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ANALYSIS OF PROPERTIES OF EPOXY COMPOSITIONS THAT OPERATE IN CONTACT WITH WATER AND OIL PRODUCTS

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Полімерозчини на основі епоксидної смоли були модифіковані з метою підвищення стійкості в агресивних середовищах і зниження вартості. Поставлена мета була реалізована за рахунок наповнення багатофракційним мінеральним каркасом і модифікацією цеолітом та фурфуролом. Варіювалися кількість фурфуролу, загальний вміст мінерального каркасу і частка в каркасі окремих компонентів. Досліджувані композиції призначені для роботи в умовах впливу сумішей води з нафтопродуктами і іншими агентами (в елементах споруд, пов'язаних з технічним обслуговуванням транспорту). Властивості композицій визначалися після експозиції окремо в повітряному середовищі, у воді і двох видах нафти.

Для пошуку оптимальних композицій використовувалася ітераційна процедура випадкового сканування полів властивостей матеріалу в п'яти координатах варійованих факторів. Поля властивостей досліджені по експериментально-статистичними моделям, які отримані за результатами натурних експериментів. ЕС-моделі використовуються для реалізації обчислювальних експериментів за допомогою методу Монте-Карло.

Підтверджено можливість визначення оптимальних (по набору критеріїв) багатокомпонентних полімерних композицій для різних умов експлуатації за допомогою ітераційної процедури випадкового сканування полів властивостей.

Отримані композиції для ремонту та захисту конструкцій, що контактують з водою: паста (композиція зниженої в'язкості без піску) і розчин (зі зніженою витратою епоксидної смоли). Суміші, що забезпечують збереження необхідних властивостей захисного розчину після тривалих впливів сумішей води з нафтопродуктами, застосовані при капітальному ремонті залізничного переїзного настилу

Ключові слова: епоксикаучукова смола, цеоліт, фурфурол, експериментально-статистична модель, метод Монте-Карло, компромісна оптимізація

1. Introduction

Materials of increased resistance are necessary to protect concrete structures, which work in contact with water, oil products and other agents. Such materials are also necessary for repair and restoration works, which are required for most of hydraulic structures, which had been in operation for many decades. Epoxy-resins based polymer solutions provide the complex of properties required for these works.

Despite the relatively high initial cost, reduction in the total cost of a life cycle of structures justifies the use of epoxy binders for repair and restoration works. Reduce of repair costs and replacement of structures, elimination of consequences of failures, environmental activities and other measures reduce the total cost of a life cycle of structures. Modifications of known materials are more actual than development of new polymers at present. Unique physical-and-chemical properties and durability of synthetic polymeric materials open wide possibilities for their use for directional modification. The cost of protective polymeric solutions with epoxy binders is currently quite high, so it is beneficial to use these materials only if we need their high strength and chemical resistance simultaneously.

The use of various modifiers and fillers makes it possible to adjust properties, increase durability and life time and reduce the cost of these materials. Therefore, the development of an optimal formulation and study on properties of filled modified epoxy compositions intended for specific operating conditions is a relevant task.

It is expedient to use the “Macro” epoxy-rubber resin produced in Ukraine as a basic component in compositions for repair and protection of concrete elements. Addition of certain dosages of furfural and zeolite can improve operation properties of solutions based on this resin (patent of Ukraine No. 5408).

2. Literature review and problem statement

The use of epoxy polymer solutions is widespread in the construction industry. Currently, repair solutions [1, 2], compositions for protection of concrete surfaces from aggressive effects [3, 4], protection of steel reinforcement in concrete [5], etc. require these materials. At present, the main trend in the industry of thermosetting plastic is not development of new polymers, but modification of known materials. There are many ways for directed modification of epoxy solutions. They include a use of fillers, variation of types and amounts of a curing agent [6], plasticization, a use of combinations of various epoxy resins and hardeners [7]. Paper [8] shows disadvantages of protective polymer solutions. The disadvantages are high shrinkage, brittleness, high cost and special production conditions. The high cost is the main disadvantage of epoxy resin based solutions for repair and restoration. Filling - is the simplest and most effective way to minimize cost. In addition, the use of fillers is one of the ways to control properties of epoxy solutions directly. There are studies on strength characteristics of epoxy composites with various types of filler [9, 10]. Authors of work [9] found that the replacement of silica sand with porous fillers and rubber crumb leads to deterioration in strength characteristics of epoxy compositions. We can observe the most significant drop in strength when rubber crumb replaces sand. It is advisable to use plasticization of epoxy resin with low molecular weight rubbers to avoid deterioration of mechanical characteristics and to reduce brittleness of polymeric solutions at the same time [11]. Therefore, we select plasticized “Macro” epoxy resin of the “Makrotech” concern (Ukraine) as the basic component for the study. It is expedient to use dense, chemically resistant fillers to obtain protective coatings [12]. The works above do not mention the use of combinations of various polydisperse fillers, likely because of the complexity of analysis of an influence of individual components of such a mineral frame on properties of a composite.

