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ДОСЛІДЖЕННЯ ДИНАМІЧНОЇ В'ЯЗКОСТІ ЕПОКСИДНИХ КОМПОЗИЦІЙ З НАНО- І МІКРОНАПОВНЮВАЧАМИ

У статті досліджено вплив нано- та мікронаповнювачів на динамічну в'язкість епоксидних композитів на основі смоли DER 331. Як нанонаповнювачі використовували вуглецеві нанотрубки (НТ) та наносажу CARBON BLACK N220 за вмісту від 0,01 до 0,1 мас.%, а як мікронаповнювачі – порошки оксиду хрому Cr_2O_3 (20 мкм) та карбіду кремнію SiC (40 мкм) за вмісту від 5 до 20 мас.%. Реологічні дослідження проводили на віскозиметрі NDJ-1S за чотирьох швидкостей зсуву (6, 12, 30, 60 об/хв).

Результати показали, що введення наповнювачів підвищує в'язкість композитів порівняно з чистою смолою, причому мікронаповнювачі мають більший вплив через вищу об'ємну частку. Наносажа суттєвіше підвищує в'язкість епоксидних композицій, ніж НТ, через схильність до агрегації. Усі композиції проявляють псевдопластичні властивості: в'язкість зменшується із зростанням швидкості зсуву. Механізм змін реологічних властивостей пояснено моделлю утворення та руйнування флокул (для нанонаповнювачів) та гідродинамічною взаємодією часток (для мікронаповнювачів).

Встановлено оптимальний вміст наповнювачів: 0.05 мас.% для наночасток та 10 мас.% для мікрочасток, що може забезпечити покращення механічних властивостей без значного погіршення технологічності. Отримані результати мають важливе значення для розробки технологій нанесення захисних покриттів у суднобудуванні.

Ключові слова: *епоксидний композит, динамічна в'язкість, нанонаповнювачі, мікронаповнювачі, реологія, псевдопластичність.*

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STUDY OF DYNAMIC VISCOSITY OF EPOXY COMPOSITIONS USING NANO- AND MICRO-FILLERS

The article investigates the effect of nano- and micro-fillers on the dynamic viscosity of epoxy composites based on DER 331 resin. Carbon nanotubes (NT) and CARBON BLACK N220 nanosoot were used as nanofillers at a content of 0.01 to 0.1 mas.%, and chromium oxide Cr_2O_3 powders (20 µm) and silicon carbide SiC (40 µm) at a content of 5 to 20 wt.% as microfillers. Rheological studies were carried out on an NDJ-1S viscometer at four shear rates (6, 12, 30, 60 rpm).

The results showed that the introduction of fillers increases the viscosity of composites compared to pure resin, with microfillers having a greater effect due to their higher volume fraction. Nanofillers significantly increase the viscosity of epoxy compositions than NTs due to their tendency to aggregation. All compositions exhibit pseudoplastic properties: viscosity decreases with increasing shear rate. The mechanism of changes in rheological properties is explained by the model of floc formation and destruction (for nanofillers) and hydrodynamic interaction of particles (for microfillers).

The optimal filler content was established: 0.05 mas.% for nanoparticles and 10 mas.% for microparticles, which can provide an improvement in mechanical properties without significant deterioration in processability. The results obtained are of great importance for the development of technologies for applying protective coatings in shipbuilding.

Keywords: *epoxy composite, dynamic viscosity, nanofillers, microfillers, rheology, pseudoplasticity.*

Problem statement. It is well known that the introduction of any fillers significantly affects the technological properties of composites, in particular their rheological behavior. Rheological properties, mainly viscosity, are a decisive factor for successful coating by spraying, dipping or casting methods. Too high viscosity makes it difficult to pour compositions into molds, leading to the formation of a poor-quality layer with air bubbles and uneven thickness.

