

# Development of fibrous materials for shielding of electromagnetic radiation

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**Abstract.** To analyze the possibility of creating polyacrylonitrile fibrous materials modified with carbon nanomaterials (CNM), the effect of CNM on the process of synthesis of a copolymer of acrylonitrile (AN), methyl acrylate (MA) and 2-acrylamide-2-methylpropane sulfonic acid (AMPS) in dimethylformamide (DMF) was studied. The deterioration of the kinetic characteristics of the process and the molecular mass properties of the obtained copolymer is established. The rheological properties of solutions of poly [AN-co-MA-co-AMPS] in DMF containing CNM were investigated. The effect of CNM on the spinning capacity of AN copolymer spinning solutions, the ability of the spun fibers to plasticization stretching and thermo-orientation one, as well as the physico-mechanical properties of the obtained fibers is shown.

## 1. Introduction

At present materials (including textile ones) with electrophysical properties that allow to screen electromagnetic radiation are of great interest. Screening of electromagnetic fields is an urgent task of protecting health, information security, electromagnetic compatibility and electromagnetic ecology of living quarters, protecting premises for servers and / or electronic equipment.

Materials, coatings, structures perform the function of shielding electromagnetic radiation, mainly due to its reflection. If radiation is reflected almost completely from metallic materials, only about 80% of the energy is reflected from the screens of conductive polymer materials, and 20% is absorbed. The ability of a medium to absorb electromagnetic radiation is determined by its electrical and magnetic properties which include specific electrical conductivity, dielectric and magnetic permeabilities [1].

At present for shielding electromagnetic radiation by means of reflection and absorption of electromagnetic energy the following items are used:

- polymeric materials with electrically conductive and magnetic components;
- polymeric electrically conductive coatings;
- structures using reflective and absorbing electromagnetic radiation of polymeric materials and coatings.



The necessary effect can be achieved by various methods. One of them is to introduce electrically conductive fillers such as carbon materials (carbon black, graphite, soot, fullerenes, carbon fibers and their various textile forms (yarns, strands, fabrics, tapes)) into the polymer base. Fibrous materials are being widely used to develop products with radio-absorbing and radio-shielding properties. When designing and manufacturing screens from fibrous materials, high technological efficiency of such products is an undoubted advantage, which, together with high productivity of modern textile equipment and relatively low cost of both raw materials and production process, makes the use of fabrics or knitted fabrics promising to create flexible screen designs and absorbers of electromagnetic radiation [2].

The use of carbon black in the form of soot is due to high dispersity of such materials. Electrically conductive carbon black can be represented as a substance formed from separate blocks. The smallest blocks are carbon particles in the form of microspheres with a diameter of approximately 30 nm, formed by layers of carbon atoms. They can be either whole or hollow. A large number of carbon particles forms the primary aggregates responsible for the structure of the substance. Their size varies from 100 to 1000 nm. Increasing the degree of filling leads to a sharp decrease in electrical resistance. However, at certain filling levels, the conductive network is saturated and further soot filling practically does not affect the electrical conductivity. As the particle sizes are reduced (down to nanoscale), their content in the compositions decreases to achieve the required level of electrical conductivity. In this connection, it is promising to use carbon nanomaterials (fulleroid multilayer carbon nanoparticles, carbon nanotubes, nanofibres, etc.) in radio absorbing materials [1].

## 2. Materials and methods

Carbon nanotubes (CNT) and technical carbon (TC) were used as additives in the study. Carbon nanotubes consisted of nanocones with a diameter of 10 to 60 nm, connected in chains up to 1000 nm in length. Technical carbon contained up to 50 % of particles 30-60 nm in size, had an average particle size of 30-35 nm and had a specific adsorption surface of  $84 \pm 4 \text{ m}^2/\text{g}$ . The structure of the TC was of spherical formations, presented by graphene layers as a "cabbage head".

Two methods were considered for the preparation of polyacrylonitrile fibers modified with carbon nanomaterials (CNM):

- introduction of highly disperse carbon additives at the stage of synthesis of the fiber-forming copolymer of acrylonitrile (AN), methyl acrylate (MA) and 2-acrylamide-2-methylpropane sulfonic acid (AMPS);
- introduction of additives into the spinning polymer solution.

