from it" the invention refers to the production of high-strength carbon bundles, used for the production of high quality composites and concerns the method of binding fiber polyacrylonitrile (PAN) material at the stages of obtaining from it CF.

The method for carrying out the stages that require continuity of the process in order to obtain from it CF or to obtain express - samples for the development of the stage modes and the study of PAN - a precursor for suitability is to bind to the long fibrous PAN-thread of short carbon yarns by the knot of a pigtail, consisting of two carbon yarns and one investigated so that the carbon yarn is an intermediate link between PAN - yarns, the length of the node is not less than 100 mm with the number of interlacing of 3-4 by 1 cm. The invention ensures high CF content in the composite and maximum realization of mechanical properties of the composite material.

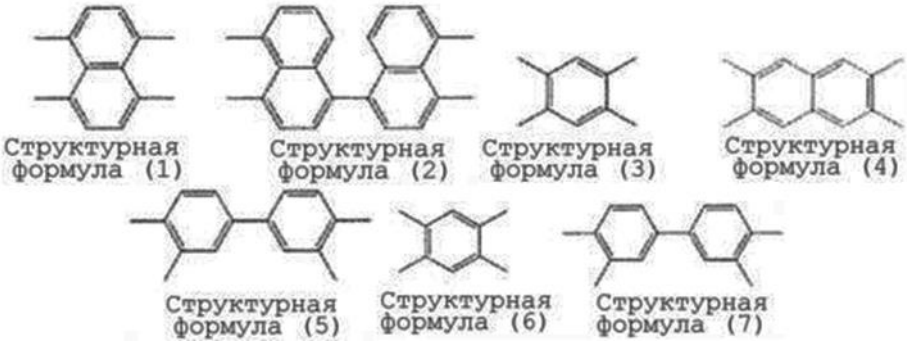
In the RF patent 2605973 [96] "Fiber-precursor for carbon fibers, carbon fiber and a method of obtaining carbon fiber" the invention refers to a fiber - precursor for CF, CF and a method of its obtaining. The precursor fiber of CF contains a polymer of the general formula (1):



Общая формула (1)

общая формула (1) - general formula (1)

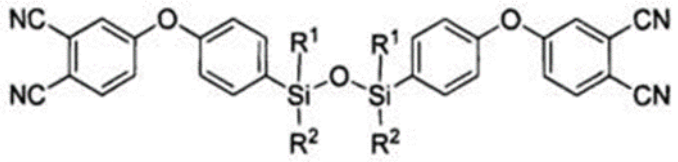
where Ar_1 is an aril group expressed by any of the structural claims (1)-(5) and Ar_2 is an aril group expressed by structural claim (6) or (7), except for the combination where Ar_1 is a group expressed by structural claim (3) and Ar_2 is a group expressed by structural claim (6) and the combination where Ar_1 is a group expressed by structural claim (1) and Ar_2 is a group expressed by structural claim (6):



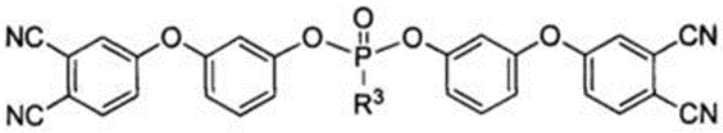
структурная формула (1)-(7) - structural formula (1)-(7)

The technical result is a carbon fibre with excellent mechanical strength and no meltdown.

In the RF patent 2694030 [97] "The appended carbon fibre and a way of its semi-precipitation" the invention concerns the field of polymeric composite materials (PCM), namely, to the apportioning of CF, intended for obtaining materials that can be used in the chemical, oil and metallurgical industries, aircraft engineering for the creation of products and elements of structures, exposed to increased tempera-rature. CF agent for CF apportionment is at least one compound of the formula



where $R^1 = R^2$ and is methyl or phenyl or, where R^1 is methyl, R^2 is phenyl; and/or at least one compound of the claim



where R^3 is selected from a group that includes aryl, ariloxy or alkyloxy substituents.

The invention also refers to an appretized CF covered with a layer of the specified agent and PCM in the form of a tape or cloth or fabric that contains the appretized CF and a phthalo nitrile binder.

The technical result is an increase in strength, as well as improved compatibility of fibres with the binder and an increase in the physical and mechanical characteristics of composite materials. Phthalonitrile monomers for UHV appretizing due to improved compatibility (adhesion) of the appretized fibers with binders allow to obtain a material that preserves its mechanical properties at high temperatures (up to 450 ºC).

In the RF patent 2034813 [98] "Composite material" the invention is intended for production of products working in oxidizing environments at high temperatures.

The task of the invention is to create a composite material containing alternating layers of silicon carbide matrix containing SiC-SiC fibers with at least one internal layer containing partially carbidized CF and binder coke in the silicon carbide matrix. The surface layer provides reliable protection against oxidation at high temperatures, while the inner layer provides increased resistance to deformation and thermal cycling of the entire material. The material is created by a known method that includes obtaining a carbon plastic billet, its carbonization and siliconization. The difference of composition in the surface and inner layers of the material is achieved when using a carbon-plastic blank prepreg made of fabric on cheap CF, respectively, does not contain or contain a barrier to liquid silicon coating, such as pyrocarbon. It is also possible to alternate the thickness of these different layers in the material, as well as alternating them in each layer of material.

In the RF patent 2560362 [99] "High Modular Carbon Fiber with Modified Surface for Composite Reinforcement and the Method of its Modification" the technology of CF production in the form of threads, harnesses is considered and concerns the high modulus carbon fiber with modified surface for composite reinforcement and the method of its modification. The fiber has a surface with comb-shaped formations in the form of corrugations, trapezoidal in cross-section along the axis of the fiber up to 1.0 μm high with rounded tops, which are arranged in an orderly manner on the forming surface of the fiber and conjugate in the bases with their forming circles with a radius of curvature not exceeding 50 nm. High-modulus carbon fiber is obtained by surface modification, which consists in changing the topography and specific surface of the fibers, subjected to ion irradiation during continuous transportation of inert gas ions.

In the RF patent 2687939 [100] "Method of hardening of polymer composite materials reinforced with carbon fiber" the technology of manufacturing of products from armoured bath CF PKM is described, namely to electrophysical hardening of finally formed products of various complexity and can be used at manufacturing of details of trans-port machines, in particular - flying machines, to which durability and endurance the increased requirements are shown. The method includes the operations of impregnation of the fibrous filler with epoxy binder, forming and curing of the workpiece under the action of a magnetic field. After the final curing and shaping of the product finally formed product is placed under the horn emitting antenna microwave technological installation at a distance from the plane of the antenna, equal to 190-210 mm, and influence it with an electromagnetic field frequency 433-2450 MHz during the time at which the surface temperature of the sample reaches a level (28-30) ºC. In the case of a large surface area of the product (for example - fuselage lining elements or truss structures of planes and stabilizer, etc.) use scanning of the emitting antenna on the surface, providing an even coating of the spot irradiation of all the necessary areas, while shifting the antenna to the next position after reaching the previous position of surface temperature equal to (28-30) ºC.

