IMPROVEMENT OF MANUFACTURING TECHNOLOGY FOR
ULTRASTRONG AND HIGH-MODULUS CARBON FIBRES

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1. The quality of CF, their strength and modulus of elasticity in particular, can be increased by the following methods: reducing the porosity of the initial PAN fibres by selecting the optimum conditions for spinning, plasticization drawing, finishing, and drying; decreasing the nonuniformity of the fibre diameter due to suppression of deformation resonance during spinning by selecting the jet formation and hardening conditions; decreasing the fibril and crystallite size by reducing the precipitator and solvent concentration gradient in the precipitation zone (spinning into mild baths); creating optimum conditions for mesophase self-ordering of the material at 450-550°C during precarbonization; increasing the cohesive energy by increasing the density to 1.8-2.1 g/cm³. 2. Replacing convective tempering of PAN twists in thermooxidative treatment by conductive tempering reduces the treatment time by 3-4 times.

Carbon fibres (CF) made from polyacrylonitrile (PAN) copolymers are the most widely used CF. This type of fibre has a set of properties (high strength and modulus of elasticity, dimensional stability, resistance to corrosion, low density) that predetermined their use in high-tech industries such as rocket-space, aviation and atomic, ship building, and production of high-quality sporting goods. However, the production volumes of these fibres is still comparatively small, 12-15,000 tons a year, which is due to imperfect technology and equipment that do not ensure the required level of quality indexes, production economy, and respect of environmental requirements. Some scientific premises and technical solutions on improving PAN CF manufacturing technology are examined below.

As for the quality indexes, together with the CF manufacturing technology, many investigators [1] believe that the properties of the initial PAN fibre, particularly its defectiveness, degree of orientation, and microfibril structure are of determining importance here.

Of the large number of defects characteristic of wet-spun PAN fibres, we distinguish the two that most strongly affect the quality of CF: porosity and nonuniformity of the filament diameter. The negative effect of porosity on the quality of CF is manifested in two ways. First, since the features of the structure of the initial PAN fibre are preserved in the structure of the CF, the porosity is also preserved, causing nonuniformity of internal stresses and brittleness in the CF. The second negative mechanism of the effect of porosity is the decrease in the thermal stability of PAN fibre, i.e., the lower value of the maximum attainable limiting temperature of thermal decomposition of the polymer. Pores serve as nuclei or centers of the onset of thermolysis of PAN fibre and do not allow attaining the temperature of 500-550°C in rapid heating required for mesophase rearrangement of the structure of the oxidized fibre during carbonization without intensive decomposition [2].

The appearance of pores in PAN fibre is predetermined by the nature of wet spinning, where the volume of solvent in the initial spinning solution is 72-84%. A polymer backbone that occupies a volume approximately equal to the volume of the initial spinning solution forms during coagulation, since the diameter of the coagulated fibre remains almost the same as the diameter of the liquid jet. The number and size of the pores are determined by the structure of the backbone formed and the conditions of its transverse and longitudinal shrinkage during plasticization drawing, washing, and drying of the fibre. The structure of the backbone is determined by the precipitation (coagulation) conditions. A high content of precipitator, usually water, in the spinning bath causes fast coagulation and formation of a rigid backbone with large pore size. The as-spun fibre

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has an unsatisfactory capacity for orientation drawing. All of this negatively affects the quality of the final carbon fibre. When the precipitator content decreases, the porosity of the PAN fibre decreases [3], which results in CF with high strength and elasticity. However, decreasing the precipitator content below a certain limit is again accompanied by an increase in the porosity and a decrease in the quality of the CF. This phenomenon is probably due to a change in the mechanism of phase decomposition of the spinning solution. At a relatively high precipitator content, the spinning solution decomposes into a solid polymer phase (backbone) and a low-molecular-weight liquid phase (mixture of solvent and precipitator). Decreasing the concentration of precipitator below the defined level is accompanied by decomposition of the spinning solution into two liquid phases — polymer and low-molecular-weight. Drops of the liquid polymer phase become the source of high porosity.

The conditions of the successive treatments of as-spun PAN fibre also effectively affect the porosity and the quality of the CF. The effect of the plasticization drawing conditions was especially important [4]. Drawing in saturated steam medium increases the porosity of PAN fibre by 15-20% in comparison to liquid plasticization treatment; the breaking strength of the CF correspondingly decreases by 5-10%. The elasticity of CF was especially sensitive. The loop strength of CF in steam plasticization treatment was 1.5 times lower than in liquid treatment.

