Study of the uniformity of mixing components of energy-saturated heterogeneous composite material

AKKryvanos¹, APhlyushchanka¹,² and YYPiatiushyk¹

¹ Research and Production Powder Metallurgy Association, 41 Platonov str., Minsk, Republic of Belarus
² O.V. Roman Powder Metallurgy Institute, 41 Platonov str., Minsk, Republic of Belarus

Email: Krivonos_ok@tut.by

Abstract. The features of mixing the components of an energy-saturated heterogeneous composite material (EHCM) were considered. The conditions for the uniform distribution of the components of the solid phase over the entire volume of the composite material were estimated and the possibility of obtaining their most dense packing was analyzed. Appropriate proportions of the particle sizes of the fine and coarse fractions of the components of the solid phase were determined, as well as their proportion. The amount of liquid phase necessary to wet the surface of the particles of the solid phase, as well as to fill the voids between them, is determined. According to the results of the calculations, the criteria were chosen for evaluating the quality of mixing EHCM components.

The calculation results are compared with observed data obtained experimentally. An appropriate technique was developed to evaluate experimental samples. The results of comparing the calculated and experimental data make it possible to build the correlation dependences of the technological characteristics of the mixing of EHCM components.

1. Introduction
A certain part of energy-saturated heterogeneous composite materials (EHCM) is an energy source in a number of technical systems that use the energy of their controlled combustion to create reactive thrust. The production of such materials is carried out by mixing the main part of the components represented by the solid phase in one or more liquid phase components. After mixing all the components of the EHCM, the resulting composition is molded and its liquid phase is polymerized. Changing the operational characteristics of the product resulted after polymerization becomes impossible (except for adjusting the linear dimensions).

According to the abovementioned, the mixing of components is one of the most critical technological operations in the general scheme for producing EHCM, which determines the quality of the final product. This circumstance makes it necessary to control the quality of mixing. Its attainment ensures the production of EHCMs with the required operational properties.

2. Formulation of the research task
For the EGCMs production, polydispersed fractions of an oxidizing agent, energy additives, catalysts and combustion stabilizers, antioxidants, technological additives and other components are introduced into the composition of the polymer combustible binder. To obtain the densest packing of particles,
oxidizer fractions of different sizes can be used (as the main component of the solid phase). Its ratio of
the sizes contributes to the maximum filling of voids [1].

During the mixing of the EHCM components, a set of tasks is solved, the results of which form its
properties. These tasks primarily include:

To achieve a uniform distribution by volume of the EHCM of all solid-phase components and
preparation of a homogeneous composition;

To produce the most dense packing of particles of the solid phase due to their rational distribution in
the volume of the EHCM, depending on the linear dimensions and properties;

To fill the voids formed in the packing of particles of solid-phase components with a liquid
combustible binder;

To clad the entire surface of the particles of the solid phase with liquid-phase components.

Stability of energy characteristics is achieved due to the uniform distribution of the components.
The absence of voids in the packing of particles of solid-phase components reduces the likelihood of a
non-controlled increase in the combustion area, and accordingly, the combustion rate and pressure
inside the chamber and the maximum dense packaging gives the best thrust per unit volume of the
resulted composite material. The formation of the EHCM structure-forming matrix is achieved by
cladding the entire surface of the particles. This provides the required physical and mechanical
properties for the EHCM product.

According to the importance of each of the above tasks in the formation of the operational
properties of EHCMS, the parameters required for control in evaluating the uniformity of mixing of
EHCM components have been determined.

The following characteristics are subject to evaluation:

- the degree of distribution uniformity the in EHCM of particles of solid-phase components;
- the absence/presence of voids in the product made of EHCM and their distribution by volume;
- the density of the produced EHCM;
- physical and mechanical properties of EHCM before and after polymerization.

The issues of uniform distribution of solid-phase components are given much attention in powder
metallurgy, pharmaceutics, agriculture, construction and other industries where the preparation of
composite materials similar in structure is carried out. In these industries, appropriate methods of
controlling the uniform distribution of components during their mixing have been introduced into the
production process [2–3]. The main part of these methods involves the use of various instrumental
methods for separating fractions or components of the mixture according to characteristic features and
an estimate of the amount of each of them in the selected sample.

Due to the presence of a polymer in the EHCM composition, which is the liquid phase at the
mixing stage, the results of studies carried out in [2–3] cannot be fully used to evaluate the uniform
distribution of solid-phase components. The mixing of polymer with polydispersed particles of the
solid phase, which are introduced to harden it, is carried out in the construction, engineering, tractor,
aircraft manufacturing and other industries to produce structural materials on a polymer base. The
mixing process of such materials was studied in [4–5, et al.]. Most of the traditionally used methods
for estimating the quality of mixing polymer-based composite materials involve burning the binder
polymer or extracting the solid phase components, followed by a quantitative estimation of the
extracted components or fractions. The use of such methods in the technology of producing EHCM is
impossible due to the reaction nature of the oxidizing agent and its decomposition at relatively low
temperatures (t>150°C).