The technical result of the invention is to increase the strength characteristics of the interlayer shear stresses by (40-48)% of the finally formed structures made of cured multilayer composite materials reinforced with HC due to the additional finishing operation of scanning influence of microwave electromagnetic field on the finally formed and processed product.

In the RF patent 2500697 [101] "The method of obtaining composite materials on a polymeric basis reinforced with carbon fibers" the invention refers to the methods of obtaining composite materials on a polymeric basis reinforced with fibers and can be used to obtain polymer matrix composites with improved physical, mechanical and tribological characteristics. The method consists in obtaining a composite on the basis of ultra-high-molecular polyethylene reinforced with HC, with a degree of filling not more than 30% of the masses, by forming the composite with a solid-phase deformation method, which consists in the joint grinding of thermoplastic powder and carbon fibers in a knife mill. Obtaining monolithic samples from composite powder is realized by thermoforming at 160 ºC and 60 MPa pressure. The result is composites with improved physical-mechanical and tribological characteristics.

In the RF patent 2687930 [102] "Method of strengthening of polymer composite materials reinforced with carbon fiber" the invention refers to the method of strengthening of articles from CF-reinforced polymer composite materials. The technical result is an increase in the strength of finished products. The technical result is achieved by the method of hardening of products made of reinforced CF PCM on the basis of an epoxy binder, which includes operations of impregnation of a fibrous filler with an epoxy binder, shaping

and hardening of the workpiece under the influence of a magnetic field. And after the final shaping and curing of the product is carried out additional impact on the microwave electromagnetic field, using a frequency of 433-2450 MHz at a thickness of the product, which is in the range from 30 to 5-7 mm, with the input power of radiation, excluding heating the product above 35-40 ºC. At the same time, the electromagnetic wave is scanned by the beam on the treated surface, ensuring the overlap of the impact spot by at least 50% and the total processing time in each spot of surface irradiation, equal to 1-2 minutes.

In the patent AC 1840615 [103] "Method for producing carbon fiber" proposed technological production of carbon fiber. The method consists in the following: heat-stabilized fiber from homo- or copolymers, acrylonitrile, heat treatment when heated to 1200-2400 °C with removal of the pyrolysis products by a countercurrent of inert gas. In the zone of maximum temperature, the gas flow rate increases 4-7 times from 18 to 72-126 m/min. The heat treatment time of the fiber in this zone is 10-20% of the total heat treatment time. Characterization of the obtained product: the sodium content decreases from 0.3% in the initial acrylonitrile fiber to 0-0.02% in CF. The temperature of the onset of CF burning rises to 480-660 °C against 450 °C if the inert gas feed rate is constant and the sodium content increases from 0.1% in the initial acrylonitrile fiber to 0.14% in CF.

In the RF patent 2535797 [104] “Method for the oxidative stabilization of polyacrylonitrile fibers filled with carbon nanoparticles” the invention relates to the field of chemistry and relates to a method for the oxidative stabilization of polyacrylonitrile fibers filled with carbon nanoparticles. The formed fibers are heat-treated in air when heated. Fibers with introduced carbon nanoparticles, which use carbon black in an amount of 0.2-10%, with a surface containing oxygen in an amount of not less than 4.8 atomic%, are subjected to oxidative stabilization with increasing temperature from 180 to 230 °C at a rate of 0.5 °C per minute per within 90-110 minutes. The invention provides a complete process of oxidative stabilization of PAN fibers filled with carbon black (carbon nanoparticles), as well as the simplification of technology by reducing the time of the process, while reducing the thermal conductivity of the fibers achieved by introducing carbon black into the fibers, which necessary for the further production of carbon material used as heat insulation of inert furnaces.

The claimed method is as follows. The spinning solution of polyacrylonitrile is injected with carbon black. From the spinning solution form a fiber of polyacrylonitrile with a linear density of 0.2-2.1 tex, filled with black carbon, while the content of black carbon is 0.2-10%. Technical carbon containing at least 4.8 atomic % of oxygen on its surface is used, which is determined by X-ray photoelectron spectroscopy data, analyzing the photoelectron line of oxygen-rod on high resolution spectra. Technical carbon has an amorphous structure with the size of particles according to scanning electron microscopy 20-80 nm, lying in the nano range. The particles form agglomerates with the size of 100-200 nm. This structure has lower thermal conductivity compared to such carbon materials used for thermal insulation of furnaces as CF, graphite, which have a crystal graphite-like structure. The polyacrylonitrile fibre filled with engineered carbon is then oxidized. The fiber is filled into a tube furnace heated to 180 ºC. The pro-process is carried out in one stage at fiber heating from 180 to 230 ºC with the speed of 0.5 ºC per minute for 90-110 minutes.

In the RF patent 2416682 [105] "The method of stabilization of carbon fiber and the method of obtaining carbon fiber" the invention refers to the field of obtaining high-strength CF, mainly made from organic source material (predecessor), in particular, to the method of stabilization of carbon fiber and the method of obtaining carbon fiber. The method of stabilization includes placing the carbon fiber in the gas medium, its treatment by microwave radiation with simultaneous heating of the gas medium. The fiber in a particular case is placed in a working chamber with a gas medium located inside it, heating the gas medium is carried out by heating the chamber (its walls) simultaneously with the processing of the fiber with microwave radiation. The method of CF production includes at least the stages of fiber stabilization and carbonization. Stabilization of the predecessor is performed by the method described above. After carbonization of the fiber, its additional graphitization is possible. It is possible to carry out complex processing by microwave radiation with simultaneous heating of the medium in which the fiber is placed for carbonization/graphy. The invention provides a reduction in the stabilization time of the precursor fibers, which results in lower energy costs and higher productivity of the CF production process.

In the RF patent 2534779 [106] “Method for the oxidative stabilization of polyacrylonitrile fibers filled with carbon nanotubes”, a method for the oxidative stabilization of polyacrylonitrile fibers filled with carbon nanotubes is proposed. The formed fibers are subjected to heat treatment in air with heating while maintaining a constant length. The content of carbon nanotubes in the fibers is 0.3-0.5%. The surface of the nanotubes contains oxygen in an amount of at least 3.5 at. %. Oxidative stabilization is carried out with increasing temperature from 180 to 230 °C at a speed of 0.5 °C per minute for 110-130 minutes. The invention provides a simplification of the technology by reducing the time of the process and increasing the strength characteristics of fibers from PAN due to the low content of carbon nanotubes.

In the RF patent 2615427 [107] "Carbon fiber for composite materials with improved electrical conductivity" the invention refers to an electrical conductive, consisting of carbon fiber threads. An electrically conductive CF composed of CF yarns that include a metallic coating in which the CF yarns include a composition based on at least one polymeric binder that contains electrically conductive nanoparticles and the concentration of the metallic coating is 8-25% wt. and the concentration of electrically conductive nanoparticles is 0.1-1% wt., counting in each case the mass of the CF equipped with a metallic coating and composition. The method of manufacturing CF for composite materials

and fiber reinforced composite material are also described. Technical result: a composite material with improved electrical conductivity is obtained.