It is possible to improve physical-and-mechanical and operational characteristics of polymer solutions based on epoxy matrix by selection of the optimal multifractional mineral frame, which includes zeolite, and by modification with furfural [13, 14].

In particular, such compositions can protect structures of transport service stations and other structures affected by mixtures of water with oil products, surfactants, etc. We should note that filled epoxy composites show good results in long-term tests for chemical resistance [15], however, authors of paper [12] note a significant deterioration in mechanical characteristics of polymeric solutions under the influence of oil products. It is almost impossible to conduct long-term tests of materials in inhomogeneous media (mixtures of water and oil products). Given the above, we propose to determine properties of compositions after exposure separately in air, separately in water and separately in two types of oil.

There is lack of studies on causes and conditions of a positive effect of zeolite on the structure of furfural modified epoxy compositions. Optimal levels of strength and durability criteria in different environments correspond to different dosages of modifying components and basic components. Therefore, a search for compromise solutions is necessary in design of compositions of a specific purpose [16]. Calculation experiments on the experimental statistical models obtained give possibility to design multicomponent polymeric solutions with a minimum content of an expensive basic component. They have guaranteed properties. It is of scientific and practical interest to investigate the possibility of extension of modification conditions for compositions intended for work in adsorption-active media. Such conditions should include an increase in dosages of furfural and zeolite, taking into account provision of a safety factor with respect to the standard requirements [17] and a change in the dispersion composition of zeolite, with an increased content of which grain size distribution may be significant.

Thus, an increase in durability and reliability of transport and hydraulic structures, which operate under constant or periodic exposure to mixtures of aggressive media, is possible through the use of protective coatings based on modified epoxy polymer compositions of optimal formulation.

3. The aim and objectives of the study

The objective of the study is a search for the optimal amount and composition of a mineral dispersed phase and conditions for modification of compositions with furfural, which ensure operation properties of epoxy rubber compositions for repair and protection of concrete surfaces in contact with water-oil media.

It was necessary to solve the following tasks to achieve the objective:

– determination of levels of mechanical properties of hardened solutions for a variety of compositions, including furfural and zeolite fractions in accordance with the plan of the experiment. Construction of experimental-statistical (ES) models, for analysis of the influence of composition factors on mechanical properties of compositions;

– determination of strength characteristics for the studied solutions after exposure to water and two types of oil for simulation of contacts with mixtures of water and oil products. Evaluation of the influence of composition factors on quality criteria of solutions after 180 days of stay in water and two types of oil using ES-models, evaluation of areas of individual optima;

– determination of optimal and compromise optimal compositions of polymeric solutions for a number of specific operating conditions (in contact with water, with mixtures of water and oil products).

4. Characteristics of the materials used and conditions of the basic experiment

We selected raw materials and determined experimental conditions based on the analysis of the main areas of regulation of properties of protective and repair epoxy compositions. Experimental conditions included variable composition factors and ranges of variation, an experimental design and measured characteristics.

As a base component was “Macro” plasticized epoxy resin produced by “Makrotech” concern (Ukraine), which is cured by 18 m.p. of monocyanoethyl diethylenetriamine – (UP-0633M).

We introduced furfural into the epoxy resin as an organic modifier. It served as a polymerization accelerator and, to a certain extent, it plasticized compositions.

We used zeolite-containing rocks from the Sokyrnitsky deposit (Transcarpathia, Ukraine) with varying degrees of grinding (fine fraction – with a specific surface S_{ss}=300 m^2/kg and coarse fraction – with a grain size of 0.315–0.14 mm) with true density ρ=2.25 g/cm^3 as a mineral modifier [14].

