Selection of optimal parameters of technological modes for the synthesis of polymer composite materials based on verified mathematical models

A V Markov and O A Oreshina

Baltic state technical university «VOENMEH», 1 1-ya Krasnoarmeyskaya Street, Saint Petersburg, 190005, Russian Federation

E-mail: olga_oresh@mail.ru

Abstract. In the modern realities of creating structural elements for various purposes, polymer composite materials are widely used. These materials are used in almost all industries, from aerospace, shipbuilding, automotive, and ending with consumer goods. The article shows the need to develop mathematical models that reflect the relationship between mechanical properties and parameters of technological modes for the synthesis of polymer composite materials, to select the optimal parameters of the technological mode of their synthesis. The article discusses the optimization of a group of mechanical properties described by mathematical models built on the basis of a full factorial experiment, in order to obtain the optimal values of the parameters of the technological modes of synthesis of a polymer composite material based on heat-resistant low-molecular-weight synthetic rubber with the addition of ferric iron oxide as a filler. The research method is optimization by the method of successive concessions. Computer experiments have been carried out to optimize the parameters of technological modes for the synthesis of materials. The performed calculations were checked with experimental data, the adequacy of the obtained models was checked.

1. Introduction
Polymer composite materials (PCM) have a number of advantages - the ability to create materials with different properties, which include temperature resistance, resistance to ultraviolet rays, the property of radio absorption of electromagnetic radiation, etc. Thus, the development of modern technology in various industries is inextricably linked with the creation of new PCMs. PCM development can be carried out by both large research institutes and universities and small business organizations. At a small enterprise, the synthesis of new materials with desired properties is carried out by a research chemist, mainly in the process of experimental research with the subsequent determination of their quality indicators. After comparing the quality indicators of the created samples of new PCMs with those specified in the technical assignment, the research chemist makes adjustments to the parameters of the technological modes of PCM synthesis. These stages of creating a new material go through several iterations, the number of which, as a rule, depends on the experience of the research chemist. In order to reduce the time spent on creating new PCM within a small enterprise, an approach can be applied that includes the use of mathematical models linking the technological modes of PCM synthesis with its properties, an algorithm for making a decision on the parameters of technological modes of PCM
synthesis, an algorithm for assessing risk in multi-criteria optimization of ranked quality indicators of PCM and special software that allows automating the decision-making process.

2. Staging
In the general case, the simulated PCM can be quantitatively characterized by vectors \( x \in \mathbb{R}^k \), \( g \in \mathbb{R}^m \) and \( y \in \mathbb{R}^n \) of input (mechanical effects on structural elements made using PCM), internal (parameters of technological modes of PCM synthesis) and output (mechanical characteristics of PCM) parameters, respectively. It should be noted that the same physical, mechanical, or other characteristics of PCM in models for various purposes can play the role of both external or internal and output parameters.

It is necessary to pay attention that when developing a mathematical model of a PCM, the values of the output parameters (mechanical characteristics of PCM) and/or the ranges of their possible change are determined in accordance with the terms of reference for the development of PCM, the input parameters characterize the operating conditions where structural elements made of PCM are used.

In the general case, the mathematical model of the PCM can be represented in the following form

\[
y = f(x, g), x \in \mathbb{R}^k, g \in \mathbb{R}^m, y \in \mathbb{R}^n,
\]

where \( f \) is a vector function of a vector argument.

The problem of verification of mathematical models describing the relationship between mechanical properties and parameters of technological synthesis modes is posed as follows: on the basis of experimental data, the values of the parameters of the function \( f(x, g) \) are calculated, which, in accordance with the selected criterion, approximates the properties of the PCM \( y = f(x, g) \) on a set of values of mechanical characteristics: \( g(k) \subset g \), \( y(p) \subset y \), where \( g(k) \) and \( y(p) \) – are the space of internal (parameters of technological synthesis modes) and output (mechanical characteristics of PCM) parameters during verification experiments; \( k \) is the number of PCM samples with different composition or parameters of technological synthesis modes; \( p \) is the number of PCM samples with the same parameters of technological synthesis modes [1-2].