In the RF patent 2343235 [108] "A method for obtaining high-strength and high-modular carbon fiber" the technology for obtaining high-strength, high-modular CF is proposed. The method includes oxidation of the predecessor and its subsequent high-temperature treatment under tension, which ensures the extraction of the fiber. The precursor fiber is pre-treated with microwave radiation. Then, at the first stage of heat treatment produces oxidation of the fibers in non-equilibrium low-temperature plasma to produce fibers with a density of 1.38-1.43 g/cm^3. At the second stage of heat treatment is conducted in an inert medium at a pressure of 20 to 750 torr or in a vacuum with a pressure below 10-2 torr, while heating the oxidized fiber to 400-450 ^{o}C. At the third stage the fibers are heated up to 600-650 ^{o}C. At the fourth stage of heat treatment the fiber is processed at the temperature of 1100-4500 ^{o}C. The obtained high-strength, high-modulus carbon fiber has the strength of 400-510 kg/mm^2 and elasticity module 39000-49000 kg/mm^2. Continuity of fiber production is provided, which allows to increase productivity and reduce energy consumption at fiber production.

In the RF patent 2658858 [110] "Carbon-carbon composite material and the method of making products from it" the invention belongs to the field of carbon-carbon compositional materials (CCCM) and can be used in rocket and space technology. Carbon-carbon composite material contains a framework in the form of needle-punched material from discrete CF along the length and a pyro-carbon matrix with isotropic structure. To obtain the CCCM discrete CF lengths are fragmented in thickness up to filaments, combined into thin sheets, from the sheets they form a framework in the form of needle-punching material and saturate the pyrocarbon with thermo gradient method at overpressure of 0.025-0.03 atm. in methane medium. The technical result of the invention is to reduce the permeability of products to tightness without increasing the duration of their manufacture.

In the RF patent 2631037 [111] "The device for measuring cutting of carbon fiber" the invention belongs to the field of mechanical engineering, namely to the device for measuring cutting of carbon fiber, and can be used in the manufacture of CF and products from PCM, reinforced CF.

The task of the invention is to develop a device for measuring cutting of CF, the technical result of which is to increase the service life due to the reduction of wear of the used knives, a significant expansion of the range of lengths of the cut CF, elimination of technological difficulties in the process of replacement of the cutting knives with a change in the range of lengths of the cut CF, as well as ensuring tightness when working with the cut and measuring CF. The technical result is achieved by the fact that the device for measuring cutting of CF, containing an CF cutting unit equipped with an electric drive, a hopper-storage of measuring CF, equipped with a filter and connected by a transport pipeline to the CF cutting unit, as well as the industrial vacuum cleaner of cyclone type, connected by a duct to the CF measurement hopper, in an explosion-proof version. The cutting unit is equipped with two guide rollers and a pressure roller, and also contains a polyurethane material with a hardness of 80-85 units. Shore guidance support shaft of the CF to be measured and the pressure rollers of the combined cutting drum, whose axis is perpendicular to the direction of movement of the CF to be cut, in this case, the pressure rotating combined cutting drum is made in the form of a two-layer cylinder located on the axis of rotation with bearings, the inner layer of which is made of metal with ring ducts on its outer surface width of 30-40 mm and a depth of 12-15 mm, and the outer ring layer is made of polyurethane with a hardness of 80-85 units. along the Shore and 5-6 mm thick, with polyurethane filled with ring ducts of the inner-root metal layer, in the outer ring layer at its entire depth are made longitudinal grooves 0.2-0 width. 5 mm, in which there are metal plate knives with tension, and depending on the given length of the cut CF the number of metal plate knives is chosen from 48 with a cutting length of 10 mm to 240 with a cutting length of 2 mm, and the knife shaft is equipped with cylindrical caps for fixing the outer ring layer of polyurethane with metal plate knives placed in it, The CF cutting unit is equipped with a slot hole located directly in the CF cutting area to extract the cut CF into the hopper through a transport pipe under the influence of the exhaust air flow of the cyclone type industrial vacuum cleaner in an explosion-proof design. The outer diameter of the combined blade shaft is 152.8 mm along the cutting edges of the metal blades.

In the RF patent 2568733 [112] "Carbon-carbon composite material and method of manufacturing of products from it" the invention is intended for use in chemical, chemical and metallurgical, aviation and space industries. They form the frame of carbon-carbon composite material from low-modulus CF, fill its pores with disperse carbon filler by growing them by a catalytic method in the gas phase of nanoscale carbon in the form of particles, fibers or tubes to its content of 3.7-10.9% of the weight of the fiber frame. Then they are saturated with pyrocarbon matrix by thermogradient method at methane overpressure of 0.025-0.03 kgf/cm2, temperature in the pyrolysis zone of 840-920 ^{o}C and speed of its movement 0.1-0.25 mm/h. The received CCKM contains the specified components in the following quantity, weight.%: HC - 38.7-46.1; nanodisperse filler - 1.7-4.2; pyrocarbon matrix - 49.7-59.6; has density of 1.41-1.55 g/cm^3. Nanodisperse carbon filler is contained in both interfiber pores of the frame and interfiber pores of CF. The technical result is the increase of strength properties of CCKM without deterioration of other operational characteristics.

In the RF patent 2687648 [113] "Method of carbon fiber separation and installation for its implementation" the invention refers to the method and device for obtaining unidirectional carbon fiber threads. The method includes laser cutting of CF and vacuum treatment of CF cutting site. Carry out continuous or periodic straight-line movement of unidirectional CF, in the process of which the density of CF, laser cutting along the axis of CF is carried out. Additional processing of the

cut CF includes appretum processing, drying and flattening and then winding the finished CF. The technical result of the invention is to provide the possibility of dividing along the unidirectional HC axis with a large number of filaments into unidirectional CF with a smaller number of filaments while preserving the microstructure of the resulting unidirectional CF and excluding the thermal shock of CF that is not in the cutting zone, while providing the necessary number of filaments in the resulting unidirectional HC.

In the RF patent 2614679 [114] "Method of obtaining tissue from carbon fiber and tissue obtained by the specified method" the invention refers to the method of obtaining tissue from CF. A method of obtaining tissue from CF is described in which a fabric (1) from CF is impregnated with a silicone, polyurethane or acrylic emulsion (4) which is then dried together with the fabric (1) in which at least one protective layer (2) containing a film, woven material or non-woven material is applied to one side of the fabric (1). The CF fabric (1) and car upholstery are also described. Technical result: a CF fabric with improved properties is obtained.