We used quartz sand from the Avdeyevsky open-cast mine (Ukraine) with a true density of 2.65 g/cm^3, a maximum grain size not exceeding 0.315 mm and clay and dust at mass content of 2.25 % as fine filler.

In addition, we used diabase flour with a specific surface S_{ss}=300 m^2/kg and true density ρ=2.9 g/cm^3 as the filler for polymeric solutions in the experiments.

We varied levels of five parameters of the dispersed system (Table 1). We presented the parameters of the investigated compositions in mass fractions and in mass parts (m. p.) per 100 m. p. of resin. We represented components of the dispersed phase among variable factors by a hierarchy of ratios, i.e. fractions of components of nested subsystems, to study the effect on properties of the system.

Table 1

Factors and levels of their variation in the experiment.

Factor of composition	Denotation	Levels		
		$X_{\min}$	X_0	$X_{\max}$
Content of the mineral frame (m. p. per 100 m. p. of "Macro" epoxy resin "Macro").	X_1	180	280	380
Mass fraction of filler (diabase + zeolite) in the frame.	X_2	0.3	0.6	0.9
Share of zeolite in the filler (fine + coarse).	X_3	0.05	0.15	0.25
Share of coarse fraction in zeolite.	X_4	0	0.25	0.5
Dosage of furfural (m. p. per 100 m. p. of resin).	X_5	2	7	12

The 27-point plan of the experiment makes it possible to describe material quality criteria under investigation in dependence on parameters of the composition with ES-models of the 2nd order (within the ranges of the component contents given in Table 1).

At the first stage of the experiment, we studied strength characteristics of the composites according to the results of tests of prism samples (2×2×8 cm) after hardening under normal conditions. At the second stage, we analyzed tensile strength in bending after exposure of samples in aggressive media.

5. Analysis of study results

5. 1. Analysis of the effect of the multifractional frame on strength of furfural-modified epoxy compositions

We obtained ES-model (1) with 18 significant coefficients (at an experimental error of 2 MPa and a risk of 10 %) according to the experimental values of prism strength R_p (MPa) for 27 compositions:

$$\begin{aligned}R_p &= 98.8+6,0x_1-2.2x_1x_2+4.2x_2-1.6x_1^2+\\&+3.8x_3^2-1.6x_3x_4+2.5x_3x_5-2.2x_4+1.1x_4x_5\\&-5.6x_5-8.8x_5^2-2.2x_1x_3-1.9x_1x_4+2.4x_1x_5-\\&-2.4x_2x_3-1.4x_2x_4+1.7x_2x_5.\end{aligned} \quad (1)$$

The model describes the total field [18] of the prism strength limit in the coordinates of all five composition parameters. Generalizing indicators of the field are: maximum $R_{p.\max}$=118 MPa at x_1=x_2=+1 (maximum volume of the frame with a high content of fine grinded filler), x_3=x_4=−1 (minimum content in the zeolite filler without coarse grains) and x_5≈−0.3 (average modification level by furfural); $R_{p.\min}$==59 MPa (x_1=x_2=x_3=x_4=−1 и x_5=+1) twice lower.

Fig. 1 shows the single-factor curves $R_p(x_i)$ (i=1,..., 5), which pass through the extreme points. The mineral frame, which perceives compressive stresses, plays a decisive role in formation of prism strength. It occupies most of the volume of the composite and has an optimal (for this external effect) multifractional grain composition. The role of the frame is particularly evident in the field of reduced compressive strength, when a decrease in filling from 380 to 180 m.p. or an increase in the proportion of sand in the frame from 0.1 to 0.7 leads to a drop in strength by 25–30 MPa.

We take into account the ultimate strength R_p in analysis of the bearing capacity of relatively massive polymer concrete structures.

