OPTIMIZATION OF INGREDIENTS UPON DEVELOPMENT OF THE PROTECTIVE POLYMERIC COMPOSITE COATINGS FOR THE RIVER AND SEA TRANSPORT

Andriy Buketov¹, Serhii Yakushchenko¹, Abdellah Menou², Oleh Bezbakh¹, Roman Vrublevskyi¹, Yaroslava Kalba³, Tetyana Cherniavskia¹, Denyo Zhyntyk¹, Olha Danylyuk³,*

¹Kherson State Maritime Academy, Kherson, Ukraine
²International Academy of Civil Aviation, Casablanca, Morocco
³Ternopil Volodymyr Hnatiuk National Pedagogical University, Ternopil, Ukraine

*E-mail of corresponding author: laboratory22b@gmail.com

Resume

It is proved that in order to increase the operational characteristics of parts of the river and sea transport, including their physical and mechanical properties, it is advisable to use the protective polymeric composite coatings. The effect of fillers on the flexural stresses of the developed epoxy composite was analyzed. The critical content of components was determined by the method of mathematical planning of the experiment: the synthesized powder mixture - 0.05 pts.wt., discrete fibers - 0.10 to 0.15 pts.wt. per 100 pts.wt. of epoxy oligomer ED-20. Introduction of such ingredients into the epoxy binder allows to increase the flexural stresses to \( \sigma = 77.4 \ldots 78.6 \text{ MPa} \). The obtained results allow to create materials with improved values of physical and mechanical properties.

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1 Introduction

Development of the river and sea transport involves creation of new materials to protect equipment parts from corrosion and wear. Use of the polymer composite materials (PCM) and protective coatings based on them is relevant in this context. Polymer composites are characterized by improved performance, which conditions a wide range of applications in the transport industry to increase the service life of machines and mechanisms [1-2]. It should be noted that nowadays the problem of improving cohesive properties of the known materials is current, which is decisive in analysis of reliability of equipment under critical conditions.

The authors [3-9] have shown that it is advisable to introduce fillers at a critical content in order to improve the properties of coatings, which are operated in the conditions of influence of corrosive environments and variable temperatures, in the complex. At the same time, it is important to choose the additives that should be active to the physical and chemical interaction with the polymer during the crosslinking. It was believed that introduction of fillers in the form of powder and discrete fibers can provide a synergistic effect in improving the material properties. In this context, it is advisable to use the method of mathematical planning of the experiment, which will reduce the number of conducted studies and optimize the content of ingredients to obtain material with the highest parameters of the studied characteristics.

Aim of the investigation - to optimize the content of dispersed and fibrous discrete fillers for the protective coatings of the river and sea transport by the method of mathematical planning of an experiment.

2 Materials and methods

The epoxide diane oligomer ED-20 was selected as the main component for the binding when forming epoxy composite materials (CM), which is distinguished by the high adhesive and cohesive strength. For the cross-linking action of epoxy compositions, polyethylene polyamine hardener was used, which allows materials’ curing at room temperatures. The PEPA is a low molecular weight substance consisting of monomer units with the following form: [- CH2-CH2-NH-]n. A micro-dispersed filler, the synthesized powder mixture (SPM) of the following composition: Fe (70%) + Ti (10%) + TiC (15%) + Fe3C (5%) and a mixture of discrete fibers (MDF) in the form of fibrous filler: modal (42%), polycryll (38%), polyanime (38%), were used for experimental studies.

Epoxy CM’s forming technology is following [3-5]:
heating of the resin up to the temperature $T = (353 \pm 2)$ K and exposure at this temperature during $\tau = (20 \pm 0.1)$ min; dosage of the filler and its further loading into the epoxy binder; hydrodynamic blending of the oligomer ED-20 and filler during $\tau = (10 \pm 0.1)$ min; ultrasonic processing of the composition during $\tau = (1.5 \pm 0.1)$ min; cooling of the composition to the ambient temperature during $\tau = (5 \pm 0.1)$ min. Then the curing of the PCM was conducted according to the mode: formation of the specimens and their curing during $\tau = (12.0 \pm 0.1)$ hours at the temperature $T = (293 \pm 2)$ K; heating with the rate of $v = 3$ K/min to the temperature $T = (393 \pm 2)$ K; holding of the PCM during $\tau = (2.0 \pm 0.05)$ hours, slowly cooling to the temperature $T = (293 \pm 2)$ K. To stabilize the structural processes to occur in the CM they were kept during $\tau = 24$ hours in the open air at the temperature $T = (293 \pm 2)$ K before testing.

