The various aspects of physicochemical modification of the components of structural materials of functional application based on classical composites and nanocomposites are analyzed. Potential applications of such materials are briefly described. Ultrasonic cavitation treatment is considered as a basic method of physical modification when obtaining the indicated classes of composites. The influence of ultrasonic treatment modes on the technological and operational properties of reactoplastic polymers, as well as on the hardening of reinforced composites based on them, is investigated. Technical means of ultrasonic cavitation processing of liquid binders and polymer composites based on them are briefly described. An effective spectrum of interrelated structural and technological parameters of ultrasonic treatment has been characterized, which is established by calculation and experimentally-statistically. The design issues of the technological processes of obtaining polymer composites of functional application are analyzed. The efficiency of creating carbon fiber composite materials, as well as the prospects for creating of these materials based on reinforcing fabric with nanomodified fillers, is described. The methods of obtaining functional nanomodified thermoplastic composite materials by extrusion method is considered. Some issues of forming products from intelligent polymer composites are analyzed. The results of the survey can be used in the design of advanced technologies for the creation of functional polymer composites of functional application.

1. Introduction

Structural polymer composite materials (PCMs) are used in various industries: aircraft, rocket, shipbuilding, automotive and electrical industry, construction, sports industry, chemical and special engineering, medicine, etc. [1]. This is due to a wide range of physicomechanical and operational properties of materials based on PCMs. For example, such materials combine low density, high modulus of elasticity and strength, durability, and other properties.

Functional PCMs, as a rule, are understood as PCMs with special properties that are determined exclusively by their application areas [2]. Moreover, such materials include both classical PCMs with macro- and microfillers and nanomodified (NM) PCMs (NM PCMs). In particular, the following materials belong to functional PCMs: thermal insulation, including foam and cellular, electrical insulation; corrosion resistant; conductive; arc resistant; friction; antifriction; hydrophobic; fire resistant; crack resistant; armoured, etc.

At the same time, additional requirements are being made for aircraft industry and rocket production for such materials. In particular, this imparts structural properties such functional properties as electrical conductivity in the longitudinal and transverse directions (to ensure lightning resistance, impart antistatic properties to the surface of the material, shielding the onboard radioelectronic equipment from external electromagnetic pulses, and superhydrophobicity (anti-icing coatings)).

An equally important area for this industry is the development of radio-absorbing PCMs. The concept of “functionality” closely correlates the concept of “intelligence.” This also applies to the PCMs, which are inherent in the above...
distinctive features. So, intellectual (smart) PCMs are able to respond to changes in operating conditions or "warn" about the occurrence of emergency situations [3–5]. Currently, IPCMs are manufactured on the basis of various types of sensors and nanomodifiers, alloys with magnetic properties, fiber-optic and piezoelectric sensors, and a number of other materials. These sensors allow you to monitor the action of external factors, in particular, pressure, temperature, strain, and the like.

At present, a large number of technical solutions have been developed, based on the principle of the effect of the memory effect of the shape of thermomaterials, for example, thermistor couplings, which are thermoshrinkable. Smart Materials were created in order not only to actively counteract the above-mentioned external factors, but also to adapt to them optimally by "evaluating" using a system of indicators characterizing both the external effect and the material's own state. In the optimum, IPCMs, primarily with continuous fibrous fillers, exhibit the ability to "analyze" and "manage" the complex of their operational characteristics according to an algorithm predetermined by the developer.

As a rule, obtaining the necessary indicators of the "state of health" of the material under operating conditions is ensured by means of intelligent sensors (IS). The system of sensors (or sensors) is essentially the "nervous system" of almost any intellectual structure. It controls the state of the structure and determines the level of mechanical load and other physical parameters (stress, strain, etc.). Ideally, the IS should detect any changes in the monitored parameters in all parts of the intellectual structure. At the same time, researchers are developing designs similar to the "biological models" of intellectual structures existing in nature. Moreover, the concept of IS is often associated with nanotechnology, where these ISs are used [3–5]. The above aspects of IPCMs are the subject of a brief review of this article.

It should also be noted that, at the present stage of development of polymer materials science and polymer technology, physical and chemical modification of the constituent components of PCMs, namely, the surface of reinforcing fillers (fabrics, fibers, particles, etc.) and liquid polymer binder (PB), is the basic direction of creating structural thermoplastic PCMs of functional application. Such a modification is carried out to improve the physicomechanical and operational properties of the resulting classical (traditional) PCMs [6] and NM PCMs.

Moreover, this task is implemented both comprehensively and individually using various modification methods. Among the latter, it is possible to single out a physical modification realized, for example, in the form of ultrasonic (US) treatment of liquid media, chemical and combined physicochemical modification [7]. Therefore, the analysis of existing methods and the development of new approaches to the implementation of such a modification, and first of all promising US modification (the rationale for the effectiveness of which is given later in the article), is an important area of current research.

