

CHEMISTRY AND TECHNOLOGY OF CHEMICAL FIBERS

PROSPECTS FOR PREPARING NANOCOMPOSITE TEXTILE YARN (REVIEW)

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Prerequisites based on experience with using a polymer concentrate (masterbatch) and providing scientific and technical information were presented and applied to the preparation of nanocomposite polyester textile yarns, which are some of the basic types of textile raw material. One of the main scientific and practical problems was considered to be the development and validation of high-tech and available nanoscale additives in the masterbatch, in particular, carbon nanopigments, nanoclays, and TiO₂ nanoparticles, using special dispersants that prevented agglomeration of the nanoparticles added to the melt.

Novel materials prepared using nanotechnology methods are being used more and more widely in various areas of science and technology. Despite the paucity of publications, developments along these lines are also beginning to affect the production of chemical fibers, where the preparation of yarns and materials based on them with fundamentally novel functional properties due to modification by nanoscale additives was predicted [1-4]. It was expected that the creation of nanocomposite textile yarns, primarily polyesters based on polyethyleneterephthalate (PETP), which are very important types of textile raw material, would prompt new opportunities for their development [1].

The promise of the developments involves the fact that the properties of a substance undergo radical changes in the nanometer range (1-100 nm) and are closely tied to the surface physics of the particles added to it [1-4]. This applies to nanoparticles or nanoclusters (compounds of pure elements, e.g., atoms, ions, molecules, and ultradispersed particles that have thread-like, plate-like, spherical, tubular, or other shapes and are considered independent units) with ordered structures and dimensions comparable with those of the polymer structures [3, 4]. Nanoparticles influence actively the structure and properties of the polymeric material owing to the exceedingly small sizes and high surface energy.

Nanotechnology includes two approaches [2-4], i.e., “top-down” and “bottom-up.” The top-down technology presupposes primarily addition of dispersed nanoscale additives in order to change the properties of the polymeric system [1-4]. An example of such an approach is the creation of ultrastrong polymeric nanocomposites [3, 4]. This can also refer to, for example, the method for changing the yarn physical structure by varying the amount of orientation drawing that is used in practice [3] or the creation of nano-sized fibrillar-porous structure by crazing in adsorption-active media [5].

The bottom-up technology presupposes a change of polymer physical fine structure (molecular and supramolecular) in the nanometer range in order to improve the macroscopic properties. This was also implemented for the production of chemical fibers [3-10]. Examples of such approaches are technical methods for controlling the fibrillar structure by varying the nanoscale sizes and the structure of alternating amorphous and crystalline oriented portions during a change of chain length (molecular weight) and with drawing in several stages with a stepwise change of temperature and thermal relaxation taking into account the spectrum of relaxation times of the structure elements [7-10]. This enables the tensile and fatigue strength of polyester yarns to be increased significantly. It is noteworthy that the

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sizes of the structural elements combined into microfibrils have the following values for amorphous-crystalline PETP yarns. The statistical segment responsible for chain flexibility in amorphous sections is about 3 nm [7]; the length of amorphous sections, 5-6 nm; the length of crystallites, 7-8 nm with a diameter of 3-5 nm and a large period of 12-14 nm [9]. The modern area of creating liquid-crystalline (mesophase) structures from rigid-chain macromolecules through their self-ordering in the straightened state during spinning from the melt or a solution of polymer to produce ultrastrong yarns also represents bottom-up technology [3].

The arbitrariness of such division of polymer technology is obvious. In both instances, the polymeric system must be perturbed for processes according to bottom-up or top-down technology. This changes the process parameters for preparing yarn (e.g., by varying the molecular weight, temperature, and amount of orientation drawing [6, 8]).

Several methods for modifying the fiber structure on the molecular and supramolecular nanoscale (arbitrarily bottom-up) are used in technical practice. We will review the method of introducing nano-sized additives to the melt before spinning yarn (arbitrarily top-down), which is not yet used in domestic technical practice.

