Modeling of structure formation of energy-saturated heterogeneous composite material

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Abstract. One of the approaches to modeling of the structure formation of an energy-saturated heterogeneous composite material (EHCM) by mixing its components represented by liquid and solid phases was considered. To develop a model of the mixing process, one of the heuristic algorithms was used, i.e. the metal annealing method. The model is formalized with the condition of averaging the particle sizes within each of the fractions, as well as the morphology of their surface. As a representative element of the model, an elementary cell is adopted in the form of hexagonally densely packed particles around one introduced into the composition of the composite material (in small amounts, from 5 to 15 %) as a modifier. The voids in the cell are filled with liquid polymer. The developed model is based on the objective function, which assumes obtaining a uniform distribution of components with the required density of their packing and filling the voids with a liquid phase while minimizing the number of mixing iterations. A comparison of the values resulted during modeling with the measured characteristics of mixing on a particular mixer will make it possible to form a matching scale of the modeling results to the operating modes of technological equipment. This will determine the appropriate modes of mixing the components at the stage of development of the technological process of EHCM production.

1. Introduction

Energy-saturated heterogeneous composite materials (EHCM) are a mixture of uniformly distributed polydisperse particles of a solid phase ranging in size from 40 to 400 microns (depending on the composition of the EHCM, some components may be nanosized particles) in an amount of 75–85 wt.% in a liquid-phase fuel-binding medium. Due to the selection of fractions of solid-phase components, their quantitative ratio, and surface morphology, their most dense packing is achieved. The most appropriate number of mixing cycles and correctly selected technological modes of operation of mixing equipment ensure uniform distribution of particles of each component in the polymer fuel-binder, filling with this binder all voids and plating them on the surface of the particles of solid-phase components.

In most cases, the methods and modes of mixing components of the EHCM are determined empirically for each type of mixer [1], taking into account the analysis of a large number of experiments involving the selection of a suitable sequence for adding components to the overall...
composition, its mixing time, rotation speed of the working body of the mixer, temperature, vacuum value in the working chamber of the mixer and other characteristics of the process. It is well known that this approach is quite time-consuming, since it involves a periodic shutdown of the manufacturing process of the composite material at a certain stage for sampling and conducting appropriate measurements. It should be borne in mind that the data obtained during the measurements are not always changed accordingly when scaling the manufacturing process of the EHCM.

The manufacture of the EHCM in the required volumes for measurements due to the high price of raw materials and the need for subsequent disposal of the experimental sample is a rather expensive research method. One of the approaches that minimize the number of experiments and, consequently, reduce the cost of obtaining the desired result, is to model the structure formation of the EHCM in order to subsequently select the necessary technological modes for its manufacture. By structural formation we understand the solution of the following tasks in the paper:

- Obtaining a uniform distribution in volume of the ecm of all solid-phase components and creating a homogeneous composition;
- Achievement of the densest packing of solid phase particles due to their rational distribution in the volume of the ecm;
- The maximum filling of voids formed in the packing of particles of solid-phase components with a liquid combustible binder;
- Cladding the entire surface of the particles of the solid phase with liquid phase components.

2. Statement of the research problem

The paper considers the mixing of particles of solid-phase components of five types – coarse and fine fractions of an oxidizing agent, an energy additive, combustion catalysts (I and II type) and an antioxidant, and also a polymer fuel-binder. In the following considerations, we will consider not the entire mixture, but the averaged unit cell of the EHCM, for which its model with a coordination number of 12 is developed, which is formed during the hexagonal dense packing of solid particles. The most acceptable description of these particles is to represent them in the form of a sphere.

For a such a unit cell, taking into account the required stoichiometry and the selected fractional composition, the basic characteristics of the EHCM components are calculated. The calculation procedure is described in [2], and the results for solid-phase components are shown in the table below.