Thus, the development of technical means (technologies and equipment) for obtaining structural PCMs with special properties, including intelligent PCMs, based on both thermosetting and thermoplastic matrices (including NM ones), as well as carbon, glass, or organic fillers, is one of the urgent problems of polymer materials science and polymer technology.

2. Purpose and Objectives of the Study

The purpose of the article is a brief analytical review of some existing and developed by the authors methodological approaches to the creation of structural classical PCMs and NM PCMs of functional application by selecting and subsequent physical and chemical modification of their constituent components, including the analysis of technical means for their production, as well as features of obtaining intelligent thermoplastic PCMs.

The following directions can be identified:

(i) the choice of nanofillers for the implementation of chemical modification of NM PCMs
(ii) features of the course of the process of US cavitation in liquid media
(iii) analysis of the effectiveness of US in the formation of PCMs of functional application
(iv) design of processes and equipment parameters for the production of PCMs
(v) equipment for low-frequency US processing of liquid polymer media and fibrous fillers
(vi) the effectiveness of the US treatment and NM thermoplastic composite materials by extrusion method
(vii) hybrid PCMs and features of their creation
(viii) features of the process of US cavitation in liquid media
(ix) production of structural electroconductive PCMs
(x) forming products from intelligent PCMs

The above aspects are shortly described in this review article.

3. Results and Discussion

3.1. Choice of Nanofiller for Chemical Modification of PCMs.

The characteristics and properties of micro- and macrofillers used for classical PCMs of functional application have been studied in sufficient detail [8]. Therefore, their choice in the design of specific PCMs, as a rule, is not a particular problem. At the same time, when designing functional NM PCMs, the choice of nanosized fillers has its own distinctive features.

Thus, at present, such groups of carbon fiber nanoparticles as carbon nanotubes (CNT), both single-walled and multiwalled, as well as carbon nanofibers (CNF) have found the greatest use as nanofillers for structural thermoplastic-plastic PCMs of functional application. Graphene, graphene airgel (GA), and other nanofillers are also intensively studied. CNTs possess a number of unique properties that fundamentally distinguish them from the traditional macro- and microfillers used for PCMs.

CNTs are among the most important objects of modern nanotechnology. This is due to the fact that they are the
foundation for the creation of a new generation of various structural materials of functional application, as well as a wide range of devices and equipment based on them [9]. For example, thin single-walled CNTs have a maximum specific surface area, according to various estimates, up to 1360 m²/g and even more, which theoretically makes them one of the most promising types of fillers [10]. At the same time, single-walled CNTs, more than other types of fillers, are subject to agglomeration under the action of Van-der-Waals forces. Moreover, the existing methods of producing single-walled CNTs do not yet allow production on an industrial scale in sufficient volumes.

Unlike single-walled CNTs, multiwalled CNTs are widely used due to the possibility of their production in industrial volumes. This is realized, as a rule, by the method of chemical precipitation on the catalyst (pyrolysis of natural gases). Thus, multilayer CNTs are much more affordable than single-walled CNTs, and their properties are more stable. At the same time, they lose in strength by single-walled CNT.

CNFs are filamentous nanoparticles without extended internal cavities. In fact, these are the same CNTs, only of large sizes and with a more developed surface. This helps to improve their interaction with the liquid polymer matrix. CNFs, unlike CNTs, due to their structure are less susceptible to aggregation. Therefore, they can be introduced into the liquid polymer without additional functionalization of their surface.

The density of CNTs and CNFs does not exceed 2 g/cm³, which allows to refer them to lightweight nanofillers [11]. Also, unlike conventional carbon macrofibres, CNTs and CNFs are not brittle. Fillers for liquid polymers with an optimal concentration of CNTs and CNFs are able to improve their interaction with the liquid polymer matrix. CNFs, unlike CNTs, due to their structure are less susceptible to aggregation. Therefore, they can be introduced into the liquid polymer without additional functionalization of their surface.

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the nature and characteristics of the demonstration of US cavitation in liquid polymer media are considered in relation to the receipt of the materials considered in the article.

3.2. Ultrasonic Cavitation Process in Liquids. The process of US cavitation consists in the formation of gas, vapor, or vapor-gas bubbles in the irradiated liquid, as well as the subsequent formation of corresponding cavities on the basis of these bubbles [18]. This phenomenon is also accompanied by effects of the first or second order, arising from the interaction of the cavities formed with the liquid medium.

During high-intensity sonication of a liquid medium, sound waves propagate in it, which alternate cyclically with the formation of high-pressure half-periods (compression half-period) and low pressure (vacuum-half-period) according to [19]. The above half cycles change with speeds that depend on the frequency of the US. During the low-pressure cycle, high-intensity US waves contribute to the formation of small vacuum bubbles or cavities in a liquid medium, due to the expansion of the liquid medium.

