Review article

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Use of nano-sized components in multilayer composite materials

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ABSTRACT

Introduction. In our country, the use of composite materials for creating parts and structural components in the construction industry is not as widespread as it could be. Composite materials are multilayer structures made of reinforcing fibers, impregnated with a polymer binder, which is also an adhesive. The strength properties of layered structural materials are achieved through various reinforcing fillers and adhesive binders. Both glass fibre and carbon fibre fabrics and fibers themselves are widely available as layered materials. Various thermosetting resins (epoxy, phenolic, polyester, polyimide, polyamideimide, polyamide, etc.) are used as binding components. Among them, epoxy resins with high strength, wettability and adhesion to various materials are widely used. Layered composite materials (LCM) are used to make polymer reinforcement for reinforcing concrete structures, various pipes, shell frames to strengthen existing metal and reinforced concrete structures, load-bearing elements in light-loaded structures of bridges and crossings. However, at the same time they have a significant drawback – low interlayer strength (propensity to layering). As a result, the connection between the layers is disrupted, which leads to a significant decrease in the rigidity and strength of the structure. This phenomenon applies to all types of fabrics and fibers. Most often, defects in the form of layering are formed under the influence of shock loads. To improve the performance characteristics of such materials, various fillers have now begun to be used - powders (micro- and nano-sized) introduced into binder compositions. Main part. The analysis of the academic literature has shown that it is possible to increase the interlayer strength in structural elements made of LCM through the use of nanofilled binders and the introduction of nanoadditives into the interlayer space of layered materials. The article reviews the related inventions in Russia, USA, etc., which can be applied in the construction industry using nanodispersed components. With the widespread use of the presented materials (in bridges, pedestrian bridges and bridge decks, etc.), significant performance advantages can be achieved compared to materials traditionally used in the construction industry. Methods and materials. By comparing the data from the submitted patents for inventions, it was revealed that the introduction of from 2% to 5% of various nanocomponents to form a nanocomposite material provides a new means of modifying the physical properties of polymer binders. Results. It was revealed that the use of nanoparticles ensures the decrease in the fluidity of prepregs and the gelation time, and the increase in residual compressive strength and specific fracture energy – indicators characterizing the crack resistance of composite materials. As a result, fracture toughness, endurance and survivability increase. Conclusion. Increasing the reliability of composite materials leads to longer service life of products and structural elements in the construction industry.

KEYWORDS: layered composite material, nanofilled binders, nanocomposite, nanopowder, epoxy composition, matrix.

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INTRODUCTION

urrently, the world market is witnessing a significant increase in the market volume of layered composite materials not only in the aviation and space industries, but also in the construction industry. The use of layered composite materials (LCM) in construction makes it possible to reduce the weight of building structures, increase resistance to adverse climatic factors, extend the time between repairs with higher strength, which provides significant advantages over materials traditionally used in the construction industry. The main areas of application of LCM are fiberglass pipes and other products produced by the winding method and used in heating networks, composite reinforcement and elements of bridge structures (pedestrian bridges, crossings, overpasses, load-bearing elements and fencing elements, decking), which are subject to high reliability requirements and durability [1]. It should be noted that the development of the domestic LCM market for construction purposes is significantly inferior to the global one. For example, in North America and Europe, various bridge structures using LCM elements have been built for more than 15 years, and the volume of construction of such bridges is increasing every year. The class of bridges is also changing - from the first experimental pedestrian bridges to road bridges up to 20 m long [2-4]. In foreign countries, the main areas of the LCM use in bridge construction are composite reinforcement, bridge decks and pedestrian bridges. Work is underway to develop prefabricated bridges using load-bearing structural elements from LCM [5–6]. According to the author of the work [3], in the construction industry the most promising areas for the widespread use of LCM are pedestrian bridges and bridge decks.

It should be noted that our country is also witnessing big interest in reducing the weight and size characteristics of the structures of heavy mechanized bridges, tank bridge laying vehicles, mechanized bridge complexes, and pontoon parks through the use of multilayer composite materials. Operating enterprises such as LLC Research and Production Enterprise "Applied Advanced Technologies" (LLC RPE "ApATeC"), Ruskompozit Group of Companies, "Opora" LLC have designed and built more than 4 dozen bridge structures, which are successfully operated in a number of facilities in Moscow, Sochi and other cities of the Russian Federation [7-8]. Unfortunately, there are not enough such enterprises in our country, although there are prospects for the further use of such materials in bridge structures. In Russia, national standards have been developed regulating the use of composites in load-bearing structures of pedestrian bridge structures [9–12]. These standards and recommendations allow the widespread use of modern composite materials in various bridge structures.