For PCM, the output parameters are the values of mechanical characteristics. Therefore, when planning an experiment, taking into account the formulation of the general verification problem, the values of hardness, tensile strength, and tensile elongation are selected as experimental data. The input data, in accordance with the formulation of the verification problem, during the planned series of experiments are the fixed values of the internal parameters of the PCM (parameters of the technological modes of synthesis). In this case, the percentage of the filler and the presence or absence of mechanochemical processing of the filler were selected as the parameters of the technological modes of synthesis.

Thus, the set of experimental data is an array of mechanical characteristics of PCMs depending on the parameters of technological synthesis modes during the experiment for one group of samples.

Using the results of experimental studies, multicriteria optimization of ranked mechanical characteristics is carried out using verified mathematical models "technological modes of synthesis - properties", as a result of which the optimal parameters of technological modes of synthesis are calculated for a group of materials under study. In accordance with this, PCM samples are made, for which the real values of mechanical characteristics are determined, which makes it possible to further determine the value of the relative error in predicting the optimized properties of PCM.

3. Materials and methods
Experimental studies were carried out with samples made of PCM, where SKTN A was used as a polymer binder (component \( x_1 \)) - synthetic rubber, heat-resistant, low-molecular, easy-flowing (grade A). The method of full factorial experiment (PFE) was chosen as the research method.

Consider the controllable factors in this group. The mass fraction of the filler (Fe₂O₃, %) in the mixture was chosen as the first controllable factor, and the mechanochemical treatment of the filler was selected as the second controllable factor.
The mechanochemical treatment of the filler is the application of a thin layer of auxiliary substances to the surface of the filler particles during their grinding (disintegration) (in this case, the processing is performed with vinylsilane). The final list of controlled factors with levels of variation is presented below:

1. The proportion of filler, % by weight - two levels (45 and 65);
2. Mechanochemical treatment - two levels (no treatment/treatment with vinylsilane).

With each of the two factors is varied at two levels, the number of experiments will be \( N = 2^2 = 4 \), and the PFE planning matrix will have the form shown in table 1.

**Table 1. Planning matrix.**

| \( \bar{N} \) | \( x_0 \) | \( x_1 \) | \( x_2 \) | \( x_1 x_2 \) |
|-------|-------|-------|-------|-------|
| 1     | +     | –     | –     | +     |
| 2     | +     | +     | –     | –     |
| 3     | +     | –     | +     | –     |
| 4     | +     | +     | +     | +     |

Table 2 shows the levels of influence of the effect of interaction of factors \( x_1, x_2 \).

**Table 2. Levels of influence of the effect of interaction of factors.**

| Level | Share of filler, % \( x_1 \) | MCT \( x_2 \) |
|-------|-----------------|------------|
| 1     | 45              | no         |
| 2     | 65              | yes/vinylsilane |

Based on the above plan of the PFE, a matrix of sample compositions was compiled for their manufacture in accordance with GOST R 54553-2019 [3] and subsequent measurement of hardness, tensile strength and elongation in tension. The resulting matrix is shown in table 3.

**Table 3. Composition matrix of samples for the experiment.**

| \( \bar{N} \) | Sample | SKTN A PMS-50, PMS-50, \( \text{mass. \%} \) | \( \text{Fe}_2\text{O}_3, \text{weight \%} (x_1) \) | Mechnochemical treatment \( (x_2) \) |
|-------|--------|-----------------|-----------------|-------------|
| 1     | 55     | 45              | –               | –           |
| 2     | 35     | 65              | –               | –           |
| 3     | 55     | 45              | yes/vinylsilane | yes/vinylsilane |
| 4     | 35     | 65              | yes/vinylsilane | yes/vinylsilane |

Checking the homogeneity of the reproducibility variance, the adequacy of the model, the significance of the polynomial coefficients is carried out according to the classical scheme of the full factorial experiment [4-5].