When these bubbles reach a critical volume at which they are no longer able to absorb US energy, the cavities burst sharply. At the same time, at the “gas-liquid” interface, the transformation of the mechanical energy of US waves into thermal energy occurs with a multiple increase in temperature and pressure in these border areas. As a result of this synergistic effect, an explosion occurs with the formation of a multitude of bubbles and hot gases.

It should be noted that the explosive processes aimed at the destruction of the internal structure of the medium.

Unlike an external explosion, implosion is an inward explosion or rarefaction. The explosion and implosion are especially characteristic demonstrations of unusual physical and chemical conditions, especially in cold liquids. According to [19], an abnormal temperature (about 5000 K) and dynamic pressure (up to 200 MPa) with heating and cooling rates $>10^{10}$ K/s and flow rates of a microjet liquid up to 280 m are reached as a result of an explosion in local areas during an explosion, although it should be noted that the above parameters, including those indicated by the authors [20], were obtained by purely theoretical calculation.

The process of high-intensity US cavitation in a liquid medium has “second-order effects,” which include a complex of phenomena in the form of strong hydrodynamic disturbances, microshock waves, cumulative microjets, and microflows of the liquid.

There are two different types of US cavitation according to [21]. The first of them includes transitional (or inertial) cavitation, which is characterized by the formation of vapor-gas cavities in a liquid medium with US intensity of $I \leq 10$ W/cm$^2$.

The second type of cavitation includes noninertial (or stable) cavitation. Its peculiarity is fluctuations of already formed and relatively stable vapor-gas bubbles, which are characterized by approximately the same equilibrium size. In this case, the intensity of the US is $I \sim (1-3)$ W/cm$^2$. Moreover, the simultaneous manifestation of the above two types of cavitation is not excluded if the inertial cavitation threshold is exceeded and taking into account the existing heterogeneity of the acoustic field in a liquid [22].

Sonochemistry studies chemical reactions when US is applied to substances, such as liquids, to change their structure and properties. Sonochemical reactions occurring in the cavitation mode are characterized by an unusual interaction between the supplied energy and the irradiated substance with hot areas inside the droplets. One of the practical applications of sonochemical reactions is the synthesis of NM PCMs of a wide range of applications [23].

3.3. Efficiency of Ultrasound Application in Forming of Polymeric Composites of Functional Purpose. Now there is widespread use of both traditional (classical) reactoplastic PCMs, in particular, based on comprehensively studied epoxy matrices [23], and the intensive development of promising technologies for creating innovative PCMs with a nanoscale filling level [24]. The promising carbon nanofillers used for functional PCMs come to the forefront of research [25]. In this regard, most of the economically developed and developing countries over the next decade declare the orientation of the industrial sectors of their economy towards the production and introduction on a large scale of NM PCMs used in the production of high technology products [26, 27].

As examples of such applications, it is possible to indicate the use of nanotechnologies in a number of technological processes in the chemical and oil and gas industry, including for oil and gas complex. In particular, nanotechnologies are used to form multifunctional nanostructured coatings and compositions. This is advisable in the implementation of the hydrophobization of external and internal surfaces of a number of structures and technological equipment, since the hydrophobization contributes to the effectiveness of their work in the long term.

As a typical example, antistatic coatings for process fuel pipelines can be given. The application of such coatings provides a long-term increase in the performance characteristics of such structural elements. For example, chemical resistance, water repellency, and anti-friction properties, as well as erosion resistance, are significantly improved.

Also promising is the use of nanotechnology in the preparation of liquid polymer compositions used to enhance potential stress concentration zones in a variety of power structures. As such zones, technological holes, cutouts, grooves, thickness differences, junctions of structural elements, and the boundaries of their loaded sections, etc., can be considered.

In the process of manufacturing and subsequent operation of such structures and process equipment, various defects, microcracks, and other typical macro- and microdamage forms often appear. In particular, it can be gaps in the holes and joints of bolted and riveted joints, which must be periodically removed and sealed to improve the performance of structural elements.

Also promising is the use of nanotechnology in the manufacture of a wide range of high-strength and corrosion-resistant structural elements of functional application based on both thermoplastic and thermoplastic carbon NM PCMs.
At the optimum, this leads to an improvement in the interfiber space during impregnation and dosed application of PCMs due to the removal of air inclusions from the saving of the molding process, as well as obtaining defect-free time of the composite, which ultimately contributes to energy savings of the molding process while ensuring resource and energy saving when they are molded on an industrial scale is an urgent task of polymer technology.