The flexural stresses of the PCM were studied in the work according to ASTM D 790 - 03 [10]. To obtain the high performance CMs, after the preliminary experiments, a method of mathematical planning of the experiment was used, which simultaneously allowed to take into account the ratio of components and technological parameters of the composition to the ambient temperature during $\tau = (60 \pm 5)$ min; introduction of the curing agent PEPA and mechanical blending of the composition during $\tau = (5 \pm 0.1)$ min; ultrasonic processing of the composition during $\tau = (10 \pm 0.1)$ min; slow exposure at this temperature during $\tau = (20 \pm 0.1)$ min; holding of the PCM during $\tau = (12.0 \pm 0.1)$ hours at the temperature $T = (353 \pm 2)$ K; slow exposure at the temperature $T = (353 \pm 2)$ K before testing.

An experiment was considered false if the experimental value of the criterion $F_p$ was found for the 5% significance level. Given $F_p < F_{p, \alpha}$, it was considered that the polynomial adequately describes the process under study [12-16].

In order to reduce the error in the study of properties and search for optimal values, five or six parallel measurements were performed and the arithmetic mean was found:

$$ y = \frac{y_1 + \ldots + y_n}{n}, $$

where:

- $y_i$ - the results of a single experiment;
- $y$ - the arithmetic mean of all parallel experiments;
- $n$ - number of parallel experiments.

To eliminate false values, the Student's criterion was used [15]:

$$ \frac{y_i - y}{S} \geq t, $$

where:

- $y_i$ - the results of a single experiment;
- $y$ - the arithmetic mean of all results;
- $S$ - quadratic error;
- $t$ - the tabular value of the Student test.

The quadratic error was determined by the formula:

$$ S = \sqrt{\frac{\sum (y_i - y)^2}{n}}. $$

An experiment was considered false if the experimental value of the criterion is greater than the table value: $|t_{exp}| \geq t_{table}$.

3 Results

The flexural stresses, as one of the main properties of composites with different content of micro-dispersed filler and discrete fibers, were investigated in order to optimize the content of ingredients in formation of the
The expanded matrix of planning of the complete factor experiment and its results are shown in Table 2. Results of study of the CM flexural stresses are shown in Table 3.

The mathematical model was formed as a regression equation [12]:

$$y = \sum_{i=1}^{N} x_i \sigma_f = (1) \sum_{i=1}^{N} x_i$$

The regression coefficients were determined by the functional layer of the protective coating. It should be noted that as a micro-dispersed filler, the synthesized powder mixture (SPM) of the following composition was used for experimental studies: Fe (70%) + Ti (10%) + TiC (15%) + Fe3C (5%). A mixture of discrete fibers (MDF) was used in the form of fibrous filler: modal (42%), polyacryl (38%), polyamide (38%). Each component (filler) was coded by units with consideration of the variation step, for standardization and for simplification of calculations (Table 1).

According to the experiment planning scheme nine experiments (N = 9) were conducted, each of which was repeated three times (p = 3) in order to exclude system errors (Table 2). In order for the planning matrix to be orthogonal [11], the corrected values of $x'$ level were entered, which were calculated by the formula:

$$x_i' = (x_i)^2 - \frac{\sum_{a=1}^{N} x_a}{N}.$$  

The expanded matrix of planning of the complete factor experiment and its results are shown in Table 2. Results of study of the CM flexural stresses are shown in Table 3.

The mathematical model $y = f (x_1, x_2)$ was formed as a regression equation [12]:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_11 x_1^2 + b_22 x_2^2 + b_{12} x_1 x_2.$$  

The regression coefficients were determined by the
The mean square error was determined as:

\[ \sigma^2 \left( \{ y \} \right) = \frac{1}{N(m-1)} \sum_{i=1}^{m} \sigma^2 \left( \{ y \} \right)_i, \quad (18) \]

where: \( \sigma^2 \left( \{ y \} \right)_i = \sum_{i=1}^{n-m} (y_i - \overline{y})^2 \);

\[ \sigma^2 \left( \{ y_{ui} \} \right) = \frac{\sigma^2 \left( \{ y \} \right)}{N}, \quad \text{or} \quad S_{u} = \frac{S_u^2}{N}. \quad (19) \]

Dispersion values are shown in Table 5.

Testing the experiment results by the Cochran test [14-15] for a fixed probability \( \alpha = 0.05 \) confirmed the reproducibility of the experiments. Dispersion of experiment results on combinations of a few factor levels: \( \sum_{i=1}^{N} S_{ui}^2 = 13.23, \sigma^2 \left( \{ y \} \right) = S_u^2 = 1.470 \).

Then, the calculated value of the Cochran test at the 5% level of significance [14]:

\[ G_{calc} = \frac{S_{u}^2}{\sum_{i=1}^{m} S_{ui}^2}; \quad (20) \]

\[ G_{calc} = \frac{2.58}{13.28} = 0.196. \]

Testing the experiment results by the Cochran test [14-15] for a fixed probability \( \alpha = 0.05 \) confirmed the reproducibility of the experiments. Dispersion of experiment results on combinations of a few factor levels: \( S_{u}^2 = 0.196 \). Calculated value of the Cochran test is \( G_{calc} = 0.196 \).