Nanofillers, such as carbon NTs and nanosoot, due to their high specific surface area, are prone to aggregation, which sharply increases the viscosity of a heterogeneous system even at low concentrations. Microfillers (chromium oxide, silicon carbide), on the contrary, are less prone to the formation of structural aggregates and affect the viscosity more predictably, mainly reducing the fluidity of compositions due to the volume effect. Thus, a contradiction arises: on the one hand, fillers are necessary to improve performance characteristics, and on the other hand, they can make the composition unsuitable for practical use. Therefore, a comprehensive study of the rheology of modified compositions is no less important than the study of the mechanical properties of polymerized materials.

Analysis of recent studies and publications. The relevance of such tests is not only in determining the influence of each type of filler separately, but also in further studying the synergistic effect in improving the properties of hybrid systems containing both micro- or nanoparticles and reinforcing fabrics [1-7]. The authors [8-10] proved that at the initial stage it is important to establish the dependence of the dynamic viscosity of epoxy compositions on the type, shape and content of fillers. For this, it was necessary to conduct research to determine the viscosity of epoxy compositions in a wide range of shear rates. As a result, to construct rheological flow curves and analyze deviations from Newtonian behavior in order to further assess the quality of dispersion of additives in the binder and the correlation between aggregation and rheology.

It should be noted that the optimal filler content was taken as the point at which the maximum improvement in mechanical properties is achieved while maintaining an acceptable viscosity for further forming of products or coatings [11, 12]. It was assumed that for nanofillers this point will probably be in the region of the percolation threshold, when a continuous strong network of nanoadditives is formed. For microfillers, the maximum permissible volume fraction at which the system still retains fluidity may be critical. As a result, it is necessary to develop recommendations for the formation of rheologically stable composite systems ready for use in the shipyard.

Therefore, the selection of the optimal content of nano- and microadditives is a key stage in the creation of new effective materials that combine high performance properties with sufficient manufacturability. The results obtained will allow in the future to control the parameters of the formation of hybrid epoxy plastics with sufficient accuracy, guaranteeing their quality and durability. This, in turn, will contribute to increasing the energy efficiency of water transport by reducing hydrodynamic resistance, corrosion protection and increasing anti-cavitation characteristics of materials. Therefore, the analysis of rheological properties is an integral and important part of the comprehensive study of epoxy CMs for marine applications.

The purpose of the work is to establish the patterns of the influence of nano- and microfillers on the dynamic viscosity of epoxy compositions.

Materials and research methods. During the formation of polymer compositions, the epoxy resin DER 331 (ISO 9001) was chosen as the basis, which is the reaction product of epichlorohydrin and bisphenol A. Polyethylene polyamine (TU 2413-357-00203447-99) was used to cure epoxy compositions. As fillers to improve the properties of composites, we used nano- and micro-sized powders. Nanofillers: MWCNT nanotubes and CARBON BLACK PowCarbon N220 nanosoot. Microfillers: chromium oxide (Cr_2O_3) and silicon carbide (SiC) powders with particle sizes of 20 μm and 40 μm, respectively.

To study the rheological properties of epoxy compositions, an NDJ-1S viscometer was used. Four rotor rotation speeds (6, 12, 30, 60 rpm) were selected according to the liquid viscosity measurement range.

Discussion of the results. Fig. 1 shows the dependence of the dynamic viscosity of epoxy compositions based on DER 331 resin on the filler content at different rotor rotation speeds. Based on the graphs presented (Fig. 1, a, c, e, g), the following analysis of the influence of nanofillers on the dynamic viscosity of epoxy compositions can be carried out. The data of rheological studies clearly demonstrate that the introduction of nanoadditives leads to an increase in the dynamic viscosity (η) of the compositions compared to the original epoxy resin (DER 331). This increase is insignificant in absolute figures, but is stably observed at all studied shear rates (6, 12, 30, 60 rpm). For both types of nanofillers (carbon nanotubes (NT) and nanosoot), the dependence of viscosity on their mass fraction (q) in the range up to 0.05 mas.% is nonlinear, which indicates the complexity of the interaction of particles with the oligomeric binder. Nanosoot demonstrates a slightly greater effect on increasing viscosity than carbon nanotubes, which is especially noticeable at higher shear rates (e.g., 60 rpm, Fig. 1, g). This may be due to the larger specific surface area and the tendency of nanosoot particles to form strong spatial aggregates-structures that effectively restrict the movement of polymer chains. Carbon nanotubes, having a sufficiently large aspect ratio, are also prone to the formation of bonds between particles, but their shape probably contributes to lower flow resistance at high shear rates compared to isometric carbon particles.