One of the main problems in the formation of NM PCMs is the difficulty of ensuring uniform distribution of the nanofiller in the liquid polymer matrix. For optimal strengthening of NM PCMs, it is necessary to ensure optimal concentration and uniform distribution of CNTs in the liquid polymer matrix. At the same time, due to the tendency of nanoparticles to mutual attraction and the resulting agglomeration, when nanofiller is introduced into liquid media, forced technological operations are first deagglomeration and then dispersion of the nanofillers used.

The lack of implementation of the above operations leads to a wide variation in the operating characteristics of the NM PCMs due to nondeterministic variation of the sizes of the agglomerates. This is due to the influence of the size of the resulting agglomerates on the technological and operational properties of nanofluids, in particular, on their dynamic viscosity and thermal conductivity. The result is nondeterminable heat transfer characteristics. Thus, the neglect of the quality of the formed dispersion of a nanofiller in a liquid polymer medium leads to a significant variation in the performance characteristics of NM PCMs obtained on its basis.

Low-frequency US is used as the most common method for deagglomeration spontaneously formed CNTs agglomerates [31]. Moreover, its use improves the dispersion of injected nanoparticles in liquid media prepared both on the basis of organic solutions and on the basis of solutions of liquid polymers. The effectiveness of US in the synthesis of GA for the formation of a three-dimensional structure should also be noted.

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In addition, the use of effective modes of US exposure allows to intensify a number of technological operations in obtaining classical PCMs [32]. As such technological operations, you can specify the operation of sonication, the impregnation PBs, impregnation, wet winding, and dosed PBs deposition in the structure of the impregnated long fibrous filler in the preparation of fibrous prepregs for the subsequent molding of classical PCMs and NM PCMs.

Also, the positive results of using optimal US treatment modes are the following: reducing the cumulative curing time of the composite, which ultimately contributes to energy savings of the molding process, as well as obtaining defect-free PCMs structures due to the removal of air inclusions from the interfiber space during impregnation and dosed application [33]. At the optimum, this leads to an improvement in the physicomechanical and operational characteristics of both classical PCMs and NM PCMs of functional application, which are obtained using US processing.

This is all the more relevant because, for PCMs of functional application, reducing the cumulative mass of the product while ensuring resource and energy saving when they are molded on an industrial scale is an urgent task of polymer technology.

### 3.4. Designing Parameters of the Technological Process and Equipment for Production of PCMs

The design of the parameters of the technological process and the equipment implementing it to obtain structural reactoplastic classical PCMs and NM PCMs of functional application involves consideration of a range of technical and economic issues [34–36]. For example, the study [37] analyzes the potential directions of development of the technology for producing polymer NM PCMs of functional application, including consideration of the economic aspects of their implementation.

Particular attention is focused on the practical uselessness of the use of US due to the difficulties of uniform distribution of nanofillers in the liquid polymer matrix by traditional methods and due to the high surface energy of the introduced nanoparticles, their mutual attraction, which leads to their coalescence and aggregation [38].

The most important factors influencing the creation of such materials are the (relatively) small size and (maximum) uniform distribution of CNT particles in the liquid polymer matrix [39]. Moreover, it was shown that the efficiency of incorporating dispersed nanoparticles into a liquid polymer medium depends on a number of factors, including their optimal dosage and technological parameters of the mixing process [40].

In addition, there are features of the introduction of nanofiller in a liquid medium upon receipt of NM PCMs. For example, in [41], it was found that, when molding reactoplastic NM PCMs, it is preferable to introduce nanofiller particles first into a less viscous liquid medium.

In this study, nanodispersed filler of annealed composite based on oligoelements (composed of minerals, salts, and metals) and PB based on an epoxy oligomer (EO) of the ED-20 brand were used. A low-molecular hardener, polyethylene polyamine PEPA, was used for crosslinking epoxy resin (ER) based on EO.

The process of dispersing nanoparticles in a liquid polymer medium under the influence of US vibrations in the cavitation mode promotes a uniform distribution of nanoparticles in a liquid polymer matrix. As a result of the US action, mechanical energy is pumped in, PB is heated, and epoxy macromolecules are activated, which leads to an additional decrease in the viscosity of the polymer system. Also, there is a uniform distribution of the dispersed nanofiller over the volume of liquid PB and the formation of free radicals.

In turn, the subsequent chemical interaction causes the formation of NM material with improved performance properties, in particular, abrasive wear. The effectiveness of US treatment depends on the effective technological parameters of sonication. As is known, frequency, amplitude, intensity, operating pressure, temperature, and volume (mass) of the liquid medium being sonicated are considered as the
main technological parameters of US treatment in liquid media.