In the RF patent 2601761 [115] "The base material from the stitched carbon fiber and a damp prepreg with its use" the invention can be used in aerospace industry, in production of sports and leisure goods. The prepreg, which has a formability, contains a backing material made from embroidered CF. Many sheet materials 1 are arranged in layers and then stitched and combined together into a stitched backing material using a stitched thread 2, woven when passing through sheet materials 1. Each sheet material 1 is formed by arranging 11 CF lines parallel to each other. The direction of the 11 CF lines of each sheet material 1 forms an angle between ±30° and ±60° with the direction of the piercing thread 2. The degree of stretching of the pierced warp material in its longitudinal direction when a certain load per inch of width of the pierced warp material is applied in the direction of pierce 2, is equal or lower than 4% when the load is 5 N and equal or higher than 10% when the load is 25 N. The prepreg is formed by impregnating the backing material from the pierced CF, in which many sheet materials 1 are arranged in layers and then pierced and joined together using the piercing thread 2, woven when passing through sheet materials 1, with a thermally curing resin in the range from 30 % wt. to 50 % wt. Invention allows to obtain the warp material from pierced CF, which has a high form stability and formability and provides convenience when processing wet prepreg, facilitates the obtaining of three-dimensional shape.

In the RF patent 2601761 [116] "Method of obtaining continuous carbon fiber with high modulus of elasticity" the invention refers to the field of metallurgy, in particular, to the methods of obtaining continuous carbon fiber with high modulus of elasticity. On the basis of complex PAN strands with a linear density of not less than 50 tex, a thick PAN braid with a linear density of 800 or 1200 tex is prepared. Then it is thermostabilized in isometric conditions in the air atmosphere by the following step mode: 180 ºC - 1 h, 200 ºC - 1 h, 220 ºC - 1 h, 240 ºC - 4 h up to the density of 1.43-1.45 g/cm^3. Further high-speed thermomechanical treatment of the obtained PAN-burner is carried out in isometric conditions in nitrogen medium at 2200 ºC for about 10 s with the temperature rise rate of 1900-2000 deg/min. Then the carbon braid is subjected to additional treatment in argon medium at a temperature above 3000 ºC. The use of the invention allows to increase production volumes of high-modulus CF at the same production facilities.

In the RF patent 2601761 [116] "Method for producing continuous carbon fiber with a high modulus of elasticity" the invention relates to the field of metallurgy, in particular to methods for producing carbon continuous fiber with a high modulus of elasticity. Based on complex PAN filaments with a linear density of at least 50 tex, a thick PAN bundle with a linear density of 800 or 1200 tex is prepared. Then it is thermostabilized under isometric conditions in an air atmosphere according to the following stepwise regime: 180 ° C - 1 h, 200 ° C - 1 h, 220 °C - 1 h, 240 °C - 4 h to a density of 1.43-1.45 g/cm3. Next, a high-speed thermomechanical treatment of the obtained PAN bundle is carried out under isometric conditions in a nitrogen atmosphere at a temperature of 2200 °C for about 10 s with a temperature rise rate of 1900-2000 deg/min. Then the carbon tow is subjected to additional processing in argon at a temperature above 3000 °C. Using the invention allows at the same production facilities to increase the production of high-modulus CF.

In the RF patent 2534794 [117] "Method of binding the fibrous pan material at the stages of obtaining carbon fiber from it" the invention refers to the production of high-strength carbon bundles used for the production of high-quality composites and concerns the method of binding the fibrous polyacrylonitrile material at the stages of obtaining CF. The method of bindings of short carbon fibrous PAN yarns to the long fibrous PAN yarn by the knot of a pigtail is the way of carrying out the stages, which require the continuity of the process in the process of obtaining from it CF or obtaining express - samples for the development of the stage modes and the study of PAN precursor for suitability, consisting of two carbon yarns and one investigated in such a way that the carbon yarn is an intermediate link between PAN-threads, the length of the node is not less than 100 mm with the number of interlacing 3-4 by 1 cm. The invention ensures high CF content in the composite and maximum realization of mechanical properties of the composite material.

In the RF patent 2042753 [118] "Method of oxidation of polyacrylonitrile threads in the production of carbon fibers and the device for its implementation" uses: oxidation of PAN threads in the production of high quality CF. The essence of the invention: the transported threads with released gaseous pyrolysis products are isolated from the direct impact of heated to 230-280 ºC circulating oxidizing medium, with gaseous pyrolysis products are removed from the oxidation zone in the suction zone. The device for realization of the method contains pre-chambers 1 with transport rollers 2 and sockets 6 and 7 for suction of gaseous products and oxidation chamber 3 with means for heating and circulation of oxidizing medium. The chamber 3 is equipped

with slotted channels 10 for thread movement and localization of gas emissions. Each slot channel is formed by two flat plates, which can be connected to one or both ends.

In the RF patent 2578283 [119] "Method of modification of carbon fibers and carbon nanotubes" the inventions refer to chemical industry and nanotechnology. CF is wound on a flat or round rotating bobbin and subjected to neutron irradiation from both sides and inside. In another version, carbon nanotubes are poured into a horizontal rotating drum, during which they are subjected to neutron irradiation. The inventions produce modified CF or nanotubes with increased strength and thermal resistance.

In the RF patent 2578283 [120] "Method of modification of CF and carbon nanotubes" the invention refers to the technology of obtaining high-modulus CF from medium-strength fibers on the basis of polyacrylonitrile flagellates and can be used to produce high quality composites. As a feedstock, medium-hard CF with a linear density of 200-1600 tex and an elastic modulus of 200-250 GPa are used.

This fiber is subjected to twisting up to the value of 30-60 twists/m with the content of apprete more than 1%. Additionally, the fiber is appretized with an appretent content of less than 1%. Then twisted braid is subjected to primary heat treatment at 2300-2500 ºC for 1-10 minutes to mod carbon braid modulus values of at least 300 GPa. Then the second heat treatment is carried out at a temperature not lower than 3000 ºC during 1-20 s at braid drawing up to 10% up to the carbon braid modulus of elasticity increase to the value not lower than 450 GPa. High quality is achieved due to the compact shape of the carbon bundles, which provides a high content of CF in the composite and the maximum realization of the mechanical properties of the composite material.

In the RF patent 2413799 [121] "Method of hardening of carbon fibers" the invention refers to the field of technological processes of CF production, in particular, their hardening by means of temperature treatment. CF hardening method contains heat treatment in two stages, including heating to temperatures of 500-1200 ºC and subsequent cooling to 30-100 ºC during 1.5-15 minutes. Heating and cooling are performed in an inert atmosphere by pulling the fibers through a gradient furnace containing various temperature zones at a speed of 2-25 cm/min. The invention allows producing carbon fibers with 1.4-1.7 times higher strength.

In the RF patent 2127335 [122] "The method of obtaining polyacrylonitrile threads suitable for the production of thin high-strength carbon tapes" the Invention refers to the production of chemical fibers, in particular, to the production of polyacrylonitrile threads suitable for the production of thin high-strength carbon tapes, and can be used in the manufacture of high-quality sports equipment, aviation. They receive a solution of copolimer by dissolving polyacrylonitrile fiber "Nitron" in the presence of 0.5-3.0% wt. chloride salt of alkaline or alkali-earth metal. "Nitron" can be pretreated with ammonia, amine or quaternary ammonium base. The solution is formed in a deposition bath with a low deposition capacity. The resulting filament is separated and dried. Made of yarns carbon tapes have a tensile strength of 154-180.3 kgf/mm^2.