| Component’s name | Particle radius, m | The amount of component mass % | kg | The volume of one particle of matter, m³ | Mass of one particle, kg | The number of particles in the unit cell, number of units | The mass of particles in a unit cell, kg | Particle surface area, m² |
|------------------|--------------------|---------------------------------|-----|----------------------------------------|------------------------|-------------------------------------------------|---------------------------------|------------------------|
| Energy additive  | 1,2·10⁻⁴          | 5,5                             | 0,18| 7,23·10⁻¹²                             | 1,31·10⁻⁸             | 1                                              | 1,31·10⁻⁸                       | 1,8·10⁻⁷               |
| Oxidizing agent  | 1,2·10⁻⁴          | 70                              | 2,32| 7,23·10⁻¹²                             | 1,41·10⁻⁸             | 12                                             | 1,69·10⁻⁷                      | 2,17·10⁻⁶              |
|                 | 2,5·10⁻⁵          | 7,5                             | 0,250| 6,54·10⁻¹⁴                             | 1,27·10⁻¹⁰            | 143                                            | 1,82·10⁻⁸                      | 1,12·10⁻⁶              |
| Combustion catalyst I | 7,7·10⁻⁶      | 1                               | 0,033| 1,91·10⁻¹⁵                             | 1,21·10⁻¹¹            | 193                                            | 2,33·10⁻⁹                      | 1,4·10⁻⁷               |
| Combustion catalyst II | 8,8·10⁻⁷      | 0,5                             | 0,016| 2,14·10⁻²¹                             | 9,08·10⁻¹⁸           | 128·10⁶                                        | 1,16·10⁻⁹                      | 1,03·10⁻⁵              |
| Antioxidant      | 0,2·10⁻⁷          | 0,5                             | 0,016| 3,35·10⁻²³                             | 1,29·10⁻¹⁹           | 90,26·10⁶                                      | 1,16·10⁻⁹                      | 4,5·10⁻⁵               |
The liquid phase in the considered EHCM is 15 mass %. The components of the liquid phase provide the filling of voids formed between the particles of the solid phase and cladding of their surface. The volume of the liquid phase of the unit cell takes on the value

\[ V_L = V_L^e - V_L^r, \]

where \( V_L^e \) – the volume of the liquid phase of the unit cell of EHCM;
\( V_L^r \) – the volume of the liquid phase of the EHCM necessary to fill the voids in the unit cell;
\( V_L^r \) – the volume of the liquid phase of the EHCM necessary for cladding the surface of the particles of the unit cell.

In accordance with the established stoichiometry, each unit cell (subject to uniform mixing) accounts for \( 3.6 \times 10^8 \) kg or \( 3.8 \times 10^{11} \) m³ of a liquid-phase polymer binder.

To calculate the characteristics of this unit cell, a representative element in the form of a hexagonal prism with a height

\[ H_c = 2 \cdot \sqrt{\frac{2}{3}} \cdot D_b \]

and square of the base

\[ S_b = \frac{3\sqrt{3}}{2} \cdot D_b^2 \]

where \( H_c \) – the height of the representative element (hexoprism);
\( S_b \) – square of the base of the representative element (hexoprism);
\( D_b \) – particle diameter of a large fraction of an oxidizing agent or an energy additive.

The view of model of a unit cell with the relative positions of the particles of the energy additive and the coarse fraction of the oxidizing agent, as well as its representative element with the relative positions of the particles of the energy additive, coarse and fine fractions of the oxidizing agent are shown in figure 1. The model does not show the remaining particles of components with sizes less than 50 \( \mu \)m.

![Image](image-url)

**Figure 1.** The model of the unit cell for hexagonal dense packing of particles with coordination number 12 (a) and its representative element (b)

In the following, to simplify the calculations, we will consider not all components of the solid phase, but only particles of the energy additive and two fractions (coarse and fine) of the oxidizing agent. We assume that the combustion catalyst I which has linear dimensions of about 10 \( \mu \)m, together with the liquid-phase polymer fuel-binder, will occupy voids formed in the laying of a fine fraction of oxidizer particles. Particles of combustion catalyst II and antioxidant are nanosized and introduced into EHCMs deposited on the
surface of particles of a large fraction of an oxidizing agent [3]. To obtain a rational EHCM structure that ensures the highest density of the composite material being manufactured, and, accordingly, the greatest momentum per unit volume of the substance, the linear sizes of these particles are selected.

