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IMPROVEMENT OF THE CHARACTERISTICS OF PROTECTIVE COATINGS INTENDED FOR THE PROTECTION OF SURFACES OF AIDS NAVIGATION WATER TRANSPORT

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Summary

Introduction. *Ensuring global communication is crucial for cargo delivery by water transport within clearly established deadlines. Thus, the reliability of ship radar systems is essential. At the same time, for the reliable operation of radar systems, it is necessary to monitor the condition of their external surfaces, particularly paint coatings.* ***Purpose.*** *Develop mathematical models for predicting the characteristics of polymer coatings intended for protecting the surfaces of ship navigation aids.* ***Results****. To create polymer coatings designed for protecting the surfaces of metal structures, particularly the surfaces of navigation equipment, the epoxy oligomer ED-20, cured with polyethylene polyamine (PEPA), was chosen as a binder. To improve the properties of protective coatings, the following were used: a nanodispersed fullerene-carbon black mixture, with a dispersion of 30…40 nm, and trimethoprim, with a dispersion of 5…10 µm. The optimal content of each filler in the polymer volume was determined based on comprehensive studies of the properties and structure of polymer coatings. To ensure the maximum effect in the form of a ratio of the structure and properties of polymer coatings, mathematical models were developed in the work using the Statgraphics Centurion 19 software, which allowed optimizing the composition of differently dispersed fillers in the matrix to ensure the desired functional properties of materials.* ***Conclusions.*** *The rational combination of micro– and nanoscale fillers allowed the structure of the* *polymer to be changed. This ensured the maximum value of the adhesive strength at separation, which is 42.0 MPa, and impact strength – 17.2 kJ/m^2 when introducing trimethoprim into the polymer volume at a content of – 10 pts.wt., and a nanodispersed fullerene-carbon black mixture – 0.050 pts.wt. The developed mathematical models and graphic response surfaces allow us to predict the final properties of polymer coatings. The developed coatings can be used to improve the operational characteristics of ship navigation aids.*

Key words: *navigation aids, polymer, adhesive strength, impact strength, optical microscopy, mathematical model.*

ПІДВИЩЕННЯ ХАРАКТЕРИСТИК ЗАХИСНИХ ПОКРИТТІВ, ПРИЗНАЧЕНИХ ДЛЯ ЗАХИСТУ ПОВЕРХОНЬ ЗАСОБІВ НАВІГАЦІЇ ВОДНОГО ТРАНСПОРТУ

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Анотація

Вступ. *Забезпечення глобального зв'язку має вирішальне значення для постачання вантажів водним транспортом у чітко встановлені терміни. Таким чином, вагомим є надійність суднових радіолокаційних систем. При цьому для надійної експлуатації радіолокаційних систем необхідно контролювати стан їх зовнішніх поверхонь, зокрема стан лакофарбових покриттів. Отже,* ***метою*** *роботи є розроблення математичних моделей для прогнозування характеристик полімерних покриттів призначених для захисту поверхонь суднових засобів навігації.* ***Результати.*** *Для створення полімерних покриттів призначених для захисту поверхонь металоконструкцій, зокрема поверхонь навігаційного обладнання, у якості зв'язувача обрано епоксидний олігомер ЕД-20, який затверджували поліетиленполіаміном (ПЕПА). Для поліпшення властивостей захисних покриттів використано: нанодисперсну фулерено-сажову суміш, дисперсністю 30…40 нм і триметоприм, дисперсністю 5…10 мкм. На основі комплексних досліджень властивостей і структури полімерних покриттів визначено оптимальний вміст* *кожного наповнювача у об'ємі полімеру. Для забезпечення максимального ефекту у вигляді співвідношення структури і властивостей полімерних покриттів у роботі розроблено математичні моделі, з використанням програмного забезпечення Statgraphics Centurion 19, які дозволили оптимізувати склад різнодисперсних наповнювачів у матриці для забезпечення бажаних функціональних властивостей матеріалів.* ***Висновки.*** *Раціональне поєднання наповнювачів мікро- і наномасштабного рівня дозволило змінити структуру полімеру. Це дозволило забезпечити максимальне значення адгезійної міцності при відриві, яка становить 42,0 МПА і ударної в'язкості – 17,2 кДж/м^2 при введенні у об'єм полімеру триметоприму за вмісту – 10 мас.ч., і нанодисперсної фулерено-сажової суміші – 0,050 мас.ч. Створені математичні моделі і графічні поверхні відгуків дозволяють прогнозувати вихідні властивості полімерних покриттів. Розроблені покриття можливо використовувати для підвищення експлуатаційних характеристик суднових засобів навігації.*

