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Functional Materials for Construction Application Based on Classical and Nano Composites: Production and Properties

Aleksandr Evhenovych Kolosov and
Elena Petryvna Kolosova

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Abstract

At the present stage of polymeric material science, the physical and chemical modification of the surface of reinforcing fibers and liquid polymer binder is the basic direction in the development of functional polymeric composite materials (PCMs) for structural purposes. In this chapter, various aspects of the physical and chemical modification of the components of reactoplastic materials of structural design on the basis of classical and nano-modified (NM) PCMs are analyzed. The choice of the most effective types of carbon nanofillers for creating functional PCMs is exemplified by the example of carbon plastics. The main emphasis is made on ultrasonic processing as the dominant method of physical modification when obtaining PCMs. It is shown that such a physical modification is aimed at the intensification of many technological operations for the production of such materials, as well as at improving the physico-mechanical and operational characteristics of the resulting products and structures on their basis. The questions of designing the technological process for the production of functional classical and NM PCMs are briefly analyzed. The aspects of creation of NM carbonocomposites in which a continuous carbon fiber is combined with a binder in the volume of which the ultradisperse carbon nanoparticles are evenly distributed are considered. The prospects of production of functional hybrid PCMs based on reinforcing fabric with NM filler are shown. Features of obtaining functional NM carbono-composites with improved physico-mechanical and operational properties, in particular, with increased strength, electrical conductivity and crack resistance are described.

Keywords: reactoplast, functionality, production, carbon, nanotube, modification, hybrid, strength, electrical conductivity, crack resistance

1. Introduction

Polymeric composite materials (PCMs), combining low density, high elasticity modulus and strength, are now widely used in various fields of industry: aircraft building, automotive industry, construction, sports industry, medicine, etc. Modification of the surface of the reinforcing fiber and liquid polymer binder (PB) to improve the physico-mechanical and operational properties of the resulting classical PCMs and nano-modified (NM) PCMs is an actual task of polymer materials science [1, 2].

This task is realized both as a complex as well as separately by various methods of modification: physical—in the form of ultrasonic (US), chemical and combined physical and chemical. The aspects of designing the technological process for the production of functional classical PCMs and NMPCMs of structural design on the basis of reactoplastics are no less relevant [3]. Moreover, exactly US treatment is the dominant method of physical modification, which is simultaneously aimed at the intensification of many technological operations for the production of such materials, as well as improving the physico-mechanical and operational characteristics of the products and structures obtained [4].

A number of studies are devoted to the issues of preparation, enhancement of physico-mechanical and operational properties and features of the use of functional reactoplastic NMPCMs. In particular, the directions in which NMPCMs production technology is developing, including economic aspects of implementing their formation nanotechnologies, were described [5]. Among a wide range of means used to produce NMPCMs, it is preferable to use technical means implementing the method of low-frequency US cavitation [6]. The advisability of such choice is primarily due to the need for a uniform (homogeneous) distribution of nanoparticles introduced into the liquid oligomer. At the same time, this process is actively hampered by the physico-chemical nature of the nanoparticles, which are characterized by high surface energy.

This, in turn, causes the mutual attraction of nanoparticles, which leads to their coalescence and aggregation upon incorporation into the liquid oligomer. It was shown that the conditions necessary to create functional nanomaterials are small size and a distribution of carbon nanofiller particles as uniform as possible in the liquid polymeric matrix [7]. The efficiency of introducing the nanoparticles into the liquid polymer medium depends on not only the dose but also the mixing parameters [8].

One of the options for improving the physical and mechanical properties of carbon PCMs is the creation of carbon plastics combined filling [9]. This is accomplished by modifying the surface of a continuous carbon fiber and a liquid PB. The chemical modification of the last one is carried out by incorporating and subsequent uniform distribution in the bulk of the liquid PB of ultradispersed carbon nanoparticles. As the latter, for example, fullerenes, astralenes, CNTs and others are used.

Thus, the above brief analysis shows that the most relevant areas of research in the field of polymer nanotechnology in relation to functional nanocomposites are, in particular, the following:

- selection of the most effective types of carbon nanofillers for the development of functional PCMs using the example of carbon plastics;

- determination of the optimal concentration of nanoparticles in the polymeric matrix;

- choice of effective methods for dispersing nanofillers during the production of functional NMPCMs based on reactoplastics;

- creation of carbon plastics combined filling;

- production of functional hybrid PCMs (HPCMs) based on reinforcing fabric with NM filler;

- production of functional NM carbonic composites with increased electrical conductivity and crack resistance.

The above aspects are briefly presented in this chapter.

2. Effective methods and means of physical modification

2.1. The method of ultrasonic modification of liquid polymeric media

As the dominant method of physical modification of liquid polymer media and reinforced classical PCMs and NMPSMs of functional purpose, US low-frequency cavitation is used in most cases. The main parameters of this action are the frequency, amplitude, intensity, pressure, temperature and volume of the liquid medium (PB) being treated. The set of interdependent optimal parameters of cavitation processing, as a rule, is set experimentally in each specific case.

In the optimum, the resulting set of parameters of US cavitation processing leads to an increase in the physico-mechanical and operational properties of solidified oligomers and reinforced PCMs based on them [10]. The amount of hardening depends on the particular type of oligomer to be processed and can vary from 40 to 50% for classical hardened reactoplastics or may increase for several times (depending on the type of nano-modifier used) as compared to the initial composite for NMPCMs [8, 11].

The influence of the developed modes of low-frequency US cavitation treatment on the operational properties of reactoplastic PCMs was investigated in comparison with the known methods. An effective range of interrelated processing parameters has been found [11]. The obtained experimental results confirmed the prospects of realization of such a modification of liquid oligomers by the example of epoxy oligomers (EOs) and epoxy compositions (ECs).

It was found that such a modification is effective not only in the low-frequency, but also in the mid-frequency US ranges, both individually and in combination [12]. Variable overpressure during the US treatment is also a promising method. In particular, this is confirmed by the results of molding epoxy couplings with shape memory effect. An increase in intensity and a reduction in time was also established, both for a separate operation of sonification the liquid polymeric composition and for the manufacture of the entire product as a whole [13].

2.2. Ultrasonic modification during production of reinforced polymeric composites

The purpose of using US modification of reinforced PCMs is to achieve a range of positive results upon completion of such a modification.

The first positive result is the US activation of the surface and the structure of the reinforcing fibrous macrofiller to improve its wettability of the liquid EC. The second positive result is the degassing of the structure of the reinforcing macrofiller immediately before it is impregnated. The third positive result is an increase in the productivity (not less than 2–2.5 times) of operations of sonification, impregnation, dosed application of liquid EC and winding while maintaining the stability of the properties of the final PCM.