Increasing the drying temperature from 80 to 140°C decreases the porosity of PAN fibre from 48 to 29 arbitrary units. Repeated wetting and drying of the fibre decrease the porosity to 20 arb. units [3]. The porosity can be additionally reduced to 10-15 arb. units in thermofixation of PAN fibre at 140-180°C.

Another type of defectiveness in PAN fibre that unfavorably affects the properties of the final CF is nonuniformity of the filament diameter. It is usually characterized by the coefficient of variation of the linear density of the filaments, K_v. The best result is obtained at $K_v = 3$-5%. Using PAN twist with $K_v > (8$-10)% is totally unacceptable. A high value of K_v means that the PAN twist contains a large number of filaments with a large diameter of 18-20 μm, i.e., ~0.3 tex, which are difficult to process with technology designed for filaments with a linear density of 0.1 tex. It should be noted that the transition in the last 15-20 years from fibres with a linear density of 0.33 tex initially to 0.17 tex and then 0.10 tex fibres allowed increasing the strength of CF from 200 to 300 and 500 kgf/mm^2 (3000-5000 MPa).

The elevated nonuniformity of the filament diameter in PAN fibres is due to deformation resonance of the spinning jets, which consists of pulsation of the jet diameter due to periodic breaking of the outer layer of the expanded part of the jet, the so-called bulb, and relaxation of the fractured layers with thickening on both sides from the point of the break. Deformation resonance can be suppressed by changing the conditions of flow of the spinning solution or precipitation of the spun fibres. In all cases, it is necessary to strive for minimum bulb deformation. This can be done by decreasing the bulb itself by increasing the spinneret hole diameter or the ratio of the length of the hole capillaries to their diameter, and decreasing the viscosity or flow rate of the spinning solution. Decreasing the bulb diameter reduces the actual spinneret drawing and correspondingly the probability of rupture of the most stressed outer layers of the bulb. Bulb deformation is also decreased by increasing or decreasing the concentration of precipitator in the spinning bath. When the concentration of precipitator is increased, the jet hardens directly on the surface of the spinneret. For this reason, the jet does not expand into the bulb shape. In this case, twists with elevated uniformity of the filament diameters are formed. But they usually have low indexes due to the high severity of the precipitation conditions.

Bulges appear in the jets when the concentration of precipitator is decreased. In this case, spinning should be conducted with a concentration of precipitator at which expansion is totally realized to prevent deformation and rupture of the surface layers, i.e., the appearance of the deformation resonance effect.

In optimal spinning conditions, the coefficient of variation for the linear density of the filaments decreases to 4-5%. The last version, where the concentration of precipitator decreases until bulb deformation stops is the most acceptable one since high strength and low porosity of the fibre are simultaneously obtained.

In addition to methods of increasing the quality of CF by decreasing the defectiveness of the initial PAN fibres, the process engineer has many other manufacturing methods for increasing the strength and modulus of elasticity of CF, including:

– decreasing the size of the structural units in the initial PAN fibres — fibrils, crystallites;

– increasing the degree of orientation of the polymer in the spinning stages of thermal stabilization and carbonization of PAN fibres;

– increasing the degree of ordering of CF by converting the material to the mesophase state and realization of the self-ordering effect that takes place here;

– increasing the cohesive energy of the treated carbon material by increasing its density by reducing the interatomic distances in high-temperature treatments (1800-2500°C).

The fibril size is decreased in PAN fibres and the structure is made more uniform over the fibre cross section in spinning in "mild" baths with a low precipitator content, so that a low solvent and precipitator concentration gradient is established in the precipitation zone and the polymer backbone formed has a uniform small-fibril structure. This topic is examined in detail in [5].

During precipitation, the precipitator diffusing into the fibre causes desolvation of the solvent, decreases the solubility of the polymer initially to the equilibrium and with an increase in the concentration, to the supersaturated or metastable state. Structure formation, i.e., the formation and growth of nuclei of the polymer solid phase, takes place in the region of the metastable supersaturated state. The rate of formation of nuclei (nucleation rate) is extremally dependent on the degree of supersaturation. As the concentration of precipitator increases, the nucleation rate increases, attaining a maximum, which results in formation of a fine fibrillar structure. When the concentration of precipitator is increased further, the growth of the new polymer phase around previously formed nuclei is simultaneously accelerated. The new nuclei are absorbed by the growing solid phase, coalescence takes place, the nucleation rate decreases, and growth of fine fibrillar structures slows.