In the RF patent 2523483 [123] "Method of Carbon Fiber Hardening" the invention refers to the technology of producing carbon fiber composite materials, in particular, the method of CF hardening, and has a wide range of applications from sports equipment to aircraft parts. The process includes impregnation of CF with C60 solution or colloidal solution (ash) of fullerene-containing soot or ink. In addition, it is possible to activate C60 fullerene or particles of fullerene-containing soot or ink applied to CF by irradiation. The use of the invention makes it possible to obtain CF with an increased value of pre-tensile tensile strength up to 11-18% and an increased value of modulus of elasticity up to 5-7%.

In the RF patent 2167225 [124] "Method of oxidation of the polyacrylonitrile harness and its implementation" the invention refers to the technology of CF production. Polyacrylonitrile harnesses are oxidized on the heat conductive surface of the heater in an air environment. The velocity of the air medium is 0.1-1.0 m/s, the temperature is 10-120 ºC below the maximum temperature of the exothermic oxidation reaction of the fibrous polymer, and the exothermic heat is used to heat the heat carrier continuously circulating in the heater. The ratio between the oxidizer speed and the heat carrier speed is 0.01-0.25 at a heat carrier speed of 4-10 m/s. Oxidation on the heater surface occurs under the normal load 0.275·10-5-1.100·10-5 n/tex.

The device for realization of the method contains an oxidation chamber with a system of contacting heaters with a bundle, with transport rollers and means for oxidizer supply and suction of pyrolysis products. The heaters are made in the form of boxes with heat-water surface having inside a distribution grid and longitudinal ribs of rigidity. The heaters are installed in height-adjustable supports. The uniformity of characteristics of a received oxidized fibre is reached. The process is intensified, energy costs are reduced, environmental safety of production is increased.

In the US patent 10442934 [125], "Methods of using N-containing compounds with carbon black to replace pan and form carbon fibers", describes a method of obtaining a PAN precursor for HCB combustion that includes carbon black modified by at least one promoter of the cyclic compound. The source of carbon black can be recycled materials such as recycled tyres or recycled plastics. The carbon black shall be modified by connecting at least one cyclic compound promoter to the outer periphery of the carbon black.

In the KR patent 20180126202 [126] «PAN PAN-based carbon fiber whose electro conductive is controlled and method for manufacturing the same» describes a method for manufacturing a PAN-based carbon fiber with adjusted electrical conductivity comprises: a first step of manufacturing a carbon nanotube-metal composite by changing kinds and amounts of metals so that a PAN-based carbon fiber has set electrical conductivity; a second step of putting the carbon nanotube-metal composite as much as the set amount into a polymer solvent to enable the PAN-based carbon

fiber to have set strength, and dispersing the same by ultrasonic waves; a third step of putting the polymer solvent in which the carbon nanotube-metal composite is dispersed into a reactor, and stirring the same; a fourth step of forming a monomer composition by mixing acrylonitrile, methyl acrylate, itaconic acid, and azobisisobutyronitrile which is an initiator; a fifth step of forming a precursor solution by adding the monomer composition to a reactor in which the polymer solvent in which the carbon nanotube-metal composite is dispersed is being stirred, and co-polymerizing the same; a sixth step of forming a coagulated yarn by spinning, washing, desolventing, and stretching the precursor solution; and a seventh step of carbonizing the coagulated yarn by oxidation stabilization.

In the CN patent 104630937 [127] «Polyacrylonitrile (PAN)-based high-strength and high-modulus carbon fiber» the invention provides a polyacrylonitrile (PAN)-based high-strength and high-modulus carbon fiber. The PAN-based high-strength and high-modulus carbon fiber is prepared by the following steps: (1) preparing a PAN spinning solution; (2) spinning a PAN fiber; (3) drafting precursor fiber; (4) preparing a PAN carbon fiber; (5) carrying out surface treatment; (6) winding to obtain the PAN carbon fiber finished product. The PAN-based high-strength and high-modulus carbon fiber has the characteristics of high strength and high modulus.

The authors in the paper [128] "Effect of additional heat-treatment temperature on chemical, microstructural, mechanical, and electrical properties of commercial PAN-based carbon fiber" in the present work are the effects of additional heat-treatment (ANT) in the range from 1800 to 2400 ºC on chemical composition, morphology, microstructure, and tensile properties, Specific electrical resistivity and thermal stability of commercial polyacrylonitrile - carbon fibers based on the carbon fibers have been investigated using elemental analysis, electron microscopy, single-fiber tensile testing, dual probe electrical resistivity testing, and thermogravimetric analysis. The results were consistent with those of other authors.

The results showed that AHT up to 2400 ºC not only increases carbon content, fiber morphology and tensile modulus, but also decreases fiber diameter, distance between graphene layers, and specific electrical resistance of CF compared to without ANT. The present study has suggested that the key properties of commercial CF based on intermediate grade PAN fibers can be improved by adding their own heat treatment without the use of voltage in the technological batch process.

In articles [129-131] "On graphitibility of carbon fibers from polyacrylonitrile fibers" by the Rietveld method (full profile analysis) the structures of graphitirovanes of CF containing the introduction of boron compound have been investigated. Rietveld's method confirmed the ability of boron-containing CF to graphite at high temperature and allowed to reveal that the structure of the fibers is better described in the rhombohedral model of graphite structure.

In the authors' abstracts [132, 133] the structure and properties of composite materials for functional purposes based on epoxy and polyamide matrixes and modified PAN precursor are considered and the processes of obtaining and thermochemical transformations of polyacrylonitrile nanofibers are studied.

In work [134] the process of electrochemical modification of CF surface for the purpose of increasing the strength of carbon plastics is developed. It is shown that the work was carried out in the following directions:

- Electrolytes development for CF electrochemical treatment on the basis of aqueous solution of hydrogen carbonate and ammonium oxalate, aniline hydrochloride, pyrrhotite. Determination of the regularities binding the KM strength on the basis of CF and polymer binder from the electrolyte composition and technological parameters of the anode treatment of CF;
- Optimization of CF electrochemical treatment processes;
- Design and creation of a pilot plant, confirmation of refinement of the obtained regularities and results at the pilot plant, optimization of the developed technical processes for industrial conditions.

In work [135] creation of fibrous materials on the basis of complex-forming water-soluble polymers by the method of electroforming has been carried out. As a result of this work compositions of molding solutions of interpolymer complexes and technologic solutions of obtaining nonwoven materials for production of distribution layers of children's hygiene means (diapers) on their basis have been proposed.