The curves in all figures show that increasing the rotor speed (shear rate) leads to a significant decrease in dynamic viscosity for all studied compositions. This behavior – a pronounced dependence of viscosity on shear rate – is a characteristic feature of non-Newtonian fluids. Epoxy resin without fillers also demonstrates a decrease in viscosity with increasing shear rate, which confirms its property of shear thinning. However, the introduction of nanofillers enhances this effect of non-Newtonian flow.

The deviation from Newtonian behavior (constant viscosity regardless of shear rate) is a direct consequence of the destruction of the internal structure formed by the filler in the polymer matrix. At low shear rates, the filler aggregates successfully resist the shear (or flow) resistance, creating additional resistance, increasing the viscosity. As the shear rate increases, these aggregates gradually break down and orient themselves in the direction of flow, which reduces resistance and leads to a decrease in viscosity.

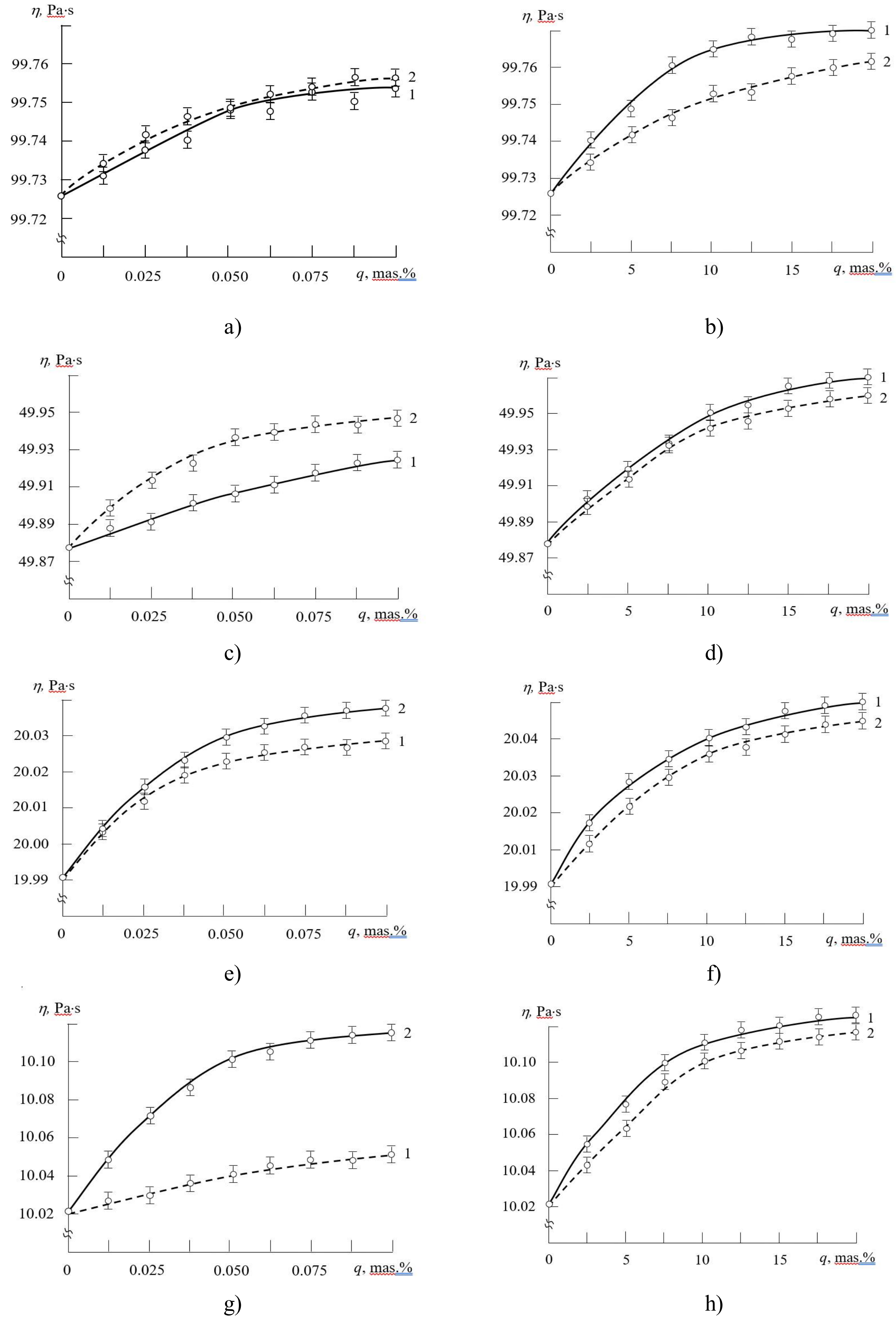

Fig. 1. **Dependence of dynamic viscosity (η) on filler content (q) at rotor speed 6 rpm (a, b), 12 rpm (c, d), 30 rpm (e, f), 60 rpm (g, h): (a, c, e, g) 1 – Nanotubes (NT); 2 – Nanosoot; (b, d, f, h) 1 – Cr2O3; 2 – SiC.**

The quality of filler dispersion directly affects rheology: better dispersed individual particles have less effect on viscosity, while large aggregates dramatically increase it and enhance non-Newtonian properties. The obtained data indicate that nanocarbon black probably has a higher tendency to aggregation compared to NT, which explains its greater effect on viscosity.

The mechanism of influence of nanofillers on dynamic viscosity can be described by the model of formation and destruction of spatial network (floccules) in a polymer matrix [11]. This model assumes that filler particles, due to their high specific surface area and Van der Waals interactions, form a strong three-dimensional structure. At rest, this structure is maximally strong, limiting the mobility of polymer macromolecules and making the composite quite viscous. When a shear load is applied, this structural network begins to collapse. At a higher shear rate, the destruction of flocs occurs more intensively, which leads to a decrease in the effective volume occupied by the filler. Accordingly, the viscosity of the composition decreases. After removing the load, the network can be restored, which is typical for the systems under study.