A number of these parameters are interrelated, for example, frequency, amplitude, and intensity, and their combination, as a rule, is established experimentally by statistical means for each case under consideration. The found set of optimal parameters of US cavitation treatment is determined based on the need to improve the performance properties of hardened oligomers or reinforced PCMs based on them [42]. In some cases, the amount of achievable hardening can vary from 40–50% for classical hardened thermosets, based on EOs and epoxy compositions (ECs), and up to 100–200% or even more for NM PCMs [43].

One of the modes of US effects on liquid polymer systems is the variation of the frequency of US. Moreover, this mode can be implemented both separately in the low-frequency and mid-frequency US bands and with their combination [44]. Another mode of US treatment is the use of variation of the working (static) pressure in the process of sonicating. Its effectiveness was experimentally tested in the formation of heat-shrinkable epoxy couplings (couplings with shape memory effect).

Thus, the purpose of the use of US modification in obtaining reinforced PCMs is to obtain a number of advantages compared with the traditional technology of molding such materials [45]. The first advantage is the US activation of the surface and structure of the preimpregnated reinforcing fiber macrofiller, which helps to improve its wettability of liquid ECs. Also, an effective US treatment of the structure of the impregnated filler contributes to the degassing of this structure.

As an undisputed advantage, it is also worth noting an increase in productivity (on average not less than 2 times) of the basic technological operations for molding classical PCMs, namely, sonicating EOs, impregnation, dozed application of liquid ECs, and "wet" winding of impregnated fiber macrofiller. At the same time, the operational properties of the resulting final composite are observed. No less important advantage of US treatment is the stabilization of the content of PB in the impregnated fiber (woven) filler with variations in the speed of its pulling in the technological operations of impregnation and dosed application [46].

Finally, the optimal parameters of US processing help to reduce the cumulative time of hardening, increase the physomechanical and operational characteristics of PCMs of functional application, allow to reduce the level of residual stresses in them, and increase the durability of their use [47].

3.5. Equipment for Low Frequency Ultrasonic Processing of Liquid Polymer Media and Fiber Fillers. Equipment for low-frequency US treatment of liquid polymer media and reinforcing fiber fillers in some cases differs in its specificity from traditional US equipment. In particular, this refers to the structures of the impregnation, dozed application, and wet-winding units on the serial impregnation and drying equipment. The technical means used in practice for US modification of liquid polymer media and contact US treatment of reinforcing fillers can be divided into two types: US concentrators and speed transformers and radiating plates.

The first of them (US concentrators) can be effectively used in the processing of liquid polymer media, including the iterative introduction of NM fillers into them. The second type (radiating plates) is used mainly in the contact US treatment of impregnated reinforcing woven fiber macrofillers with a width of up to 2000 mm.

Due to the difference in the objects of use, for both of the above types of US technical equipment, it is necessary to determine their effective design and technological parameters using, e.g., experimental and calculation methods [48]. In the absence of these parameters, the appearance of defective parts of the molded classical PCM and NM PCMs is not excluded.

For US treatment of impregnated fabrics, US cavitators are used based on magnetostrictive or piezoceramic transducers attached to a radiating plate, which as a result makes longitudinal and transverse bending vibrations [49].

The typical tasks of designing technology parameters and the equipment implementing it to produce traditional PCMs and NM PCMs of functional application aimed at identifying and subsequent study of the relationship between structural-mechanical and geometric parameters of molded products, on the one hand, and technological factors of their production, on the other hand. In particular, analytically obtained kinetic equations of longitudinal and transverse impregnation of oriented and woven fibrous fillers with liquid ECs, given in [50], allow us to predict the impregnation time and pulling speed of the fibrous filler through the impregnating bath, as well as to design its dimensions.

Analysis of experimental and statistical results on the effect of technological modes of impregnation of fibrous fillers with liquid PB on the strength of impregnated and hardened fibrous fillers makes it possible to predict the optimal tension force of the impregnated fibrous fillers under circumferential "wet" winding [51, 52].

To optimize material and time costs when designing technical means of forming the studied technological objects, it is advisable to use an approach based on the methodology of structural-parametric geometric modeling and engineering approach [53]. According to this approach, within the framework of the synthesis, the selected enlarged blocks and their constituent structural elements are analyzed, which simulate the structural and technological parameters of the technology and equipment (instruments) for sounding liquid polymer media and for producing, e.g., reactoplastic PCMs, as well as structural and technological interconnections between them.

Different aspects of simulation of the parameters of an ultrasonic dosed cavitator with radiative plate were studied in works [54–56]. In particular, in study [54] analysis of effective technical means of US exposure and a technique of variant structural-parametric design was provided. This paper [54] describes an adapted method for constructing US cavitators in contact with rectangular emitting plates. The use of this technique allows us to predict the optimal dimensions of the radiating plates for the rational use of their features in a particular technological process.