In view of the foregoing, three types of particles are subject to consideration (an energy additive, as well as coarse and fine fractions of an oxidizing agent). The volumes of these particles are denoted by \( V_1 \), \( V_2 \) and \( V_3 \) respectively. The volume of possible empty voids is \( V_0 \). Then the volume of the whole mixture of EHCM (\( V_c \)) will take on the value

\[
V_c = V_0 + V_1 + V_2 + V_3 + V_f. \tag{4}
\]

In this model, the number of particles of the energy additive and the coarse fraction of the oxidizing agent are \( n_1 = 1 \) and \( n_2 = 12 \), respectively. In this case, between approximately the same \( 13 = n_1 + n_2 \) spheres, 13 octahedral and 26 tetrahedral voids will occur (which corresponds to a certain packing density). These voids are filled with particles of a fine fraction of an oxidizing agent in an amount of \( n_3 \). In real terms, \( n_2 \) varies in the range from 39 (provided that at least one particle of a small fraction of the oxidizing agent gets into each formed void) to 143.

A representative element includes one particle of an energy additive (\( n_1 = 1 \)) and 18 segments of a large fraction of an oxidizing agent; we assume that the remaining components are distributed proportionally. Using the capabilities of the KOMPAS-3D software product, it was determined that all segments of the particles of the coarse fraction of the oxidizing agent included in the representative element are equivalent in volume to 5 particles of the coarse fraction of the oxidizing agent (\( n_2 = 5 \)), and the ratio of the linear sizes of the representative element and the selected unit cell, is \( 6/13 \). Then, taking into account expressions (2) and (3), the unit cell volume will be

\[
v_c = 6.5 \sqrt{2} D_b^3, \tag{5}
\]

and the volume of the components of the solid phase in this cell

\[
v_f = 6.5 \sqrt{2} D_b^3 \phi, \tag{6}
\]

where \( v_c \) – the volume of unit cell;

\( v_f \) – the volume of the solid phase of the unit cell;

\( \phi \) – the density of the particles in the unit cell.

3. Formalization of the process of mixing the solid phase of EHCM.

The process of mixture formation is presented as a random process of filling an elementary cell with particles of three types and a liquid polymer fuel-binding agent and we will reproduce it using the metal annealing algorithm [4].

We assume that the volume \( (v_1) \) of an individual particle of the first type with an average diameter \( d_1 \) is:

\[
v_1 = \frac{\pi d_1^3}{6}, \tag{7}
\]

the volume of particles of the second \( (v_2) \) and third \( (v_3) \) type with average diameters \( d_2 \) and \( d_3 \) will be

\[
v_2 = \frac{\pi d_2^3}{6}, \quad v_3 = \frac{\pi d_3^3}{6} \quad \text{accordingly.} \tag{8}
\]

And the total volume of particles in the unit cell, taking into account the specific example shown in table, will be

\[
v_f = v_1 + v_2 + v_3 = \frac{\pi (d_1^3 + 12d_2^3 + 143d_3^3)}{6}. \tag{9}
\]

Imagine that we randomly select and return particles of each type from the source material and on this basis we form a unit cell with the required number of \( n_1 \), \( n_2 \) and \( n_3 \) spheres. Let us estimate the probability that a particle of the first type gets into the unit cell during this process.
Following this rule, for the probability of particles of the second and third type entering the unit cell, we can write, respectively

\[ p_2 = \frac{12v_2}{v_c}, \quad p_3 = \frac{143v_3}{v_c}. \] (12)

The values of the probabilities found will allow us to determine the initial unit cell, densifying it by annealing, we create the possibility of obtaining the highest (required) packing density \( \phi_{\text{max}} \) of the particles of solid-phase components of the EHCM. Then, from the normalization condition, the probability of the formation of voids within the selected unit cell \( (p_0) \) will take the value

\[ p_0 = 1 - p_1 - p_2 - p_3. \] (13)

The process of compaction of the cell is the search for such a combination of selectable particles, in which the volume of voids is the smallest, that is \( v_c \rightarrow v_{c \text{min}} \). In accordance with expression (1), the voids in the unit cell are filled with the liquid-phase component of the EHCM. In this case, the part of the fuel-binder remaining after filling the voids is intended for cladding the surface of the particles of solid-phase components of EHCM. The volume of this part of the liquid phase spent on the complete cladding of all particles will be proportional to the surface area of the particles of each type, their quantity, as well as the thickness of the cladding layer and will be

\[ v_p = h(n_1 s_1 + n_2 s_2 + n_3 s_3) = h s_c, \] (14)

where \( s_c \) – the total surface area of the particles of solid-phase components of the unit cell;

\( s_1, s_2, s_3 \) – the surface area of the particles of the corresponding type (taken from the table);

\( h \) – cladding thickness.

