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FIBRE COMPOSITES

CARBON NANOTUBE FILLED POLYACRYLONITRILE FIBRES. PRODUCTION AND PROPERTIES

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The results of studies of fibre spinning from polyacrylonitrile filled with carbon nanotubes are reported and the recommendable concentrations of nanoparticles in the spinning solution are determined. It is demonstrated that incorporation of carbon nanotubes in the polymer enhances physicomechanical indexes of the fibres vis-à-vis unfilled ones.

Amongst the modern structural materials, carbon fibre reinforced plastic composites, in which high-modulus and high-strength carbon fibres produced by high-temperature treatment of polyacrylonitrile (PAN) fibres, occupy a prominent place [1-3]. The choice of this precursor is dictated by several factors, such as high carbon yield on carbonization of PAN fibres, plasticity, linear unbranched structure of the polymer, etc. [4]. As is well known [5-7], the properties of original PAN fibres exert a direct effect on the quality of the obtained carbon fibres (CF), namely, elastic modulus, elasticity, and strength, so the fibres earmarked for processing into CF must possess high physicomechanical properties.

In general, the companies producing PAN fibres – the precursors of carbon fibres – synthesize special copolymers for such products. Fibres from these copolymers possess higher physicomechanical indexes compared to textile variety of fibres. At the same time, there is a potential and a necessity of using “unary” PAN fibres for CF production. On the other hand, in the literature [8-11] special routes are proposed for augmenting strength properties of PAN fibres from usual polyacrylonitrile copolymers usable for manufacture of textile yarns, for instance, by incorporating carbon nanotubes (CNT). In this work, we have demonstrated the possibility of using CNT for reinforcing PAN fibres to enhance their physicomechanical properties.

Manufacture of PAN-CNT composite fibres is based on use of CNT-B carbon nanotubes (a product of ODO Technology of Chemical Physics, Minsk, Belarus), copolymer PAN-C (a product of OOO SNV, Saratov, Russia), and dimethyl formamide (DMF) solution, which are feed products. Before the spinning solutions are prepared for fibre spinning, the feed components, which enter the PAN-CNT fibre forming block, are analyzed, prepared, and batched. After the fibres are formed and dried, their physicomechanical properties are studied and, if necessary, they are conditioned. A specific feature of preparation of spinning solutions containing CNT is that after addition of nanotubes to the solution, they are dispersed by a Hielscher UP200S ultrasonic disperser. The CNT was dispersed in DMF and the PAN solution in DMF was prepared before loading into the mixing tank.

An experimental line (Fig. 1) consisting of individual blocks (modules) was developed for producing composite fibres.

In the first stage of the study, the optimum polymer concentration in the spinning solution was determined. Such parameters as spinning solution feed rate, temperature, and composition of the setting bath as well as the rate of winding of the thread on a spool remained constant.

In the first series of experiments, the fibres were spun without carbon nanotubes (Table 1). The investigations demonstrated that for this experimental line the conditions of fibre formation without CNT must be the following:

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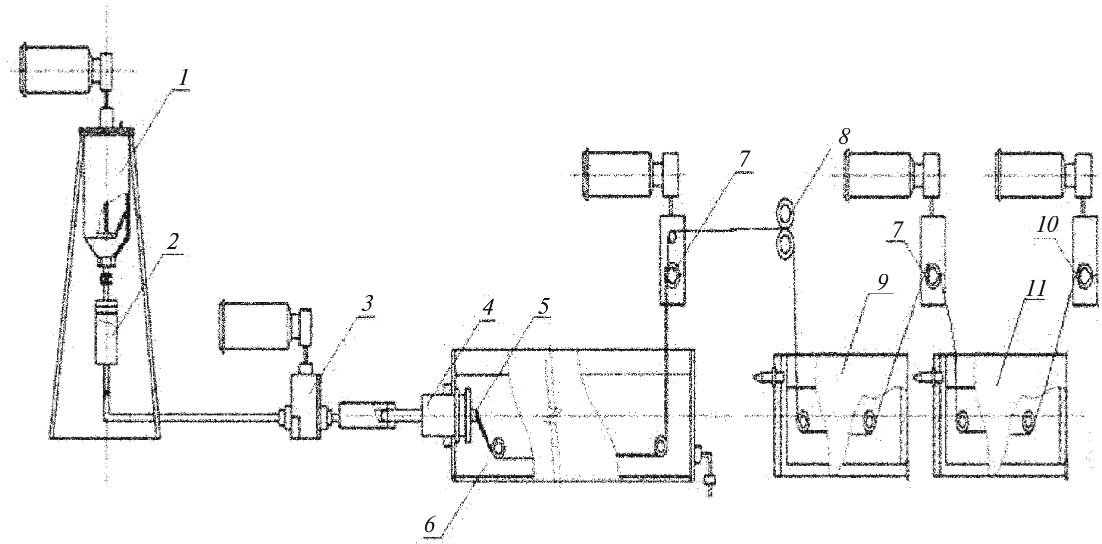

Fig. 1. Schematic layout of the experimental line for producing PAN-CNT composite fibres: *1* – mixing tank, *2* – filter, *3* – spinning pump, *4* – spinneret assembly, *5* – spinneret, *6* – setting bath, *7* – pulling rolls, *8* – guide rollers, *9* – two successive rinsing baths, *10* – winding device, and *11* – three successive plasticization pulling baths.