Ключові слова: *засоби навігації, полімер, адгезійна міцність, ударна в'язкість, оптична мікроскопія, математична модель.*

Introduction. To protect the surfaces of navigation aids (antennas, echo sounders, radars, compasses) for water transport, polymer coatings are used, particularly epoxy-based ones, since they contain hydroxyl, ether, and epoxy groups. These groups are polar and not only interact with the metal substrate but also contribute to the diffusion process due to their interaction with metal oxides. Despite the protective functions of polymer coatings, the condition of the paint coating on ship navigation equipment is inspected annually in accordance with the requirements of the International Maritime Organization (IMO), the International Convention for the Safety of Life at Sea (SOLAS, chapters IV, V), and the regulations of classification societies (DNV, Lloyd's Register) [1–5]. Therefore, there is a need to search for new ingredients for the development of protective coatings for the navigation complex that will comply with the requirements of international organizations, classification societies, associations, and conventions.

Statement of the problem. When developing protective coatings, there is a possibility that a single filler will not be able to simultaneously improve multiple properties. This can be achieved by introducing several fillers into the epoxy matrix [6–9]. The combination of micro- and nanoscale fillers ensures a uniform distribution of mechanical stresses within the polymer volume, preventing the formation and propagation of micro- and macro-cracks, and ecnhancing rigidity and resistance to deformations through the formation of a multi-level coating structure.

Analysis of recent research and publications. One of the effective methods for creating coatings with the required set of properties is modification of materials by introducing polydisperse fillers into the matrix [10–12]. In this case, nanocarbon and dispersive fillers are introduced into the matrix to reinforce epoxy composites and coatings based on them [13–15], ensuring a wide range of industrial applications. To maximize the effect on the structure and properties of polymer coatings, it is essential to develop mathematical models that will optimize the composition of ingredients within the matrix to achieve the desired functional properties of materials.

Purpose: develop mathematical models for predicting the characteristics of polymer coatings intended for protecting the surfaces of ship navigation aids.

Presentation of the main material. Materials and methods. To create polymer coatings intended for the protection of metal structures surfaces, in particular surfaces of navigation equipment, the following ingredients were selected: binder – epoxy oligomer ED-20; hardener – polyethylene polyamine (PEPA), with a component ratio (wt. parts) – ED-20: PEPA – 100: 10.

To improve the properties, the following were used:

– nanodispersed fullerene-carbon black mixture (NFCM) (YongFeng Chemicals, Hefei, China). NFCM is a nanocarbon material obtained by synthesizing fullerenes using laser evaporation of graphite technology. The size of NFCM is 30…40 nm;

– filler trimethoprim $C_{14}H_{18}N_4O_3$ (TMP) (CAS: 738-70-5), a synthetic antibiotic capable of inhibiting microorganisms and bacteria. The size of the TMP is 5…10 μm;

The formation of coatings was performed in a specific sequence, as outlined in the works [6, 7, 15].

The adhesion strength of the matrix to the metal base was investigated according to ASTM D897-08.

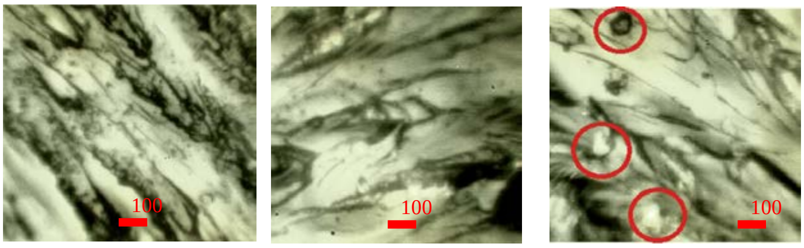
The impact strength (W) was determined by the Charpy method according to ASTM D6110–18.

The study of the structure of the composites was carried out on a microscope model XJL-17AT and Versamet 2. For digital image processing, the software “Levenhuk ToupView” was used.

The deviation of the values in the studies of the adhesion strength and physical and mechanical properties of the developed polymers was 2…5% of the nominal.