The cladding process is a search for such a combination of the distribution of the combustible binder, in which the area of the cladding layer \( (s_p) \) will correspond to the surface area of the particles of the solid-phase components of the unit cell, that is \( s_p \rightarrow s_c \).

Thus, the cyclic step-by-step \( (i = 1, 2, ...) \) procedure for obtaining the desired cell consists of:

- the formation of the densest stacking of particles of each type with the volumes and quantities \( n_1, n_2 \) and \( n_3 \) chosen for them;

- the maximum filling of the space between the particles of the solid phase with the liquid-phase component of the EHCM and, accordingly, minimizing the volume of voids, \( v_0 \rightarrow 0 \) (or minimize the volume of the cell itself, that is \( v_c \rightarrow v_{c \text{min}} \));

- cladding the surfaces of each of the particles with a liquid-phase component of the EHCM, the area of which for the cell is \( s_c \).

The desired cell, representing the final solution of the problem, will be characterized by a vector that has coordinates

\[ X^{\text{opt}} = X[n_1, n_2, n_3, v_0 \rightarrow 0, s_p \rightarrow s_c]. \] (15)

At the first step of the iterative procedure, the cell volume takes on the value

\[ v_c^1 = v_c = 6,5\sqrt{2}D_b^3\phi^1, \] (16)
This expression will be characteristic of a unit cell formed by particles having a spherical shape with the same linear dimensions. At the same time, the particles of the oxidizing agent and the energy additive most often have a shape close to spherical with a shape factor of $k_f \geq 0.9$ and some discrepancies in linear sizes determined by the difference between the cell sizes of the used sieves. Subsequently, taking into account the value of the form factor $k_f \geq 0.9$, this indicator can be neglected when describing individual particles in the form of balls with a random diameter:

$$d_{10} = d_1 + \Delta d_1(\xi_1 - 0.5);$$
$$d_{20} = d_2 + \Delta d_2(\xi_2 - 0.5);$$
$$d_{30} = d_3 + \Delta d_3(\xi_3 - 0.5),$$

where $\Delta d_1, \Delta d_2, \Delta d_3$ – the maximum deviation of the diameters of the particles of the corresponding type from their average values;

$d_{1r}, d_{2r}, d_{3r}; \xi_1, \xi_2, \xi_3$ – random variables with a uniform distribution law in the interval $[0; 1]$.

4. Algorithm for constructing a particular solution.

The procedure for forming the contents of a unit cell is represented by the following steps.

Using a random number sensor, select a number $\xi$, uniformly distributed on the interval $[0;1]$.

When $\xi \in [0, p_1]$, then we make a decision about the first type of particle entering the unit cell.

When $\xi \in [p_1, p_2]$, then we make a decision about the second type of particle entering the unit cell.

When $\xi \in [p_2, p_3]$, then we make a decision about the third type of particle entering the unit cell.

When $\xi \in [p_3, 1]$, then we make a decision about not a single particle falling into the unit cell (that is, about the presence of a void in this cycle of the procedure).

Such calculations are repeated $N = n_1 + n_2 + n_3$ the number of times corresponding to the number of all particles that should be part of the future “ideal” cell. As a result, at the first step of the iterative procedure, a cell is characterized by a vector $X^1 = X^1[n_1^1, n_2^1, n_3^1, v_1^1, v_2^1, v_3^1, s_p^1]$.

According to the above scheme, at each $i$-th step of the iterative procedure, cells with a random structure are formed, that is, the so-called partial $i$-th solution is constructed, which, in accordance with the metal annealing algorithm, should be further improved (that is, the cell will become denser) as it mixes.

We denote $n_1^i, n_2^i, n_3^i$ - randomly selected into the unit cell during mixing at the $i$-th step, the number of particles of the first, second and third type, respectively. We will characterize such a cell with a vector having coordinates $X^i = X^i[n_1^i, n_2^i, n_3^i, v_1^i, v_2^i, v_3^i, s_p^i]$. Then we can write

$$v_1^i = \frac{4}{3}\pi n_1^3, \quad v_2^i = \frac{4}{3}\pi n_2^3, \quad v_3^i = \frac{4}{3}\pi n_3^3.$$  (18)

To obtain the value of the void volume, we use the relation

$$v_0^i = v_1^i - (v_2^i + v_3^i).$$  (19)

By value of the magnitude $\Delta v = v_0^{i-1} - v_0^i$ and the results of its comparison with the permissible value $(\Delta v < \Delta v_0)$ we decide to stop the cladding process.