Table 1. Influence of Polymer Concentration in Spinning Solution on Fibre Formation

PAN concentration in solution, wt. %	Spinning characteristics
20	Fibre breakup in spinneret 5 min after start of spinning, gelling of solution in spinning pump
18	Fibre breakup in spinneret 10 min after start of spinning, solution passes through spinneret holes with difficulty
17	Frequent breakups of individual filaments, a lot of spinneret wastes is formed
16	Stable spinning, rare filament breakups
15	Stable spinning, prolonged polymer coagulation in setting bath, "glued" thread, difficult to separate filaments from one another

Table 2. Influence of Carbon Nanotube Concentration on Fibre Formation

CNT concentration in polymer, wt. %	Spinning characteristics
0.1	Stable spinning, no breaks, light-gray fibre
0.2	Ditto
0.4	Stable spinning, no breaks, gray fibre
0.8	Ditto
1.2	Periodic breaks of individual filaments, dark-gray fibre
1.6	Partial breaks, clogging of spinnerets, dark-gray fibre

spinning solution feed rate 3 cm^3/min, setting bath composition – DMF to water ratio 60:40, and setting bath temperature 10-15°C.

The recommended PAN concentration in DMF for further experiments is 16% because at this polymer concentration in the solution the thread bundle is found to be stable right until winding on spool. Individual filaments can be easily separated from the bundle, which indicates complete coagulation of the polymer in the setting bath.

The fibres formed from 16% solution were rinsed, dried, and their physicomechanical properties were investigated. The experiments demonstrated that the strength of the formed fibres lies in the 50-55 cN/tex range.

In the second stage of the studies, the influence of carbon nanotube (CNT) concentration in the spinning solution on the stability of complex thread formation was determined. The CNT concentration was varied within 0.1-1.6 wt. % with respect to the polymer. The formation conditions were the following: spinning solution concentration 16%, spinning

Table 3. Influence of Plasticization Pulling Frequency on Properties of PAN Threads

CNT-B concentration in polymer, wt. %	Pulling frequency	Strength, cN/tex	Breaking elongation, %
0	0	20.2 ± 3	8.0 ± 0.2
	2	24.1 ± 2	8.4 ± 0.3
	4	26.8 ± 4	8.3 ± 0.3
	8	30.7 ± 3	8.5 ± 0.1
0.2	0	27.6 ± 2	13.8 ± 0.4
	2	34.8 ± 6	14.6 ± 0.2
	4	35.2 ± 3	15.5 ± 0.3
	8	37.8 ± 3	16.0 ± 0.5
0.4	0	43.5 ± 5	16.3 ± 0.3
	2	50.4 ± 2	17.2 ± 0.5
	4	56.5 ± 4	18.0 ± 0.4
	8	59.1 ± 5	18.5 ± 0.7
0.8	0	44.2 ± 4	19.1 ± 0.4
	2	53.6 ± 6	19.7 ± 0.5
	4	59.5 ± 5	20.5 ± 0.8
	8	64.9 ± 7	21.8 ± 0.5

solution feed rate 3 cm^3/min, DMF to water ratio 60:40, formation rate 3 m/min, without pulling. The experimental results are cited in Table 2.

The studies demonstrated that in the 0.1-0.8 CNT concentration range spinning is stable without breakups. Further increase in CNT concentration in the spinning solution causes partial filament breakups, which may arise from clogging of spinneret holes due to agglomeration of nanotubes or discontinuity of polymer jets on account of detachment from CNT particles.

In order assess the influence of plasticization pulling on the properties of complex PAN threads, the rate of feeding freshly formed thread into the plsticization bath and the rate of thread spooling were varied. The pulling frequency is a quantity that characterizes the difference between the feeding and spooling rates. The experimental results are furnished in Table 3.

The studies conducted demonstrated that increase in CNT concentration in the polymer enhances thread strength even without plasticization pulling; with addition of 0.8% CNT, this parameter rises by 1.5 times (from 44.2 to 64.9 cN/tex) compared to unfilled sample. Also clearly evident is the fact that the pulling frequency enhances strength properties of fibres regardless of the quantity of filler added. Note that the maximum breaking stress is observed when the quantity of CNT added is 0.8% and the pulling frequency is 8. The breaking elongation of the fibres increases with increase in pulling frequency and CNT content in the samples, and the latter may indicate some plasticizing effect of CNT on the polymer.

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