Statistical methods: the statistical processing of the obtained results was performed using the software package for statistical data processing: Statgraphics Centurion 19, with the definition of Cochrane’s, Student’s, Fisher’s criteria.

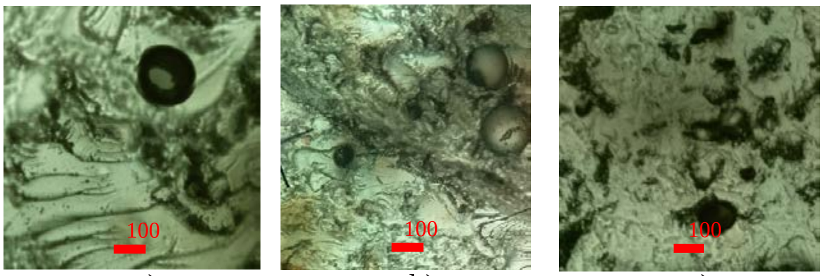
Analysis of properties and structure of polymer materials. Based on the study's previous results, the maximum values of adhesive and cohesive strength were established for polymer materials filled with a nanodispersed filler (fullerene-carbon black mixture) and a dispersed filler (trimethoprim $C_{14}H_{18}N_4O_3$). The maximum values of adhesive (σ_a = 36.5 MPa) and cohesive (W = 15.2 kJ/m^2) strength were observed when a nanodispersed fullerene-carbon black mixture was introduced with content of – q = 0.050…0.075 pts.wt. In this case, changing the content of the nanodispersed filler from q = 0.050 pts.wt. to q = 0.100 pts.wt. provide a change in the structure and, therefore, the properties of the protective coatings (Fig. 1, a-b). The surface of the polymer material, which was not subjected to mechanical treatment, was investigated using optical microscopy. Based on the analysis of fracture fractograms, it can be stated that the structure of polymer materials with the content of NFCM q = 0.050 pts.wt. and q = 0.075 pts.wt. (Fig. 1, a, b). is characterized by the presence of straight and, in some cases, parallel cleavage lines. This indicates a uniform distribution of internal stresses in the polymer system. In comparison, increasing the content of nanofiller to q = 0.100 pts.wt. creates conditions for forming brittle areas in the polymer volume (Fig. 1, c). The value of the mechanical strength of such materials decreases to W = 13.6 kJ/m^2.



a) b) c)

Fig. 1. Fracture structure of polymeric materials with different contents of nanodispersed fullerene-carbon black mixture: a) q = 0.050 pts.wt; b) q = 0.050 pts.wt; c) q = 0.100 pts.wt.

The dispersed filler TMP showed the maximum values of the adhesive (σ_a = 37.0 MPa) and cohesive (W = 12.8 kJ/m^2) strength were observed when trimethoprim was introduced at a content of – q = 10 pts.wt. As in the previous case, a change in the structure of polymeric materials was observed when a dispersed filler was introduced. Analysis of the fracture structure of the polymer (Fig. 2, a) allowed us to identify a relief surface structure with the presence of trimethoprim particles.



a) b) c)

Fig. 2. Fracture structure of polymeric materials with different trimethoprim contents: a) q = 5.0 pts.wt.; b) q = 10.0 pts.wt.; c) q = 15.0 pts.wt.

The nature of the filler distribution in the polymer binder is not uniform. We analyzed the fracture structures of a polymeric material filled with trimethoprim at a content of – q = 10 pts.wt. (Fig. 2, b). This allowed us to identify more particles in the polymer volume, the lateral surface of which borders on the cleavage lines. This indirectly indicates the formation of physicochemical bonds around the particles of the dispersed filler, which changes the trajectory of crack propagation under the influence of impact loading. When the filler content increases to q = 15 pts.wt. (Fig. 2, c), an uneven distribution of particles in the polymer volume was observed. The brittle nature of the fracture changes to a more viscous one.

So, based on the analysis of the structure and properties of polymeric materials filled with dispersed and nanodispersed fillers, the following can be stated:

– to ensure adhesion strength, it is possible to use both dispersed and nanodispersed fillers since the values of the adhesion strength are sufficient for application in the protection of water transport surfaces;

– to improve the physical and mechanical properties of protective coatings, it is advisable to use a nanodispersed filler since the mechanical properties differ from those of a polymeric material filled with a dispersed filler. However, taking into account the properties of trimethoprim (a synthetic antibiotic capable of inhibiting microorganisms and bacteria), it is advisable to use it when filling coatings for anti-corrosion and anti-fouling protection of surfaces of ship navigation aids. Therefore, one of the methods of increasing mechanical characteristics, and as a consequence of protection from aggressive external factors, is to combine fillers of different physico-chemical nature and dispersion.