The mathematical model for hardness \( (\tilde{y}_{\text{hard}}) \), has the form:

\[
\tilde{y}_{\text{hard}} = 45.4 - 3.8x_2 - 0.9x_1x_2
\]

The mathematical model for ultimate tensile strength \( (\tilde{y}_{\text{strength}}) \), has the form:

\[
\tilde{y}_{\text{strength}} = 0.4 - 0.14x_1 - 0.21x_2
\]

The mathematical model for tensile elongation \( (\tilde{y}_{\text{el}}) \), has the form:

\[
\tilde{y}_{\text{el}} = 11.8 - 0.74x_1 + 1.23x_2
\]
To optimize the mechanical characteristics of the polymer composite material, the method of successive concessions was applied. It is most suitable for the case when the mathematical models describing the relationship "technological modes of PCM synthesis - PCM properties" can be ordered in descending order of their importance [6-8].

The maximum value of the Shore hardness is 45.4 conventional units with the following values of the parameters of the technological modes of synthesis:

- $x_1 - 45\%$ (percentage of filler);
- $x_2 - 0$ (lack of mechanochemical processing of the filler).

After finding the maximum value of the first criterion in importance (Shore hardness) in the range of admissible solutions, the maximum value of the second most important criterion (ultimate strength) is found. However, in this case, the following condition must be met - the value of the first criterion should not deviate from its maximum value by more than the amount of the permissible concession (in this case, $\delta_1 = 12$).

Thus, the problem is solved

$$Z_2(\bar{X}) \rightarrow \max \quad Z_1(\bar{X}) \geq 33.4, \quad (2)$$

When solving it, the maximum value of the ultimate strength is $0.34 \cdot 10^6$ Pa with the following values of the parameters of the technological modes of synthesis:

- $x_1 - 45\%$ (percentage of filler);
- $x_2 - 0$ (lack of mechanochemical processing of the filler).

The next step is using the value of the assignment $\delta_2$ according to the second criterion, which, together with the first assignment, is applied when finding the conditional maximum of the third particular criterion

$$Z_3(\bar{X}) \rightarrow \max \quad Z_1(\bar{X}) \geq 46.35 \quad Z_2(\bar{X}) \geq 0. \quad (3)$$

The maximum tensile elongation is 13% with the following values of the parameters of the technological synthesis modes:

- $x_1 - 45\%$ (percentage of filler);
- $x_2 - 1$ (presence of mechanochemical processing of the filler).

The values of the parameters of the technological modes of synthesis obtained at the last stage are optimal (figure 1).

The target values of the functions and the values of the parameters of the technological modes of synthesis are given in tables 4 and 5, respectively.

**Table 4.** Target values of functions by calculations for a group of samples.

| $Z_1$ | $Z_2$ | $Z_3$ |
|-------|-------|-------|
| 41    | 0.13  | 13    |
Table 5. Values of parameters of technological modes of synthesis for a group of samples.

| $x_1$ | $x_2$ |
|-------|-------|
| 0.45  | 1     |

The values of the parameters of the technological modes of synthesis obtained at the last stage are optimal. This result is displayed in the software tab "Optimization of the composition of radio-absorbing polymer composite materials".

Figure 1. Output of results for a group of silicone-based samples.

4. Results and discussion

To verify the developed mathematical models of the properties of PCM, samples of PCM were made in accordance with the requirements given in GOST R 54553-2019, for which, as a result of experimental studies, the real values of mechanical characteristics were determined. Thus, in accordance with table 3, samples were made in the amount of five copies for each composition and experiments were carried out to determine their mechanical characteristics. The confidence limits of the random error of the measurement result were determined at a confidence level of 0.95 and with four degrees of freedom. The measurement results and optimal values are listed in table 6.