The quality of the obtained cells (the effectiveness of each particular solution $X_i$) will be characterized by the proximity of the vector $X^i = X^i[n_1^i, n_2^i, n_3^i, v_1^i, v_2^i, v_3^i, s_p^i]$ to the vector $X^\text{opt} = X[n_1, n_2, n_3, v_1^\text{min}, v_3^\text{min}, s_p^\text{min}]$.

For this, we calculate the value

$$E_i = [(n_1 - n_1^i)^2 r_1^3 + (n_2 - n_2^i)^2 r_2^3 + (n_3 - n_3^i)^2 r_3^3],$$  (20)

and at each subsequent $(i + 1)$-th step the difference is determined

$$\Delta E_{i+1} = E_{i+1} - E_i.$$  (21)

The algorithm for constructing a particular solution in accordance with the considered methodology is shown in figure 2.
Figure 2. Algorithm for constructing a particular solution
If $\Delta E_{i, i} < 0$, then the new solution is better than the previous one and it is remembered. Otherwise, before discarding it and proceeding to the next iteration, the probability of preserving the resulting "bad" solution is estimated. This probability depends on the so-called "annealing temperature". The unit cell volume is taken as an analogue of "annealing temperature" $v^i_{c+1}$, which decreases from iteration to iteration. The law of changing the volume of the mixture (i.e., the law of compaction of the unit cell) is proposed to be adopted as follows:

$$v^i_c = v^i_{co}[1 + \frac{1}{i^a}], \quad i = 1, 2, \ldots$$  \hspace{1cm} (22)

in this case, $a \in [1; 2; 3]$ - tuning coefficient, regulating the annealing rate; $v_{co}$ - limit value of the unit cell volume.

At the end of each $i$-th iteration, the volume $v^i_c$ is adjusted (in accordance with the expression $v^i_c = v^i_{co}[1 + \frac{1}{i^a}]$ ) and recalculated the probability of choosing particles of each type according to the following formulas

$$p^{i+1}_1 = \frac{v^i_1}{v^i_c}, \quad p^{i+1}_2 = \frac{v^i_2}{v^i_c}, \quad p^{i+1}_3 = \frac{v^i_3}{v^i_c}.$$  \hspace{1cm} (23)

Considering following normalization conditions $p^{i+1}_0 = 1 - p^{i+1}_1 - p^{i+1}_2 - p^{i+1}_3$.

The process of forming the contents of the unit cell is repeated, that is, the $(i + 1)$ -th iteration is performed. Calculations continue until the value $\Delta E_{i+1, i}$ with a predetermined accuracy does not approach 0, that is $\Delta E_{i+1, i} \approx 0$.

The number of iterations (mixing cycles) $i$, at which the above condition is fulfilled, characterizes the required time of mixing of the energy additive and two fractions of the oxidizing agent. Further comparison of the values obtained during the simulation with the measured values of the results of mixing on a specific mixer will make it possible to obtain predicted values for specific technological equipment.

5. Conclusion
The article discusses the approach of modeling the process of mixing components of the EHCM based on the use of one of the heuristic methods – "metal annealing". In the course of the review, the process of obtaining a uniform distribution of all components, the densest packing of the particles of the components of the solid phase, as well as filling the voids with a liquid-phase fuel-binder and cladding the surface of the particles laid in the unit cell with them, is formalized. Based on the research results and formalization of the process of mixing the components of the EHCM, an algorithm for the adoption of the private was developed.

The proposed modeling method avoids local errors in the study of the process of forming the densest packing of particles of solid-phase components during their mixing, filling the voids formed with a liquid-phase polymer combustible binder and cladding the surface of the mixed particles with it. The presence of such a model makes the mixing process more predictable, providing the manufacturer of the EHCM with the required technological information. This allows the manufacturer to improve the process by obtaining appropriate modes at the stage of its development and thereby obtain the methodological basis for the formation of a quality management system in production.
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