Herein we present the prerequisites and discuss the potential of using nanotechnology methods in the production of polyester textile yarns, the preparation methods of which could become fundamental for the development of similar yarns from other polymers. It is assumed that the most acceptable method for introducing nano-sized additives is to use them as polymer concentrates, i.e., a masterbatch (MB). From the viewpoint of consistency of properties and their functional lifetime, introducing nano-sized additives to the polymer mass is more effective [1] than surface treatment of textiles. However, these methods should certainly co-exist considering the broad areas of application. Surface application of nanolayers onto textiles is still used more frequently [4].

In our opinion, several scientific and practical problems must be solved in order to introduce nano-sized additives into the polymer mass using MB during the production of textile yarns. In particular, MB with well dispersed, technical, and cost-effective nano-sized additives must be developed and the expected changes of the yarn physicochemical and mechanical properties must also be predicted. The main problem, besides the commercial aspect, consists of the development of technical MB with nano-sized additives that would firstly not disrupt the yarn production process stability and be safe and, secondly, impart fundamentally new properties to the yarns [1]. Such MB do not yet exist on the Russian market although there is certainly interest in them.

It is noteworthy that the method for adding polymeric concentrates (MB) to the main melt that was developed several decades ago continues to be elaborated and improved. The gamut of dyes and other functional additives, e.g., soluble dyes, luminophores, optical bleaches, pigments, TiO_2 , antipyrenes, and antimicrobial and antistatic additives, is expanding. Special apparatuses for gravimetric dosing of MB by mixing it with the main granules are already widely used in foreign and domestic practice. In several instances, side extruders for dosing MB melt into the main polymer melt are used. Two injectors are used on new apparatuses in order to facilitate introduction of two different additives, e.g., a dye and a functional additive. The equipment at several domestic plants for producing polyester textile yarns includes injectors for introducing MB that, in our opinion, can be used technically to introduce MB with nano-sized additives and for research in this area.

Below we present literature examples of the problem of introducing into fibers various nano-sized additives that attest to the urgency and prospects of developing this area.

According to Sezen [1], who represents the famous company Cortex, the use of MB with nano-sized functional additives that change radically the polymer properties is currently not nearly the main area for developing a variety of polyester textile yarns. He considered such additives to be, in particular, nanoparticles with Ag and Zn ions in addition to oxides such as TiO_2 , CuO, ZnO, and SiO_2 . Additives such as modified nanoclays, nanoceramics, and carbon nanotubes were also highly interesting [1]. He also paid attention to the preparation of MB, in particular, the need for surface treatment of the nanoparticles in order to prevent their agglomeration and achieve the required effect. Sezen thought justifiably that the relationships among the polymer properties, nano-sized additive dispersions, viscosity, melt behavior, fiber-forming stability, and final yarn properties should be established empirically.

Research on the introduction of nano-sized additives of metal oxides (TiO_2 , Al_2O_3 , ZnO, MgO) in order to produce fibers with photocatalytic activity, UV protection, antimicrobial properties, electrical conductivity, dirt-repellant properties, and wear resistance was also reported [2].

Serkov and Radishevskii discussed aspects of the use of nanotechnology for the production of chemical fibers [3]. Special attention was paid to new carbon compounds, i.e., fullerenes and nanotubes, that were discovered in recent

decades and to their possible introduction into fibers. Fullerenes are spherical carbon clusters consisting primarily of six-membered carbon rings. Nanotubes, hollow fibers of diameter 2.5-30 nm and length 2-5 μm , have been more widely developed. Both structures are produced by vaporizing carbon and precipitating it on graphite electrodes by using an electric arc. The carbon-carbon bonds in planes of ordinary graphite are the strongest of all chemical bonds. However, the interplane bonds (van-der-Waals forces) are weak. Therefore, graphite layers can slide relative to each other. The graphite base planes in nanotubes are concentric closed structures. This makes the nanotubes exceptionally rigid and strong and enables them to be used to fabricate special and especially responsive composites. According to the literature [3], the use of nanotube additives in various areas, including in chemical fiber technology, is of great scientific and practical interest. Fibers filled with nanotubes are 6 times stronger than steel and 100 times lighter than it [2, 4]. Also, electrically conductive fibers can be prepared.