To determine the relative error in predicting the optimized properties of the PCM by the $i$-th optimized parameter, the following formula was used

$$
\varepsilon_i = \frac{|y_i^m - y_i'|}{y_i'}, \quad i = 1, n,
$$

where $y_i^m$ and $y_i'$ are the optimal value found using the mathematical model and the real value of the $i$-th value of the mechanical characteristic, respectively.
### Table 6. Comparison of measurement results and calculated optimum values for silicone-based samples.

| Name of characteristic and unit of measurement | Calculated optimum values | Measurement results | Arithmetic mean | Standard deviation | Confidence limits |
|------------------------------------------------|--------------------------|---------------------|-----------------|-------------------|------------------|
| Shore hardness, conventional units             | 41                       | 35                  | 37              | 0.707             | 1.963            |
|                                                |                          |                     |                 |                   | 36               |
|                                                |                          |                     |                 |                   | 38               |
|                                                |                          |                     |                 |                   | 36               |
|                                                |                          |                     |                 |                   | 34               |
|                                                |                          |                     |                 |                   | 36               |
|                                                |                          |                     |                 |                   | 38               |
| Tensile strength, MPa                         | 0.13                     | 0.13                | 0.16            | 0.009             | 0.025            |
|                                                |                          |                     |                 |                   | 0.025            |
|                                                |                          |                     |                 |                   | 0.025            |
|                                                |                          |                     |                 |                   | 0.025            |
| Tensile elongation, %                         | 16                       | 13                  | 17              | 0.707             | 1.963            |
|                                                |                          |                     |                 |                   | 15               |
|                                                |                          |                     |                 |                   | 13               |

The values of the relative error in predicting the optimized properties of PCM for each mechanical characteristic are given in table 7.

### Table 7. Relative modeling error.

| Mechanical characteristic name | Relative modeling error, % |
|--------------------------------|----------------------------|
| Shore hardness                 | 9.8                        |
| Tensile strength               | 7.1                        |
| Tensile elongation             | 13.3                       |
5. Conclusion
Based on the results of carrying out and processing the experimental data, mathematical models of Shore hardness, tensile strength, tensile elongation of PCM based on silicone rubber with trivalent iron oxide were obtained. The parameters of the technological modes of synthesis corresponding to the optimized mechanical characteristics have been determined.

Thus, the optimization by the method of successive concessions can be successfully applied to obtain the values of the parameters of the technological modes of synthesis of a new material at an enterprise engaged in the creation of new functional materials.

As a result of the experimental studies, the error of modeling the optimized properties of PCM was determined, which does not exceed 14%, which proves the possibility of using the developed mathematical models when creating new polymer composite materials.

References
[1] Markov A V and Oreshina O A 2020 The concept of mathematical modeling of physical and mechanical characteristics of composite materials 12 (Moscow: Flight) pp 3-6
[2] Markov A V, Efremov N Y and Oreshina O A 2020 Modeling the properties of polymer composite materials used in aircraft structures 6 (Moscow: Flight) pp 12-16
[3] State Standard GOST R 54553-2019 “Rubber and thermoplastic elastomers. Determination of elastic-strength properties under tension” (approved by the Federal Agency for technical regulation and Metrology from September 11, 2019)
[4] Oreshina O A 2020 Full factor plan application to polymer composites hardness investigation JOP Conference Series: Metrological Support of Innovative Technologies. Krasnoyarsk Science and Technology City Hall of the Russian Union of Scientific and Engineering Associations. (Krasnoyarsk: ICMSIT). C. 42031
[5] Gorsky V G, Adler Y P and Talalay A M 1978 Planning for industrial experiments (Moscow: Metallurgy) p 112
[6] Sidnyaev N I 2019 The theory of experimental design and analysis of statistical data: a textbook and workshop for universities 2nd edn. (Moscow: Yurayt Publishing House)
[7] Berikashvili V S 2019 Statistical data processing, design of experiment and random processes (Moscow: Yurayt Publishing House) p 164
[8] Lemeshko B Y 2018 Criteria for testing homogeneity hypotheses. Application guide (Moscow: INFRA-M) p 207