Synthesis of model copolymers of AN was carried out by the homophase free-radical synthesis method under conditions simulating a standard production process for obtaining in the reactor an ideal mixing of a continuous type of fiber-forming copolymer in dimethylformamide (DMF). The reaction mixture contained 90 % AN, 9 % MA and 1% AMPS (based on the weight of the monomers). As the initiator of free radical synthesis, azobisisobutyronitrile (AIBN) was used. As the CNM, TC was used, which was introduced into the reaction mixture after preliminary dispersion into DMF by ultrasonic action with a frequency of 22 and 44 kHz. The synthesis temperature was 70 °C and 80 °C. Dynamics of the synthesis of poly [AN-co-MA-co-AMPS] was estimated by the gravimetric method. The molecular weight characteristics of the polymer samples obtained were evaluated by the viscometric method.

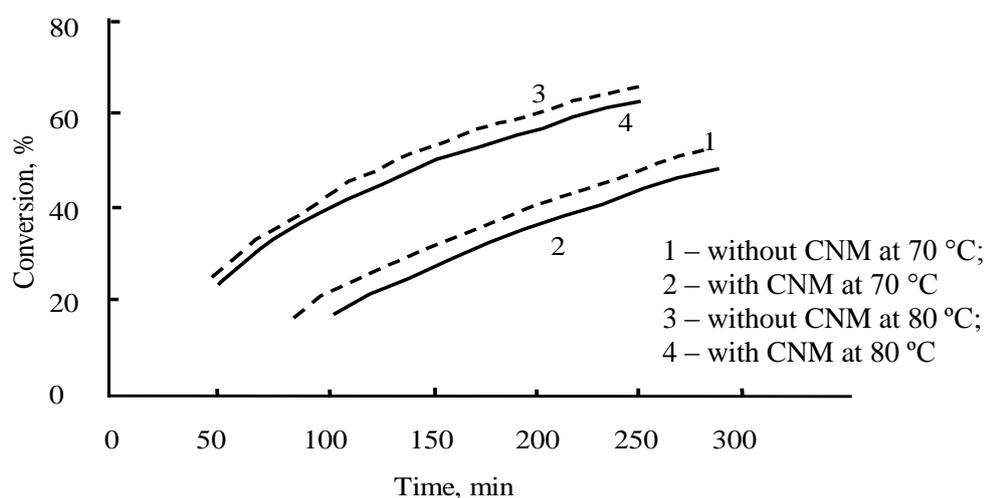
To assess the effect of the content of carbon additives of different morphology on the physico-mechanical properties of fibrous materials, model fibers were obtained by wet-molding from solutions in DMF. For this purpose, a specially developed laboratory pilot plant was used, which allows modeling various production processes for obtaining fibers and threads and studying the influence of various technological factors on the properties of finished fibrous materials. Spinning solutions were prepared on the basis of poly [AN (90%) -co-MA (9%) -co-AMPS (1%)]. The polymer content in the spinning solution was 21%. The path length of the fiber in the precipitation bath was 0.9 m, the temperature of the precipitation bath being about 12 °C. The precipitation bath consisted of 55 % (by weight) of DMF and 45 % (by weight) of water. Further, the fibers were stretched in a plasticizer bath, dried and stretched again. The plasticizing stretching temperature in a 5% aqueous solution of DMF was 95 °C.

The drying temperature and subsequent thermal orientation stretching of the fibers was 95 and 135 °C, respectively. As a result, at each stage of the technological process, fiber samples were obtained, which made it possible to evaluate the effect of highly dispersed carbon additives on the formation of the structure and properties of modified fibers. The tensile deformability, strength, elongation at break of model fibers were determined. The evaluation of the physico-mechanical properties of the fiber was carried out in accordance with the current standards. The spin-purity of solutions of poly [AN-co-MA-co-AMPS] in DMF was evaluated by determining the maximum rate of reception of fiber on the take-up tray from the precipitation bath before fiber breakage.