It is known from [13–16] that it is possible to increase the strength properties of composite materials in building structures and their rigidity characteristics by introducing nanodispersed components into their composition, which will significantly improve the operational characteristics of structures.

The analysis of the research literature has shown that the interlayer strength in structural elements made of composite materials is increased through the use of nanofilled binders and through the introduction of nanoadditives into the interlayer space of layered materials. An additive (nano particles with the diameters from 1 to 100 nm) is often introduced to improve one or more properties of the polymer binder. Polymer nanocomposite binders are formed by mixing fillers, which are nano-sized particles, and thermosetting or thermoplastic polymers. The properties of polymer nanocomposite adhesives compare favorably with the those of conventional binders. When using such matrices, the operational characteristics of LCM change: i.e. increased strength and rigidity, deformation heat resistance, resistance to ultraviolet radiation, barrier characteristics of membranes and coatings, as well as thermal and electrical conductivity.

The purpose of this study is to review patents for inventions on materials and promising technologies that can improve the strength and performance characteristics of LCM for building structures through the use of nanoparticles.

MAIN PART

NANO-FILLED BINDERS

Prepreg and a product made from it [17]

The method for producing a nanomodified binder is as follows: Fullerene C_{60} (0.01 parts by weight), carbon nanotubes NTA (0.1 parts by weight), fulleroid multilayer nanomodifier NTC – Astralen (0.5 parts by weight) and an amino derivative fullerene C_{60} (0.02 parts by weight) is dispersed in an organic diluent and the resulting suspension is subjected to ultrasonic treatment (frequency -35 kHz, time -30 minutes). The resulting suspension of carbon nanoparticles is introduced into 100 parts by weight. epoxyamine resin ECD (N, N, N', N' – tetraglycidyldiamino-3,3'-dichlorodiphenylmethane, and add 44 parts by weight of the hardener - 4,4'-diaminodiphenylsulfone, mix and thus obtain a polymer binder. The introduction to the polymer binding of amine derivatives of fullerenes together with other nanoparticles makes it possible to mobilize their potential for targeted interaction with modification objects the "dispersed phase-dispersion medium" boundary in the supramolecular structure of the polymer matrix and the "reinforcing fiber-polymer matrix" interface.



It is these interphase boundaries that are responsible for the mechanical properties of the polymers, polymer composite materials and, accordingly, for the endurance and survivability of products made from them.

The proposed technical solution provides a reduced fluidity of prepregs by 10-40%, less gelation time by 5-10 times, an increased residual compressive strength by 10-15% and more specific fracture energy by 40-50% – indicators characterizing the crack resistance of composite materials. As a result, their fracture toughness, endurance and survivability increase. Increasing the reliability of composite materials makes it possible to increase the service life of products and structural elements.

Method for producing a nanomodified binder, binder and prepreg based on it [18]

The nanomodified binder is prepared as follows. A concentrate is prepared by dispersing nanomodifier particles in a condensation resin with a viscosity of more than 600 cP by ultrasonic exposure with a radiation power of 1 to 5 kW and an amplitude of 20 to 80 μ m. Next, the resulting concentrate is introduced into the binder based on a condensation resin. To intensify the dispersion process, ultrasonic action is used, which promotes the effective destruction of particle aggregates, however, stabilization requires the presence of a resin that has functional groups and a viscosity of more than 600 cP to prevent subsequent aggregation. Adjusting the parameters of ultrasonic exposure, such as amplitude from 20 to 80 microns and radiation power from 1 to 5 kW, allows you to select optimal modes for each type of resin.

Nanoparticles of metals and alloys, their oxides, nanotubes and nanofibers of various structures can be used as nanomodifiers. The best effect is achieved by using nickel, copper, aluminum and nanotubes as nanomodifiers, but this list of nanomodifiers is not exhaustive. Nanomodifiers are catalysts for curing processes based on the functional groups of both amine and anhydride curing resins, as well as the formation of crosslinking in phenolic and polyimide resins. Therefore, their introduction into the polymer matrix leads to an increase in strength indicators and contributes to a more complete curing process.

