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Cure modeling and optimization of the composition of the polymer matrix for magnetostrictive composites

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Abstract. The paper explores the curing processes of unfilled epoxy resins ED-16. Mathematical modeling of curing processes has been performed and mathematical models of curing processes are presented in the form of full quadratic polynomial models. Separately, the degree of curing of unfilled epoxy compositions is studied. As a result of exploring the obtained models and performing optimization procedures for the ED-16 resin, theoretical aspects of curing high-viscosity epoxy systems were developed and recipe-technological parameters for obtaining a high-strength polymer matrix based on the high-viscosity ED-16 resin were proposed, which makes it possible to obtain epoxy composites with specified parameters structures and properties. Keywords: composite materials, mathematical modeling, optimal structure, optimization of properties.

1 Introduction

At present, modern construction for the manufacture of building structures, finishing elements of buildings and structures is in dire need of composite building materials that are distinguished by high performance characteristics and have a strictly specified structure and properties. For example, composite building materials for radiation protection must have some specific properties: high average density, the presence of elements with large atomic numbers, the absence of a crystal lattice, a minimum content of elements that form long-lived nuclides, etc. [1, 2].

Greatest practical interest is the possibility of obtaining composite building materials with high physical, mechanical and operational properties with minimal time and material resources. The solution of this problem is not possible without an optimal polymer matrix in all senses. Such a polymer matrix should have optimal rheological characteristics [3, 4] and high physical and mechanical properties. The factors that have the strongest influence on the physical and mechanical parameters are the concentration of the hardener and the heating of the polymer matrix [5], which, at an optimal ratio, provide the maximum degree of curing of the epoxy resin.

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2 Research methods and principles

When creating epoxy composites for radiation protection, ED-16 grade epoxy-diane resin cured with polyethylene polyamine (PEPA) was used as a binder. The choice of resin is due to the higher molecular weight compared to other brands, which should provide better protection against high-energy radiation.

To assess the degree of curing of the epoxy resin, the method of differential scanning calorimetry (DSC) [6] was used, based on measuring the heat released during the curing reaction of epoxy resins using a PerkinElmer DSC6000 device.

The degree of curing is a value (%) characterizing the degree of the curing reaction of the epoxy resin. The degree of curing is calculated by the formula (1).

$$Degree\ of\ curing = \left(1 - \frac{H_S}{H_T}\right) \cdot 100, \qquad (1)$$

here: HS – total heat of reaction of the tested (partially) cured epoxy composition, J/g; HT – total heat of curing reaction determined in preliminary test, J/g [6].

The total heat of reaction is the total amount of heat (J/g) released by the uncured epoxy composition during the complete course of the curing reaction, determined by DSC [6].

For most real materials science, recipe-technological and technical-economic problems, it is advisable to use polynomial models [7], therefore, in this work, polynomial experimental-statistical models (ES models) of the form were used to describe the behavior of the system:

$$\overline{Y} = b_o + \sum_{i=1}^{k} b_i \cdot x_i + \sum_{i<j} b_{ij} \cdot x_i \cdot x_j + \sum_{i=1}^{k} b_{ii} \cdot x_i^2 + \ldots + \varepsilon\text{'} \qquad (2)$$

here b_o, b_i, b_{ij}, b_{ii} – are defined as statistical quantities in a normalized form according to experimental data; ε – a random variable that takes into account the totality of experimental errors.

Moreover, taking into account the accuracy of the devices and instruments used in the experiments, a second-order regression equation is sufficient. When using equations of higher degrees, the accuracy of estimates of the coefficients of the regression equations will exceed the accuracy of determining the experimental data, and the regression equation will be inadequate when tested by the Fisher criterion. Based on this, in this work, full quadratic ES models were used. Such models make it possible to perform a complete regression analysis, the result of which is the solution of the optimization problem of the first type – finding the optimal conditions for the functioning of the system at any resource consumption and the second type – finding the minimum resource consumption to ensure the required level of the system quality indicator [7].

To optimize the polymer matrix, a nine-point compositional symmetric plan FFE 3^2 is having high efficiency in criteria D, A, E and Q, which is easy to analyze and allows you to present the results graphically. It is advisable to use it whenever the direction of the search is unknown and there are no strict restrictions on resources. The factors and intervals of their variation were chosen as follows:

factor X_1 – PEPA hardener concentration, variation intervals:
+1 = 30 % – by weight of resin ED-16;
X_1 = 0 = 18% – by weight of resin ED-16;
–1 = 6% – by weight of resin ED-16;

factor X_2 – sample heating temperature, variation intervals:
X_2 = +1 = 80 ^{0}C – during 5 hours;

$0 = 60\ ^0\mathrm{C}$ – during 5 hours;
$-1 = 40\ ^0\mathrm{C}$ – during 5 hours.