### 3. Results and discussion

From a practical point of view, the introduction of carbon modifiers into the fiber-forming polymer at the stage of synthesis could reduce the number of technological operations, and possibly increase the degree of its dispersion, stability and uniformity of the suspension. To assess this possibility, the synthesis of fiber-forming copolymers of AN with the introduction of CNM into the initial reaction medium was studied. The results of the study of the effect of (CNM) on the dynamics of the copolymerization of AN, MA, and AMPS in DMF are presented in figure 1. The quantitative analysis of the kinetic parameters of the synthesis of poly [AN-co-MA-co-AMPS] is shown in table 1.

The experimental data characterizing the dynamics of synthesis (figure 1) indicate, first of all, the extensification of the process of obtaining fiber-forming poly [AN-co-MA-co-AMPS] in the presence of CNM at all the synthesis temperatures. Based on the data of table 1, the extensification of the synthesis process is observed, primarily, as a result of an increase in the duration of the induction period of the polymerization process in the presence of CNM. Simultaneously, there is a slight decrease in the rate and its temperature dependence, as well as the overall conversion of monomers in the presence of CNM in the reaction mixture. The possible reason for the negative effect of CNM on the synthesis of poly [AN-co-MA-co-AMPS] can be that the CNM with its graphene (polynuclear aromatic) structure can act as a "trap" of free-radical particles generated as a result of the initiator decay, which reduces the efficiency of initiation.



**Figure 1.** Dynamics of the synthesis of poly[AN-co-MA-co-AMPS].

This assumption is confirmed by the results of studying the rheological properties of dilute solutions of poly [AN-co-MA-co-AMPS] samples synthesized in DMF. Thus, from the data presented in table 1, it follows that in the presence of CNM in the reaction mixture, a significant increase in such an index of the molecular weight characteristics of the polymer as the intrinsic viscosity is observed. This may be the reason that the effective concentration of free radicals in solution in the presence of CNM

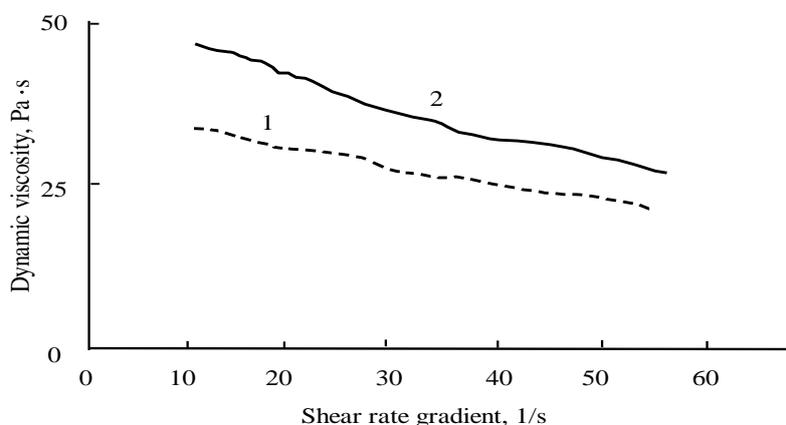
decreases, and the trapped by CNM radicals may be the cause of the formation of branched macromolecular structures. Such structures should contain particles of CNM at the branch nodes. The significant growth of molecular weight and the presence of branched macromolecular formations make it difficult to process the polymer into fiber and do not provide the possibility of obtaining fibers of the required quality.

**Table 1.** Kinetic parameters of synthesis of poly[AN-co-MA-co-AMPS].

Indicator	without CNM		in the presence of CNM	
	70 °C	80 °C	70 °C	80 °C
Induction period, min	19,6	7,4	40,9	13,6
Copolymerization rate, mol·dm <sup>-3</sup> ·s <sup>-1</sup>	3,23·10 <sup>-4</sup>	1,21·10 <sup>-3</sup>	3,11·10 <sup>-4</sup>	1,10·10 <sup>-3</sup>
Conversion of monomers over 300 min, %	57	64	54	60
Apparent activation energy, kJ/mol	140		120	
Characteristic viscosity, dl/g	0,91	0,76	2,43	1,81

One of the methods for modifying fibers with highly disperse materials is to introduce them into the spinning solution at the stage of preparation of the latter. However, the high tendency of CNM to self-agglomeration is a significant difficulty for their dispersion and reduces the stability of their dispersion. In this paper, this problem was solved in a complex manner by gradually increasing the viscosity of the concentrated dispersion of CNM in DMF. To this purpose the dispersion of CNM in DMF was subjected to alternate long-term action of ultrasonic oscillations of different frequencies, which was accompanied by the introduction of poly [AN-co-MA-co-AMPS] into the slurry of the CNM. The obtained CNM dispersion concentrate (CCNM) containing a certain amount of polymer was used to prepare spinning solutions intended for obtaining fibers with a specified content of CNM. The results of systematic microscopy of films cast from CCNM confirmed the high degree of dispersion of CNM in CCNM and the stability of this dispersion.