Table value of the Cochran test is \( G_{tab} = 0.478 \).

That is, Equation (20) is satisfied:

\[ G_{calc} = 0.196 \leq G_{tab} = 0.478. \]

Subsequently, the coefficients significance of regression
The adequacy of the model was checked by the Fisher test [17]:

\[ F_{S} = \frac{S_{\text{reg}}^{2}}{S_{\text{error}}^{2}} \leq F_{(f_{1}, f_{2})}, \quad (24) \]

where \( S_{\text{reg}}^{2} = 2.59 \) - calculated value of dispersion of adequacy (Table 5),

\[ S_{\text{error}}^{2} = \frac{\sum_{i=1}^{N} S_{b_{i}^{2}}}{N}, \quad (25) \]

\( S_{\text{reg}}^{2} \) = 1.470 - mean square error,

So: \( F_{S} = 0.415 \),

\( F_{(f_{1}, f_{2})} \) - table value of the Fisher test in 5% significance level (\( f_{1} = N \cdot (k + 1) = 9 \cdot (5 + 1) = 3 \), \( f_{2} = N \cdot (n - 1) = 9 \cdot (3 - 1) = 18 \)). So: \( F_{(f_{1}, f_{2})} = 3.16 \) [18].

Calculated value of Fisher test is less than the table one, so Equation (21) is satisfied. It is possible to assume that equation adequately characterizes the composition.

Interpretation process of the obtained mathematical model, as a rule, is not just determination of factors influence. A simple comparison of absolute value of linear coefficients does not determine the relative degree factors.
Substituting these values in accordance with Equation (26) into the regression equation and transforming it, one obtains the following regression equation with the natural values of the variables:

\[
\sigma_f = 44.63 + 44.33q_1 + 577.0q_2 - 1030.0q_1q_2 - 2200.0q_1^2 .
\]  

Given equation in natural values allows only predicting the output value for any point in the middle of the range of factor variations. However, with its help it is possible to construct graphs of dependence of the output value (flexural stresses) from any factor (or two factors). Geometric interpretation of the response surface is shown in Figures 1-3.

4 Discussion

Dependencies that connect normalized and natural values of the variables are as follows:

\[
x_i = \frac{q_i - q_{i0}}{\Delta q_i} ,
\]  

(26)

where:

- \( q_i \) - value of \( i \) experiment factor,
- \( q_{i0} \) - value of zero level,
- \( \Delta q_i \) - variation interval.

Substituting these values in accordance with Equation (26) into the regression equation and transforming it, one obtains the following regression equation with the natural values of the variables:

\[
\sigma_f = 44.63 + 44.33q_1 + 577.0q_2 - 1030.0q_1q_2 - 2200.0q_1^2 .
\]

Figure 1 Standardized Pareto chart (a) and main effects (b)

Figure 2 Estimated surface \( \sigma_f = f(q_1,q_2) \)

Figure 3 Contours of estimated response surface, which illustrate dependence of the flexural stresses on the content of the two fillers in the complex
Based on the experimental studies, it has been found that both factors are significant. It should be noted that effect of content of the SPM on values of the flexural stresses is higher compared to the MDF (according to the Pareto chart). It was determined that the optimal values of the flexural stresses have a developed epoxy composite with the SPM and the MDF at the following contents: the SPM is 0.05 pts.wt., MDF - 0.10 to 0.15 pts wt. ($\sigma_f = 77.4$ to 78.6 MPa) by analyzing the calculated response surface.

The obtained results indicate that both factors of the regression equation are significant. It should be noted that the greatest influence on the output parameters of the composite have a quadratic dependence of the first factor and linear dependence of the second factor. In the course of the analysis, it was found that values of the flexural stresses have the maximal values at the optimal content of components. In particular, from Figure 2 it is noticeable that an additional increase in the flexural stresses is possible when the content of the SPD filler is increased.

The developed PCMs will be used for the repair of equipment, mechanisms and systems of a marine vessel [19], such as:

- pipeline systems characterized by the corrosion damage;
- deck mechanisms (cargo devices).

5 Conclusions

The critical content of the dispersive and fiber fillers: the synthesized powder mixture is 0.05 pts.wt., the mixture of discrete fibers - 0.10 to 0.15 pts.wt. per 100 pts.wt. of epoxy oligomer ED-20 was found by the method of mathematical planning of the experiment. Introduction of such ingredients into the epoxy binder allows to increase the flexural stresses of the epoxy composites from $\sigma_f = 48.0$ MPa (for epoxy matrix) to $\sigma_f = 77.4$ to 78.6 MPa.

It was analyzed that with increasing the content of the synthesized powder mixture it is possible to increase values of the flexural stresses. These studies will be presented in the future works. The obtained results allow to create materials with improved physical and mechanical properties in the complex. The obtained materials can be used as the protective coatings to increase the performance and for repairing of the vehicle parts.

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