The invention makes it possible to obtain a binder with good redispersibility and stability of nanoparticles during storage. Prepregs based on a nanomodified binder have an improved set of physical and mechanical properties by 15-30%, depending on the resin used.

Polymer nanocomposite and method for its preparation [19]

The composite contains epoxy resin, hardener and filler – glass spheres and nanomodifier. The nanomodifier – aluminum oxide and zirconium oxide and/or yttrium

oxide, is prepared by performing sol-gel synthesis, which is carried out by reverse coprecipitation of aluminum and zirconium and/or yttrium hydroxides. The nanocomposite is obtained by mixing epoxy resin and nanomodifier, introducing a hardener and gradually introducing glass spheres. The polymer composition includes epoxy resin, hardener and filler, based on the weight of the resin, glass spheres in an amount of 1-16.5 wt.% and 1-3 wt.% of a nanomodifier, which is aluminum oxide and zirconium oxide and/or yttrium oxide. To uniformly distribute the nanomodifier in the volume of epoxy spheroplastics, dried nanomodifier powder is introduced into the epoxy base and mixed thoroughly. A hardener is added to the resulting system, mixed with the gradual introduction of predried glass spheres in air until a visually homogeneous mass is formed. Further mixing is continued in a vacuum mixer to remove air bubbles formed during the previous stages of preparation.

Polymer composites obtained using this composition have improved heat and chemical resistance, ignition resistance, and combustion retardation.

Composite materials obtained with this binder can be used, for example, in the construction of bridges, ships, the manufacture of vehicle parts (for example, cars or aircraft), in electronics, in the production of construction and structural materials.

Nanomodified epoxy composite [20]

Nanomodified epoxy composite, including epoxy resin, hardener, inorganic filler and nanoparticles of aluminum oxide, or zirconium oxide, and/or yttrium oxide as a nanomodifier, where it contains quartz or silica fabric of volumetric weave as a filler, and the nanomodifier is made in the form of spheres obtained by evaporation-condensation method, with the following ratio of components, parts by weight: epoxy resin 100, hardener 10, filler 60–65, spherical nanoparticles Al_2O_3 , or ZrO_2 , and/or Y_2O_3 17–22.

To produce a nanomodified epoxy binder, epoxy resin type KDA or KDA-2 is used as a base according to TU 2225-661-11131395-2005. A weighed amount of epoxy resin is loaded into the mixer and mixed at a rotor speed of 750 rpm. Mixing is carried out until the resin temperature reaches 35-40°C. Then aluminum oxide nanopowder in an amount of 20 wt. is introduced into the mixer in small portions of no more than 100 g/min. hours in relation to the introduced amount of epoxy resin (100 parts by weight). To produce the binder, nanopowders are used, consisting of weakly aggregated spherical particles with an average size of 30-50 nm. Such powders are obtained, for example, by the method of electric explosion of a wire in a mixture of argon and oxygen gases. Uniform mixing of the mixture components at a mixer rotor speed of 750 rpm is carried out for 1 hour. After mixing is completed, the re-



sulting mixture is poured into a sealed container for shipment to the consumer. Immediately before starting the manufacture of the body parts, a hardener of the TEAT-1 type TU 6-09-11-2119-93 in an amount of 10 wt. parts in relation to the weight of epoxy resin is mixed into the binder., and then applied to the reinforcing filler.

The invention is intended to be used in mechanical engineering, construction, aviation and space fields, since it has the improved physical and mechanical characteristics and higher erosion resistance.

Epoxy composition [21]

The epoxy composition contains an epoxyanhydride mixture and aluminum oxide nanoparticles with sizes of 5-20 nm in the following component ratio (wt.%): epoxyanhydride mixture 70.0-99.5, aluminum oxide nanoparticles 0.5–30.0. The composition is pre-treated with ultrasound at a frequency of 22 kHz for the time that ensures uniform distribution of nanoparticles throughout the composition. The epoxyanhydride mixture contains epoxy diane resin ED-20, anhydride hardener - isomethyltetrahydrophthalic anhydride (iso-MTHFA), plasticizer EDOS, accelerator UP-606/2 at a ratio (parts by weight) of 100:80:5:1.5, respectively. Aluminum oxide nanoparticles have high surface energy, which leads to the high degree of agglomeration. However, under certain conditions ultrasonic treatment of an epoxyanhydride mixture filled with aluminum oxide nanoparticles ensures uniform distribution of particles throughout the composition. The distribution of aluminum oxide nanoparticles in the polymer matrix is ensured using the IL-10-0.1 ultrasonic generator with the frequency of 22 kHz and the power of 1000 W. Aluminum oxide nanoparticles have a specific set of acid-base properties (point of zero charge, surface complexation constants (pKa), forming the charge and potential of the surface), which determines their physical and chemical activity and expands the scope of application of the claimed composition.