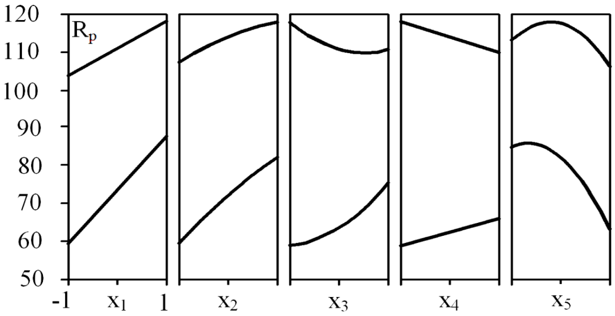

Fig. 1. Dependences of the prism strength on composition factors in the zones of minimum and maximum

Constructors often use polymer composites for protective, restorative, decorative and other coatings in practice, so polymer composites work in relatively thin layers. Therefore, a priority for such compositions is the characteristic of mechanical properties – the tensile strength.

We evaluated this characteristic of fine grinded polymer composites by the tensile strength in bending in this study, following paper [19].

We can describe a full field of ultimate strength at bending of R_b (MPa) by model (2) with 17 significant estimates of coefficients (with an experimental error of 1.2 MPa):

$$\begin{aligned}R_b &= 30,5-1,2x_1+1,8x_1^2-1,3x_1x_2-\\&-2,2x_2^2-0,4x_3-1,1x_3x_4+0,5x_3x_5-1,0x_4\\&+1,3x_4x_5-0,9x_5-1,4x_5^2-\\&-1,6x_1x_3-1,0x_1x_5-1,2x_2x_3.\end{aligned} \quad (2)$$

Fig. 2 shows the single-factor curves $R_b(x_i)$, which pass through the extreme points of the field – the maximum $R_{b.\max}$=37 MPa, x_1=x_3=−1, x_2≈0, x_4=−1, x_5=0.44, and the minimum $R_{b.\min}$=24 MPa at x_1=0.86, x_2=x_3=x_4=+1, x_5=−1.

We should note that these dependencies differ significantly from similar dependencies for the prism strength, both in compositions corresponding to the extremums of the property and in the nature of the influence of ratios between ingredients.

First of all, an increase in the share of the mineral frame in the modified epoxy composite leads to a decrease in tensile strength in the zones of both extremums. We observe the effect of a decrease in R_b in the region of the minimum (in contrast to $R_{p.\min}$ zone – Fig. 1) with an increase in the

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proportion of filler and the content of zeolite grains in it. The only of 5 factors, which contributes to an increase in this mechanical characteristic, is the amount of furfural (in the range under study). This modifier lengthens the period of gelatinization and hardening of epoxy compositions, which reduces internal stresses and, consequently, leads to an increase in tensile strength.

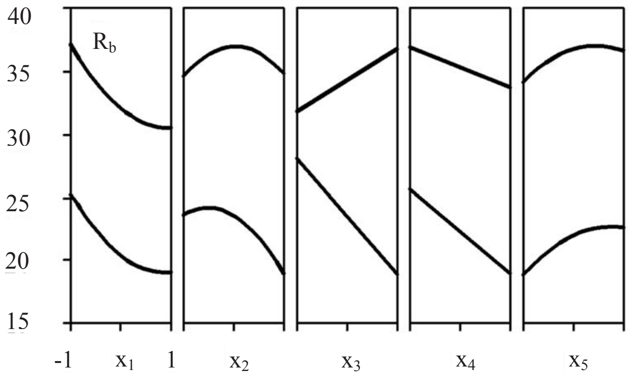

Fig. 2. Dependences of tensile strength on composition factors in the zones of minimum and maximum

"Cubes on a square" diagram (Fig. 3) provides the possibility of additional analysis of the influence of factors. The traditional factors form a bearing square and determine "Mineral frame" polymer composite.

These are, first of all, ratios between all mineral ingredients and the polymer (the degree of its filling), secondly, between sand and fine grinded filler.

We constructed nine cubes with equiscalar surfaces at characteristic points of the square (with fixed frame factors). The equiscalar surfaces reflect the influence of three other factors that change from a frame to frame. We can join them into "matrix modifiers" group – these are shares of fine and coarse grains of zeolite and an amount of furfural.