Mathematical modeling of properties of protective coatings. Considering the above, the problem of improving the characteristics of protective coatings designed for the protection of water transport surfaces was addressed by optimizing the composition of polydisperse fillers in the epoxy binder when setting up an active experiment, i.e., using an orthogonal plan of the 2nd degree 3^2. The content of the ingredients was selected based on previous comprehensive studies of the adhesive and physico-mechanical properties of epoxy composite materials. The primary levels of change in the content of TMP and NFCM components are given in Table. 1.

Table 1

Variable levels in conventional and natural scales

Name of ingredients	Factor	Intermediate level, q, pts. wt.	Variation step, Δq, pts.wt.	Value of content of variable parameters/ingredients, pts.wt.		
				-1	0	+1
Trimethoprim $C_{14}H_{18}N_4O_3$ (TMP)	x_1	10.0	5.0	5.0	10.0	15.0
Nanodispersed fullerene-carbon black mixture (NFCM)	x_2	0.050	0.025	0.025	0.050	0.075

According to the complete factorial experiment (CFE) design, a series of 9 experiments (N = 9) was conducted, each of which was repeated five times (p = 5). The experiment was carried out randomly according to the experimental scheme in [6, 7] to exclude systematic errors. The CFE design matrix and its results are given in Table 2.

Table 2

Results of research on the properties of polymer materials

№ Experiment	Component content, q, pts.wt.		Adhesion strength, σ_a, MPa	Impact strength, W, kJ/m^2
	x_1	x_2	y_1	y_2
1	5.0	0.025	39.8	15.1
2	15.0	0.025	36.1	15.2
3	5.0	0.075	37.2	15.4
4	15.0	0.075	35.0	15.0
5	10.0	0.050	41.3	17.2
6	15.0	0.050	38.0	17.0
7	5.0	0.050	42.0	17.1
8	10.0	0.075	36.3	15.8
9	10.0	0.025	37.5	16.3

The mathematical model of the dependencies $y = f(x_1, x_2)$ was expressed in the form of a regression equation:

$$y = b_0 + b_1x_1 + b_2x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1x_2 \quad (1)$$

The formula determined the regression coefficients for adhesive strength and impact strength according to [6, 7], the values of which are given in Table 3.

Table 3

Regression equation coefficients

Marking	**Regression equation coefficient for adhesion strength**	**Regression equation coefficient for impact strength**
b_0	40.67	17.52
b_1	-1.65	-0.07
b_2	-0.82	-0.07
b_{11}	-0.35	-0.63
b_{22}	-3.45	-1.63
b_{12}	0.37	-0.13

Based on the calculations performed, the following regression equations were obtained for the two properties under study: adhesive strength at separation (y_1) and impact strength (y_2):

$$y_1 = 40.67 – 1.65\, x_1 – 0.82\, x_2 – 0.35x_1^2 – 3.45x_2^2 + 0.37x_1x_2$$

$$y_2 = 17.52 – 0.07\, x_1 – 0.07\, x_2 – 0.63x_1^2 – 1.63x_2^2 – 0.13x_1x_2$$

For statistical processing of the obtained experimental results, a test of the reproducibility of the experiments was carried out according to the Cochrane's test:

$$G = \frac{S^2_{u\max}}{\sum_{u=1}^{N} S_u^2} \le G_{(0.05;f_1;f_2)} \quad (2)$$

The formula determined adequacy variances:

$$S_{ui}^2 = \frac{\sum_{i=1}^{m}\left(y_i - \overline{y_i}\right)^2}{m-1} \quad (3)$$

where y_{im} – the value obtained from each parallel experiment; $\overline{y_i}$ – the average value of the quantity obtained in parallel experiments.

The formulas determined the reproduction variances:

$$\sigma^2\{y\} = \frac{\sum_{i=1}^{N=9}\sigma^2\{y\}_i}{N(m-1)}; \quad (4)$$

where $\sigma^2\{y\}_i = \sum_{i=1}^{m=5}(y_i - \overline{y_i})^2$;

$$\sigma^2\{y_a\} = \frac{\grave{a}^2\{\acute{o}\}}{N},\ S_{b_0}^2 = \frac{S_0^2}{N} \quad (5)$$

The values of the obtained calculations of the variances of adequacy and reproduction are given in Table 4.