As a function of the degree of supersaturation, two types of coagulation can be distinguished in wet spinning of PAN fibres: frontal and bulk. In spinning into severe spinning baths, a boundary zone of important supersaturation where crosslinking nuclei instantaneously arise according to a spinodal mechanism and growth of fibrillar structures begins is formed on the surface of the spun fibre. Fibrils growing from neighboring centers collide and reciprocally inhibit their growth in all directions except for perpendicular to the contact surface of the spinning solution with the spinning bath, where the precipitator concentration gradient and correspondingly the degree of supersaturation are greatest. A boundary line — coagulation front — is formed which moves to the axis of the fibre during diffusion of the precipitator. This is frontal coagulation. It results in formation of radial rod-shaped structures.

Bulk coagulation takes place in spinning in mild baths. The ratio $C_p < 2C_c$ is the criterion of the onset of mild baths, i.e., the concentration of precipitator in the bath C_p must be less than two critical concentrations C_c. In this case, a concentration below C_c is established on the surface of the fibre and the boundary line of the critical concentrations begins after the time required for accumulation of precipitator on the surface of the fibre to C_c. As a result, a liquid segment is formed in the spun fibre, and this causes the appearance of a metastable region and the possibility of implementing conditions for formation of crosslinking nuclei in the bulk and finally formation of a fine fibrillar structure and improvement of all physicomechanical properties.

Mild baths with a precipitator content in a narrow concentration range are the most promising of the spinning baths examined. The use of mild baths in spinning PAN fibres leads to formation of a fine fibrillar structure of the fibre and an increase in the physicomechanical indexes of the CF.

PAN twists with a 500-tex linear density, 10.8 μm filament diameter, strength of 52.5 cN/tex, and elongation of 18% were obtained by implementing this principle. The CF made from these twists had a strength of 456 kgf/mm^2 (~4560 MPa) and modulus of elasticity of 26.3 ton-force/mm^2 (~263 GPa).

Increasing the quality indexes of CF by higher orientation drawing in the PAN fibre fabrication stage and thermooxidative treatment is most effective and has been used since PAN fibres have been manufactured. The possibilities of this method have been exhausted to a significant degree. Attempts to further increase orientation drawing are frequently unsuccessful. This is due to the nonuniform deformation capacity of the filaments. Some fibres, 5-15%, do not withstand this kind of drawing and break, decreasing the quality of the entire carbon fibre. This phenomenon becomes especially unacceptable when drawing is conducted in the form of a woven ribbon, where breaking of filaments in the ribbon remains unnoticed even at high degrees of drawing and the final CF has low strength in the plastic.

The structure of the polymer backbone in PAN fibre is such that even at 12-14-fold drawing, the angle of disorientation does not drop below 10-12°. A further increase in the reciprocal ordering of the macromolecules can be obtained by converting the material to the mesophase (liquid-crystalline) state where an effect of spontaneous ordering of the material is realized [2].

Elevated chain rigidity and the presence of mesogenic groups are a necessary condition for mesophase transition of a polymer. The rigidity of PAN macromolecules is increased in thermooxidative treatment due to formation of naphthyridine rings in polymerization of nitrile groups, which simultaneously play the role of mesogenic sites due to the high polarity. The mesophase transition takes place in the 450-550°C temperature range. The strength increases by 3.5-4.0 times, to 200 kgf/mm^2 (~2000 MPa), and ordering of the material is observed. However, at the very time of rearrangement of the structure, the strength of the material drops, which is characteristic of the mesophase transitions of other polymers.