Another positive result is the stabilization of the content of the PB in the impregnated woven filler, with variation in the speed of its stretching in the impregnation and dosing operations [14]. Finally, the effective parameters of US treatment contribute to increasing the deformation-strength and adhesion characteristics of PCMs, to lower the level of residual stresses, to increase the durability and to reduce the cumulative hardening time [15].

As a result of practical use of the methods of US cavitation processing, the designs of the impregnation, dosing and winding units on the serial impregnating and drying equipment were improved. The above mentioned results once again confirm the choice of US treatment as the main method of physical modification of liquid (including polymeric) media and reinforced fibrous PCMs of functional purpose at the main stages of their production.

Despite the existence of a huge range of US cavitation processing tools, the technical means used for US modification of liquid polymeric media and reinforcing fillers based on them can be conditionally divided into US concentrators, speed transformers and radiating plates.

US concentrators (dispersants) are effectively used primarily for processing liquid polymeric media, including when nanomodifiers are introduced into them. Radiation plates are used mainly for processing impregnated woven fibrous fillers up to 2000 mm wide.

Despite on the difference in the objects of application, for both of the above mentioned types of US technical means it is necessary to determine the effective design and technological parameters [16]. Otherwise, the appearance of defective areas of the resulting final PCMs (both classical and NM) is possible.

In this case, during the treatment of impregnated tissue, the US cavitators are based on piezoceramic transducers with a radiating plate that undergoes bending vibrations [17]. In addition, it is necessary to eliminate the non-uniformity of bending vibrations of radiating rectangular plates by calculation-experimental methods [16, 17]. Otherwise, there is a high probability of obtaining defective PCMs.

2.3. Designing the technological process of ultrasonic production of polymeric composites

The tasks of designing the technology and equipment for the production of classical PCMs and NM functional PCMs are aimed at identifying and studying the interrelations between

the structural, mechanical and geometric parameters of products, on the one hand, and the technological factors of their production, on the other. For example, obtained analytically kinetic equations of longitudinal and transverse impregnation of oriented and woven fibrous fillers with liquid PBs make it possible to predict the impregnation time and the speed of broaching the fibrous filler through the impregnating bath, and also to design its dimensions [18]. Design of the optimal tension force of impregnated fibrous fillers in circumferential winding allows the study of experimental results on the influence of technological impregnation regimes on the strength of impregnated and cured fibrous fillers [19, 20].

Moreover, in order to minimize material and time costs, as a rule, the methodology of structural and parametric modeling of design and technological parameters of technology and equipment (tools) for sonification of liquid polymeric media and for producing reactoplastic PCMs is used [3]. In turn, the geometric parameters of the model of oriented classical PCMs, which are considered as structurally inhomogeneous media, are the basis for designing technological manufacturing parameters and predicting the stress-strain state of solidified classical PCMs [21–23]. **Figure 1** shows an innovative scheme for producing of unidirectional reactoplastic classical PCMs and NMPCMs for functional purposes using low-frequency US treatment.

For example, the investigated traditional structural scheme for impregnation and dosing of a polymer (epoxy) binder on a long fibrous filler using US modification (**Figure 1**) can be conveniently divided into such separate structured blocks: I—the block for sonification the EO and preparing an impregnation EC based on it; II—the block of "free" impregnation of oriented (woven) fibrous filler with liquid EC; III—the block of dosed application of liquid EC to impregnated fibrous filler.

The main stages of innovative production of unidirectional reactoplastic PCMs for functional purposes using US are as follows (**Figure 1**). Prior to the impregnation step, US treatment of the epoxy resin in reservoir 17 is carried out using an US concentrator 16. The US concentrator 16 is connected to a magnetostrictive transducer 15, which is powered by an US generator 14 (block I in **Figure 1**). Depending on the selected geometry of the US concentrator 16, a certain value of the amplitude A and intensity I_o of the US vibrations introduced into the liquid epoxy resin is obtained at the output. In the case of preparing a NM EC, for example, CNTs are added thereto. Controlled parameters of US processing are: time τ, temperature T, amplitude A and intensity I_o.

After US treatment of the epoxy resin, a hardener of epoxy resin enters the reservoir 17 from reservoir 18. Here, the epoxy resin is mixed with its hardener with the same US concentrator for a few seconds, resulting in an impregnating composition. Next, the tap 19 is opened and the impregnating composition is fed to the bath 1. After this, the dry long fibrous material 4 is rolled up from the bobbin 5, which, after passing the enveloping roll 6, enters the bath 1, where it is impregnated with the liquid PB 2, which has already been treated with US (block II in **Figure 1**). In this case, several structural forms of the placement of long fibers in the cross section of the impregnated filler, which affect the kinetics of the impregnation process, are possible.