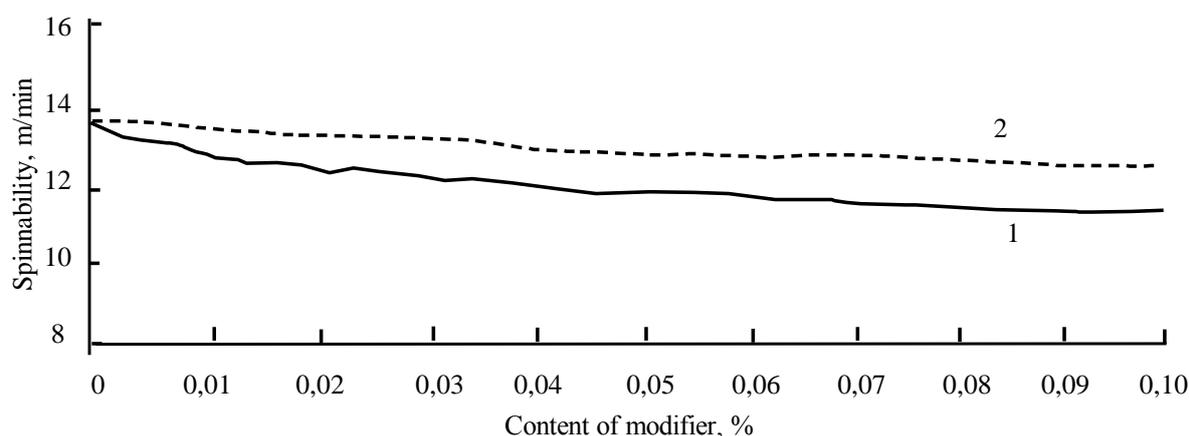
In preparing spinning solutions for the production of fibers modified with CNM, a significant increase in viscosity and anomalies in the rheological behavior of the spinning liquid was observed even when small amounts of additives were introduced (figure 2). This fact is very important, since it leads to high shear stresses during extrusion through the holes of the spinnerets and changes the behavior of the spinning-liquid jet drawn in the spin bath during fiber spinning.



**Figure 2.** Rheograms of solutions of poly [AN-co-MA-co-AMPS] in DMF at 20 °C without CNM (1) and with 0.1 % of CNM (by weight of polymer) (2).

An increase in the content of CNM leads to a decrease in the ability of the jet of the spinning liquid to deform the stretching (figure 3). However, when the content of the modifier in the spinning solution was up to 0.1 % (by weight of the polymer), no disturbance in the filament stability was observed. Reduction of spinnability when introducing a modifier appears is due to the fact that with an increase in the number of particles of CNM and in their total surface area, the proportion of the polymer phase to which the filler effect extends increases. As a rule, the near-surface phase has a high packing density of polymer macromolecules, which reduces its ability for high viscous-flowing and highly elastic deformations. This is most revealed when the spinning liquid of a CNT is modified. It can be explained by much higher anisotropy of the CNT form, compared with the spherical particles of the TC. On the one hand, this creates more hydrodynamic resistance for deformation, and on the other hand, it also significantly increases the contact area between CNT particles and the total energy of their interaction with the polymer phase in the spinning liquid.

Despite the decrease in the spinnability of solutions of poly[AN-co-MA-co-AMPS] in DMF as the content of CNM increases and when the morphology of the carbon modifier is varied, practically there was no revealed the effect of these factors (table 2) on the maximum possible values of drawing ratio and basic physico-mechanical properties of fibers even with an increase in the content of CNM in the fiber to 1 %.