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In article [136] "Influence of $KMnO_4$ concentration and treatment time on PAN precursor and the resulting carbon nanofibers' properties" the authors considered polyacrylonitrile nanofibers obtained by electroforming and which were impregnated with $KMnO_4$ in different concentration and time conditions. Morphological structures, chemical and thermal properties were studied by scanning electron microscopy, infrared Fourier transform spectroscopy and differential scanning calorimetry. The initial and preoxidized samples were stabilized and carbonized. Coloration, weight gain were also evaluated and solubility in *N*,*N*-dimethylformamide was also evaluated.

The purity of the peak at 2340 cm^{-1} corresponding to the coupling MnO_4-C=N, together with a wide peak at 1650 cm^{-1}, was detected in the infrared spectrum of preoxidized samples. Based on the results of DSC, cyclization reactions in preoxidized samples were accelerated by initiating an exothermic reaction at lower temperatures. The modified samples had higher reaction times and ΔH values, wide exotherms, shorter initial induction times and lower Ti values than the untreated samples.

In article [137] "PAN precursor fabrication, applications and thermal stabilization process in carbon fiber

production: experimental and mathematical modelling" the authors chose polyacrylonitrile, which is a universal artificial polymer and has been used in large quantities as a product since its first mass production in the mid-40s. This article is the first comprehensive review that provides a general understanding of the relationships between the structure of PAN fiber, the properties and process of its stabilization, along with the use of mathematical modeling as a powerful tool for predicting and optimizing the processes involved.

In article [138] "Simulation Model for Stabilization of Carbon Fibres" the authors stated that at present there is no model for mathematical description of stabilization model. The first steps to the analysis were taken by Dunham and Eddie in 1992 to describe the stabilization method by means of the differential equation. This project uses a numerical approach based on their work. However, there are some problems that need to be addressed before the stabilization process is understood and described.

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In article [139] "State and Perspectives of CF Production and Consumption from Oil Flows" the analysis of literature data on the state of CF production, market and consumption is performed. It is shown that the demand for CF at the world market has grown considerably in recent years. This trend will continue in the future. The advantages of using oil raw materials for producing carbon fibers are shown. It is noted that production of CF from oil furnaces is currently set up and intensively developed by a number of foreign companies. In Russia there is no industrial production of CF from oil furnaces.

In article [140] "Modified sorption-active carbon fibrous materials" modification of carbon fibrous materials which are further used as sorbents is considered.

In article [141] "PAN based carbon fibre manufacturing" in production of carbon fibre the PAN precursor obtained in the process of three-process polymerization, carbonization and thermal treatment is usually used. The oxidation process is the first and the very first stage of PAN production, and then it undergoes carbonization. Before carbonization, an important stage of the process is the stabilization process, which is carried out as part of the oxidation process. Stabilization is carried out using temperatures from 200 ºC-250 ºC. The obtained CF has a density of 1.75-1.76 g/cm^3 and tensile strength of 3.5-3.8 GPa.

In article [142] "Fabrication and Properties of Carbon Fibers" the author examines the research and development carried out over the past few decades on carbon fibers. The two most important precursors in CF in industry are polyacrylonitrile and mesophase paking. The structure and composition of the precursor significantly influence the properties of the resulting CF. Although the main CF production processes are similar, different precursors require different processing conditions to achieve improved performance. In this overview, efforts to optimize the process are discussed. The review also attempts to cover research on other developed precursor materials, mainly with the aim of reducing costs.

Works on CF have also been reported at many conferences and published in applied chemistry journals [143-147].

There are a lot of works on research and use of CF, which find its application in different environments and become the objects of conference reports, objects of researches presented in abstracts and articles. One of the priority directions is CF modification.

2.3. Carbon fiber surface modification

The modern scientific community recognizes the need to modify existing polymer fibers and materials from them in order to give them additional operational and technological properties. Fiber modification is carried out at different stages of production: during the synthesis of fiber-forming polymer; in the process of processing the polymer into a fiber or thread; at the stage of finishing the molded fiber or immediately before using the finished fiber.

The choice of modification method depends on the structure of the polymer, economic aspects and the purpose of the finished product. Methods for the modification of fibers, filaments and materials from them are usually divided into the following groups:

- methods of chemical modification;
- methods of composite modification;
- methods of physical (structural) modification;
- methods of electrophysical (surface) modification [3, 148].

So, [149] activated hydrocarbons are promising sorption materials for removing various components from aqueous solutions, and are also effective as supports for catalysts due to the developed porous structure, large specific surface area, and high sorption capacity. They have good kinetic characteristics and a special surface reactivity [150-153].

To obtain ion exchangers from hydrocarbons, the fibers are subjected to oxidative treatment with reagents or electrooxidation. Moreover, the sorption capacity with respect to metals substantially depends on the selected processing method [151], which is associated with a change in the surface chemistry of the fiber [150, 151], and in the case of oxidative treatment, with a change in the pore structure [154]. Another technique for modifying hydrocarbons is the deposition of additional components on the fiber surface - films of metal oxides or polymers - to produce thin-bedded inorganic sorbents (TIS) [155].

Traditional methods for studying the texture of finely dispersed and porous bodies (adsorption, mercury porosimetry, x-ray methods, and others) cannot be applied for various reasons to the study of complex composite materials to adequately describe their texture. In this case, the term texture refers to the structure

of the porous space, the solid phase framework, the spatial arrangement and size distribution of all components, phases, and other geometric characteristics of the atomic scale [156].

The universal methods of visual analysis of the shape and relative position of pores and particles are electron microscopy methods [156, 157], as well as, in particular, atomic force microscopy [158] and scanning tunneling microscopy [159], which have been actively developed over the past two decades.

The fibers were studied using a German LEO-430 electron scanning microscope (ESM) and an NT-MDT atomic force microscope (AFM) (Zelenograd, Russia). AFM surveys were carried out by contact and semi-contact methods; images were selected in the most informative representations.

Samples of the studied thin-layer inorganic sorbents were obtained by the chemical modification of carbon materials according to the method described in the patent [160] and by electrochemical deposition of titanium hydroxide on a carbon material by the method [161].

For the initial hydrocarbon treatment, we used AKTILEN-B carbon fiber tow produced by the *LenNII «Khimvolokno»*.

According to the data obtained by atomic force microscopy, the ACTILEN-B HC has no less than a two-level hierarchical block structure. A system of micropores and submicropores is formed between blocks of various levels. Micropores taper down. The macropore system is formed at the points of fiber breaks and between microfibrils.

The surface of the fiber, including the surface of macro- and micropores, is covered with submicropores.

The oxidation of ACTILEN-B fiber is accompanied by deformation of microblocks, manifested in their swelling, and an increase in the size of macropores.

The coating based on titanium hydroxide on ACTILEN-B fiber, obtained by the electrochemical method, is formed mainly in the form of a relatively even film composed of blocks of approximately the same height. But there are also individual “island” particles of micron-sized sizes.

Modification of the fiber with titanium hydroxide leads to the creation of a double sieve, which includes a pore system in the coating and below it a pore system of the original fiber.