3 The main results

The formation of the structure of high-density epoxy composites was carried out using the main provisions of the polystructural theory, the theory of optimal control, and methods of system analysis. The essence of the polystructural theory lies in the representation of the material as polystructural, that is, in the selection in a single structure of many interdependent structures growing one into another (according to the "structure in structure" principle). The selection of systems and subsystems, the hierarchy of quality criteria, the optimization of the modes of formation of individual structures into polystructures – all this determines the recipe and technology for manufacturing composites [8].

Calculation of coefficients of regression equations, their estimates, confidence intervals, verification of Student's and Fisher's criteria, etc. were carried out in accordance with the procedure described in [7] using the program Mathcad v.14. After carrying out all the statistical calculations, the final regression equation was obtained:

$$Y = 112 + 17{,}2 \cdot X_2 - 10{,}1 \cdot X_1^2 - 5{,}1 \cdot X_1 \cdot X_2 . \tag{3}$$

In its natural form, equation (3) has the form:

$$R_{comp}(C,T) = 112 + 17{,}2 \cdot T - 10{,}1 \cdot C^2 - 5{,}1 \cdot C \cdot T , \tag{4}$$

here $R_{comp}(C, T)$ – compressive strength of unfilled specimens of size 20×20×20 mm; C – PEPA concentration in % – an optimized factor X_1; T – warm-up temperature in °C – an optimized factor X_2.

After researching and solving this extremum regression equation, the following values were obtained $R_{comp}(C, T)$, C and T:

- $R_{\max} = 129{,}79 \approx 130$ MPa – the limit of compressive strengh;
- $C = -0{,}252 \approx 15$ % – hardener concentration based on resin weight;
- $T = 1 \approx 80$ °C – product heating temperature.

Based on these data, the isolines of the resulting function (areas of equal estimates) were constructed, on which the optimization results are displayed (Fig. 1). As can be seen from Figure 1, equation (4) has a clearly defined maximum corresponding to 15% (by weight of the resin) concentration of the hardener and the product heating temperature of 80°C for 5 hours.

To verify the results of mathematical modeling and optimize the recipe-technological parameters of the polymer matrix of epoxy composites, the degree of curing of the unfilled resin was determined under conditions of the levels of variation of the second factor by the DSC method [6].

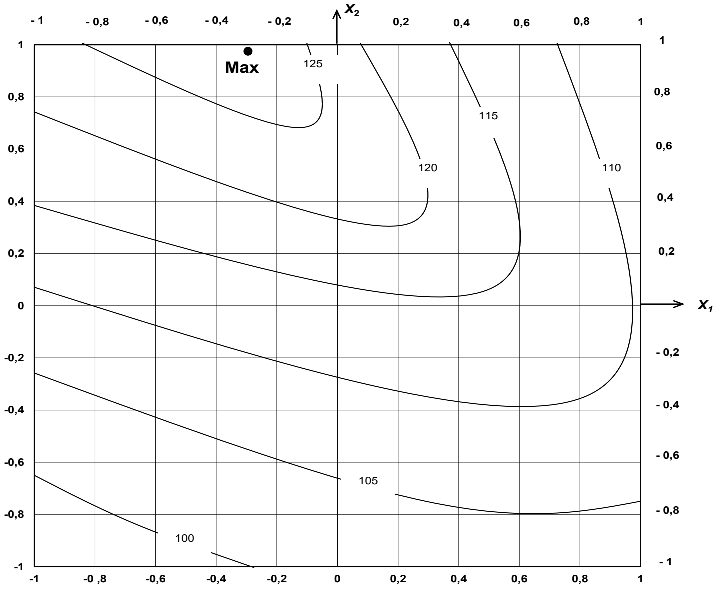

Fig. 1. Isolines of the strength of the polymer matrix.

The procedure of performing a cure rate measurement is shown in Figure 2.

The start of the exothermic reaction was taken as the moment when the heat flux on the DSC curve deviated from the baseline (the left limit of integration of the DSC curve); Figure 3. Due to the significant difference in baseline heights before and after the curing process, integration was performed using a sigmoidal baseline, Figure 3.

The degree of curing of a partially cured epoxy composition was determined by the ratio of the heat of reaction of this composition to the total heat of reaction of the uncured epoxy composition according to the formula (1).