After exiting the impregnation bath 1, a preliminary uncontrolled application of the PB 2 to the long fibrous material 4 is provided. This material in the dosing zone (block III in **Figure 1**)
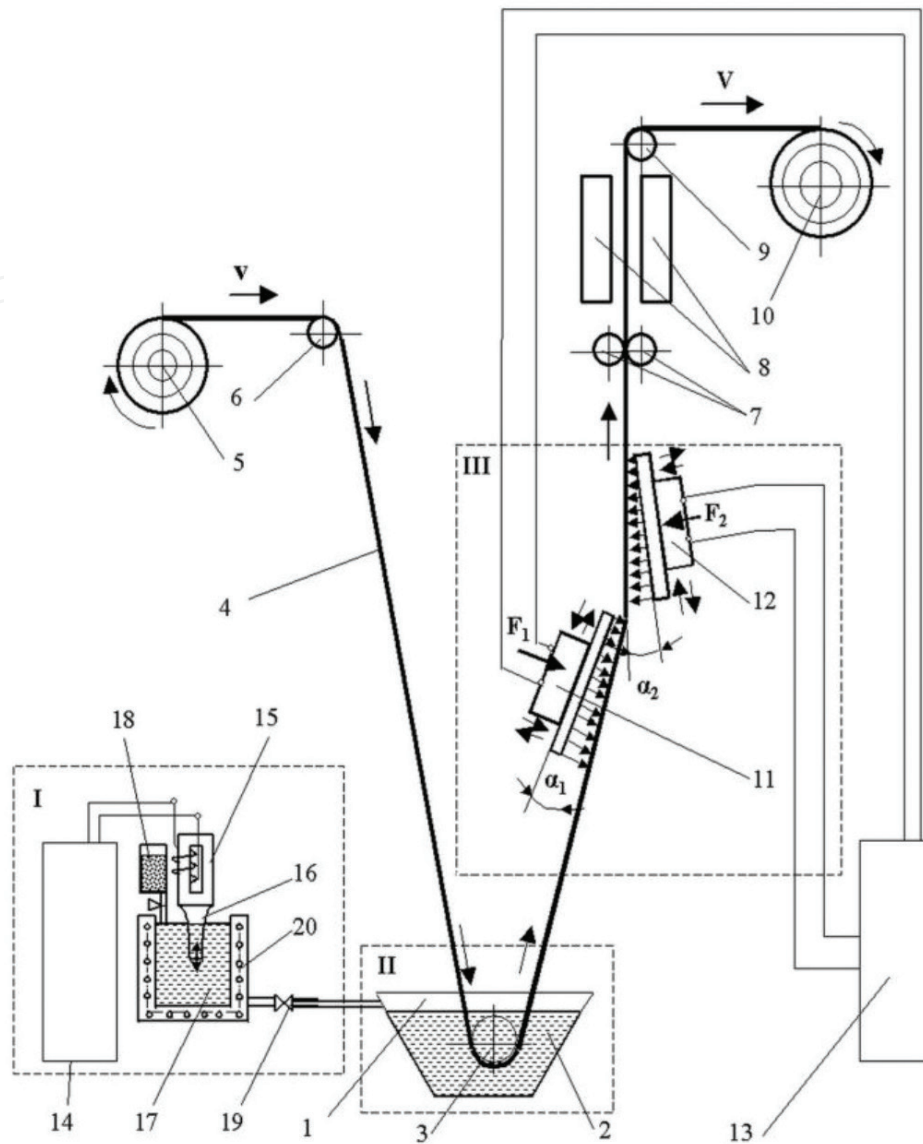
Figure 1. Scheme of impregnation and dosed deposition of PB on long-length fibrous material: 1—impregnating bath; 2—liquid PB; 3—envelope roll in impregnating bath; 4—long-measuring fibrous material; 5—bobbin with a dry fibrous material; 6, 9—enveloping rollers; 7—squeezing rollers; 8—drying chamber; 10—take-up bobbin; 11, 12—a pair of working US instruments (emitting US plates); 13, 14—US generators; 15—magnetostrictive transducer; 16—waveguide-concentrator US; 17—reservoir with epoxy resin; 18—reservoir with curing agent of epoxy resin; 19—the tap; 20—thermoregulating cell; F_1 and F_2 are the forces of pressing working tools 11 and 12 against the impregnated fibrous material; α_1 and α_2 are the slopes of the working tools 11 and 12 to the surface of the impregnated fibrous material; v—broaching speed.

is processed on both sides by US instruments in the form of US rectangular plates 11 and 12 emitting US having individual drives from the US generator 13. These plates 11 and 12 contact the material 4, which was impregnated and processed by the edge of the plate edge, with varying pressing forces F_1 and F_2, respectively. The US vibrations propagate both along the width and along the length of the plates 11 and 12. Moreover, the tools 11 and 12 are disposed with respect to each other along the length of the material 4, processed on both sides relative to it, and at different angles of inclination α_1 and α_2 to the plane of the material.

In turn, working US instruments 11 and 12 consist of several successively located structural elements of various shapes and sizes made of different materials.

Varying the content of the PB, uniformity of its distribution in the material, and removal of the excess PB are achieved by adjusting the angle of inclination α_1 and α_2 of the radiating plate to the surface of the material 4, by varying the power (intensity I_1 and I_2) applied to the transducers, and by dosing the pressing forces F_1 and F_2. The final spinning of the PB from the impregnated material is carried out by a means of squeezing the material made in the form of two rolls 7. The impregnated and squeezed material then enters the drying chamber 8, and after drying passes through the envelope roller 9 and is wound onto the take-up reel 10. When using the developed innovative technology and equipment, the dependence of the deposit on the speed of drawing the impregnated material is largely eliminated, as well as the degassing of the air from the structure of the impregnated material due to the contact US action.

Then, within the synthesis framework, only the above mentioned enlarged blocks I–III and their constituent structural elements are analyzed, as well as structural and technological interrelations between them. Implementation of the developed approaches to the use of effective US devices allows obtaining a wide range of practically defect-free classical PCMs and NM PCMs for functional purposes. Effective hardware for connection and repair of polyethylene pipelines using US modification and heat shrinking are studied in [24–28]. The epoxy-glue compositions and banding, fiberglass tape impregnated with epoxy compositions, thermistor couplings with shape memory and surface-treatment methods for polyethylene pipes are investigated. The results obtained in these studies are another example of the creation of functional materials for construction application based on classical reactoplastics and thermoplastics used in gas-pipeline repair.

3. Functionality of carbon plastics based on reactoplasts

A set of specific requirements to the constructional materials based on PCMs, which are used in highly loaded structural elements, are set [29, 30]. Among them are the simultaneous provision of high strength and rigidity; resistance to alternating dynamic loads; small mass; high long-term strength. No less important indicators are heat resistance and corrosion resistance, while ensuring a high degree of reliability of the designed construction as a whole. The above complex of requirements is satisfied, for example, by classical and NM PCMs in the form of carbon plastics based on thermoset (epoxy) matrices [31, 32].

For example, the spectrum of application of NMPCMs based on carbon fibers and HD modified with nanoparticles (CNTs) is highly loaded materials, products and structures intended primarily for use in chemical, shipbuilding, machine, engineering, building, aviation, rocket and aerospace and other industries [33–36]. The advantage of using carbon plastics in comparison with traditionally used metals, fiberglass and organic fibers, is that it provides increased compressive strength, high elasticity modulus and fatigue strength, low creep and dimensional stability of the molded article due to the low temperature coefficient of linear expansion. Not less important advantages are high indicators of chemical and radiation resistance,

as well as good workability (manufacturability) [37]. The above mentioned set of advantages also determines the advisability of processing carbon plastics on serial production equipment at low labor and energy costs.

It should be noted that in the CIS countries, a wide range of unidirectional structural carbon plastics for functional purposes was created (**Table 1**) [9, 31, 32].

In the CIS countries, aircraft component parts and units are usually manufactured by an autoclave solvent polymer impregnation processing technique [38]. However, foreign companies usually use nonsolvent processing technique. Molding without autoclave (e.g. infusion molding or vacuum and pressure impregnation) sufficiently decreases the PCM production costs.

In the reinforcement plane, the properties of the PCMs are determined mainly by the properties of the reinforcing material. And in the perpendicular plane, the properties of the PCM are largely limited by the strength characteristics of the PB and the adhesion value between the PB and the reinforcing filler. This often leads to the destruction crack initiation and propagation in the interlayer space of PCM under the influence of normal and tangential loads arising during the operation of products.