The authors [11] noted that flocs (or aggregates) are spatial, three-dimensional clusters of filler particles (in our case, nanotubes or nanosoot particles), united among themselves mainly by physical Van der Waals forces. They are formed spontaneously after the filler is introduced into the polymer. This is not a stable chemical compound, but a dynamic physical structure. The accumulation of particles occurs mainly due to their high specific surface area and energy. It is flocs that are the main reason for the sharp increase in viscosity even with small additions of nanofillers. In this case, polymer chains cannot move freely through this dense network, since they increase the effective volume of the filler particles. The floc includes not only the filler, but also the resin around the particles in the form of soft surface layers. Thus, a composition with 0.05 mas.% filler can behave like a composition with 5 mas.% additive content, creating much greater flow resistance.

Based on the analysis of the graphs (Fig. 1, a, c, e, g), it can be additionally stated that the flocculated structure is not strong. Under the action of shear stresses (rotation of the rotor in our case), these weak bonds between the particles are destroyed. At low shear rates (V=6 rpm), the floc structure remains almost intact, therefore the viscosity is maximum. At high shear rates (V=60 rpm), the forces that destroy exceed the forces that hold the flocs. The aggregates disintegrate, the particles are oriented along the flow, the effective volume of the filler decreases sharply, and the viscosity decreases. This is a manifestation of the thinning of the compositions during shear (pseudoplasticity). On the contrary, after stopping the experiment, the particles again begin to move randomly (due to Brownian motion), restoring the flocculated network. This ability to recover the structure after the load is removed also implies a change in the thixotropic properties of the materials.