In addition to the existing treatments of the mechanism of the transition to the mesophase state based on an analysis of entropic changes, the energy approach also merits attention. The mesophase transition examined is a thermotropic transition
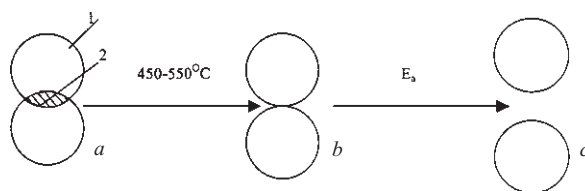
Fig. 1. Diagram of the activation thermotropic mesophase transition in carbonization of oxidized PAN fibre: a) interaction of macromolecules in oxidized fibre [1] segment section; 2) interaction energy]; b) mesophase state; c) isotropic state; E_a: activation energy of transition to isotropic state.

observed with a change in the temperature. An increase in the temperature is accompanied by an increase in the distances between polymer chains up to a state where the outer chain surfaces will not be overlapped by projections and depressions due to thermal motion, i.e., the segments of the molecules can freely move over the surface relative to each other. Macromolecules with a different segment size behave differently. According to molecular-kinetic theory, the kinetic energy of the molecules and in the case examined, the segments of macromolecules which are independent kinetic units, is a function of the temperature and molecular mass of the segment:

$$E_k = 3/2RT = Mv^2/2, \tag{1}$$

where E_k is the kinetic energy; R is the gas constant; T is the absolute temperature; M is the molecular mass of the segment; v is the root-men-square velocity of the segments of the macromolecules.

Segments with a lower molecular mass obtain greater acceleration at the same temperature so that they separate and pass into the isotropic liquid state, while segments with a higher mass will continue to move over the surface relative to each other. The factor of anisodiametry and mesogenic groups comes into effect here. "Floating" over the surface relative to each other, the rod-shaped segments with strongly polar mesogenic groups will be attracted to each other, forming an anisotropic mesophase (liquid-crystalline) structure which significantly increases the physicomechanical properties of CF.

The examined mechanism, which is essentially an activation mechanism, is similar to the well-studied activation of viscous flow [6]. In both cases, the "elementary event of the process consists of the fact that the molecular-kinetic unit overcomes the potential barrier in passing from one position to another, for which it must have sufficient energy — activation energy." The higher the chain rigidity, the higher the activation energy. The empirical dependence of the activation energy of viscous flow E_a on the chain rigidity thermodynamic parameter σ has been established:

$$E_a = 4.31\sigma^4. \tag{2}$$

For flexible-chain polyethylene, rigidity parameter $\sigma = 1.62$, and for more rigid-chain polystyrene, it is 2.19. The activation energy of viscous flow is correspondingly equal to 29.8 and 98.7 kJ/mole. The high energy barrier for separation of rigid naphthyridine chains from each other thus inhibits their transition to the amorphous state and allows being in the intermediate, i.e., mesophase (liquid-crystalline) state. The duration of existence of this state is probably low due to the high temperature (500°C), but is sufficient for the chains to unfold and mutually orient due to reaction of mesogenic groups. The scheme of the activation thermotropic transition to the mesophase state is shown in Fig. 1. The reaction of naphthyridine chains 1 in the initial oxidized fibre is indicated by hatched area 2. On heating to 450-500°C, the intermolecular interaction energy decreases due to thermal expansion and the segments are in contact only by the outer electron shells, which allows them to execute azimuthal motion and because of attraction of the mesogenic groups, to pass into the oriented state. The segments cannot move away from each other because of the high activation energy due to the elevated rigidity of the naphthyridine chains. If energy greater than or equal to E_a is directly supplied, the segments separate (state c) and the material passes into the amorphous state.

As a result of mesophase strengthening, the qualitative indexes of CF increase significantly, but further progress in increasing the strength and modulus of elasticity is made by increasing the cohesive energy due to an increase in the density of the CF to 1.8-2.1 g/cm^3 by high-temperature treatments at 1200-3000°C.

Carbonization takes place in three temperature zones called precarbonization, high-temperature carbonization, and graphitization. During precarbonization, structural rearrangement takes place [7-8] related to mesophase transformation of the naphthyridine polymer [2], a necessary condition for attaining high physicomechanical indexes of CF. In high-temperature carbonization, the structure formed during precarbonization basically remains unchanged.

Heat treatment of PAN twists in multipass furnaces is one of the longest and most power-consuming stages in manufacture of CF. Its duration reaches 3 h at 180-300°C, which inevitably results in large heat losses. They can be eliminated by going from convective to conductive (contact) tempering [9, 10].

The high rate of heat exchange between the twist and the tempering surface allows narrowing the temperature range to $\pm 2^\circ$C, increasing the treatment temperature, and reducing the treatment time by 3-4 times.

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