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ORIENTATION OF ANISOTROPIC CARBON PARTICLES IN THE MATRIX OF REINFORCED PLASTICS BY AN AC ELECTRIC FIELD

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In order to increase the shear strength of glass-fibers-reinforced plastics, a method has been developed for orientation of conductive carbon nanoparticles by an electric field applied transversely to the reinforcing fibers. Results of our research confirm the efficiency of the method offered — the shear strength the composites increased significantly, up to 35%, without reducing their other characteristics.

Introduction

Reinforced plastics on the basis epoxy matrices and high-strength continuous fibers of various nature find a rather wide application in modern engineering. Such materials possess high elastic-strength characteristics in tension and compression in the fiber direction due to characteristics of the reinforcing fibers. At the same time, the low strength of these materials in the transverse direction — the shear strength and specific fracture toughness (crack resistance), are caused by the properties of epoxy matrices. The purpose of the given research was to develop an effective method for increasing the shear strength and crack resistance of reinforced plastics.

There are several ways to improve the characteristics mentioned. For example, modifying the polymeric matrix by addition of disperse mineral particles of shungite, calcium oxide, and montmorillonite clays, and heat-resistant thermoplasts — polyamides, polyimides, polysulfones, and other components [1-3]. Addition of rubbers and active thinners considerably reduces the heat resistance of the material [4], the use of heat-resistant thermoplasts greatly complicates their technology owing to the high viscosity of binder [5-9], and the disperse mineral additives are of low efficiency [10, 11]. Great hopes were connected

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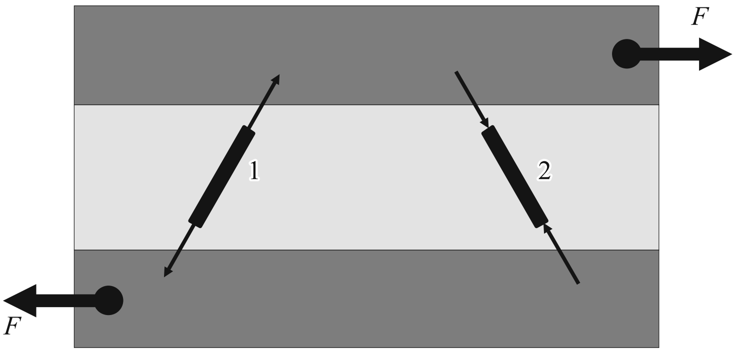


Fig. 1. Schematic of nanotube orientation in the interfiber space at interlaminar shear. 1 — tension and 2 — compression.

with the use of carbon nanoparticles, mainly carbon nanotubes (CNTs) as modifiers. But the effect of their application also appeared to be insignificant [12-14]. Authors of the present work have conjectured that positive results could be achieved by orientation of anisotropic filler particles perpendicularly to the reinforcing fibers, which would allow one to maximally utilize the elastic-strength characteristics of the particles. A method to orientate current-conducting disperse particles with the help of an electric field has been developed. Earlier, in [15-17], the possibility of orientation CNTs by an electric field in a liquid polymer environment has already been shown. At the same time, the efficiency of use of this method to increase the shear strength by orientation CNTs in matrices of reinforced plastics was shown by authors of the present work, apparently, for the first time. A great advantage of the use of CNTs to modify a matrix is their small size — they are arranged in the interfiber space of composite and do not break down the structure of the basic fibers in the material.

As current-conducting filler, carbon nanotubes of various diameter and length and graphene nanoplates (GNPs) [18] were used. Being good elastic conductors, carbon particles, under the action of an electric field applied, form induced dipoles, which are oriented in the direction of its force lines [19]. Hardening of the binder fixes the oriented filler particles in a direction close to perpendicular to the reinforcing of fibers. Thereby, the physicomechanical properties of a composite are bound to be improved. On Fig. 1, a schematic of the conjectured strengthening mechanism of a composite modified by oriented nanoparticles is shown. Under the action of shear stresses in the composite, the nanoparticles located in the interfiber matrix space and oriented in relation to the reinforcing fibers at angles close to 90º, take up tensile (1) and compressive (2) loads (depending on their orientation) and thereby hinder the shear of layers. For such a modified material, a patent [20] has been received.