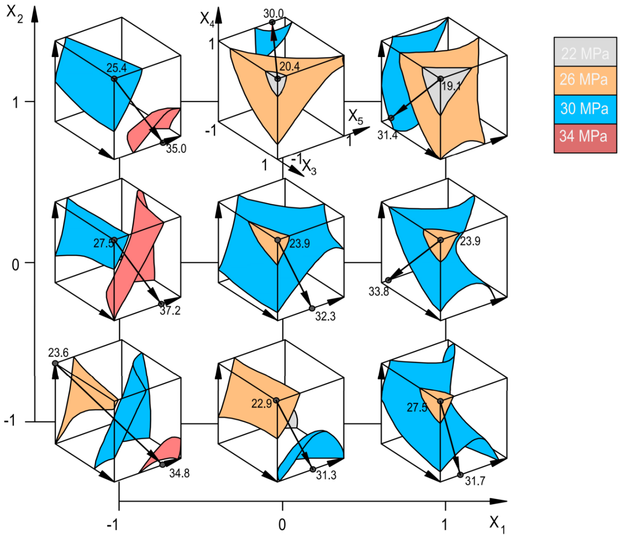

Fig. 3. Local R_b fields depending on the basic factors of the "mineral frame"

First of all, we should state: the effect of modifiers (fine and coarse zeolite, furfural) on the bending strength significantly depends on the total share of the frame and the share of filler in it. Changes in a shape of equiscalar surfaces, coordinates of the extremes, and a direction of vectors of averaged gradients reflect this.

We can observe the maximum level of R_b=37.2 2 MPa (Fig. 3) at a low filling of epoxy resin (180:100 m. p.) with a frame with the average filler content (60 %). We can provide this by the modification of only fine dispersed zeolite (upper level, 25 %) in combination with the introduction of about 10 m.p. of furfural. Such modification gives not only 35 % excess over the minimum R_b (with the fixed frame x_1=–1, x_2=0), but also it gives an increase of 18 % relative to the composite with low modification levels (x_3=x_4=x_5=–1).

As the degree of filling and the share of filler increase, the modification efficiency decreases. There are zones, where the vector of growth of R_b turns towards a smaller modification, in the area of these factors (the bearing square in Fig. 3).

5. 2. Analysis of strength characteristics of the investigated polymeric solutions after exposure to water and two types of oil for simulation of contact with mixtures of water and oil products.

We determine special characteristics of repair solutions and protective coatings, in particular, water and oil absorption, in addition to general technical properties, for each of 27 compositions specified in the experiment plan. We determine the bending strength (MPa) after exposure of samples under normal conditions (R) and separately in three media: water (R_W), "light" oil (R_{PL}) and "heavy" oil (R_{PH}) for 6 months.

R_{PL} and R_{PH} strengths correlate with R_W (risk is less than 1 %). The statistical linear relationship (with a risk of more than 1 %) between R_{PL} and R_{PH} is weaker, and we can accept the hypothesis about correlation with R only for R_{PH}. This indicates that formulations, which that provide the best levels of some strength criteria, may not meet the requirements of others. It may be necessary to find a compromise.

ES-models built on the experimental data for 27 compositions make possible to perform the search for acceptable, optimal and compromise compositions. The models describe fields $Y(x)$ of quality criteria of the polymer solution in region Ω_x of five normalized coordinates of the composition $X_i=(X_i-X_{i.o.})/\Delta X_i$. $|x_i|\leq 1$. In particular, models (3) to (5) with significant coefficients represent prescription fields of material strength for bending after exposure to water, light oil, and heavy oil at risk of 5, 10 and 10 %, respectively.

We should note that the best and worst strength levels evaluated by (3) to (5) correspond to different filling levels and dosages of modifiers after exposure to different media:

$$R_{W\max}=33.1\,\text{MPa}\,(x_1=x_2=x_3=+1, \mathrm{x}_4=-1, x_5=-0.3),$$

$$R_{PL\max}=25.3\,\text{MPa}\,(x_1=-1, x_2=x_4=+1, \mathrm{x}_3=-0.7, x_5=0.9),$$

$$R_{PH\max}=22.9\,\text{MPa}\,(x_1=x_4=-1, x_2=0.4, \mathrm{x}_3=x_5=+1),$$

$$R_{W\min}=17.3(x_1=-0{,}1, x_2=x_3=x_5=-1, x_4=+1),$$

$$R_{PL\min}=14.7(x_1=x_2=x_3=x_4=x_5=-1),$$

$$R_{PH\min}=10.9(x_1=-0.2, x_2=x_3=x_4=x_5=-1),$$

$$\begin{aligned}R_W &= 23.8+0.7x_1+2.0x_2+0.7x_3-\\ &-0.7x_4+5.1x_1^2-2.3x_5^2-0.6x_1x_5-\\ &-0.7x_2x_3-1.1x_3x_4+0.6x_4x_5,\end{aligned} \quad (3)$$