The coating based on titanium hydroxide obtained by a chemical method has a pronounced relief appearance with respect to such a coating obtained by an electrochemical method, and is composed largely of associates of micron-sized particles.

The study of the adhesion of components in carbon plastics, depending on various methods of surface modification in the manufacture and operation of PCMs, is very relevant and helps to solve the problem of creating high-strength structural composites. Therefore, the most important task today, in the field of creation and use of reinforced plastics, is to improve the methods of surface treatment of fibrous fillers, to find the possibilities of a correlation dependence of the strength of CMs on the strength of adhesive interaction based on the laws of physicochemical interaction of plastic components [162].

Interface [163] protective coatings based on nanosized refractory compounds on carbon bundles and tapes were studied. The possibilities of applying thin layers consisting of refractory oxides of aluminum, zirconium, silicon to continuous hydrocarbons and tapes using the sol-gel method are considered. For the application of two-layer coatings consisting of carbide and zirconium oxide, gas transport chemical reactions were used. Morphological features, phase and elemental composition of coatings were studied using high-resolution X-ray phase, electron microscopy analysis and high-quality energy dispersive analysis. It is shown that coatings based on refractory oxides are uniformly distributed over the thickness and length of individual fibers. They have good adhesion to the fiber, do not exfoliate, the thickness does not exceed 200-300 nm. The oxidative stability of carbon materials with coatings of various types was studied.

Thus, the authors of [164] considered the processes of hydrocarbon modification by ion beam treatment with argon, nitrogen, and oxygen ions. It is shown that the method [165-170] is promising for controlling the surface structure and adhesive properties of carbon fiber materials. The change in the hydrophilic-hydrophobic properties of hydrocarbons was studied by controlling the contact angle depending on the modification parameters (time, ion energy, processing medium), and the morphology of the hydrocarbon surface was studied by scanning electron microscopy. It has been established that the most effective removal of contaminants from the surface of a hydrocarbon occurs during ion-beam treatment in argon and nitrogen.

Using the method [171] of electrochemical treatment of CF obtained by two-stage thermal stabilization and carbonization of polyacrylonitrile fiber, we modified its surface in order to enhance adhesion with an epoxy matrix.

Thus, in a number of works [172-174], the effect of low-temperature plasma treatment in a high-frequency capacitive discharge at a reduced pressure of carbon fabrics on the mechanical properties of carbon-based materials based on them was studied. An increase in the indicators of mechanical properties is established.

Modified hydrocarbons [175-181] were chosen as objects of study. The structure, composition and methods of forming inorganic porous materials and composites based on them are considered, the areas of their potential application are given. Composites based on activated hydrocarbons with metal oxides (Ti, Mn, Ni) and the natural chitosan biopolymer are characterized.

The physicochemical principles of surface modification of cellulose, carbon, and ceramic materials by nanosized metal oxides were analyzed [183], and the mechanisms of interparticle interaction of nano-objects and the effect of the modification on the sorption and catalytic properties of materials were studied.

In the RF patent 2560362 "High-modulus carbon fiber with a modified surface for reinforcing composites and a method for its modification" the invention relates to a technology for producing hydrocarbons in

the form of threads, bundles and relates to a high-modulus carbon fiber with a modified surface for reinforcing composites and a method for modifying it. The fiber has a surface with comb-like formations in the form of corrugations that are trapezoidal in cross section along the fiber axis up to 1.0 μm high with rounded vertices that are ordered on the fiber surface forming surface and are mated in the bases with their generators in circles with a radius of curvature of not more than 50 nm. A high-modulus CF is obtained by modifying the surface, which consists in changing the topography and specific surface of the fibers, and is subjected to ion irradiation during continuous transport by inert gas ions [184].

In the RF patent 2012696 "Method for processing the surface of carbon fibers" use: technical materials. Summary of the invention: a stimulating agent is applied to the surface of a carbon fiber material from a solution of a halide compound in an organic solvent. It is dried, the halide compound is reduced to the corresponding element in a stream of hydrogen at 600-1273 K and a pressure of 0.25-13.5 kPa. Then carry out the deposition of the coating of silicon carbide and whiskers at 1473-1673K and a pressure of not more than 13.5 kPa using a gas mixture of silicon tetrachloride, monosilane, methane, argon and hydrogen in a ratio of 1: 20: 160: 180: 200 to 1: 10: 200: 200: 1000. The halides are iron, nickel, cobalt, antimony, bismuth, lanthanum, tellurium, silicon chlorides [185].

In the RF patent 2578283 [186] “Method for modifying carbon fibers and carbon nanotubes”, carbon fibers are wound on a flat or round rotating spool and are subjected to neutron irradiation from both sides and from the inside. In another embodiment, carbon nanotubes are poured into a horizontal rotating drum, during which they are subjected to neutron irradiation. Effect: inventions provide obtaining modified CF or nanotubes with increased strength and heat resistance.

In the RF patent 2538687 [187] “Method for determining the degree of impregnation of hydrocarbon bundles with pitch and installation for its implementation” the invention relates to the field of production of carbon-carbon composite materials for various purposes, is intended for comparative assessment of the impregnation of hydrocarbon bundles with pitch melts and can be used in testing the production of carbon-carbon composite materials having various properties, by modifying or replacing the pitch binder and / or carbon fiber, for example, in scientific laboratories, in particular during laboratory work. To determine the degree of impregnation of the hydrocarbon bundles with pitches, the hydrocarbon bundle is placed in a glass tube so that the end of the bundle protrudes from the glass tube, and the hydrocarbons in the bundle are oriented along the axis of the glass tube, while the thickness of the bundle is chosen so that it is held tightly in the glass the protruding end of the carbon fiber tow is brought into contact with the molten pitch and held in this position, then the hydrocarbon tow is removed from the tube and the impregnation height of the hydrocarbon tow is determined. A simplification and acceleration of determination is achieved.

In the RF patent 2475463 [188] “Method for modifying the surface of an inorganic fiber, modified fiber and composite material” the invention relates to the modification of the surface of an inorganic fiber by forming a highly developed surface of the inorganic fiber used as a filler by forming carbon nanostructures on the fibers (CNS) and may find application in the production of high-strength and wear-resistant fibrous composite materials A method of modifying the surface of an inorganic fiber includes the following steps: (a) impregnating the inorganic fiber with a solution of the pitch fraction α2 in organic solvents; (b) subsequent drying of the impregnated fiber; (c) heat treatment of the impregnated inorganic fiber at 300-600 °C; (d) applying to the surface of a heat-treated transition metal salt in accordance with step (c); (e) reduction of a transition metal salt to produce transition metal nanoparticles; (e) carbon deposition on transition metal nanoparticles to produce carbon nanostructures on the surface of the fiber. The composite material contains a modified fiber made by the above method, and a matrix of polymer or carbon. The technical result of the invention: increasing the strength of the composite material in the transverse direction relative to the reinforcement plane by preventing the destruction of the surface of the fibers when modified with carbon nanostructures.