Table 4

Calculation results

№	Adequacy variances			Reproduction variances		
	Symbol	Value for y_1	Value for y_2	Symbol	Value for y_1	Value for y_2
1	S_{u1}^2	0.043	0.030	$\sigma^2\{y\}_1$	0.087	0.060
2	S_{u2}^2	0.053	0.063	$\sigma^2\{y\}_2$	0.107	0.127
3	S_{u3}^2	0.003	0.010	$\sigma^2\{y\}$	0.007	0.020
4	S_{u4}^2	0.043	0.013	$\sigma^2\{y\}_4$	0.087	0.027
5	S_{u5}^2	0.010	0.003	$\sigma^2\{y\}_5$	0.020	0.007
6	S_{u6}^2	0.013	0.010	$\sigma^2\{y\}_6$	0.027	0.020
7	S_{u7}^2	0.023	0.070	$\sigma^2\{y\}_7$	0.047	0.140
8	S_{u8}^2	0.043	0.010	$\sigma^2\{y\}$	0.087	0.020
9	S_{u9}^2	0.023	0.040	$\sigma^2\{y\}_9$	0.047	0.080

At the same time:

$$\sum_{i=1}^{N} S_{ui}^2 = 0.257\,(y_1);\; \sum_{i=1}^{N} S_{ui}^2 = 0.250\,(y_2);$$

$$\sigma^2\{y\} = S_0^2 = 0.029\;(y_1);\; \sigma^2\{y\} = S_0^2 = 0.028\;(y_2);$$

Then, the estimated value of the Cochrane's criterion at a confidence level of $P_d = 0.95$ was determined by the formula:

$$G_c = \frac{S_{u_{\max}}^2}{\sum_{i=1}^{N} S_{ui}^2}; \tag{6}$$

$$G_c = \frac{0.053}{0.257} = 0.208\;(y_1);\; G_c = \frac{0.070}{0.250} = 0.28\;(y_2)$$

Verification of the experimental results according to Cochrane's criterion [6, 7] for a confidence level P_d = 0.95 confirmed the reproducibility of the experiments for the investigated initial parameters (y_1) and (y_2). In this case, the dispersions characterizing the dispersion of the experimental results on the combination of factor levels are $S_{u\max}^2 = 0{,}053\,(y_1);\, 0{,}070\,(y_2)$. Calculated values of Cochrane's criterion: G_c = 0.208 (y_1), G_c = 0.28 (y_2). Then, as the tabular value of the Cochrane criterion: G_{tab} = 0.478.

That is, condition (2) is fulfilled:

$$G_c = 0{,}208 \le G_{tab} = 0{,}478$$

$$G_c = 0{,}28 \le G_{tab} = 0{,}478$$

The significance of the regression equation coefficients was further determined by analyzing the results according to the experimental plan (Table 5).

Table 5

Results of the study of adhesive strength and impact toughness

№	Adhesion strength, σ_a MPa					Average property value
	1	2	3	4	5	6
1	39.7	39.7	39.8	39.7	40.1	39.8
2	36.5	36.1	35.7	36.1	36.1	36.1
3	37.0	37.5	37.1	37.2	37.2	37.2
4	34.9	35.3	35.0	35.1	34.7	35.0
5	41.2	41.4	41.2	41.3	41.4	41.3
6	38.0	37.9	38.1	38,1	37.9	38.0
7	42.0	42.1	42.1	42.0	41.8	42,0
8	36.1	36.3	36.3	36.2	36.6	36.3
9	37.5	37.6	37.3	37.5	37.6	37.5
Impact strength, W kJ/m²						
1	15.1	15.1	15.2	15.2	14.9	15.1
2	15.2	15.1	15.0	15.2	15.5	15.2
3	15.2	15.3	15.4	15.5	15.6	15.4
4	14.9	14.9	15.0	15.0	15.2	15.0
5	17.2	17.1	17.2	17.3	17.2	17.2
6	17.0	17.0	17.1	17.0	16.9	17.0
7	17.1	17.1	17.0	16.9	17.4	17.1
8	15.8	15.8	15.8	15.9	15.7	15.8
9	16.3	16.3	16.3	16.5	16.1	16.3

Further, the variances of the regression coefficients (Table 6) were determined using the formula:

$$S_{b_i}^2 = \frac{S_0^2}{\sum_{u-1}^{N} x_{iu}^2} \quad (7)$$

The Student test [6, 7] determined the significance of the regression coefficients' significance. In this case, the tabular (t_t) and calculated (t_c) Student tests were determined (Table 6). For a confidence level of $P_d = 0.95$, the tabular value of the Student test is $t_t = 2.028$.