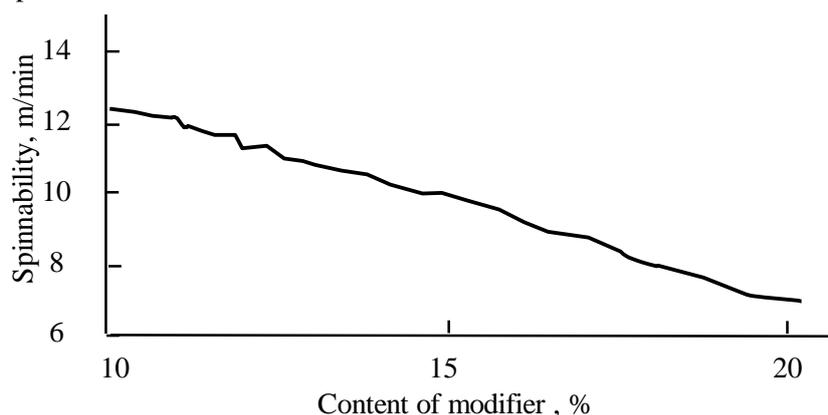
**Figure 3.** Spinnability of solutions of poly [AN-co-MA-co-AMPS] in DMF with CNT (1) and TC (2).

**Table 2.** Parameters for the production of modified fibers and their physical and mechanical properties of fibers.

Indicator	Modifier				
	CNT	TC	CNT	TC	
	Content of CNM,% of polymer				
	0,1		1,0		
	<i>Maximum fold of drawing, times</i>				
plasticization drawing	9,0±0,3	8,8±0,3	8,9±0,3	no data	no data
thermal orientation drawing	2,2±0,2	2,2±0,2	2,2±0,2	no data	no data
	<i>Plasticization drawing by 5 times</i>				
Specific breaking load of fiber, cN / tex	38±2	44±2	43±2	45±2	44±2
Elongation at break,%	19,8±1	22,0±1	21,8±1	21,9±1	21,7±1
	<i>Plasticization drawing by 5 times, thermal orientation drawing by 2 times</i>				
Specific breaking load of fiber, cN / tex	68±3	75±3	72±3	77±3	73±3
Elongation at break,%	14,3±0,5	13,9±0,5	13,5±0,5	13,6±0,5	13,4±0,5
Fiber color	white	light-gray		dark-gray	

At the same time, in order to make fibrous materials capable of shielding electromagnetic radiation, it is necessary to create conditions for having at least tunnel electrical conductivity. This requires the introduction of a larger amount of CNM into the polymer base.

Analysis of the possibility of increasing the content of carbon filler in the spinning solution by the example of the use of TC revealed the possibility of increasing this parameter to 15-20 %. In this case, the shrinkage of the filaments formed in the precipitation bath is substantially reduced, as well as spinning (figure 4) and drawing ratio of the fiber. The properties of such fibrous materials will be presented in other papers.



**Figure 4.** Influence of the TC content in the fiber on the spinner.

#### 4. Conclusions

The study of the possibility of modifying fibers obtained from solutions of poly[AN-co-MA-co-AMPS] in DMF with the addition of CNM, with a view to further developing of the technology for the production of textile materials for shielding electromagnetic radiation, showed:

- the introduction of CNM into the polymer structure of the fiber at the stage of obtaining fiber-forming copolymers of AN by the method of free radical synthesis is not technologically advisable, since it substantially extensifies this process and impairs the technological characteristics of the fiber-forming copolymer;
- modification of the fiber by CNM is more expedient to carry out by dispersion in spinning liquids;
- the most effective way of dispersion of CNM in liquids is ultrasound treatment;
- the effective viscosity and anomaly of the viscous properties of spinning solutions containing CNM in the investigated range of the shear rate gradient and the shear stress are much higher as compared with unmodified solutions;
- the introduction of up to 1 % (by mass) carbon materials of nanometric sizes into the fiber and their morphology do not significantly affect the plasticization and thermo-orientation stretching of modified polyacrylonitrile fibers, as well as their specific tensile load and elongation at break.
- the maximum possible content of CNM in a fiber is actually limited by the spinnability of solutions of polymers, while the physico-mechanical properties of the fibers are also reduced.

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