The growth of such cracks under the action of alternating, static and shock loads leads to a catastrophic destruction of PCM components. Therefore, the low impact strength of carbon composites significantly reduces the area of their possible application. The standard method for increasing the crack resistance is to introduce a thermoplastic polymer into the epoxide matrix which is soluble in it, for example, a polysulfone, whose concentration exceeds 20%

Physico-mechanical properties	Structural carbon-fiber brand					
	KMU-11 m	KMU-31n	KMU-41	KMU-4e	KMU-5e	KMU-6-36
Tensile strength $\sigma_t \cdot 10^{-1}$, MPa	80	75	70	100	80	70
Compression strength $\sigma_{cs} \cdot 10^{-1}$, MPa	60	60	60	100	80	70
Shear strength $\tau_s \cdot 10^{-1}$, MPa	5.9	5.5	5.5	8.0	6.0	5.7
Elasticity modulus $E \cdot 10^{-1}$, MPa	14,500	15,000	14,000	12,000	12,000	12,500
Fatigue strength $\sigma_{-1} \cdot 10^{-1}$ based on $I0^7$ cycles, MPa	50	45	50	70	55	50
Stress coefficient $K_{1c} \cdot 10^{-1}/0.31$, MN·m$^{3/2}$	—	68	126	—	—	94
Maximum operating temperature, °C	180	100	150	150	80	150

Table 1. The nomenclature of unidirectional carbon-fiber plastics for functional purpose [9, 31, 32].

(by weight) [38]. At the same time, the viscosity of the PB becomes extremely high, which makes this method unacceptable for the manufacture of PCM by infusion methods.

Especially emphasized should be the promising constructional NM carbon composite of brand VKU-18tr [39]. It is produced on the basis of the polymeric binding grade ENFB-2 M, an equiprobable fabric of Porcher Ind. (art. 3692). Nanoparticles of astralene of NTS brand in the amount of 0.5% of the mass fraction of the cured polymer matrix are used as the nanomodifier of the liquid PB. Carbon plastic of the brand VKU-18tr was compared with its closest analog in the form of carbon-plastic KMU-4-2 m-3692, obtained on the basis of the same components, but without the astralean nanoparticles.

The results of comparative tests of these carbon plastics are given in **Table 2**.

The results of **Table 2** indicate that the VKU-18tr NM carbon plastic surpasses the number of operating parameters of its analog material, for example, strength, including at higher temperatures. So, for example, at a temperature of 170°C, the strength of the VKU-18tr NM carbon plastic produced by compression is 54% higher. With an interlayer shifting, this excess is 32%, and with a bending, 20%. The same trend is observed with an increase in temperature: hardening at room temperature is from 10 to 15%, and at a temperature of 170°C it increases to 30–50%. Even more, as the temperature rises, the strength of the VKU-18tr NM carbon plastics increases under compression.

Property	Reinforcement direction	Material		Improvement of carbon nanofiber properties, %
		Carbon-fiber plastic VKU-18tr	Carbon-fiber plastic KMU-4-2M-3692	
Tensile strength, MPa	[0°]	780	750	4
	[90°]	600	550	8
	[0°, 90°, ±45°]	640	490	23
Tensile elasticity modulus, GPa	[0°]	65.4	64	—
	[0°, 90°, ±45°]	55.5	45	—
Shear strength, MPa	[0°]	768	700	10
	[90°]	660	600	10
	[0°, 90°, ±45°]	450	405	11
Interlayer shear strength, MPa	[0°]	46	42	10
Shear strength in sheet plane, MPa	[±45°]	93	82	13
Operating temperature, °C	—	170	120	42
Tropical stability after exposure in a tropical chamber for 3 mo., percent retention of compression properties	[0°, 90°, ±45°]	96	55	41

Table 2. Several parameters of VKU-18tr and KMU-4-2 M-3692NM carbon plastics for functional purpose [9, 39].

The above confirms the urgency of developing new, cost-effective and technologically advantageous methods for modifying the surface of carbon fiber and liquid PB. The ultimate goal of such a modification is to improve the physico-mechanical and operational properties of carbon composites.

4. Production of functional hybrid polymeric composite materials

One of the promising directions for improving the physico-mechanical and operational characteristics of elements of load-bearing unit made from reinforced reactoplastic PCMs is the creation of functional reactoplastic hybrid NMPCMs (HNMPCMs). The latter are obtained by incorporating nanoparticles into the structure of a liquid polymeric matrix and a reinforcing macrofiller [40, 41]. In investigations it was established that the nanomodification of the liquid PB, carried out with the help of optimal US action prior to impregnation of the reinforcing macronutrient, improves the processability of the PB and the strength of the solidified polymeric matrix [7, 37].

This, in turn, favorably affects on the hardening of the obtained NMPCMs, especially under the action of tensile loads [9]. At the same time, the nanomodification of only the liquid polymeric matrix does not have a significant effect on the strength characteristics of the PCM structural elements, the functional purpose of which is mainly in the perception of external force loads. This can be explained by the fact that when impregnating the reinforcing strands of the macrofiller with the NM liquid polymer matrix, the nanoparticles do not enter the inter-fiber space of the reinforcing macrofillers and filtering out on their boundaries.

Figure 2 shows a structural model of a functional HNMPCM, the reinforcing fabric of which contains fibers coated with CNTs [40]. The connection of CNTs grown on the surface of each individual fiber during interaction between parallel reinforcing fibers and transverse layers of reinforcing fabric is shown.
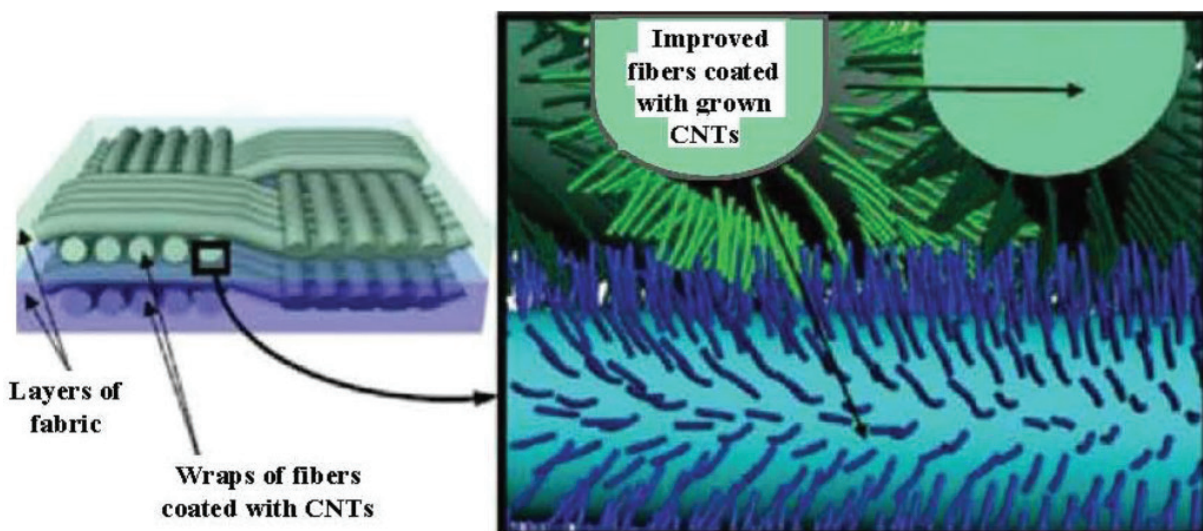

Figure 2. Scheme of a functional hybrid nanocomposite with grown CNTs on monofilaments [40].