When constructing a mathematical model for predicting adhesion characteristics, the calculated values of the Student's test t_{0p}, t_{1p}, t_{2p}, t_{11p}, t_{22p}, t_{12p} (Table 6) are more significant than t_t.

Therefore, it was considered that all coefficients of the regression equation are substantial, and thus, the equation remains unchanged:

$$y_1 = 40.67 - 1.65\, x_1 - 0.82\, x_2 - 0.35x_1^2 - 3.45x_2^2 + 0.37x_1 x_2$$

Then, when constructing a mathematical model for predicting impact toughness, the calculated values of the Student's test t_{1p}, t_{2p}, t_{12p} (Table 6) are less than t_t. Therefore, the equation takes the form:

$$y_2 = 17.52 - 0.63x_1^2 - 1.63x_2^2$$

Table 6

Dispersions of the regression coefficients (S_b^2) and calculated values of the Student test (t_p)

№	Dispersions of regression coefficients			Calculated Values of Student's test		
	Symbol	Value for y_1	Value for y_2	Symbol	Value for y_1	Value for y_2
1	$S_{b_0}^2$	0.003	0.003	t_{0p}	701.22	302.58
2	$S_{b_1}^2$	0.005	0.005	t_{1p}	23.93	0.98
3	$S_{b_2}^2$	0.005	0.005	t_{2p}	11.85	0.98
4	$S_{b_{11}}^2$	0.014	0.014	t_{11p}	2.93	5.37
5	$S_{b_{22}}^2$	0.014	0.014	t_{22p}	28.89	13.86
6	$S_{b_{12}}^2$	0.007	0.007	t_{12p}	4.4	1.5

The adequacy of the obtained model was checked using Fisher's test [6, 7] :

$$F_c = \frac{S_{u\,max}^2}{S_y^2} \le F_{(0.95;f_{\grave{a}\sigma};f_y)} \qquad (8)$$

Therefore, the following values of the Fisher's calculation criterion were obtained:

$F_c = 1.827$ (y_1), $F_c = 2.5$ (y_2).

Based on the calculations, it was found that the calculated value of the Fisher's test is less than the tabular value, i.e., condition (8) is fulfilled. This makes it possible to state that the obtained mathematical models for predicting adhesion and physical and mechanical properties adequately describe the composition.

To convert the conditional values of the variable parameters into natural values, the following equation was used [6, 7]:

$$x_i = \frac{q_i - q_{i0}}{\Delta q_i} \qquad (9)$$

where q_i – the value of the ith factor of the experiment,

q_{i0} – the value of the zero level,

Δq_i – the variation interval.

By substituting these values according to formula (9) into the regression equation and transforming it, we obtained the following mathematical models with the natural value of the variable parameters:

$$\sigma_a = 31.9 - 0.2q_1 + 489.333q_2 - 0.014q_1^2 + 3.0q_1q_2 - 5520.0q_2^2$$

$$W = 8.22222 + 0.543333q_1 + 268.667q_2 - 0.0253333q_1^2 - 1.0q_1q_2 - 2613.33q_2^2$$

The obtained mathematical models allow for predicting the values of the output quantities (y_1, y_2) for the presented points in the middle of the factor variation area. The geometric interpretation of the response surface is given in Fig. 3, 4.