1. Experimental part

The initial investigations were carried out on model samples with carbon- and glass-fiber microplastics. As a binder, we used a composition of an ED-20 epoxy resin and with an active E-181 thinner (1:1), but having a rather low viscosity. As a disperse filler, we employed multiwall CNTs. Their amount in the binder was ~0.5 wt.%. To achieve a homogeneous distribution of the CNTs, they were dispersed in chloroform by ultrasound during 1 h using a 100-V ultrasound generator. Then, the epoxy was added to the dispersion, and the chloroform was removed by heating to 100°C and vacuumizing. Directly prior to the experiment, 10% of a polyethylene polyamine (PEPA) hardener was added to the binder to reach a considerable increase in viscosity of the composition in 1-1.5 h. Cuts of fibers, impregnated with this binder in a stretched state, were placed in the field of an alternating electric current of strength 50 W/mm. This strength corresponded to that mentioned in the literature [16]. On completion of the exposition in the electric field, the microplastics were thermally processed during 2 h at 160°C to terminate the hardening of binder.

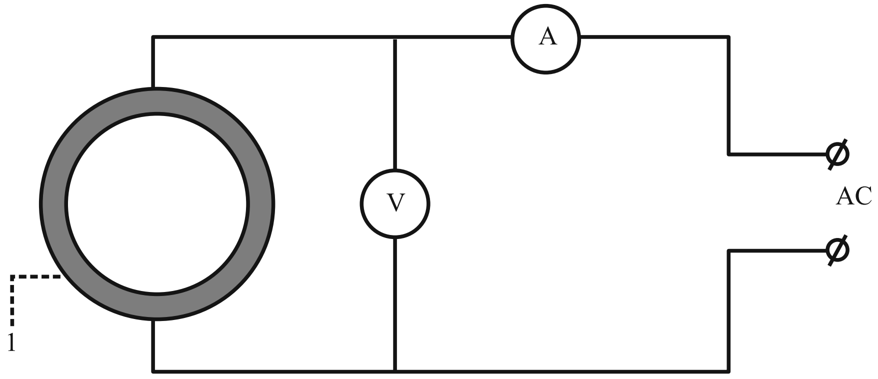


Fig. 2. Schematic of processing of glass-fiber plastic samples by an electric current: 1 — ring sample with flexible electrodes.

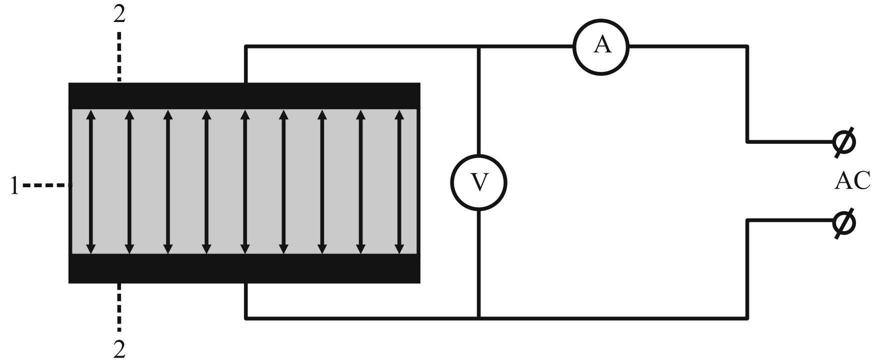


Fig. 3. Cross section of a glass-fiber plastic sample: 1 — sample and 2 — electrodes. Arrows show power lines of the electric field.

The orientation of CNTs in the composite was determined by the methods of electron microscopy and by measuring the shear modulus G of the microplastic. This modulus was determined on a torsion pendulum of type MK-3 (Khimautomatika, Russia) from its vibratio period T' by the formula

$$G = A/T'^2 ,$$

where A is a constant.