Aspects of optimization of design and technological parameters of US equipment were discussed in study [55], where parametric visualization of the variant design method
of US cavitation devices with radiating plates is given. In continuation of the methodological approaches outlined in [55], results of computer-aided variant 3D-design were presented in study [56]. This study describes the basic techniques of computer-based three-dimensional variant design of US device parameters using the developed method of structural-parametric modeling of a metering device with a rectangular radiating plate.

3.6. Efficiency of Ultrasonic Treatment under Production of Nanomodified Thermoplastic Composite Materials by Extrusion Method. As is known, the exceptional properties of NMPCMs are due to the optimal combination of the “soft” phase (polymer matrix) and the functional phase (dispersed in it by nanofillers).

In this case, an effective dispersion of CNTs in the liquid polymer matrix is necessary.

The latter, however, is difficult because of the attraction of nanoparticles to each other by particles with the formation of stable agglomerates. Agglomeration is also facilitated by the lack of affinity between the nanoparticles and the liquid polymer matrix.

To solve this problem, the initial components—liquid polymers, as well as CNT—were preprocessed (physicochemical modification) before making nanocomposites based on them.

The physicochemical modification aimed at minimizing the difference in free energy between the components of the nanocomposite to ensure the maximum realization of their individual properties in the molded material.

For example, the use of high-frequency sound waves in the pretreatment of a liquid polymer matrix, as well as in the operations of homogenization and mixing this matrix with a nanofiller, is widely used as the dominant method of physical modification. Such a modification leads to an improvement in the distribution of the dispersion of functionalized CNTs in liquid PBs.

The article in [57] provides examples of preliminary US treatment of nanoparticles in a liquid solution using US probe, including the process of deagglomerating nanoparticles in the open air under laboratory conditions. This forms a fluidized air layer, and nanocomposites are obtained by mixing the polymer melt with the treated nanoparticles.

In the process of extrusion when mixing the melt, it is possible to use US in the working chamber both at one fixed frequency and at several variable frequencies of the low frequency range. Such an impact suggests the presence of a resonant frequency (frequency range), due to the length of the polymer chain of macromolecules and its mechanical vibrations.

The diversification of the distribution of the lengths of polymer chains leads to the application of the spectrum of different US frequencies, which cause a change in the distribution of such chains from a random conformation to an extended one. Therefore, at the termination of the use of a specific US frequency, the conformation of the polymer chain can be randomly weakened to an arbitrary conformation. This effect improves the mobility of the polymer chain with the introduction of CNTs into it, which also increases the efficiency of dispersion of CNTs in the liquid polymer matrix.

In the investigation [58] describes approaches and technological aspects and also presents some results of the use of low-frequency US treatment in the preparation of high-viscosity melts of thermoplastics. The analysis of this work indicates a lack of knowledge of the mechanism of US action on highly viscous polymer melts. Apparently, this is due to the fundamental differences in the rheological properties of low-viscosity liquid thermoplastics and high-viscosity melts of reactoplastics. Nevertheless, in this work, directions of further research are indicated concerning the features of the study and the manifestation of both chemical and physical effects in the US processing of polymer melts.

3.7. Hybrid Polymer Composite Materials. One of the promising methods for modifying the surface of carbon fiber and PB to improve the physicomechanical and performance properties of the final product is the creation of carbon plastics of combined filling (the so-called hybrid PCMs: HPCMs). In HPCMs, continuous carbon fiber is combined with PB. At the same time, ultradisperse carbon nanoparticles are preliminarily uniformly distributed in the volume of the used liquid PB [59].

The main problem that arises when attempting to impart certain functional properties (for example, electrical conductivity) to a HPCM is that an increase in the concentration of CNT in a liquid PB entails a sharp increase in viscosity and a corresponding transition of the liquid PB to the thixotropic state. This circumstance makes it impossible to use traditional methods of producing prepreg on the basis of such PB.

To solve this problem, a new approach was developed, described in [60]. It consisted in applying PB, modified CNTs, from dispersion. Moreover, a volatile solvent (acetone) is used as a dispersion medium. The particles of the dispersed phase contain native CNTs or CNTs covalently modified with functional groups, an EO and a hardener. In the case of using nonfunctionalized CNTs, the modifier (compatibilizer) is included in the dispersion. At the same time, polymers are used as a modifier, providing noncovalent functionalization of nanotubes and regulating interaction in the subsystems “CNT–CNT”; “CNT–polymer matrix.”

Compared with the traditional covalent modification of the nanofiller, the developed approach has several advantages, which are as follows. Despite the fact that the interaction between each link of the block and the surface of the CNT is weaker than the covalent interaction between the functional group and the CNT, a large number of blocks that are part of the copolymer provide for its stronger attachment to the surface of the nanotube.