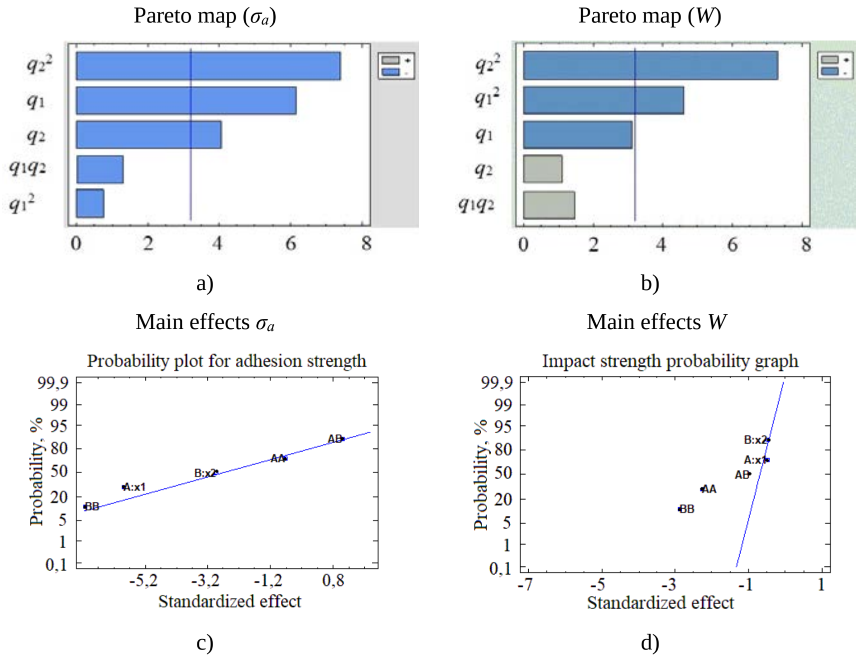


Fig. 3. Pareto maps (a, b) and main effects (c, d):
$AA - q_1$; $BB - q_2$; $Ax1 - q_1^2$; $Ax2 - q_2^2$; $AB - q_1q_2$

Based on the presented Paretto maps (Fig. 3, a, b), which were obtained when analyzing the experimental database using the Statgraphics Centurion 19 software, it can be stated that the most statically significant effects that affect the initial parameters under study (y_1 and y_2) are those that cross the vertical line (corresponding to a confidence level of 0.95). Therefore, it can be stated that the most significant factors for improving the adhesion characteristics are q_2^2, q_1, and q^2, i.e., the square value of the content of the fullerene-carbon black mixture, the value of the content of trimethoprim and the nano dispersed fullerene-carbon black mixture. The most significant factors for increasing the impact strength are q_2^2 and q_1^2, i.e., the square values of the content of the two additives. Based on the Pareto maps, it can also be stated that the influence of the main filler's content is stronger than the additional one.

Additional analysis of the graphs for diagnosing errors in the obtained values allows us to state that the maximum deviation of factors from a direct distribution indicates their significance in forming a mathematical model. Thus, it can be noted that all aspects in the mathematical model (y_1) are significant (consistent with previous calculations) since they are as close as possible to a direct distribution. Then, when analyzing the probability graph for the mathematical model (y_2), we observed some deviation of factors from a direct distribution, which allows us to state their indirect influence in predicting impact toughness. In this case, the most significant are their quadratic values of the ingredient content.

Based on mathematical modeling and Statgraphics Centurion 19 software, response surfaces and their contours for the studied output parameters y_1 and y_2 (Fig. 4).

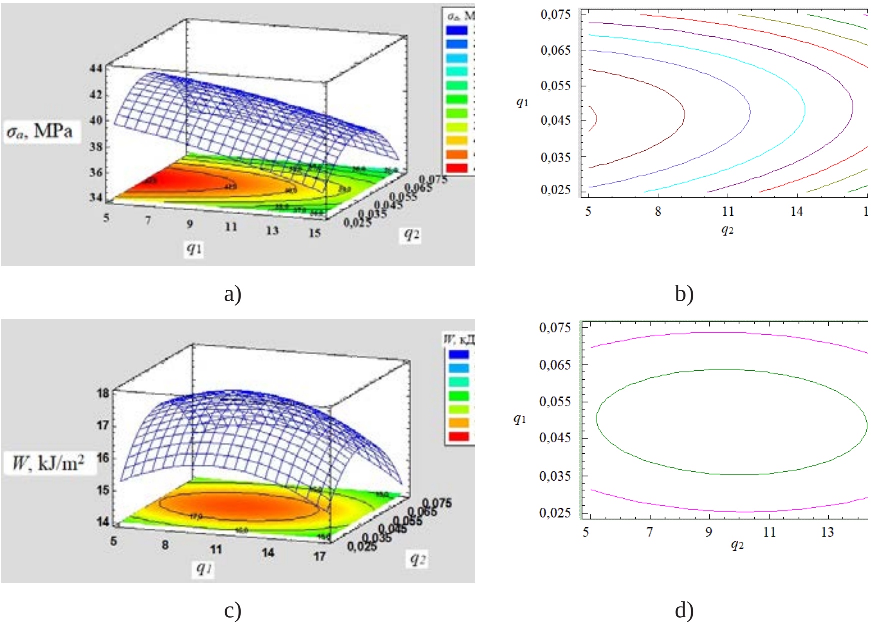


Fig. 4. Calculated response surface and response surface contours σ_a / $W = f(q_1, q_2)$