4.1. Synthesis of carbon nanotubes on reinforcing macrofibers

The search for new efficient technologies has already led to original methods. One of them is growing of CNTs on monofilaments of reinforcing fabrics (**Figure 3**).

With this method, the classical technology of manufacturing composite products [40], practically is not changed, which is an undoubted advantage of the developed technology [41]. The principal possibility of growing CNTs on reinforcing fibers before their subsequent impregnation with a liquid PB was investigated. For the study, dry fiberglass and dry twill rope twill weave were used (type Twill of the brand: 3k, 2 × 2 Twill Weave Carbon Fiber Fabric, 5.7 Oz/Sq Yd, 50″ wide, .012″ thick and 3k, 2 × 2 Twill Weave). In **Figure 3a** and **b** shows the surface of the fiber before and after application of CNTs.

Growth of CNTs on carbon fibers was carried out by pyrolysis of gases (CVD process) [41]. The length of CNTs, as a rule, was much greater than the distance between the layers of tissue (~10 μm) and between the fibers in strands (~1–5 μm). CNTs grown on fiber reinforcing fibers were studied using a scanning electron microscope (SEM). It was found that the CNT grew uniformly and densely in the radial direction on the surface of each individual fiber in the reinforcing fabric (**Figure 3b**).
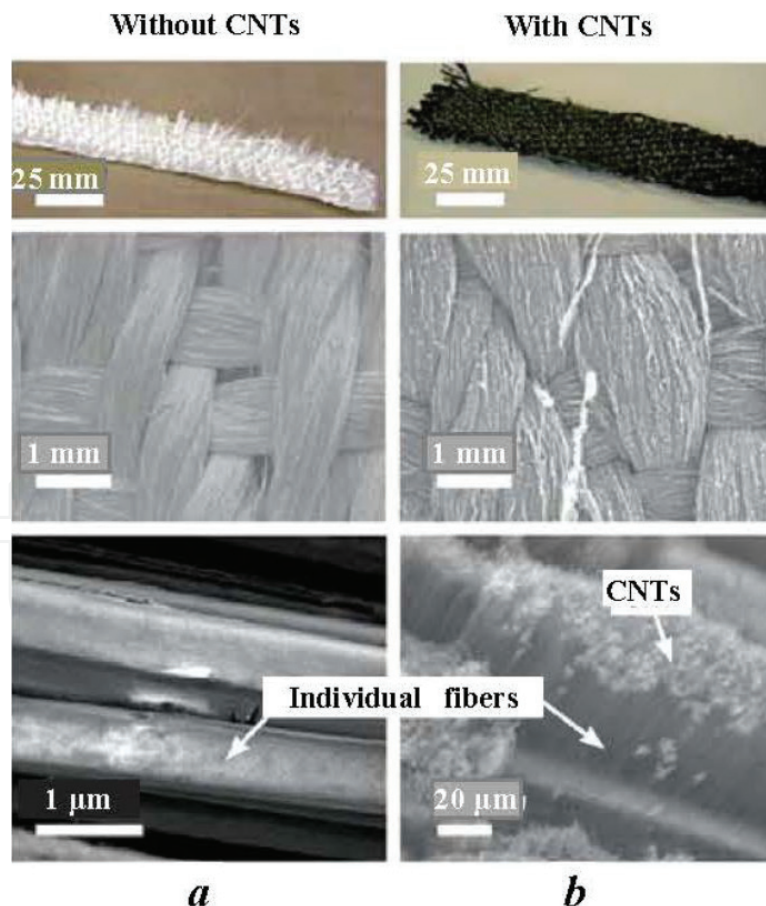

Figure 3. SEM image of glass fabrics and carbon fabrics used in laminate production [40]: a—without CNT; b—with CNTs grown along the radius on the surface of the fiber, as well as individual fibers coated with CNTs; resolution on the lower images of a and b ~20 μm.

Morphology (uniformity of growth, distribution along the fiber and throughout the laminate), the diameter of CNTs and the uniformity of their distribution were evaluated using a transmission electron microscope (TEM). The TEM analysis of multilayer photos showed that CNTs grown on fiber reinforcing fibers have an outer diameter of ~17 ± 2 nm and eight concentric layers (**Figure 4**).

As a result of impregnation with a polyester binder reinforcing NM fabric, a new structure is obtained—a HNMPCM, where nanoadditives are present not only in the polymeric matrix, but also in fibers. It is called free reinforced plastic (FFRP). When studying the wettability of CNTs with a reactoplastic polyester adhesive, it was found that CNTs are easily impregnated with such binding capillary method (free impregnation method) [41]. Improved adhesion between CNTs and reactoplastic material creates a strong functional nanocomposite for power purposes. Thus, due to the synthesis of CNTs directly on macrofibers, the solidified polymer fixes uniformly distributed CNTs on the surface of dry macrofibers, creating a functional nanocomposite of increased strength (the shear strength of HNMPCMs based on the polyester matrix increased by 60%).

It is known that one of the main problems during the process of making samples was the impregnation by PB of reinforcing woven layers, which contain single CNTs. Images obtained from optical and scanning electron microscopes demonstrate the presence of CNTs throughout the entire laminate section and the absence of differences between laminates with and without CNTs (**Figure 5**).

The PB under impregnation under the influence of vacuum completely impregnated all reinforcing macrofibers together with CNTs. The sections of the laminate without CNTs (**Figure 5c**) and with CNTs (**Figure 5d**) at the same scale indicate a qualitative structure and a uniform impregnation of the hybrid layers with a PB. This is confirmed by the absence of voids in the structure and the quasiregular distribution of the fibers after vacuum impregnation.