The use of the invention claimed will improve the quality of products due to improved tribological, mechanical properties and characteristics of the epoxy composition, which can be used in mechanical engineering and construction.

The method for preparing a nanosuspension for the production of a polymer nanocomposite [22]

The method involves preparing a nanosuspension by introducing 0.5-10.2 wt. % carbon nanotubes (CNTs) into a thermoset binder under ultrasonic (US) influence with the intensity in the cavitation zone ranging from 15 to 25 kW/m². Moreover, the dispersion of carbon nanotubes in the binder is carried out with simultaneous photographic recording of changes in the color intensity

of the nanosuspension. When the nanosuspension reaches color intensity values corresponding to the values of the normalized degree of dispersion in the range from 0.9 to 0.99, the ultrasonic treatment is stopped. It has been found that the degree of dispersion of CNT nanoparticles at a given concentration corresponds to the color intensity of the nanosuspension, which changes as the dispersion process is carried out under ultrasonic influence. The best strength properties of the composite are obtained when the particles are evenly distributed throughout the volume of the binder. In this case, the color intensity of the nanosuspension takes on the maximum steady-state value for a specific ratio of CNTs and binder, and does not change with the further exposure to ultrasound. As the particles deagglomerate and are evenly distributed in the binder, the color intensity of the nanosuspension changes from a transparent state, through gradual turbidity until the color intensity reaches a steady-state value. A steady-state level of intensity is achieved at a certain treatment time, beyond which either the remaining agglomerates are no longer destroyed, or all CNT nanoparticles are distributed evenly (there are no agglomerates in the nanosuspension in this case). Continuing the process of ultrasonic exposure beyond this value is useless from the point of view of achieving better dispersion and harmful from the point of view of the safety of CNTs, which, with prolonged ultrasonic exposure, can violate their integrity.

The method makes it possible to optimize the degree of dispersion of carbon nanotubes in the binder and reduce the production time of nanocomposites that have increased strength due to the uniform distribution of nanoparticles in the nanocomposite. Such composites can be used as structural materials in space, aviation, construction and other industries.

Nanocomposite material based on polymer binders [23]

The nanocomposite material contains a polymer binder, filler and a fraction of nanoparticles. The nanoparticle fraction includes multilayer torus-shaped carbon particles ranging in size from 15 to 150 nm, in which the ratio of the outer diameter to the thickness of the torus body is in the range (10-3):1. The filler is selected from the group consisting of glass, carbon and organic and boron fibers. The binder is selected from the group consisting of epoxy resins, epoxy novolac resins, epoxy phenolic resins, polyesters, polyimidazole or polyoxybenzimidazole. The use of a fraction of nanoparticles in the composition of a nanocomposite material makes it possible to achieve effective compaction and strengthening near the filler/binder interfaces and increase its average density, elasticity, rigidity and strength. The indicated torus-shaped carbon particles are preferably of the fulleroid type. The interlayer distance in



such particles is 0.34-0.36 nm. It is advisable that these torus-shaped particles are particles from the cathode deposit crust obtained by evaporation of a graphite anode in an arc process and subjected to gas-phase oxidation, which are subject to the action of the electric field. It is optimal when the nanoparticle fraction in the proposed nanocomposite material is present in an amount of up to 25% by weight of the polymer binder. In this case, the desired effect is achieved when such particles are present in an amount of 0.02% by weight of the binder.

Nanocomposite material with improved mechanical properties can be used in the manufacture of various parts and products for mechanical engineering, construction and transport.