Issues of nanotechnology as applied to fibers, textiles, and the coloring process, e.g., the use of thermotropic and phototropic dyes for “smart” textiles that change color depending on the temperature and illumination, were discussed in detail in the monograph of Krichevskii [4]. It was emphasized that the polymer yarn became a nanocomposite upon adding the nano-sized additive (polymer + nano-sized additive = nanocomposite). It is important to note that the term nano-sized additives means, as already mentioned, additives with particles sizes 1-100 nm, i.e., with an upper limit of 100 nm. The total particle surface area and, correspondingly, their surface energy and activity increase sharply for such small dimensions. This affects the system structure formation and properties. Carbon nanotubes and especially the more available mineral clays of plate-like structure were considered to be promising nano-sized additives for fibers. Introduction of them into the melt could radically change the mechanical properties of the chemical fibers and their thermal and fire resistance.

Important information that the Japanese company Toyota still uses nanocomposite yarns with nano-sized additives of aluminosilicates (Al_2O_3 and SiO_2 , the principal part of clays, corundum, and kaolin) for the production of nylon automobile safety belts in order to improve their operational properties was published [4]. For this, nanolayers of clay about 1-nm thick can be dispersed well in the fiber polymer matrix. The polymer-nanoclay-nanocomposite technology is very simple and inexpensive. Montmorillonite clays, fine-grained sedimentary rocks that are dusty when dry and plastic when moist, are used more often than not. Addition of them to polymeric matrices of nano-sized TiO_2 can increase the protection of fibers and textiles from the action of UV light because of its photoactivity and also the fire resistance, improve the antiseptic properties, and produce self-cleaning textiles. For this, TiO_2 with well dispersed nanoparticles must be obtained (it is noteworthy that TiO_2 of particle size $\sim 1 \mu\text{m}$ is now used to give a matte finish). Dispersed nano-sized carbon pigments could turn out to be exceedingly promising. The fact that an exceedingly small amount of nano-sized additives, approximately from one to several percent, was required for a radical change of properties was surprising [4].

It was reported [2] that fibers acquired electrical conductivity, fire-protection properties, and increased strength if they were filled with corundum. In particular, polyamide fibers containing 5% corundum nanoparticles had 40% greater tensile strength and 60% greater bending strength. For example, this was important for preparing hard hats. Reducing the size of the corundum particles to the nanoscale could enhance this effect. The possibility of using another type of clay, kaolin, as a nano-sized additive should also be evaluated. It is now used as a filler in polymer composites [11].

The creation of nanocomposite fibers is just beginning. Therefore, there are more questions than answers. Many scientific and technical aspects, in particular, the properties of nano-sized additives and how the primary and secondary amorphous-crystalline yarn structure is formed upon introducing nano-sized additives in high-speed spinning processes and orientation drawing must be studied in order to predict the properties. In our opinion, it would be advisable in the first stage at least to focus attention on the development and validation of the MB of the most available types of nano-sized additives, i.e., nanocarbons, nanoclays, and TiO_2 nanoparticles.

MB additives that are characterized mainly by micro-sized and not nano-sized particles are used in industrial practice. However, the use in production of, for example, soluble dyes or separate brands of black pigment with initial carbon particle sizes of 18-20 nm enable the discussion of an approach to nanocomposites, i.e., a transitional period from micro- to nano-sized MB active additives.

Let us address several technical features and prerequisites for designing studies on the preparation of nanocomposite yarns. We will briefly examine the properties of the MB and its behavior during yarn formation.

The basic requirement for a polymeric carrier of MB is known to be compatibility with PETP. Polybutyleneterephthalate (PBT) is usually used as the polymeric carrier, sometimes in combination with cheaper PETP with 30-40% added dye pigments and other additives. It is thought that PBT, which has a lower melting point than PETP, provides more facile melt processing. The use of dyes that are soluble in the polymer melt is relatively rare. Pigments are used more often than not. Apparently, this is due to the broader coloring and technical potential of pigments.