At the same time, the distance between macrofibers in the HNMPCM is slightly larger than in the base sample due to the expansion of the fibers by growing CNTs. Thus, the creation and
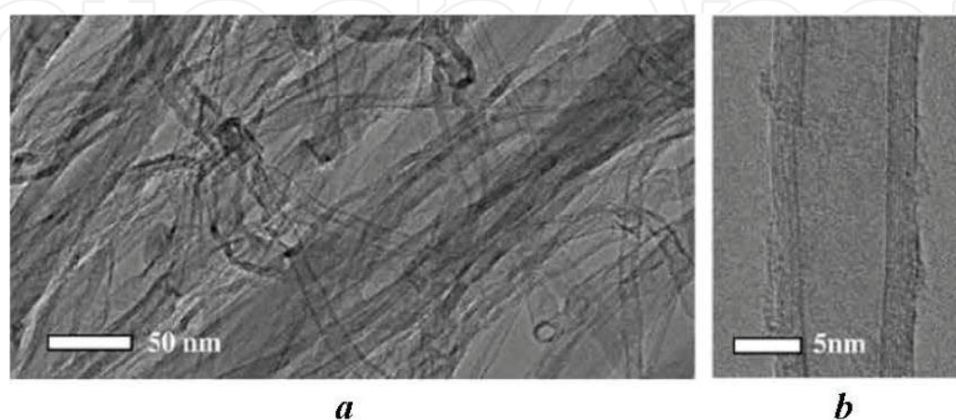

Figure 4. TEM images of CNTs grown on a carbon fiber with a low (a) image resolution and a single high-resolution CNT (b) (concentric layers in the CNT structure are shown) [41].
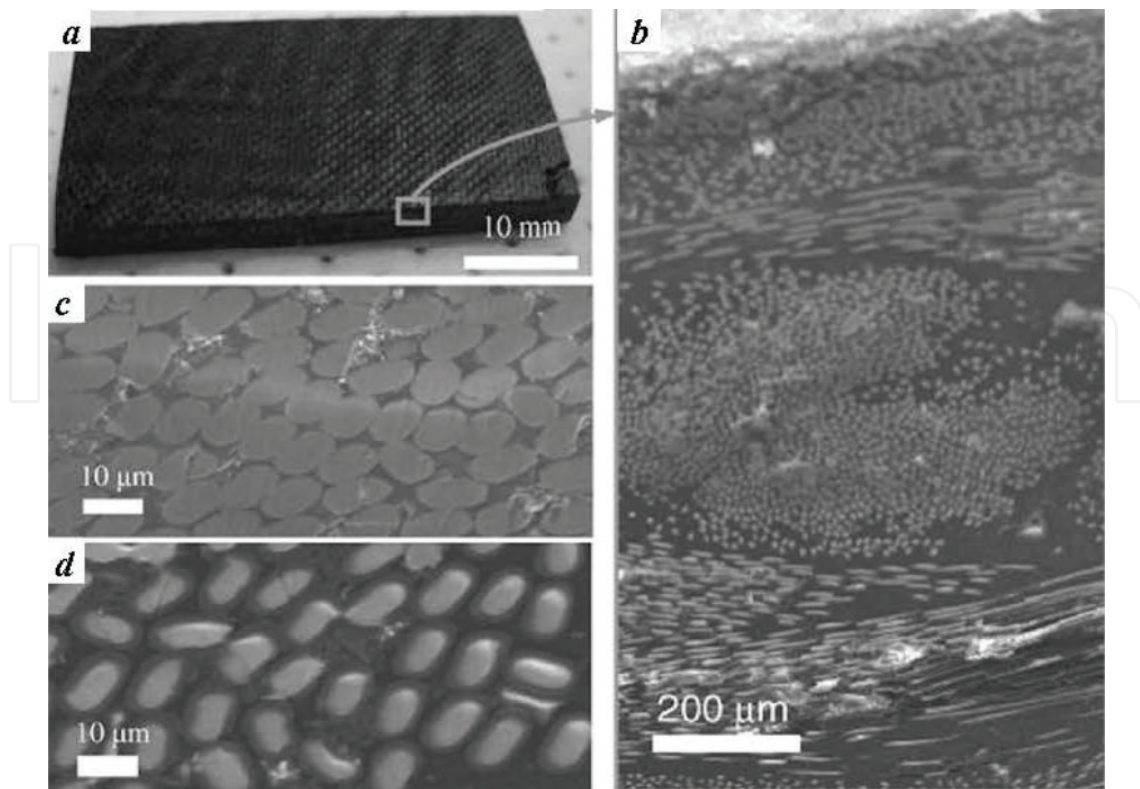
Figure 5. Hybrid composite samples based on a nanocomposite with a CNT content of 0.2% [41]: a—three-layer laminate after trimming; b—SEM image of intersecting tissue layers impregnated with a nanocomposite binder; c—SEM image of the section of composites without CNTs; d—cross section of reinforced CNT hybrid NMPCMs.

study of functional HNMPCMs has shown that the application of the method of gas-phase growth of CNTs ensures their uniform distribution on reinforcing macrofibers of the filler, and vacuum impregnation with a PB reliably binds CNTs with reinforcing macrofibers.

5. Production of functional nano-modified carbonocomposites with crack resistance

In the past 10 years in the CIS countries the possibility of using CNTs for additional reinforcement of PCM has been intensively studied. As a result of these studies, HNMPCMs are created, in which CNTs are contained along with a reinforcing macrofiller, carbon or glass fiber [33, 42]. These studies provide the basis for the creation of functional NM carbonocomposites with increased crack resistance. According to the data of the studies of a number of investigators, CNTs exert maximum influence on the value of the ultimate strength at interlayer shear and the fracture toughness of reinforced PCMs [43–45].

At the same time, the characteristics of PCM, which depend on the properties of the reinforcing filler (elasticity modulus and tensile strength), change slightly. Still, it should be noted that the results of the study of the effect of CNTs on the crack resistance of the HNMPCMs, obtained by various authors, differ significantly. The use of PB modified by CNTs in the

composition of the HNMPCM allows increasing the crack resistance coefficients G_{1c} and G_{2c} by an average of 15–40% [46–49]. At the same time, it is possible to obtain an increase in the crack resistance coefficient up to 120–180% if a thermoplastic polymer is incorporated into the PB together with the CNTs, which acts as a non-covalent CNT modifier [50, 51].

When using films based on a partially cured EC filled with CNT [40], or a mixture of CNT and thermoplastic polymer [52, 53], it is possible to increase the coefficient of crack resistance by 2–3 times. The resulting films were placed between the layers of the reinforcing filler. In addition, the crack resistance is affected by the method of obtaining HNMPCM [52]. In the first embodiment, the nanofiller was functionalized with silane groups. Before the winding on the reinforcing fiberglass, a PB (EC) modified with short CNTs and nanofibers was applied, after which the coefficient of crack resistance of the obtained monolithic HNMPCM sample was determined.

In the second variant of the winding, two separate plates were made on the basis of a modified PB, which were then glued together with a PB containing a functionalized nanofiller. The crack propagated along the gluing layer. Despite the practically identical composition of the modified binder, in the first case the crack resistance coefficients in the reinforcement direction G_{1c} and in the perpendicular direction G_{2c} increased by 5–14% compared to the initial values (monolithic plate based on the unmodified PB), and in the second by 79–109%, respectively. The influence of the degree of aggregation of CNTs and the type of functional groups covalently attached to their surface on the crack resistance of HNMPCM obtained by the vacuum forming method was investigated [38]. A binder based on an epoxy amine resin and an amine curing agent was used.