In the RF patent 2402584 [189] “Modified carbon products and their use”, a modified carbon product includes a carbon carrier, an organic functional group with a cyclic moiety attached to its surface, and a metal group covalently attached to the specified functional group. The metal group is a source of metal selected from silver, copper, nickel, europium, iron, aluminum, rhodium, cobalt, ruthenium, magnesium, calcium and platinum. The carbon carrier may be carbon black, activated or bulk carbon, carbon flakes, hydrocarbons, or carbon nanotubes. To obtain a modified carbon product, the following stages are carried out: preparing a carbon carrier, modifying it with a functional group, attaching a metal group to it. The stage of accession can be carried out in a liquid medium, in the vapor or gas phase. The invention allows to obtain a wide range of materials that have advantages over the known.

After analyzing the patent base, it becomes clear that China is becoming the leader in patenting its inventions. The chemical modification method is described in patents [190-193] CN 106867199 "Oriented graphene oxide modification carbon fiber composite material and preparation method thereof", CN103321035 "Surface modification method of carbon fiber plasma grafted graphene oxide", CN101348953 "Surface modification method of polyacrylonitrile fiber for producing high performance carbon fiber”, CN1250116 “Active carbon fiber surface modifying method”, as well as the physical modification method, for example with plasma, which is described in CN101412592 “Surface modification method for basalt fiber by using plasma treatment and carbon nano-tube coating” [194].

The invention, according to patent CN101412592 [194], it provides a method for modifying the surface of an HC of a carbon nanotube with a plasma graft, and the method includes the following steps: placing the carbon fiber material in a plasma atmosphere, wherein

the power of the plasma generation device is 100-1000 W. and the processing time is 10-900 s; drying the treated carbon fiber material in vacuum at 40-60 ° C to a constant weight; then the addition of an aminated carbon nanotube to the organic solution and ultrasonic treatment for 10-50 minutes to obtain a sol solution with a concentration of 0.01-10 g / l; finally, adding carbon fiber material to the sol of a carbon nanotube, adding a surface-active agent to the mixture, where the mass ratio of surface-active agent to carbon nanotube amination is 1: 1, ultrasonic treatment of the resulting mixture with a solution for 10-50 minutes, raising the temperature to 50-100 °C, carrying out the reaction at a constant temperature for 9-12 hours, as well as washing and drying. According to the invention, a carbon nanotube is used as a material for grafting a CF surface; the surface of the hydrocarbon is modified by plasma; Many polar groups are introduced onto the surface of the fiber; therefore, the hydrocarbon is grafted using an aminated carbon nanotube; then a carbon nanotube is grafted.

An increase in the output of high-quality polymers with specified technical characteristics, including synthetic fibers, is one of the main tasks of the economic and social development of our country for the long term. At this stage, it is necessary to modify existing polymer fibers and materials from them in order to give them additional operational and technological properties.

The properties of polyacrylonitrile fibers can be changed within wide limits using various methods for their modification. Of the modified fibers, the following are of most interest:

- fibers from acrylonitrile copolymers;
- fibers from grafted copolymers of polyacrylonitrile;
- fibers from mixtures of polyacrylonitrile with other polymers.

Consequence

The results of the study indicate that a significant increase in the volume of hydrocarbon production and improvement of its quality requires a set of measures aimed at solving key technological problems. The main efforts should be focused on increasing the strength of CF, reducing the cost of their production and improving the quality of CF-based composites.

The key technological tasks are the development of technologies and equipment for obtaining high-strength CF, the development of technologies and equipment to reduce the cost of production of CF, the development of technologies to improve the quality of composites based on CF.

Ways to address them is to develop a technology for the production of PAN precursor to produce high-performance CF by wet-spinning, working out "dry-wet" method of producing PAN, the development of high-performance equipment for technical PAN precursor in the form of bundles, development of technologies and equipment for efficient regeneration and utilization of waste heat and emissions generated from production of hydrocarbons, development of new formulations of precursors and the transition to the material a greater linear density, optimization of the structure of CFRP, with the aim of increasing strength, the development of technology and creation of production of modern types of adhesives, including with the addition of nanoparticles.

According to the results of the study revealed that it is reasonable to extend the use of hydrocarbons in industry to manufacture equipment with high performance, in particular in the automotive industry (for example, to significantly reduce the weight of the car), shipbuilding (mainly to skins).

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THE MODELING OF MANAGEMENT DECISIONS IN EMERGENCY SITUATIONS AND MAN-MADE ENVIRONMENT

Sokolova A.
M.Sc.
University of Civil Protection, Ministry of Emergencies of the Republic of Belarus
г. Minsk
Sokolova S.
Doctor of Philosophy,
International State Ecological Institute
Sakharov International State Ecological Institute, Minsk, Minsk, RU D. in Philosophy, Doctor of Sciences,
Associate Professor at the A.D. Sakharov International State Ecological Institute
of the Belarusian State University
г. Minsk
https://doi.org/10.5281/zenodo.6654277

Abstract

The article presents the author's view on the topical issues of modeling of management decisions in emergencies in the context of the technogenic environment, emerge updated forms of communicative quasi-social relations between man and technology, which brings to the fore the problems of self-organization, innovative robotic, cybernetic systems and technobiotic stage of human civilization.

Keywords: modeling methods, automated information-management systems, "Liquidator" program, man-made environment.

Today against the background of in Ukraine crisis there is an intensification of competition for resources between "centers of power", aggressive sectional policy of Euro-Atlantic alliance, which dynamically changes international standards, imposes sanctions, uses "dirty" information technology, which actualizes the problem of modeling management decisions in emergencies [1, p. 46-51].

The beginning of the 21st century was marked not only by global crises (migration, food, military, economic, energy, coronary crisis,) but also by hybrid wars (information war, sanction war, network-centric warfare, cyber warfare, economic warfare) [2, p. 90]. Consequently, in such complex conditions of transformation of the geopolitical world, of particular importance are the issues associated with the emergence in the technogenic environment of self-organization phenomena of complex robotic, cybernetic systems and technobiotic stage of evolution of human civilization (neocybernetics). Let us note that the adoption and implementation of management decisions in emergencies is the responsibility of the manager, as the management activity is the product of making timely decisions (system analysts, managers, experts), including in emergencies. The central place is occupied by the problem of developing an algorithm, modeling of managerial decisions in emergency situations, which is associated with innovative programs (software product), based on educational technology [3, p. 68].

The multidimensional process of making management decisions is structured and aimed at solving a problem situation: goals (the subject of management makes a decision); consequences (the direction of action is chosen); division of labor (there is a certain division of labor in the organization); professionalism (not every employee of the organization has professional knowledge, experience and is empowered to make certain decisions independently, especially in emergency situations). Managerial decision making is a dynamic process, which proceeds in time and is carried out in several stages, and the result of the management process is the activity of the head of the organization to implement the chosen decision (development of self-organizing robotic systems and design of complex technical systems) [4, p. 25].