The orientation patterns of the current-conducting particles in the matrices of wound reinforced plastics were examined on ring samples of glass-fiber plastics. As a binder, we used the EDT-20 epoxy resin. The resin was filled with the multilayered carbon nanotubes manufactured by the Chinese company already mentioned, multilayered carbon nanotubes of the mark “Taunit-M” produced by the OOO “NanoTwkhTsentr” (of diameter 8-15 nm and length more than 2 μm), and graphene nanoplates (GNPs) received at the IChF RAN of the Russian Academy of Sciences (flakes of diameter 1 μm and thickness no more than 0.5 nm). The ranges of degrees of filling were from 0.005 to 3 wt.% for the CNTs and from 0.1 to 0.5 wt.% for GNPs. To obtain a homogeneous distribution of particles in the binder, they were dispersed during 30 min in acetone by ultrasound of power 60 Wt. Then, the epoxy resin was introduced into dispersion, and the mixture was exposed to the action of ultrasound of power 100 Wt during 1.5 h using an UZTA_0.2/22_OM “Volna” device. Thereafter, to remove the solvent from the mix of components, it was vakuumzed at 70°C during 5 h. Directly before winding, 10 wt.% of the PEPA polyethylene polyamide or a triethanolaminotitanate (TEAT) hardener was added to the binder.

The unidirectionally reinforced ring samples of glass-fibers plastics were made by winding a binder-impregnated glass fiber, with a linear of 400 tex, on an individual mandrel made of an insulating material (textolite). The thickness of the ring was about 5 mm. To act on the ring samples by an electric field, flexible electrodes made of an aluminum foil (Fig. 2) were employed, to which a 50-Hz stress of 270 V was delivered during hardening of samples in a heat chamber. The electric field power lines were directed perpendicularly the reinforcing fibers (Fig. 3), thus imparting the necessary orientation to the carbon particles, which, apparently, was also affected by electrophoretic phenomena in the binder [17]. The action with the electric field lasted 3 h, during which changes in amperage of the current passing through the sample were registered, which can be interpreted from the viewpoint of orientation of carbon particles: a growth in amperage indicate that the particles are being oriented. As the sample hardened, the amperage decreased (see Fig. 3).

Depending on the type of hardener, various hardening modes were used. At cold hardening (with PEPA), samples were held during 24 h at room temperature (20°C) and then in a heat chamber during 2 h at 160°C. At hot hardening (with TEAT), the most effective appeared to be the step mode: 2-h smooth heating from 100 to 160°C and 6-h holding at 160°C (Fig. 4). Various hardeners and hardening modes were used to compare the efficiency of particle orientation and to choose optimum conditions for increasing the mechanical characteristics. All samples had an identical technological and thermal prehistory. Calculations of the volume content of fibers, porosity, and density showed that the content of fibers practically did not depend on the composition of binder.

The shear strength and specific fracture toughness (crack resistance) of the glass-fibers plastic were determined on segments cut out from ring samples. The shear strength was determined by the method of bending a short beam in three-point loading [21]. The sizes of the samples were 5 × 6 × 40 mm, and the ratio of the distance l between supports to the sample thickness h was 6.5. The calculation were performed by the known Zhurawski formula

$$\tau = \frac{3P}{4lh}.$$

For quasi-static tests, with a deformation rate of 11 mm/min, a universal Instron-1122 testing machine was used, and for low-speed impacts (4 km/s) — an installation based on a spring impact testing machine [22].

The specific fracture toughness G_{IR}, which characterizes the crack resistance, was determined with the help of a universal testing machine of Instron type by delaminating double-cantilever beam samples with a cut [23]. The samples were ring segments of length 110-115 mm, width 10 mm, and thickness 2 mm. The initial length of crack ≈ 10 mm. The crack was created during winding by means of a teflon film placed in sample midlayers. During the tests, the relation between the F displacement D was registred in the digital form. The breakdown process was also photographed to determine the bending angles α_1 and α_2 of cantilevers. The energy was calculated by the formula [23]

$$G_{IR} = F_C\,(\sin\alpha_1 + \sin\alpha_2)/w,$$

where w is sample width and F_C is the critical force at which the crack begins to grow.