Thus, after optimizing the content of fillers of different physicochemical natures and dispersion, an increase in the protective coatings' adhesion and mechanical strength by 1.1 to 1.3 times was observed (compared to composites with only a single filler). Additional analysis of the structure of the polymer material, which contains trimethoprim – 10.0 pts.wt. and a nanodispersed fullerene-carbon black mixture – 0.050 pts.wt. (Fig. 5), allows us to state that the increase in impact strength is associated with the maximum densification of the polymer structure.

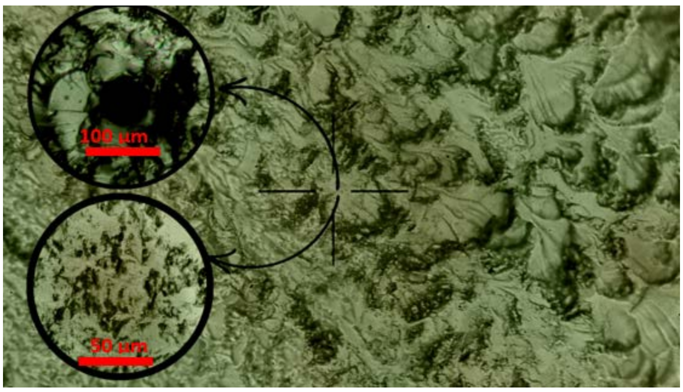


Fig. 5. Fracture structure of polymeric materials with an optimal content of trimethoprim (10.0 pts.wt.) and nanodispersed fullerene-carbon black mixture (0.050 pts.wt.)

At the same time, the synergy between particles of different dispersion and physicochemical nature ensures the filling of voids with nanofiller, thus increasing the density of the material, and, as a result, creates conditions for a uniform distribution of mechanical loads in the material. This, in turn, allows us to reduce the likelihood of the spread of microcracks, which create the prerequisites for forming large prominent cracks, destroying the polymer.

Conclusion. Setting up an active experiment using an orthogonal plan of the 2nd degree 3^2 allowed us to obtain results, with the help of which mathematical models were created that describe the dependence of the adhesive strength and impact strength of polymeric materials on the content of fillers of different dispersion and physicochemical nature.

Based on the mathematical model and its graphic representation in the form of response surfaces projected onto a plane in the form of a set of lines (which correspond to the optimization parameters), it was established that the adhesive strength increases with an increase in the trimethoprim content to 7.0 pts.wt. Increasing the content of more than 7.0 pts.wt. of trimethoprim provides a linear decrease in the studied property. Regarding the nanodispersed fullerene-carbon black mixture, the concentration curves pass through a maximum at an additive content of 0.040…0.050 pts.wt. While the impact strength increases with increasing trimethoprim content in the range of 8.0 wt. parts to 15.0 pts.wt., and 0.035…0.065 pts.wt. of nanodispersed fullerene-carbon black mixture, respectively. However, the maximum values of the initial parameters (σ_a = 42.0 MPa, W = 17.2 kJ/m^2) were observed when the ingredients were introduced at the following content: trimethoprim (d = 5...10 μm) – 5...10 pts.wt., nanodispersed fullerene-carbon black mixture (d = 30...40 nm) – 0.050 pts.wt. per 100 pts.wt. of epoxy oligomer ED-20 and 10 pts.wt. of hardener PEPA.

It is proven that the increase in adhesive and physico-mechanical properties (compared to the unfilled matrix – σ_a = 24.4 MPa, W = 7.0 kJ/m^2) by 1.7…2.4 times is associated with a change in the polymer structure, which is due to the physicochemical interaction of the ingredients and mechanical compaction. This makes it possible to use the developed materials to form functional coatings for protection against external factors of ship navigation aids.

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