Further, noncovalent functionalization by changing the ratio between the blocks that make up the copolymer and the structure of the functional linkage block allows you to precisely control the interaction energy with the polymer matrix. The use of a number of copolymers with a known ratio of blocks and their structure makes it possible to investigate the fundamental laws of the influence of the interaction energy of the “CNT–polymer matrix” system on the functional and structural properties of NMPCMs.
Thus, this approach allows a controlled way to change the degree of CNTs aggregation and the architecture of the resulting nanostructures. And if, to obtain a nanocomposite with a high level of physicomechanical properties, a uniform distribution of CNTs in a polymeric matrix is required, then, to obtain electrically conductive nanocomposites with a minimum concentration of CNTs, their partial aggregation is more preferable.

In addition, noncovalent functionalization of CNTs is a more technologically advanced and cheaper way to obtain the starting components for the preparation of a nanocomposite compared with the traditionally used covalent functionalization. In this paper [60], a method was also proposed for creating a hydrophobic, electrically conductive PCM based on epoxy binder and a reinforcing filler of glass fabric. The method consisted in the simultaneous introduction into its composition of nanoscale objects—CNTs functionalized in the gas phase and a solution of telomers of tetrafluoroethylene in acetone.

The EC contained CNTs functionalized in the gas phase (7 wt.%), telomers of tetrafluoroethylene (7 wt. parts), and ER with a hardener (100 wt. parts). HPCM, obtained by pressing the prepreg, impregnated with this EC, has a number of the following set of functional properties. The value of the specific volume resistance of the studied HPCM sample along and across the plane of laying the reinforcing filler is 19 Ohm-cm and $6.7 \cdot 10^2$ Ohm-cm, respectively. It was found that the HPCM plate with a thickness of 0.68 mm attenuates electromagnetic radiation in the range 27–34 GHz by 100 times. The share of reflected radiation is 75–80%. The surface of the HPCM can be given hydrophobic properties, characterized by a high value of the wetting angle (136°).

Another approach to the creation of HPCM is described in [9, 61, 62]. In these works, it was proposed to carry out the nanomodification of a liquid PB simultaneously with its US treatment before impregnation of the reinforcing macrocell. It was determined that such a combined physicochemical modification leads to an improvement in the technological properties of a liquid PB and also contributes to the hardening of the hardened polymer matrix.

Also, a feature of the developed approach was the synthesis of CNTs directly on the reinforcing macrofibre tissue. In this case, the hardened polymer fixes uniformly distributed CNTs on the surface of dry macrofibres. It is established that this method of molding contributes to the creation of high-strength NM HPCM of functional application. For example, the shear strength of an NM HPCM molded on the basis of a polyester matrix increased by an average of 60%.

3.8. Production of Structural Electroconductive Polymeric Composites. As is known, in classical PCMs reinforcing macro- and microfillers traditionally play the role of a reinforcing element. Recently, when creating constructional NM of PCMs of a new type, nanomodifiers in the form of CNTs are also often endowed with an amplifying function due to their functional use. For example, one of such functions is high electrical conductivity [63]. Moreover, the conductivity of nanocomposites based on CNTs depends on many factors, for example, on the type of CNT and their concentration, the composition of the ingredients of the polymer matrix, and also the technology for producing NM PCMs.

In work [64], the following method for forming NM PCM is described. An array of vertically oriented CNTs was grown on an aluminum oxide substrate. Then they were cut from the substrate and squeezed in the direction perpendicular to the axis of orientation of the CNTs.

After that, the deformed CNTs impregnated the ER and cured, thus obtaining NM PCM. The measured value of the electrical conductivity of the obtained NM PCM in the direction of the orientation of the CNTs with their concentration in the composite about 6% was 10 S/cm.

In the work of other researchers [65], even greater values of the electrophysical and physicomechanical characteristics of NM PCMs were declared. At the same time, the array of vertically oriented CNTs was pulled in the direction perpendicular to their growth, thus obtaining stretched sheets of CNTs. Next, these sheets were impregnated with EC using the method of vacuum infusion at a concentration of CNTs of 8%. NM PCM was obtained on the basis of impregnated sheets, which were oriented in mutually perpendicular directions and then layered into layers, obtaining a composite based on 1750 stretched sheets. The obtained NM PCM is characterized by the following set of functional characteristics: tensile strength 117 MPa, modulus of elasticity 7.45 GPa, and electrical conductivity 2205 S/cm.

Of particular note are the fundamental technological differences in the production of NM PCMs of functional application based on reactoplastics and thermoplastics. In particular, due to the cardinal differences in the structure and properties, especially rheological, of these two classes of polymers, the use of an injection molding method and an extrusion method is effective for producing NM PCMs based on thermoplastics in the form of multiphase polymer matrices. This is due to the significant values of tangential stresses arising during the flow of polymer melts in the working bodies of thermoplastic equipment.