Nanomodified epoxy binder for composite materials [24]

Nanomodified epoxy binder for composite materials includes epoxy diane resin and amine hardener. As a hardener, it contains polyamine of the Aramin-T brand, which is a modified aromatic polyamine. The composite material contains silicate-type nanoparticles, which are organophilic clay of the "Monamet 1E1" brand, and carbon-type nanoparticles, which are carboxylated carbon nanotubes of the "Taunit-M" brand. If necessary, it contains a plasticizer-flotation agent oxal T-92, which is a mixture of dioxane alcohols and their high-boiling ethers. The composite material contains an active diluent, which is a condensation product of aniline and epichlorohydrin (epoxyaniline resin brand EA).

The indicated components are contained in the composite material in the following ratio (wt.%): epoxy resin (4.12-72.44), silicate-type nanoparticles (0.51-1.81), carbon-type nanoparticles (0.02–0. 45), plasticizer (0.0–0.56), active diluent (3.78–65.52), aromatic amine hardener (22.69-28.1). 0.02 wt.% of Taunit-M carboxylated carbon nanotubes are added to 72.44 wt.% of ED-20 epoxy resin and the resulting mixture is dispersed by ultrasonic exposure using a submersible emitter UZDN-2T for 45 minutes at an exposure frequency of 22 kHz. Then, the resulting dispersion of Taunit-M carboxylated carbon nanotubes in ED-20 epoxy resin is loaded into a 50-liter mixing reactor, equipped with heating and a mechanical stirrer, and 3.78 wt.% of the active diluent – epoxyaniline resin grade EA and stirred with a gradual rise in temperature to $(50\pm5)^{\circ}$ C for (20 ± 5) minutes from the moment of loading. Next, while continuing stirring, small doses of 0.26 wt.% silicate-type nanoparticles are loaded – organophilic clay of the Monamet 1E1 brand and stirring is continued for (85 ± 5) minutes at a temperature of $(50\pm5)^{\circ}$ C. The finished resin part is poured into metal drums or flasks.

Preparation of the hardener: 22.69 wt.% of the Aramin-T hardener is loaded into the container equipped with heating and a stirrer and heated to the temperature of $(80\pm5)^{\circ}$ C while stirring. Then, continuing mixing, small doses of 0.25 wt.% silicate-type nanoparticles are loaded – organophilic clay of the Monamet 1E1 brand, 0.56 wt.% oxal flotation reagent T-92 and mixed until a homogeneous composition is obtained for (90±10) min at the temperature of (80±5)°C. The product cooled to (50±5)°C is poured into metal drums or flasks.

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Preparation of the composition: 76.5 wt.%. resin part and 23.5 wt.% hardener, preheated to the temperature of $(50\pm5)^{\circ}$ C, are loaded into a reactor equipped with a mechanical stirrer and stirred for (15 ± 5) minutes. Curing is carried out at the temperature of $(160\pm5)^{\circ}$ C for (20 ± 2) minutes.

The technical result of the invention is to reduce the curing time of the binder, to increase the heat resistance and strengthen the characteristics of the cured compositions, and to expand the range of epoxy compositions with improved technological and operational characteristics. The invention can be used in the production of fiber-glass pipes and other products produced by the winding method and used in heating networks, hot water supply systems with network water, water supply systems with the operating temperature of up to 150°C.

The polymer binder, the composite material based on it and the method of its manufacture [25]

The polymer binder contains N,N,N',N'-tetraglycidyldiamino-3,3' dichlorodiphenylmethane (ECD), and additionally the open carbon nanotubes and a fulleroid multilayer nanomodifier astralen in the following component ratio (parts by weight):

N,N,N',N'-Tetraglycidyldiamino-3,3'-dichlorodiphenylmethane (TU 6-05-1725-75) – 100; 4,4'-Diaminodiphenylsulfone (TU 6-02-1188-79) – 44;

Fullerene C_{2n} , where n is not less than 30 (TU 31968474.1319.001-2000) - 0.01-1.0;

Open carbon nanotubes (TU 31968474.1319.001-2000) – 0.1–1.5;

Fulleroid multilayer nanomodifier astralen (TU 31968474.1319.001-2000) - 0.5-10.

A composite material made of the polymer binder and carbon fiber filler, is characterized in that the proposed polymer binder is used as a polymer binder in the following ratio of components, wt.%:

Polymer binder -36-42;

Carbon fiber filler -58-64.