The preparation of MB with additives of pigments that are suitable for introducing into the melt during fiber spinning is a rather delicate and responsive process. They are prepared as follows. Pigments and polymeric carrier are ground to powders, dried, mixed (approximate ratio 60-70% polymeric carrier and 40-30% pigment), and fed in this form into a two-headed extruder where the polymeric carrier and additive are fused and stirred vigorously. This forms a homogeneous MB melt. After the extrusion, filaments of the MB melt are cooled in water and cut into granules of a given size (the evenness of the MB granule dimensions is important for subsequent accurate gravimetric dosing).

Next, MB granules pass a special filter test that consists of an evaluation of the dynamics of the melt pressure increase during passage through a calibrated sieve and filter. It is considered acceptable if the MB melt pressure increases by less than 0.1 bar/g. It is noteworthy that the filter-test value depends on the pigment particle size and its tendency to agglomerate. The finer the particles are, the greater their surface energy is and the greater the tendency to agglomerate. As already mentioned, several MB suppliers use initially nano-sized carbon particles (18-20 nm). However, their initial nanoscale size in the yarn cannot be maintained without treatment by a special dispersant that prevents them from agglomerating. The fact that carbon particles can agglomerate in the melt was proven in practice. For example, a filter with 20-25 μm openings became plugged during processing of the carbon particles. This depended mainly on the type of carbon and the MB production technology at different companies. Apparently, agglomerates could form during preparation of the polymer concentrate and during storage in the melt on the spinning machine. The possibility of establishing a dynamic equilibrium between agglomeration (coalescence) of carbon particles and their decomposition in the melt under the influence of shear stresses could be proposed.

Technical practice showed that even an insignificant change of the melt temperature and viscosity affected its ability to be filtered. The effectiveness of filtration increased (pressure after the filter decreased) if the temperature was lowered and the viscosity was increased for a melt colored with carbon. It was especially important that the particles did not coalesce at the moment of melt extrusion from the spinnerets in order to avoid plugging the spinneret openings and breaking the filaments. Modern spinning machines have dynamic (on the auger) and static (in the melt tube) homogenizers. Special spinneret assemblies with homogenization and fine filtration are used. These certainly reduce breakage and stabilize the spinning process. However, even enhanced homogenization cannot completely prevent particle agglomeration without treating them specially during MB preparation.

It is well known that several companies add pigments of particle size 0.1-0.2 μm , i.e., approaching nanoscale, in order to increase the coverage and deepness of the color during special sizing and selection of a disperser [4]. Therefore, it can be assumed that it will be possible in the near future to produce well dispersed nanoparticles, including carbon pigment.

As indicated above, introduced pigment particles in an actual technical process have microscale dimensions and can agglomerate. As a result, the spinning process can become unstable. The thickness of a spun standard elemental yarn is 15-20 μm . Therefore, the particle size should not exceed half the filament cross section [6] in order to avoid breaking it. This is especially important in preparing multi- and microfilament yarns with filament fineness of 10-12 μm and less, where the size of the added particles should not exceed 5 μm [6]. For example, particles of the matrix-forming agent, TiO_2 of about 1- μm size, do not cause difficulties in spinning if the particles do not coalesce. Coloring pigments should have about the same average size. The added dispersed particles should be reduced to nano-sized dimensions in order to stabilize the process and minimize the breakage. Thus, reducing the coloring and functional additives introduced into the melt to nanoscale sizes can turn out to be an effective method for increasing the technology level of preparing nanocomposite yarns.

What is the possible interaction mechanism of nano- and microparticles with the polymer? As indicated, nanoparticles are commensurate with the dimensions of the polymer structural elements. Therefore, their interaction can in principle change the structural and mechanical properties of the produced fibers. Apparently, the nanoparticle sizes enable them to be incorporated into diffuse amorphous (intercrystallite) regions and interlayers of microfibrils (if the nanoparticle size is less than several nanometers) or to occupy interfibril space, forming joint structures with the polymer.