Therefore, the term "flocculant" characterizes only dynamic aggregates of nanoparticles that form a temporary three-dimensional network inside the epoxy resin. It is the process of their formation and destruction that is the main mechanism that explains the significant dependence of viscosity on shear rate and its sharp increase even at negligible concentrations of nanofillers.

Based on the analysis of the results obtained, it can be stated that the optimal content for both selected nanofillers should be considered 0.05 mas.%. At this content, a noticeable strengthening of the material is achieved (as can be assumed), but the technological properties (viscosity) remain at an acceptable level, suitable for gluing tissues. A further increase in the particle content will lead to a sharp increase in viscosity and aggregation, which will make the material unsuitable for practical use. It should be noted that for nanocarbon black, due to its greater influence on viscosity, the upper limit of the optimal content may be even lower.

Thus, nanofillers significantly affect the rheology of epoxy composites, enhancing their non-Newtonian behavior due to the formation and destruction of a spatial network of aggregates. Carbon nanotubes have a slightly smaller effect on the increase in viscosity compared to nanocarbon black at the same mass content. The quality of dispersion is a critical factor determining rheological behavior; poor dispersion leads to excessive viscosity increase. The optimal content for both types of nanofillers in this study does not exceed 0.05 mas.%. The results obtained are important for the selection of technological parameters for forming products and preventing problems with their quality.

The work also obtained the dependence of dynamic viscosity (η) on the content of microdispersed fillers at different shear rates. Based on the analysis of Fig. 1, b, d, f, h, the following conclusions can be drawn regarding the influence of microfillers on the dynamic viscosity of epoxy compositions. The introduction of microparticles of chromium oxide (Cr_2O_3) and silicon carbide (SiC) at a content of 10 mas.%

leads to a moderate increase in dynamic viscosity compared to the original resin. This increase is more significant than in the case of nanofillers, which is explained by the higher volume fraction of microparticles. The curves in all graphs demonstrate a clear tendency to decrease in viscosity with increasing rotor rotation speed, which indicates a pronounced non-Newtonian behavior of the composites.

The increase in viscosity with the introduction of microfillers is associated with an increase in the volume content of the dispersed phase and a decrease in the distance between the particles, which limits the mobility of polymer chains. The effect of a decrease in viscosity with an increase in the shear rate is explained by the destruction of temporary structures and the orientation of the particles in the direction of flow. The data indicate that the compositions with microfillers exhibit the properties of pseudoplastic liquids (the viscosity of which decreases with increasing shear rate), which is typical of concentrated suspensions.

A comparison of the effects of the two types of microfillers shows that chromium oxide (20 μm) causes a slightly greater increase in viscosity compared to silicon carbide (40 μm), which may be due to the smaller particle size and larger specific surface area. The deviation from Newtonian behavior confirms the presence of interactions between the filler particles and the formation of temporary structures. The quality of dispersion of microfillers is satisfactory, as evidenced by the smooth nature of the viscosity change and the absence of sharp jumps in the curves.

The mechanism of the influence of microfillers on the rheological properties can be described by the model of concentrated suspensions, where hydrodynamic interactions and random formation of aggregates play a key role [12]. According to this model, filler particles create hydrodynamic fields that interact with each other, which leads to an increase in viscosity even in the absence of direct contact. In concentrated systems, such as compositions with 10 mas.% microfiller, the distance between particles becomes insignificant, which contributes to their additional interaction. Random formation of aggregates (in particular, in the case of chromium oxide) occurs due to the forces of physical interaction, which leads to the formation of temporary structural formations. These structures create additional resistance to flow, which manifests itself as an increase in dynamic viscosity. Under the action of shear stresses, these aggregates are partially destroyed, and the particles are oriented along the flow, which explains the decrease in viscosity with increasing shear rate. The efficiency of this process depends on the size, shape and content of the particles. For example, smaller Cr_2O_3 particles (20 μm) have a larger specific surface area compared to SiC (40 μm), which enhances agglomeration and viscosity increase. The model also predicts that viscosity increases significantly with increasing filler volume content, when particle motion is restricted. This behavior is consistent with experimental data, where the viscosity increase is moderate but significant. Thus, the rheology of microparticle compositions is determined by the balance between hydrodynamic effects and physicochemical interaction of the particles.