To regulate the rheological properties of the binder, an unsaturated polyester resin modifier and a radical polymerization initiator was used. The modification of the chemical structure occurred according to the type of interpenetrating polymer networks. The method of preparation of the concentrate (1.5% by weight) of CNTs "Taunit-M", covalently functionalized with carboxyl (CNT-COOH) and amide groups (CNT-CONH2) in the epoxy amine oligomer, is described by [54]. Four types of concentrates of functionalized CNTs (COOH-1, COOH-2, $CONH_2$-1 and $CONH_2$-2) were used in the epoxy amine resin, which differed in the types of functional groups and the degree of aggregate dispersion. The aggregate size in concentrates COOH-2 and $CONH_2$-2 was 3–20 μm, and in concentrates COOH-1 and $CONH_2$-1 does not exceed 3–5 μm. As the reinforcing filler, a uniform fabric firm Toray was used: weav-twill, thickness of the bundle 3k (3000 filaments).

Six layers of filler were used to assemble the pack, each of which was applied with a previously prepared binder in equal proportions in such a way that its mass fraction in the finished cured sample was 36–40%. It was found that the modification of the epoxy binder by carboxylated and amidated nanotubes leads to a decrease in the glass transition temperature T_g (maximum of 8°C). And with an increase in the degree of aggregation, the difference between the glass transition temperatures T_g in the modified functionalized CNT (FCNT) and the control sample decreases. The maximum hardening of the modified epoxy binder was 20%. The use of a binder modified with well-dispersed carboxylated nanotubes makes it possible to increase the value of the energy of interlayer destruction of carbon-plastic G_{IR} by 63% as compared to the initial sample. The likely reason for the increase in G_{IR} is the change in the propagation path of the crack in the modified FCNT samples from the HPCM.

For HNMPCMs prepared using a binder with uniformly distributed CNTs functionalized with amide groups, an increase in the G_{IR} value compared to the starting plastic is 41%. Aggregation of carboxylated FCNT leads to a decrease in the effect—an increase in the G_{IR} value is only 17%. **Figure 6** shows the results of a fractographic study of the surface of the HNMPCM after separation of the sample with a COOH-1 concentrator and a sample of reinforced plastic made using a SEM at various magnifications.

As can be seen from **Figure 6**, on a scale of up to 10 μm, the pattern of destruction of the initial and modified sample is practically the same. However, on a larger scale, there are significant differences: a large number of "pyramidal" formations are observed on the surface of a modified sample with FCNTs. In addition, the number of fibers destroyed during the stratification of the sample increases. It was found that when modifying the epoxy binders of the FCNT, the values of the elasticity modulus E and the tensile strength σ_t of the HNMPCM decrease on average by 35 and 25%, respectively. This is explained by a decrease in the volume fraction of the reinforcing fiber in the samples of HNMPCM (an average of 20%) compared to the control sample.
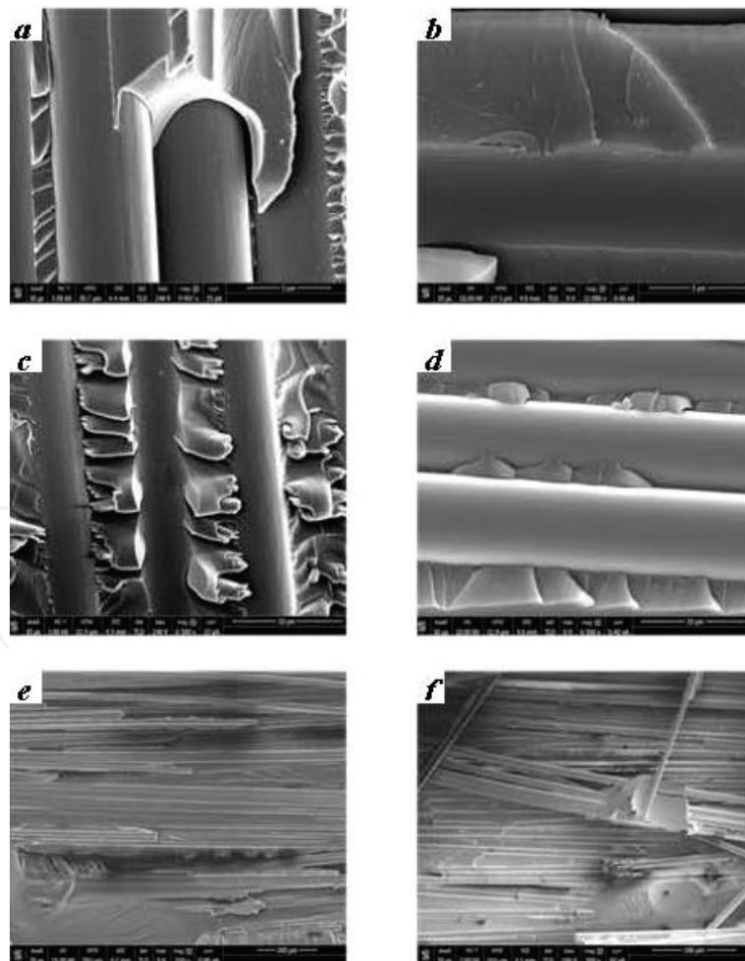

Figure 6. Results of fractographic investigation of the surface of the HNMPCM after separation, obtained with the help of SEM [38]: a, c, and e—control sample; b, d, and f—sample of HNMPCM with COOH-1 concentrate.

6. Production of structural electro conductive polymeric composites

In recent years, the efforts of researchers in the field of polymer nanotechnology are concentrated in the direction of the creation of functional constructional PCMs of a new type. In such PCMs, the CNTs themselves are used as the reinforcing element. In particular, one of the most important functions of such PCMs is a high level of electrical conductivity [55]. So, it is shown that the conductivity of the CNT-filled composites depends not only on CNTs type, concentration and polymer matrix composition, but also on the nanocomposite production method.

For example, for materials that can be manufactured by pressure die casting methods, the task of creating nanocomposites that combine a high level of functional and physico-mechanical properties can be solved by using multiphase polymer matrices and extruders. This is necessary to ensure a high level of shear stresses. In particular, the authors of the paper used the following method [56]. An array of vertically oriented CNTs that were grown on an alumina substrate was sheared off the substrate and then compressed in a direction perpendicular to the CNT orientation axis. Then the resulting deformed nanofiller was impregnated with ECs, which are used for the manufacture of PCM and cured.