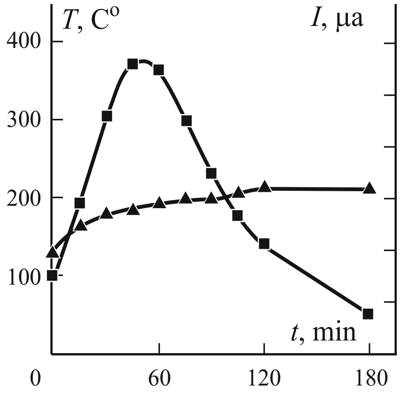
All the experimental values given in tables and figures are averages from five-eight samples.

2. Results and Their Discussion

2.1. Properties of microplastics

The orientation of CNTs was estimated using the electron microscopy (Fig. 5). The microplastic was cut crosswise on a low-temperature microtome. In the microphotos, the ends of carbon fibers, cracks, and delaminations around them are visible. In the cracks, CNTs located perpendicularly to fibers are visible. It is also seen that the CNTs are oriented along lines power of the electric field applied. After processing by the electric field, the vibration period T' decreased roughly 1.5 times, that corresponded to a two-fold increase in the shear modulus G (Table 1).

The data presented point to a considerable increase in the shear modulus of the microplastics owing to the orientation of CNTs in the transverse direction under the action of the electric field. Further, we will consider the results found on ring samples of wound glass-fiber plastics.



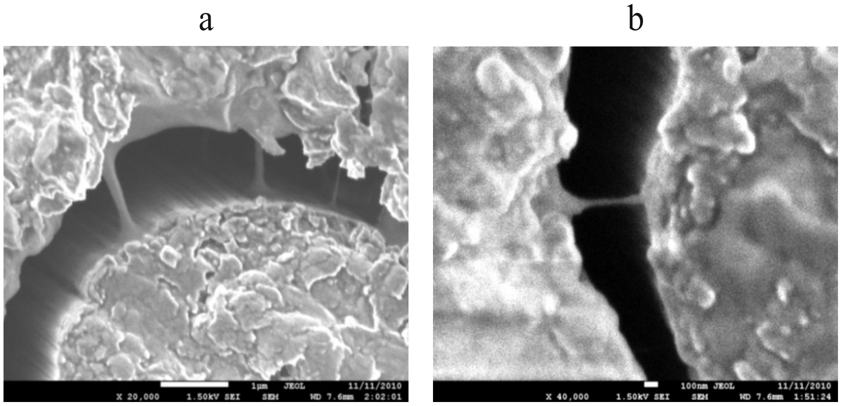


Fig. 4. Amperage I (■) of the current flowing through a ring sample and the hardening temperature T (▲) as functions of time t (for the initial stage of hardening).

Fig. 5. CNTs in cracks of a microplastic on the basis of carbon fibers. a — 1-μm and b — 100nm scale.

TABLE 1. Shear Modulus G_{cu} in Conditional Units of Microplastics in Relation to the Conditions of Action of the Electric Field (e.f.)

Binder composition	Carbon-fiber plastic		Glass-fiber plastic	
	T', s	$G_{\text{cu}} \cdot 10^3$	T', s	$G_{\text{cu}} \cdot 10^3$
ED-20	10.5	10±1	4.5	49±3
ED-20 (e.f.)	8	15±1	-	-
ED-20 +CNTs	8.5	14±1	3.5	82±3
ED-20 + CNTs (e.f.)	6.9	21±2	3	111±5

2.2. Properties of epoxy glass-fibers plastics hardened by PEPA

In Table 2, the physicomechanical properties of epoxy glass-fibers plastics hardened PEPA are given. These results show a considerable growth in the shear strength at the usual chaotic distribution of CNTs in the epoxy matrix. At quasi-static loading, the shear strength increased by 40% and the specific fracture toughness by 5%. The orientation of nanoparticles in the matrix by the electric field has led to a greater growth in the parameters — by 16 and 24%, respectively.

From the data presented, it can be concluded that, by changing the orientation of CNTs in the matrix of glass-fiber plastics hardened by PEPA, it is possible to considerably increase the physicomechanical characteristics of composites in comparison with those having a matrix with nonoriented CNTs.