In the investigations [65, 66], other methods for obtaining NM PCMs on the basis of CNTs were described, which are characterized by a high level of functional and physicomechanical properties, namely, density 1.25 g/cm³, tensile strength equal to 3.8 GPa, the elasticity modulus which is 293 GPa, and the electrical conductivity which is 1230 S/cm.

The low density of the obtained NM PCM and the high level of electrical conductivity (which characterizes the resistance to lightning discharge) determine the prospects of using the material obtained in the structural elements of aerospace technology. According to the authors, the proposed methods are potentially applicable for large-scale industrial production.

However, due to the high shear stresses that occur during the molding of such NM PCMs, it is advisable to use extruders.

Another way to impart the electrical conductivity of NM PCMs is to use CNTs, the surface of which is decorated with electrically conductive metal nanoparticles [63, 67]. Thus, the electrical conductivity of nanocomposites with CNTs depends on the following factors: the type of nanotubes,
the composition of the polymer matrix, and the NM PCMs’ obtaining technology.

The effective modes of US treatment [68] predetermine the effectiveness of the modification of polymer liquid media, the deterministic distribution of CNTs over the volume of the composite, which, in turn, affects the amount of contact resistance between the CNTs. At the same time, the above-described technologies for producing NM PCMs from an elongated array of vertically oriented CNTs allow one to obtain (so far, however, mainly in laboratory conditions) functional nanocomposites, which are characterized by extremely high values of electrical conductivity and physicomechanical properties.

3.9. Forming Products from Intelligent Polymer Composites. It should be noted that the design of technical tools for molding of thermoplastics and reactoplastics does not have unified approaches, since there are features and differences in the design for each of the above class of PCMs. Therefore, such design should be considered in each individual case with respect to a particular technology. This is especially true for IPCMs; i.e., PCMs are a new generation due to the following prerequisites. Around the world, over the past decades, there has been a high demand for intelligent (smart) materials, primarily for innovative IPCMs and products made from them [69].

For example, for the molding of IPCM products using the injection molding method, a mold design was developed (see Figure 1), which contains a die 1 and a die 2, which form the molding cavity 3. In the wall of the matrix 1 is mounted the possibility of reciprocating movement of the probe 4 with the neck 5 for loading embedded parts 6 in the form of IS. Probe 4 is equipped with a drive 7, which ensures its progress. In the internal cavity of the probe 4 is mounted actuator 8, for example, in the form of a hydraulic cylinder, which drives the ejector 9.

The prepared portion of the viscous polymer under a certain pressure is injected into the forming cavity 3 of the mold formed by the matrix 1 and the punch 2 until it is filled. Probe 4 is currently in its original position. The insertion part 6 is fed into its internal cavity due to the fact that the hole in the wall of the mold and the hole 5 on the surface of the probe 4 are connected.

At this point, the actuator 11 moves the valve 10, opening the outlet of the probe 4. After that, the actuator 7 of the probe 4 moves it in the direction of the forming cavity 3 by a specified amount. Next, the actuator 8 moves the ejector 9 through the internal channel of the probe 4 and pushes the embedded part 6 into the filled forming cavity 3 by a predetermined stroke of the telescopic probe 4.

After pushing the embedded part of the probe 4 together with the ejector 9 it is moved to its original position by the actuator 7, and the valve 10 is closed by the actuator 11. Next is the exposure of the material in the molding cavity 3 and the cooling of the product from IPCM. After that, the mold is opened, and the product is removed from the molding cavity.

The proposed technical solution provides input IS in any given point of polymer products. This, in turn, allows to reduce the number of accidents during the operation of structural products from IPCMs. The latter is provided due to the early receipt of signals from the IS, introduced into the polymer material, about the onset of the critical state of the product under the action of alternating mechanical loads, temperature, and other operational factors.

4. Conclusions

The results of the studies described in this article confirm the effectiveness of physical, chemical, and combined physicochemical modification methods as the basic direction for improving the physicomechanical and operational characteristics of structural constructional classical PCMs and NM PCMs of functional purpose.

Development and design of effective technical means of low-frequency US cavitation processing is an effective direction for the implementation of physical modification technology. It is shown that in the optimum such a physical modification aimed at intensifying many technological operations for producing such materials, as well as at improving the physicomechanical and operational characteristics of the resulting products and structures based on them.

Also the use of molded intelligent materials allows to reduce the number of accidents during the operation of such products due to the early receipt of signals from the entered ISs on the onset of a critical state.

Further areas of research in the field of creation of reinforced PCMs of functional purposes are the improvement of the properties of nanomodifiers used, the improvement of the technology of their deagglomeration, and the subsequent homogenization of the components of nanocomposites, as well as the development of innovative methods for the synthesis of carbon plastics of combined filling in the form of hybrid carbon composite materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.
References