It is shown that the electrical conductivity of such a deformed nanocomposite in the CNT orientation direction is 10 Sm/cm at a CNT concentration of about 6%. Other authors reached significantly larger values of the electro-physical and physico-mechanical characteristics [57]. In contrast to the method described in [56], they stretched an array of vertically oriented CNTs in a direction perpendicular to their growth. The resulting stretched sheets were impregnated with an EC by vacuum infusion. For PCM, obtained on the basis of 1750 stretched sheets oriented in mutually perpendicular directions, the following physico-mechanical and operational (electrical conductivity) characteristics were obtained: tensile strength of 117 MPa, elasticity modulus of 7.45 GPa, electrical conductivity of 2205 Sm/cm at concentration of CNTs at the level of 8%.

Other researchers demonstrated a different way of obtaining PCM with a high level of functional and physico-mechanical properties [58, 59]. It is declared that this method can be used in the future for large-scale industrial production. According to this method, an array of vertically grown CNTs (7–9 nm in size) was subjected to orientational stretching and impregnation with a solution of bismaleinimide resin (**Figure 7**).

The complex filament was collected by successively stacking several layers of oriented and impregnated nanotubes. From the obtained filaments, a prepreg was prepared, which was then pressed (the proportion of PCM being 50–55%).

Figure 8 shows a comparison of the dependence of the tensile strength of PCM on its elasticity modulus for materials reinforced with standard carbon fibers and CNTs.

□—high-strength plastics; ■—high-modulus plastics; •—developed plastics.

It was studied that such HNMPCMs due to the use of CNT as a reinforcing filler are characterized by a complex of high functional characteristics. In particular, the tensile strength is 3.8 GPa, elasticity modulus of 293 GPa and the electrical conductivity reaches 1230 Sm/cm. At
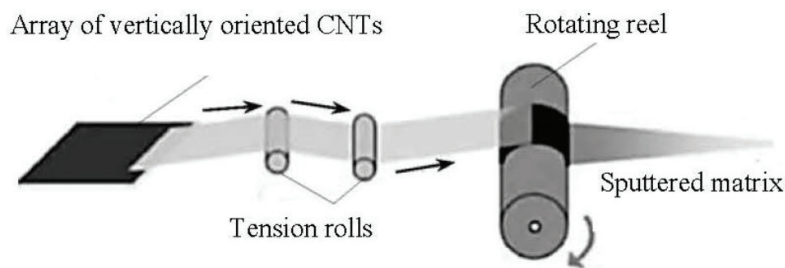
Figure 7. Scheme of the technological process of obtaining a complex filament from the CNT's array [58].
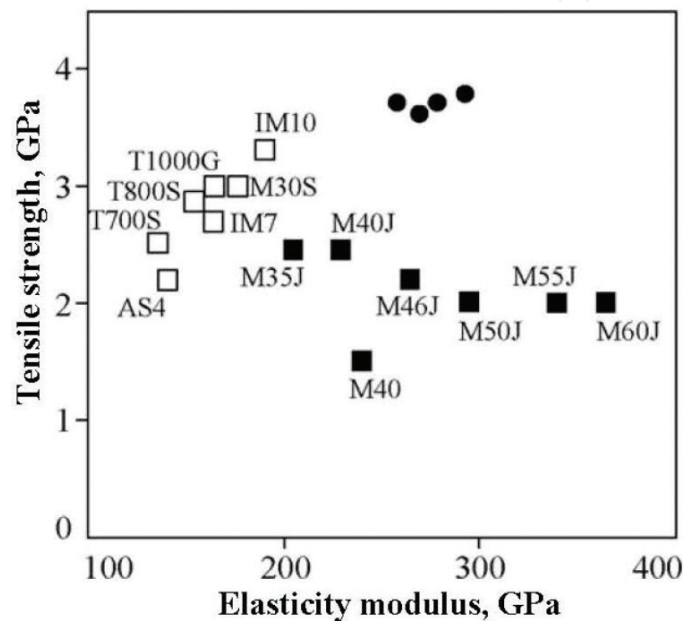

Figure 8. Comparative dependence of the tensile strength on the value of the elasticity modulus for materials reinforced with standard carbon fibers and CNTs [58].

the same time, during the production of such materials, it is advisable to use extruders in point of view of the need to obtain high shear stresses during the shaping of the such HNMPCMs.

Taking into account the fact that the density of the PCM is only 1.25 g/cm³, this material is extremely promising for use in the design of aviation and space technology. Also, a high level of electrical conductivity ensures the stability of the resulting HNMPCM to the effect of a lightning discharge. In addition, one of the possible ways to impart electrical conductivity to classical PCM based on reinforcing fillers is the use of CNTs decorated with metal nanoparticles [55, 60].

Thus, based on the foregoing, it can be concluded that the electrical conductivity of nanocomposites with carbon nanotubes is influenced by: the type of nanotubes, the composition of the polymeric matrix, and the technologies for obtaining the NMPCMs, including US treatment for modifying liquid polymeric media [61]. The last one forms the distribution of CNTs by the bulk (volume) of the composite and affect the value of the contact resistance between CNTs. At the same time, the technology of obtaining composite materials from a stretched array of vertically oriented nanotubes makes it possible to produce functional PCMs with a record level of electrical conductivity and physico-mechanical properties.

7. Conclusions

The results of the studies described in this chapter confirm the effectiveness of physical, chemical and combined physico-chemical methods of modification as a basic direction of improving the technological and operational characteristics of classical PCMs and NM liquid polymer media and reinforced PCMs of functional purpose on their basis. The choice of the dominant method of physical modification of liquid polymer media and reinforced classical PCMs and NM PCMs of functional purpose in the form of US low-frequency cavitation has been experimentally confirmed.

The effective spectrum of interrelated regime parameters of US processing is characterized, which is established exclusively by an experimental method. The efficiency of creation of carbon plastics of combined filling is shown, as well as the prospects of creating HNMPCMs on the basis of reinforcing fabric with NM filler, which is used as CNT. Methods for obtaining functional NM carbonocomposites with improved physico-mechanical and operational properties, in particular, with increased strength, electrical conductivity and crack resistance are described. Potential applications of such materials are briefly described.

Further directions of research in the field of creation of reinforced PCMs on functional purpose are improving the properties of nanomodifiers used in the form of CNTs, improving the technology of de-agglomeration and subsequent alignment of nanocomposite components, and developing innovative methods for the synthesis of carbon plastics of combined filling and hybrid coal composites.

Author details

Aleksandr Evhenovych Kolosov[1]* and Elena Petryvna Kolosova[2]

*Address all correspondence to: a-kolosov@ukr.net

1 National Technical University of Ukraine, Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine

2 Faculty of Physics and Mathematics, National Technical University of Ukraine, Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine

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