$$R_{PL} = 20.4 + 1.2x_2 + 0.6x_3 + 0.5x_4 - \\ -0.7x_1x_2 - 0.6x_1x_3 - 0.5x_1x_4 - 0.7x_1x_5 + \\ +1.0x_2x_4 - 0.8x_3x_4 - 1.1x_3x_5 \quad (4)$$

$$R_{PH} = 15.8 + 1.5x_2 + 0.4x_3 - 0.9x_4 + \\ +0.3x_5 + 2.7x_1^2 - 1.7x_2^2 + 1.1x_3^2 - \\ -0.6x_1x_3 - 0.3x_1x_5 - 1.2x_2x_3 - 0.6x_2x_4 + \\ +0.6x_2x_5 - 1.1x_3x_4 - 0.6x_3x_5. \quad (5)$$

The analysis of the models (3)–(5) and the single-factor local fields described by them in the zones of extremums show that:

– the role of furfural is different for different media; the maximum dosage is useful for work in oil, but it can reduce the strength in water;

– the amount of filler affects the bending strength with different intensity in water, light oil and heavy oil;

– the positive overall effect of zeolite is ambiguous in compositions of increased strength, and the addition of coarse grains can be justified in the maximum zone; this confirms the need for a compromise.

5. 3. Search for optimal and compromise optimal polymer solutions for a number of specific operating conditions.

The iterative procedure [20, 21] of random scanning of property fields (quality criteria, resource saving, etc.) makes possible to solve a number of optimization problems using the Monte-Carlo method. There were the following requirements set in the optimization problems: $R_b(x) \geq 25$ MPa; $R_W(x)$, $R_{PL}(x)$, $R_{PH}(x) \geq 20$ MPa taking into account the typical characteristics of repair polymer solutions.

The technological limit on the effective viscosity ($150 \leq \eta(x) \leq 500$ Pa-s at the shear rate of 1 s^{-1}) significantly depends on consumption of epoxy resin (g/kg), determined by "criterion of resource saving" $E(x_1, x_5)$ – the degree of filling and the amount of furfural.

Fig. 4, 5 show the search for a solution to the problem, where it is necessary to maximize R_{PL} and R_{PL} in order to ensure the same stability of compositions in different media.

There were 10,000 randomly distributed in Ω_x of x random vectors (in 5s normalized coordinates of the composition in the interval from –1 to +1, Fig. 4, *b*) at the initial stage ("1–0") of the 1-st iteration. We added $2^5=32$ peaks of this 5-dimensional cube to them. We estimated levels of the criteria fields R_b, R_W, R_{PL}, R_{PH}, η according to the corresponding models and calculated E at each of N=10,032 points.

At the stage "1–1", after sorting of points (options of compositions according to values of criteria), we excluded points with unacceptable levels $R_b<25$, R_W, R_{PL}, $R_{PH}<20$ MPa (Fig. 4) and η outside the specified interval. The remaining points fall within the range of acceptable solutions Ω_{1-1} (Fig. 5).

At the last stage of the iteration ("1–2"), the lower levels of the optimality criteria R_{PL} and R_{PH} increased (Fig. 4), we eliminated options that did not meet the new requirements (Fig. 5), and thus, the acceptable region reduced (to $\Omega_{1-2}<\Omega_{1-1}$).

At the initial stage of each subsequent iteration, the boundaries of the search area for each coordinate expanded by 0.1–0.2 relatively to the achieved boundaries (Fig. 4), which could lead to the criteria going beyond the level of restrictions. Thus, at the stage ("2–0"), the lower level of R_{PH} (Fig. 4) was less than 18 MPa (below the required 20). The points (10 000) generated in the new region were added to the options left after the previous iteration (in particular, 3 after "1–2" stages).