The optimal content for microfillers should be considered to be 10 mas.%, since this will provide (in our opinion) a noticeable improvement in mechanical properties without excessively complicating the processing process. Therefore, microfillers slightly increase the viscosity of epoxy compositions, while maintaining the possibility of their further processing by standard methods.

Table 1 systematizes data on the dynamic viscosity of epoxy resin DER 331 and compositions based on it with different fillers at four shear rates (6, 12, 30, 60 rpm). The table data confirm the general trend: an increase in the shear rate leads to a decrease in viscosity for all the studied materials, which is a sign of non-Newtonian behavior (pseudoplasticity). The viscosity of the pure resin decreases from 99.728 Pa·s at 6 rpm to 10.021 Pa·s at 60 rpm, which demonstrates its shear thinning property. The introduction of nanofillers (0.05 mas.%) increases the viscosity compared to the pure resin at all shear rates.

Table 1

Viscosity of epoxy compositions with optimal content of nano- and microfillers

Rotation speed, V, rpm	Viscosity of compositions, Pa·s				
	Resin DER 331	NT (0.05%)	Nanosoot (0.05%)	Cr_2O_3 (20 μm) (10%)	SiC (40 μm) (10%)
6	99.728	99.747	99.749	99.765	99.749
12	49.875	49.899	49.932	49.946	49.941
30	19.991	20.020	20.030	20.039	20.036
60	10.021	10.038	10.102	10.115	10.109

Nanosoot has a greater effect on viscosity than carbon nanotubes (CNTs). For example, at 60 rpm, the viscosity of the composite with nanosoot (10.102 Pa·s) is higher than with CNTs (10.038 Pa·s). Microfillers (10 mas.%) cause a significantly greater absolute increase in viscosity compared to nanofillers due to their higher volume fraction. Chromium oxide (Cr_2O_3) shows a slightly greater effect on viscosity than silicon carbide (SiC), which is explained by the smaller particle size (20 μm versus 40 μm) and, accordingly, the larger specific surface area. For example, at 6 rpm, the viscosity is 99.765 Pa·s for Cr_2O_3 versus 99.749 Pa·s for SiC.

The relative increase in viscosity due to the introduction of additives is more significant at low shear rates (6 rpm) and decreases at high (60 rpm), which confirms the destruction of aggregates of filler particles under the action of shear forces. The difference in viscosity between the compositions and the pure resin also decreases with increasing shear rate, which indicates the leveling of rheological properties under conditions of intense loading. The obtained data are of important technological importance for coating processes requiring high speeds (e.g. spraying), the viscosity of different composites will be close, which simplifies their application. However, for low shear rate coating methods (e.g. vacuum infusion), the choice of filler type and content will critically affect the processability of the material.

Conclusions. Based on the above, it can be stated that the rheological properties of epoxy compositions significantly depend on the type, size and content of the filler, as well as on the technological conditions of product formation (shear rate). Nanofillers (0.05 mas.%) moderately increase the viscosity, and nanocarbon black has a more significant effect due to its tendency to aggregation. Microfillers (10 mas.%) cause a significantly greater absolute increase in viscosity, and smaller particles (Cr_2O_3, 20 μm) increase it more than larger ones (SiC, 40 μm).

All compositions exhibit pseudoplastic properties, which makes them convenient for creating compositions for the purpose of further forming hybrid composites: they reduce flow resistance during application and retain their shape after its termination.

The optimal filler content was established: 0.05 mas.% for nanoparticles and 10 mas.% for microparticles, since with such a filling it is possible to achieve a useful strengthening effect without a sharp deterioration in technological properties. The results obtained are the basis for the development of technological regulations for applying high-quality protective coatings and forming hybrid composites for water transport. The study confirms that rheological control is a key tool for optimizing both operational and technological properties of composite materials. By selecting the type and content of the filler, it is possible to purposefully control the rheology of epoxy compositions to ensure their effective use in shipbuilding.

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