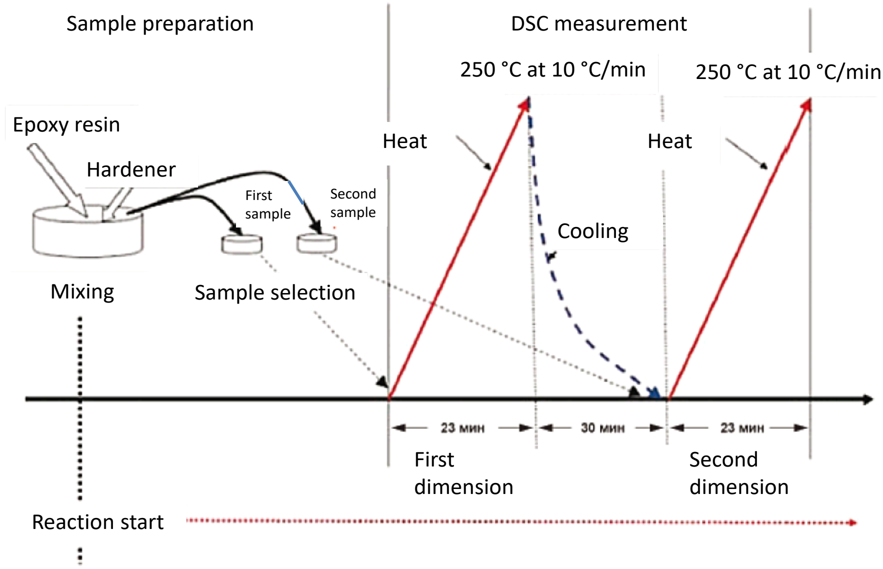

Fig. 2. Procedure of performing a cure rate measurement.

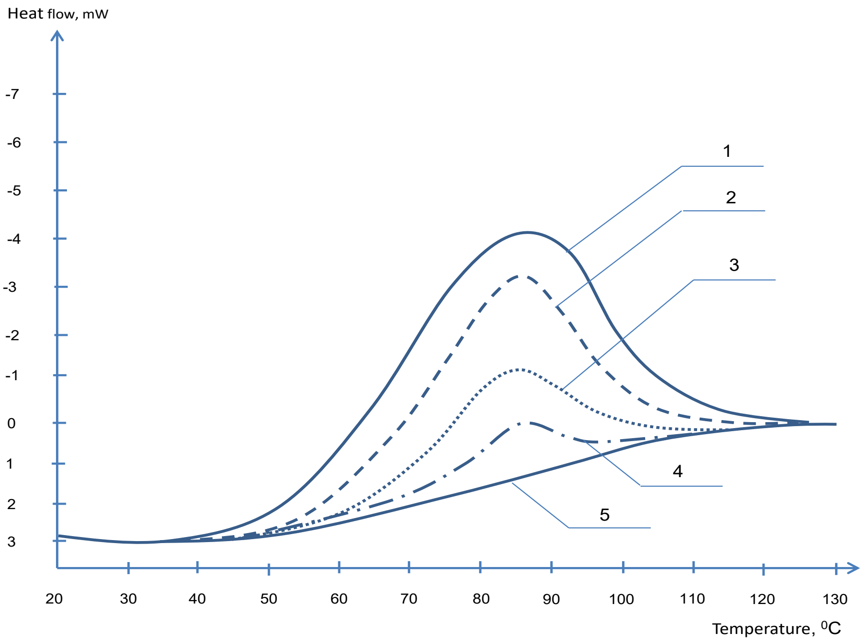

Fig. 3. Determining the area between DSC curves and sigmoid baseline:

1 – uncured epoxy composition, 2 – heating at temperature 40 °C for 5 hours,
3 – heating at temperature 60 °C for 5 hours, 4 – heating at temperature 80 °C for 5 hours,
5 – baseline corresponding to the complete curing of the epoxy composition.

After processing the experiment according to the method described in [6], the following results were obtained:

- 72.4% cure rate when heated at 40°C for 5 hours;
- 85.1% cure rate when heated at 60°C for 5 hours;
- 98.5% cure rate when heated at 80°C for 5 hours.

4 Conclusions

According to the partial derivatives of both variables in equation (3), it can be seen that the dependence of strength on the heating temperature is directly proportional, and on the concentration of the hardener it is parabolic. This can be explained by the fact that, by increasing the heating temperature, we reduce the size of the globules of the three-dimensional network and increase the degree of polymerization of the resin, which leads to the ordering of the structure and the improvement of the physical and mechanical properties. The nuclei of the polymer phase formed during the hardening process are dispersed throughout the volume and actually play the role of fillers. Thus, at a certain stage of structure formation, hardening unfilled polymer systems can be considered naturally filled. Considering that at a certain stage of hardening, two-phase polymer systems tend to reach a state of thermodynamic equilibrium due to cluster formation, the parabolic dependence shows the existence of such an amount of hardener at which the appearance of nuclei of the polymer phase, their self-organization - cluster formation, and, consequently, the achievement of thermodynamic equilibrium occurs in the shortest time and in the fullest extent. Experiments to determine the degree of curing confirm the technological parameters of thermal heating of epoxy compositions selected in the course of mathematical modeling.

The methodology for optimizing a polymer matrix based on epoxy compositions, outlined in the article, has been repeatedly tested by various scientists in the synthesis of composite materials with specified parameters of structure and properties [1, 3, 4, 9-17].

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