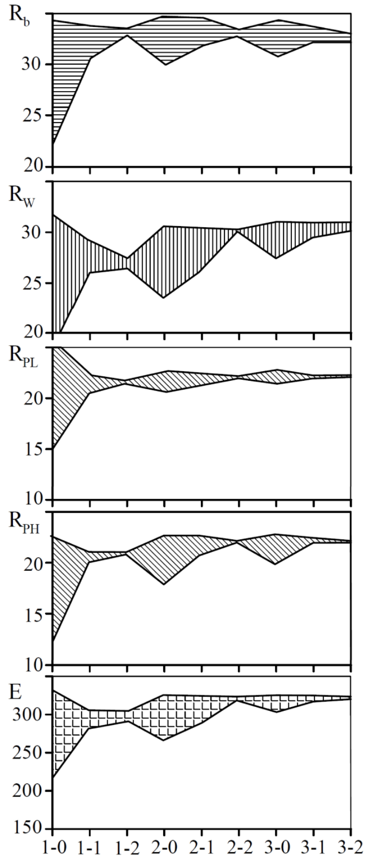

Fig. 4. Changes in the ranges of quality criteria at the stages of search for a compromise

We determined not the initial requirements for the criteria, but their worst levels improved by the previous iteration at the initial stages of iterations of the boundary of acceptable area. In particular, the lower value R_{PL}=21.5 (Fig. 4) at the stage "3–1" and it was not 20 (at "1–1").

At the final stages, a step-by-step approach to individual maxima occurred due to the upward movement of lower bounds of the optimality criteria and exclusion of compositions, which did not fall into the new boundaries.

Thus, at the "2–2" stage, it was possible to raise both R_{PL} and R_{PH} to 22 MPa (Fig. 4). Averaging of the coordinates of the best points of the last iteration (3-rd one in this task) gave compromise optimal values:

$$x_1=-0.99,\ x_2=0.88,\ x_3=1.00,\ x_4=-0.93,\ x_5=0.51.$$

We obtained the following results after return to natural values of the input variables and rounding to technically feasible values: the content of the mineral frame was 180 m. p. ($x_1=-1$); the share of the filler in the frame was 0.85 ($x_2=0.8$); the share of zeolite in the filler was 0.25 ($x_3=+1$), without coarse grains ($x_4=-1$), 10 m.p. of furfural per 100 m. p. of "Macro" resin ($x_5=0.6$). This composition (with a viscosity of about 220 Pa-s) corresponded to R_b=34.3, RW R_W=30.6, R_{PL}=22.0, R_{PH}=22.5 MPa at a sufficiently large consumption of resin, E=324.7 g per 1 kg of solution.

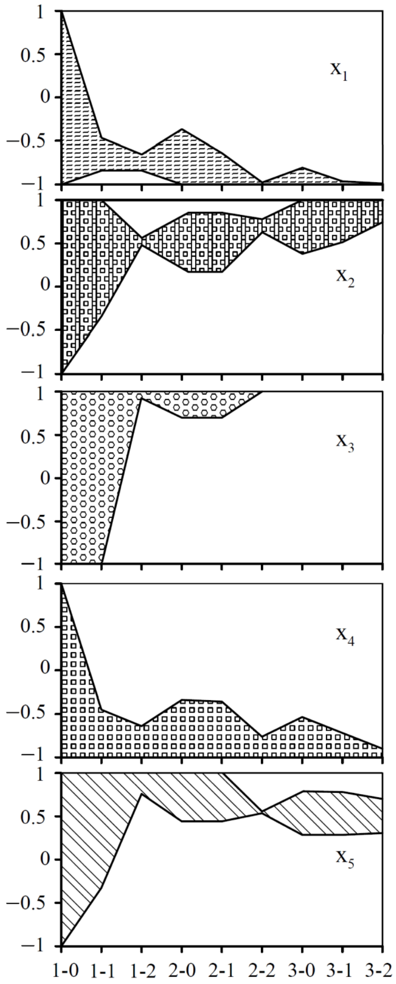

Fig. 5. Changes in the ranges of the boundaries of factors at the stages of search for a compromise

A search for a compromise between strength maxima in light oil and heavy oil and minimum resin, that is, for three criteria of optimality: R_W, R_{PH} and E provide more economical formulations with E=303 g/kg. If it is sufficient to fulfill the requirement R_{PL}, R_{PH}>20 MPa, the solution to the problem of minimization of resin consumption leads to compositions with E=270 g/kg.