2.3. Properties of epoxy glass-fiber plastics hardened by TEAT

A simple modification of matrices of glass-fiber plastic with CNTs did not increase the fracture toughness G_{IR} of composites in comparison with that of reference samples (Table 3). For the samples subjected to the action of electric field, the fracture toughness increased by 40% at .5 wt,% of S-MWNT-4060 CNTs in the matrix.

The crack resistance of the glass-fiber plastic with a CNP matrix grew by 20% in comparison with that of reference samples. The action of the electric field on composite samples did not increase the fracture toughness.

TABLE 2. Physicomechanical Properties of Glass-Fibers Plastic Hardened by PEPA, with 0.5 wt.% of S-MNT-4060 CNTs in the Binder

Property	Binder composition		
	ED-20	ED-20 + CNTs	ED-20 + CNTs (e.f.)
Shear strength τ, MPa	35±3	50±2	58±2
Fracture toughness G_{IR} , kJ/m^2	1.26±0.06	1.32±0.04	1.64±0.05

TABLE 3. Fracture Toughness G_{IR} (kJ/m^2) of Glass-Fiber Plastic Hardened by TEAT (Modifier Concentration 0.5 wt.%)

Binder composition				
ED-20 (without a modifier)	ED -20 + CNTs S-MWNT-4060	ED -20 + CNTs S-MWNT-4060 (e.f.)	ED -20 + GNPs	ED -20 + GNPs (e.f.)
1.17±0.05	1.23±0.1	1.65±0.06	1.51±0.04	1.55±0.03

As is seen from the data given in Table 4, the shear strength at quasi-static deformation (11 mm/min) of glass-fiber plastics on the basis of matrices modified by nonoriented S-MWNT-4060 CNTs remained practically unchanged in comparison with that of reference samples at all the filler concentrations considered. At processing the samples with the electric field, an appreciable growth in the shear strength (by 20% in comparison with that of reference samples) was observed only at a high (3 wt.%) concentration of the modifier. Since the introduction of the filler in amounts exceeding 1 wt.% leads to technological difficulties at winding samples (due to the high viscosity of the modified resin), the use of S-MWNT-4060 CNTs as a modifier for increasing the shear strength is inexpedient.

The use of the "Taunit-M" SNTs as a modifier allowed us to achieve a more significant growth in the shear strength of the glass-fiber plastic. In quasi-static loading, already at concentration 0.5 wt.% of the modifier in the matrix, the shear strength the samples exposed to the electric field grew by 35% in comparison with that of reference samples. At impact loading (4 km/s), the growth in the shear strength of the samples processed by the electric field amounted to 15% compared with that of the reference sample.

The different results obtained on using various kinds of CNTs as a modifier were supposedly caused by their geometrical sizes. Not improbable is also the variant of different reaction of CNTs on the ultrasonic action during their dispersion. This question requires further investigations.

In our work, besides the already convential CNTs a novel disperse modifier, grapheme nanoplates (GNPs), obtained at the IKgF of the Russian Academy of Sciences, was used to increase the shear strength of the glass-fiber plastic. The procedure of its creation is described in [18]. At all the filler concentrations considered, the shear strength of the glass-fiber plastics with GNP-modified matrices remained the same as that of the reference samples on the basis of unmodified matrices (see Table 4). On exposure of samples to the electric field, their shear strength grew with concentration of filler in the matrix. At o.5 wt.% GNP, the shear strength was by 30% higher than that of both the reference samples and the samples not exposed to the electric field. It can be assumed that this effect was caused by reorientation of GNPs under the action of the electric field.

2.4. Comparison of the efficiency of different fillers

The results found confirm the conclusion that, at hot hardening, the modification of composite matrices with disperse carbon particles (CNTs or GNPs) by itself does not improve their shear properties. It is only the application of the method of orientation of disperse particles by an electric field that allows one to considerably improve the characteristics of a composite in the transverse direction. From the data given in Table 4, it is evident that the most significant increase in the shear strength was reached with "Taunit-M" CNTs and GNPs. In this case, a moderate concentration of modifier (0.5 wt.%) allowed us to

TABLE 4. Shear Strength τ (MPa) of Glass-Fiber Plastics Hardened by TEAT at Different Deformation Rates (ED-20 Binder)