The question of whether nanoparticles can be incorporated into polymer crystallites or act as centers of fiber crystallization is exceedingly controversial [12]. Only if the nanoparticles are isomorphous with the polymer crystal unit cell can they be incorporated into crystallites. This is certainly a subject for special research. The mechanism could be different for microparticles. Because the size of the used microparticles, even 1-2 μm , is incommensurate with the size of the polymer fiber structural elements (recall that the total length of the amorphous and crystalline sections is 12-14 nm), these particles can probably occupy only the fiber interfibril space. Thus, on one hand, added microparticles cannot be polymer nucleation centers but, on the other, interphase layers involving the polymer can apparently be formed on the surface of these particles as a result of intermolecular adsorption interaction.

Microparticles in the melt have a different size and are situated randomly in the isotropic polymer matrix that is disoriented by thermal effects. As we already pointed out, microscopic additives can change their dimensions under the influence of melt layer shifts in the transverse flow velocity gradient field (dv/dr) until extrusion of the melt. The greater the transverse velocity gradient is, the better the homogenization is [6]. The transverse velocity gradient changes to a longitudinal velocity gradient (dv/dl) after the melt is extruded from the spinneret. The extruded filaments elongate and the chains are partially oriented in this field from the spinneret to the point of hardening. A primary structure appears. Local ordered oriented regions form in the amorphous poorly oriented matrix during high-speed spinning. These are responsible for the structure and properties of partially oriented yarn (POY) [6]. With this, microparticles can be situated between macromolecules of the amorphous matrix. A secondary oriented structure with alternating amorphous and crystalline regions combined into microfibrils arises with subsequent drawing or drawing with texturing of the yarn (DTY). Added microparticles can be situated between these. This affects the structural and mechanical properties of the yarn. The surface (frictional) properties of the yarns can change because of this. This is important to consider during production of DTY. It can be assumed that molecules of soluble dyes can penetrate into amorphous regions, thereby weakening the interaction between chain sections. Apparently, nano-sized additives can also interact with the polymeric matrix in the same manner. However, interaction of a different nature is also possible.

We published previously preliminary results of research on the effect of coloring pigment additives with micron-sized particles added to MB on the processing and properties of polyester yarns [12]. Unfortunately, there are no other publications in the literature although work in this area is most probably being conducted. It should be noted that this study area, which is related to the nature of the interaction and effect on fiber structure formation of pigment particle additives, is a poorly studied topic of theory and technology, despite the lengthy practice of using MB for mass coloring. Only the influence of polymer concentrate additives on the technical process and the properties of polyester yarns were reported [12]. This concerned the decrease of melt viscosity and forced reduction of spinning temperature in addition to a change of the bending and strength properties of spun POY and their structural changes detected from the sample melting point. The load–stretch plot presented before [12] showed that the bending properties of polyester POY spun with various dyes differed significantly. First, the forced elasticity limit decreased upon adding dyes. Second, the length and shape of the neck growth region changed in the neck-spinning zone. The change of bending properties was undoubtedly related to the influence of coloring additives on structure formation [12]. Values of the heat of fusion of uncolored and colored POY samples are given below and were obtained by differential scanning calorimetry:

Color	MB additive, %	ΔH , kJ/kg
Uncolored	–	43
Black	3.3	49.5
Red	4.0	62
Blue	3.5	50

It can be seen that the heats of fusion of colored POY samples increased relative to that of the uncolored sample although to different extents depending on the pigment type and concentration. Apparently, this was due to increased crystallinity due to an increase of the array of crystalline structures and the creation of interphase ordered polymer–pigment structures, i.e., an increase of system polymorphism. Special physicochemical research is needed for a more detailed discussion.

Previous work [12] demonstrated the effect of physical modification of polyester yarns with very small additives of pigments with micron-sized particles. Only 1-1.5% of coloring pigments (3-4% of MB containing about 30% pigment to PETP melt) with MB was added to the spun polymer. Apparently, the effect of nano-sized additives will be considerably enhanced and, possibly, have a different nature. In our opinion, the results obtained in this stage can serve as scientific

and practical prerequisites and a basis for further technical research and studies on the production of nanocomposite textile yarns by introducing nano-sized additives. Modern analytical instruments can be used to estimate the sizes of nanoparticles in MB granules and yarn [1, 13].

We reviewed the production aspects of nanocomposite textile yarns, allowing the discussion of several issues related to the initial development stage of this area of chemical fiber technology.

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