A composite material differs in the following: ropes, tapes, and fabrics are used as carbon fiber filler.

A composite material made of a polymer binder and organofiber filler, differs in that the proposed polymer binder being used as a polymer binder in the following ratio of components, wt.%:

Polymer binder -47-50;

Organofiber filler -50-53.

A composite material is distinguished by the fabrics used as an organ-fiber filler.

A composite material made of the polymer binder and glass fiber filler is characterized with the proposed polymer binder used as a polymer binder in the following ratio of components, wt.%:

Polymer binder -24-30;

Fiberglass filler -70-76.

A composite material is distinguished by the glass fabrics used as a fiberglass filler.

The method for producing a composite material includes fullerene C_{2n} , where n is not less than 30: open carbon nanotubes and a fulleroid multilayer nanomodifier astralen in the form of a suspension in acetone are mixed with N,N,N',N'-tetraglycidyldiamino-3,3'-dichlorodiphenylmethane by ultrasonic action, followed by the introduction of 4,4-diaminodiphenylsulfone, then the resulting polymer binder is used to impregnate carbon, organo-, or glass fiber filler, the surface of the described filler being pre-finished with a solution of fullerene in a solvent (aromatic hydrocarbon), afterwards the resulting prepreg is dried and the composite material is formed.

The proposed polymer binder, a composite material based on it and the method of its manufacture will make it possible to create promising products with increased strength properties.

Epoxy composition [26]

For gluing and repairing fiberglass structures epoxy composition includes epoxy diane resin, modifier, filler and amine hardener, while silane-modified polyurethane (SPU-polymer) is used as a modifier, and silicate-type nanoparticles, which are organophilic clay powder based on modified montmorillonite MOHAMET 1E1, aromatic polyamine of the Aramin trademark is used as a hardener with the following component content in parts by weight: epoxy resin 100, SPU polymer 5–25, silicate type nanoparticles 10–50, hardener – aromatic polyamine 40-50.

The SPU polymer combines the advantages of curing by the silanes mechanism and the properties of the polyurethane matrix, as well as the use in the composition of organophilic clay MOHAMET 1E1 and a hardener – an aromatic polyamine of the Aramin trademark. It can significantly increase the adhesive strength of the composition when gluing fiberglass parts or repairing fiberglass structures, especially in wet conditions – when applied to damp and wet surfaces.

The invention relates to cold-curing polymer epoxy compositions and can be used for gluing and repairing fiberglass building structures, including wet conditions, when applied to damp and wet surfaces.

INTRODUCTION OF VARIOUS FILLERS INTO THE INTERLAYER SPACE OF COMPOSITE MATERIALS

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The phase boundary is the weakest point of the layered material; it is here that the destruction in the form of layering begins, both under mechanical loads and under other hit impacts. Defects in the form of layering can be reduced by introducing particles of thermoplastic polymers or nanoadditives into the intermediate layers.

Thermoset resin composites containing interlayer impact-increasing particles [27]

Polyamides and copolyamides in the powder form are the preferred thermoplastic materials for structured thermoplastic layers. Insoluble thermoplastic powders with particle sizes from 35 to 60 microns are used in amounts up to 15% by weight. The use of smaller particles is not effective because the particles migrate into the fibrous layers during formation and curing, and larger particles pose a problem regarding possible destruction of the interlayer zone during curing of the product due to their relatively large size. Thermoplastic polyamide particles are used, having a melting point of up to 170°C, which are applied to the interlayer space. Heat treatment of bags is carried out at the temperatures from 170 to 190°C. The method makes it possible to obtain a composite material containing thermoplastic particles that increase impact resistance and have improved compression characteristics under the conditions of higher temperature and humidity.

Structured thermoplastic in the intersheet zones of composite materials [28]

There is a method known where thermosetting resin and fibrous layers are combined in such a way that between the layers there is a structured thermoplastic layer, which is a non-woven material with a thickness of 0.5 to 50 microns and a weight of no more than 20 g/m^2 . Nonwoven material in the form of veils is made from hydrowoven or randomly oriented fibers of polyamides, copolyamides, polyesters, copolyesters, and polyurethanes. The veil layer is attached to dry unidirectional layers by partially melting or softening the veils and simultaneously pressing the veils with unidirectional fibers. The resulting structural elements made by this method have high structural strength and resistance to damage.