Modifier concentration in the binder, wt.%	Modifier					
	S-MWNT-4060	S-MWNT-4060 (e.f.)	Taunit-M	Taunit-M (e.f.)	GNPs	GNPs (e.f.)
			11 mm/min			
0	55±2	55±2	58±1	58±1	55±1	55±1
0.05	57±1	58±1	-	-	-	-
0.1	-	-	-	-	55±2	58±3
0.2	-	-	-	-	56±2	67±3
0.5	57±1	59±1	56±2	74±2	57±2	70±2
1	58±4	60±3	-	-	-	-
2	57±2	60±3	-	-	-	-
3	60±2	65±1	-	-	-	-
			4 m/s			
0	-	-	80±2	80±2	-	-
0.5	-	-	79±1	91±2	-	-

obtain reinforced plastics with increased shear characteristics without a significant complication of winding technology and without a decrease in other parameters, such as the glass-transition temperature. In particular, it is known [24] that the introduction CNTs in an amount of 0.5 wt.% greatly raises the heat resistance of epoxycomposite matrices; however, at a further increase in their content in the matrix, the glass-transition temperature is reduced.

Conclusion

The results obtained confirm the efficiency of orientation of current-conducting filler particles by an electric field improve the physicomechanical properties of wound composites: the crack and impact resistance reinforced plastics increased considerably without reducing the glass-transition temperature, as this occurs on plasticization of matrices with rubbers and active thinners, and also without a great complication of the technological winding process, as it happens in the case of modifying composite matrices with highly viscous heat-resistant thermoplasts. When using S-MWNT-4060 CNTs as a filler, the crack resistance increased considerably (to 40%) at a small (5-10%) increase in the shear strength. More effective for increasing the shear strength turned out to be "Taunit-m" CNTs and GNPs as modifiers. In this case, the shear strength increased by 35% in quasi-static loading and 15% in impact loading.

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REFERENCES

1. M. L. Kerber, V. M. Vinogradov, G. S. Golovkin, et al., Polymer Composite Materials: Structure, Properties, Technology [in Russian], SPb, Professia (2008).
2. N. N. Trofimov, M. Z. Kanovich, E. M. Kartashov, et al. [in Russian], Physics of Composite Materials, M., Mir (2005).
3. V. I. Solodilov, R. A. Korohin, Yu. A. Gorbatkina, and A. M. Kuperman, "Comparison of fracture energies of epoxy-polysulfone matrices and unidirectional composites on them," Mech. Compos. Mater., **51**, No. 2, 177-190 (2015).

4. V. I. Solodilov, Yu. A. Gorbatkina, A. M. Kuperman, “The effect of an active diluent on the properties of epoxy resin and unidirectional carbon-fiber-reinforced plastics,” Mech. Compos. Mater., **39**, No. 6, 493-502 (2003).

5. V. I. Solodilov, I. V. Bessonov, A. V. Kireinov, N. Yu. Taraskin, and A. M. Kuperman, “Properties of glass-fibers plastic on the basis of an epoxy binder modified by a furfurolacetone resind and polysulfone,” Kompozity i Nanostruktury, **8**, No. 2, 77-87 (2016).

6. R. A. Korokhin, V. I. Solodilov, Yu. A. Gorbatkina, and A. V. Shapagin, “Rheological and physicomechanical properties epoxy-polyetherimide compositions,” Mech. Compos. Mater., **51**, No. 3, 313-320 (2015).

7. Yan Zhang, Fenghua Chen, Wei Liu, Songmei Zhao, Xianggui Liu, Xia Dong, and C. Han Charles, “Rheological behavior of the epoxy/thermoplastic blends during the reaction induced phase separation,” Polymer, **55**, Iss. 19, 4983-4989 (2014).

8. V. I. Solodilov and Yu. A. Gorbatkina, “Properties of unidirectional GFRP based on an epoxy resin modified with polysulfone or an epoxyurethane oligomer,” Mech. Compos. Mater., **42**, No. 6, 513-526 (2006).

9. V. I. Solodilov and Yu. A. Gorbatkina, “Properties of unidirectional GFRP on the basis of an epoxy resin modified by polysulfone or an epoxyurethane oligomer,” Mekh. Kompoz. Mater. Konstr., **14**, No. 2, 224-235 (2008).