6. Discussion of results of studying the properties of epoxy compositions after exposure to various media

One of the main criteria for selection of base modifying components and fillers was their availability. Ukraine has significant reserves of zeolites. And furfural obtained by processing of agricultural waste is one of the cheapest organic solvents. The aim of the above study is development of cost-effective compositions by maximization of the content of epoxy resin with provision of the required level of performance properties of protective compositions.

The positive effect of the organic modifier, furfural, on strength characteristics of polymeric solutions before and after exposure to aggressive media manifests itself with different intensities. This modifier activates the pre-gel stage of structure formation and slows down the process at later stages. In filled epoxy systems, this contributes to relaxation of emerging stresses and formation of a dense boundary layer. This eliminates conditions for formation of cracks and pores and leads to an improvement in mechanical properties of material. Furfural influences properties of polymeric solutions due to its plasticizing effect, which leads to an improvement in adhesion of a polymer matrix to filler and creates a dense and impermeable structure. Zeolite influences strength after exposure to aggressive media due to the known effect of the “molecular sieve” [22], however, the analysis of data obtained from experimental-statistical models indicates the ambiguous effect of this modifier. An analysis of fields of material properties [18] revealed areas, where replacement of part of the fine dispersed zeolite with a larger fraction is expedient, but the composition range is very limited, and the increase in strength is insignificant. There are various optimal dosages of modifiers and fillers for all the described material quality criteria. Selected media contain a wide range of aggressive ingredients. Therefore, determination of the component of media, which has a negative impact on the studied compositions, is a very difficult task. However, it is not possible to model an influence of media, which affects material under actual operating conditions, in the laboratory. Experimental statistical modeling makes it possible to determine the optimal ratio of components for individual material quality criteria. It became possible to determine composites with a given set of properties with regard to the requirements for repair materials by compromise optimization.

It is possible to repeat the procedure of the Monte Carlo method to meet the new requirements for repair solutions, if necessary. For example, if we need to introduce a new material quality criterion or to toughen the criteria described above. At the same time, if we are talking about search for a compromise between the previously studied characteristics, there is no need for new field experiments. In addition, if necessary, we can extrapolate the obtained mathematical models extrapolated for other calculation experiments (built on different plans for analysis of new properties of the studied compositions). All of the above makes it possible to obtain maximum information on the behavior of material under various conditions at minimal cost and test scientific hypotheses with a high degree of confidence.

Currently, there is a tendency to the use of man-made waste as fillers for polymer solutions based on epoxy resins [9, 10]. The use of such fillers provides reduce in the cost of material, and the use of iterative numerical methods makes possible to obtain the compromise-optimal compositions with guaranteed properties. We should continue laboratory tests of polymeric solutions with the indicated modifiers and expand spectrum of fillers and the studied quality criteria, since we studied the complex of properties of the compositions described above very limitedly.

7. Conclusions

1. We determined the values of mechanical properties for hardened epoxy solutions of 27 compositions (according to the 5-factor experimental design). These values are the limits of prism compressive strength (in the range from 67 to 114 MPa) and flexural tensile strength (23.4–33.6 MPa).

2. The nonlinear experimental statistical models obtained made possible to estimate an influence of amount and composition of the mineral frame and a dosage of furfural on mechanical properties of composite, to determine the opti-

mal ratios of components, which are different for different material quality criteria. Thus, for R_b, which increases with the introduction of furfural, modification of the maximum amount of finely dispersed zeolite and 10 m. p. of furfural at low filling and an average proportion of filler in the frame (60 %) provide the maximum level of 37 MPa. The excess over the minimum durability is 35 %, and the relative minimally modified composite is 18 %.

3. Analysis of ES-models described by R_b, R_W, R_{PL} and R_{PH} fields in composition coordinates showed that the best and worst strength levels after exposure to different media correspond to different filling levels, different frame compositions and furfural dosages. The influence of the ratio of components on these operational properties is contradictory. In particular: the effect of the content of the frame on the strength in 4 media corresponds to different parts of the generalized curve "degree of filling – strength."

4. We obtained rational (optimal and compromise-optimal) component ratios for a number of protective and repair compositions, taking into account different requirements for material using iterative random scanning of property fields in five coordinates of the composition.

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