Method for producing layered plastic [29]

To obtain layered plastic, impregnation of the carbon filler with an epoxy binder, assembly of a prepreg package and molding are used, while when assembling the package, additionally between the layers of prepregs there placed a thermoplastic polyamide or polysulfone film

with a surface energy of at least 50 mJ/m² in an amount of 1-10 wt.% on 100 wt.% binder in the form of continuous layers, strips or mesh. The use of these films in the interlayer zone leads to a significant increase in the fracture toughness and residual compressive strength after a normalized impact and makes it possible to adjust the properties of the material depending on the magnitude of the most probable damage from impact loads with different energies. The use of the film in the form of strips with a certain pitch or meshes with a certain cell size allows you to regulate the maximum allowed size of a probable defect or permissible operational damage. Due to insufficient wettability of the film surface, the use of thermoplastic films with the surface energy of less than 50 mJ/m² sharply reduces the interlayer strength and fracture toughness of carbon fiber plastic. The thickness of the thermoplastic film used is selected depending on the thickness of the carbon fiber monolayer, but it is preferable to use films with a thickness of 40-75 microns. The use of thermoplastic film in an amount of less than 1 wt.% causes technological difficulties when placing the film to assemble the package, and the increase in the amount of film above 10 wt.%, in turn, leads to the decrease in the strength characteristics of carbon fiber plastic.

Method for producing layered plastic [30]

The invention deals with the technology for manufacturing layered composite materials to be used in all industries and concerns the method for connecting prepregs. Fiber filler (glass or carbon fabric) is impregnated with an epoxy binder and a prepreg is obtained, then the prepreg is cut into pieces of the required size and a prepreg package is assembled, during which additional prepreg is placed between the layers of the prepreg, silicon dioxide nanoparticles are pre-applied with an aerosol on both sides and then molding is carried out. The authors found that there is an optimal number of nanoparticles distributed on the surface of the prepreg, which allows to increase the strength properties of layered composites, which depends on the size of the nanoparticles, the concentration of particles in the aerosol space and the time the prepreg is in the aerosol space.

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The present invention makes it possible to obtain layered composite materials with the stronger characteristics of manufactured products by increasing the interlayer strength of the composite.

CONCLUSION

From the presented patents for inventions [17-30], it has been revealed that the introduction of from 2 to 5% of various nanocomponents to form a nanocomposite material is a new means of modifying the physical properties of polymer binders. The use of nanoparticles in the binder ensures the decrease in the fluidity of prepregs and gelation time, the increase in residual compressive strength and specific fracture energy – the indicators that characterize the crack resistance of the composite materials. As a result, the fracture toughness, endurance and survivability of the structure, as a whole, increases by 10-30%, depending on the patent for the invention used. Increasing the reliability of the composite materials makes it possible to increase the service life of products and structural elements in the construction industry.

REFERENCES

1. Keller T. Material-tailored use of FRP composites in bridge and building construction. *CIAS international seminar*. 2007; 319-333.

2. Ushakov A., Klenin Y., Ozerov S. Development of modular arched bridge design. *Proceedings of the 5th International Engineering and Construction Conference* (IECC 5). Irvine, CA, USA. 2008; 95-101.

3. Peng Feng, Lieping Ye. Behaviors of new generation of FRP bridge deck with outside filament-wound reinforcement. *Third International Conference on FRP Composites in Civil Engineering* (CICE 2006). Miami. 2006; 139–142.

4. Klenin Yu.G., Pankov A.V., Sorina T.S., Ushakov A.E. Application of composite materials for bridge structures. *Introduction of experience of applied advanced technologies in industry and transport*: collection of papers. Issue 3. M.: Publishing house TsAGI. 2004; 5-12.

5. Bannon D.J., Dagher H.J., Lopez-Anido R.A. Behavior of Inflatable Rigidified Composite Arch Bridges. *Composites Polycon-2009. American Composites Manufacturers Association*. Tampa. 2001; 1–6.

6. Rapidly-deployable light weight load resisting arch system: pat. 20060174549 A1 US; published 10.08.2006.

7. Ushakov A.E., Klenin Yu.G., Sorina T.G., Khairetdinov A.Kh., Safonov A.A. Bridge structures made of composites. *Composites and nanostructures*. 2009; 3: 25–37.