10. R. A. Korokhin, V. I. Solodilov, and Yu. A. Gorbatkina, “Properties of GFRP on the basis of an aerosol-filled resin,” Mekh. Kompoz. Mater. Konstr., **15**, No. 3, 437-447 (2009).

11. R. A. Korokhin, V. I. Solodilov, Yu. A. Gorbatkina, and A. V. Otegov, “Physicomechanical properties of dispersedly epoxies,” Plast. Massy, No. 4, 37-41 (2013).

12. V. A. Bol’shakov, V. I. Solodilov, R. A. Korokhin, S. V. Kondrashov, Yu. I. Merkulov, and T. P. Dyachkova, “Investigation of crack resistance of polymer composite materials made by the infusion method with the use of various concentrates on the basis of modified CNTs,” Tr. VIAM, **55**, No. 7, 9 (2017).

13. R. A. Korokhin, V. I. Solodilov, Yu. A. Gorbatkina, and A. V. Otegov, “Effect of ultrasonic processing of nanomodified binders on the fracture toughness hardened compositions,” Mekh. Kompoz. Mater. Konstr., **17**, No. 4, 527-538 (2011).

14. R. A. Korokhin, V. I. Solodilov, Yu. A. Gorbatkina, and A. M. Kuperman, “ The use of carbon nanotubes as modifiers of epoxypolysulfone matrices of wound organoplastics,” Mech. Compos. Mater., **49**, No. 1, 77-86 (2013).

15. C. A. Martina, J. K. W. Sandler, A. H. Windle, M.-K. Schwarz, W. Bauhofer, K. Schulte, and M. S. P. Shaffer, “Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites,” Polymer, **46**, 877-886 (2005).

16. Cheol Park, John Wilkinson, Sumanth Banda, Zoubeida Ounaies, Kristopher E. Wise, Godfrey Sauti, Peter T. Lillehei, and Joycelyn S. Harrison, “Aligned single-wall carbon nanotube polymer composites using an electric field,” J. Polym. Sci., Part B, Polym. Phys., **44**, 1751-1762 (2006).

17. Kunitoshi Yamamoto, Seiji Akita, and Yoshikazu Nakayama, “Orientation and purification of carbon nanotubes using ac electrophoresis,” J. Phys. D: Appl. Phys., **31**, L34.-L36 (1998).

18. E. F. Sheka, I. Natkaniec, V. Mel’nikov, and K. Druzbicki, “Neutron scattering from graphene oxide paper and thermally exfoliated reduced graphene oxide,” Nanosystems: Physics, Chemistry, Mathematics, **6**, No. 3, 378-393 (2015).

19. Z. Z. Latypov, “Anisotropic strengthening the properties of nanocomposites by the methods of electromagnetic orientation nanoparticles in the matrix,” Nauch. Priborostr., **21**, No. 1, 50-52 (2011).

20. D. A. Bulgakov, A. Ya. Gorenberg, and A. M. Kuperman, Patent on invention № 2468918, A composite reinforced material and a way of its production.

21. Composite Materials [in Russian], eds V. V. Vasilyev and Yu. M. Tarnopolskii, M., Mashinostroenie (1990).

22. A. V. Antonov, E. S. Zelenskii,y A. M. Kuperman, O. V. Lebedeva, and A. V. Rybin, “Behavior of reinforced plastics based on a polysulfone matrix under impact loading,” Mech. Compos. Mater., **34**, No. 1, 12-19 (1998).

23. V. I. Solodilov, S. L. Bazhenov, Yu. A. Gorbatkina, and A. M. Kuperman, “Determination of the interlaminar fracture toughness of glass-fiber-reinforced plastics on ring segments,” Mech. Compos. Mater., **39**, No. 5, 407-414 (2003).

24. E. N. Kablov, S. V. Kondrashov, G. Yu. Jurkov, “Prospects of using carbon-containing nanoparticles in binders for polymer composite materials,” Ros. Nanotekhnol., **8**, No. 3-4, 28-46 (2013).