8. Internet resource: http://www.apatech.ru/bridge_engineering.html

9. GOST R 54928-2012. Pedestrian bridges and overpasses made of polymer composites. Technical conditions.



10. GOST 33119-2014. Polymer composite structures for pedestrian bridges and overpasses. Technical conditions.

11. GOST 33376-2015. Composite polymer decking sections for pedestrian and road bridges and overpasses. General technical conditions.

12. Industry road methodological document: ODM 218.2.058-2019. Recommendations for the use of composite materials in the designs of bridge structures and transition bridges.

13. Brusentseva T., Zobov K., Filippov A., Bazarova D., Lkhasaranov S., Chermoshentseva A., Syzrantsev V. Introduction of nanopowders and mechanical properties of materials based on epoxy resins. *Nanoindustry*. 2013; 3 (41): 24-31.

14. Pokrovsky A.M., Chermoshentseva A.S. Experimental study of the influence of nanoadditives on the properties of composite materials with interlayer defects. *Bulletin of the Moscow Aviation Institute*. 2017; 24 (3): 150-159.

15. Bokhoeva L.A., Baldanov A.B., Rogov V.E., Chermoshentseva A.S., Amin T. Effect of adding nanopowders on the strength of multilayer composite materials. *Factory Laboratory. Diagnostics of materials.* 2021; 87 (8): 42–50. DOI: https://doi.org/10.26896/1028-6861-2021-87-8-42-50 10

16. Chermoshentseva A.S., Pokrovskiy A.M., Bokhoeva L.A., Baldanov A.B., Rogov V.E. Influence of modification by nanodispersed powders on layered composite aerospace hulls and protective shields. *IOP Conference Series: Materials Science and Engineering*. Novosibirsk, 2019; 012178.

17. Kablov E.N., Gunyaev G.M., Ilchenko S.I., et. al. Prepreg and a product made from it. Patent 2278028 RF MKS P. 1. 2006; 17.

18. Yablokova M.Yu., Serbin V.V., Avdeev V.V. Method for producing a nanomodified binder, binder and prepreg based on it. Patent 2415884 RF MKS. P 2. 2011; Bull. 10.

19. Konakov V.G., Nikolaev G.I., Sudareva N.G., et al. Polymer nanocomposite and method for its production. Patent 2414492 RF MKS P. 2. 2011; 8.

20. Abdrakhmanov F.Kh., Beketov I.V., Koytov S.A., et al. Nanomodified epoxy composite. Patent 2661583 RF MKS P. 1. 2018; Bull. 20.

21. Belykh A.G., Vaseneva I.N., Sitnikov P.A. et al. Epoxy composition. Patent 2633905 RF MKS C 1. 2017; 29.

22. Tarasov V.A., Stepanishchev N.A., Stepanishchev A.N., et al. Method for preparing a nanosuspension for the production of a polymer nanocomposite. Patent 2500695 RF MKS. P. 1. 2013; 34.

23. Ponomarev A.N., Olga Meza. Nanocomposite material based on polymer binders. Patent 2437902 RF MK. P. 2. 2011; 36.

24. Kosolapov A.F., Bal M.B., Natrusov V.I. Nanomodified epoxy binder for composite materials. Patent 2584013 RF MKS. P. 1. 2016; 14.

25. Kablov E.N., Gunyaev G.M., Ilchenko S.I., et al. Polymer binder, composite material based on it and the method for its manufacture. Patent 2223988 RF MKS. P. 2. 2004; 5.

26. Kosolapov A.F., Bal M.B., Seleznev V.A. Epoxy composition. Patent 2618557 RF MKS. P. 1. 2017; 13.

27. Aerts Vincent J., Bonneau Mark, Elder Judith. Thermoset resin composites containing interlayer impactincreasing particles. Patent 2641004 RF ISS. P. 1. 2018; 2.

28. Mortimer Stephen. Structured thermoplastic in intersheet zones of composite materials. Patent 2602159 RF MKS. P. 1. 2016; 31.

29. Kablov E.N., Rumyantsev A.F., Raskutin A.E. Method for producing layered plastic. Patent 2271935 RF MKS. P. 1. 2006; 7.

30. Rogov V.E., Bokhoeva L.A., Chermoshentseva A.S. Method for producing layered plastic. Patent 2715188 RF MKS. P. 2. 2020. 6.

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