The use of non-destructive testing methods for polymer-based composite materials considered in
[6], due to the high explosiveness of EHCM and the features of the technological stages of its
production, requires their adaptation taking into account the properties of the material under study. At
the same time, each of the technological stages of producing EHCM has its own characteristics that
determine the properties of the studied material and, accordingly, the methods for their evaluation. In
view of the foregoing, the objective of the study is to choose methods for estimating the quality of
mixing EHCM components, determine the algorithms for their application, verify these methods using
the existing technology for producing EHCMs, formalize input data and resulted final values, as well as to develop rules for interpreting the results.

3. Materials and discussion
In accordance with the thermodynamic calculations carried out in [1], the composition of the EHCM was chosen in which the liquid phase was 14 wt. %. The solid phase is micrometer and nanoscale particles. Moreover, in order to achieve the densest packing, the particles of the oxidizing agent (the main component of the solid phase) are chosen by two fractions. Their median sizes were 240 and 50 μm. To formalize the objective function of the process of mixing EHCM components, a unit cell model with a coordination number of 12 was developed, which is formed during tight hexagonal packing of solid particles. To simplify the calculations of the criterial characteristics of this unit cell, a representative element in the form of a hexagonal prism was chosen with a height

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

and a base area

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

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

The developed unit cell model describes the position of particles of coarse and fine fractions of the oxidizing agent and the energy additive. It is assumed that other components of the solid phase with a particle size of less than 10 μm (including those having a nanoscale) together with liquid-phase components will fill voids formed between the particles of the oxidizing agent and the energy additive. A view of the unit cell model with the mutual arrangement of the particles of the energy additive and the coarse fraction of the oxidizing agent, as well as its representative element with the mutual arrangement of the particles of the energy additive, as well as coarse and fine fractions of the oxidizing agent are shown in figure 1.

![Image of unit cell model](image.png)

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

In [7], criteria for estimating the quality of mixing EHCM components were determined for this unit cell, which are subsequently used for instrumental control at all stages of producing the EHCM.
For the calculated number of components and the chosen fractional composition, the technology for producing the EHCM was developed.

Due to the impossibility of achieving uniform mixing when introducing solid-phase components, the particles of which are nanoscale, into the composition of the liquid binder, the production of the EHCM was carried out by mixing the components in two stages. At the first stage, nanoscale components from an alcohol suspension were deposited on the surface of particles of a coarse fraction of the oxidizing agent [8]. During the deposition, the uniformity of the distribution of nanoscale components on the powder surface was studied.

To estimate the uniformity of distribution, sampling and analysis of changes in the surface area of interacting particles were periodically performed. Estimation of the changes was carried out by measuring the specific surface and calculating the surface area of the particles, intended for subsequent cladding with a liquid-phase combustible binder. The specific surface was measured by the BET method on a surface area and pore size analyzer SA 3100 of BECKMAN COULTER (USA). For example, the results of measuring the specific surface area and the total particle area of the chosen samples of the oxidizing agent (coarse fraction) and antioxidant before, after 2 and 4 hours of deposition are presented in table 1.

**Table 1. Surfacodynamics.**

|                          | Specific surface m²/g | Mass kg | Total surface area m² |
|--------------------------|------------------------|---------|-----------------------|
| **Before adhesive deposition** |                        |         |                       |
| Oxidizing agent (coarse fraction) | 0.425                  | 2.985   | 1417.9                |
| Antioxidant              | 430                    | 0.015   | 6450                  |
| **After two hours of adhesive deposition** |                     |         |                       |
| Oxidizing agent (coarse fraction) with deposited antioxidant | 2.17                  | 3       | 6491                  |
| **After four hours of adhesive deposition** |                     |         |                       |
| Oxidizing agent (coarse fraction) with deposited antioxidant | 1.965                 | 3       | 5868                  |

The results obtained were evaluated against the background of changes in the surface morphology of the particles of a coarse fraction of the oxidizing agent. The imaging of the surface morphology was made by means of Mira high-resolution scanning electron microscope (Tescan, Czech Republic). So, the results of morphological analysis of the particle surface of a coarse fraction of the oxidizing agent before, after 2 and 4 hours of deposition of antioxidant particles, are presented in figure 2.

It is noticeable that after two hours of operation of the technological equipment, the total surface area of the particles decreased by 17.5%. However, the study of the morphology of the surface of the oxidizing particles revealed the presence of agglomerates (figure 2b) of the antioxidant. Taking into account the obtained values, the process of mechanical effect on the deposited surface and nanoscale particles of the antioxidant continued until their relatively uniform distribution was obtained. So, during the next two hours, the total surface area of the particles decreased by another 6.7% and a more uniform distribution of antioxidant particles on the deposited surface was obtained (figure 2b).
Figure 2. The results of morphological analysis of the surface of the particles of a coarse fraction of the oxidizing agent a) before the deposition of nanoscale additives; b) after two hours of operation of technological equipment; c) after 4 hours (completion of adhesive deposition) of operation of the technological equipment.

At the second stage, according to the results of mixing the components of the liquid and solid phases, the uniformity of the distribution of the EHCM components was determined through the study:

- nature of the distribution of polydispersed fractions of solid-phase components;
- physical and mechanical properties of EHCM;
- homogeneity of EHCM after polymerization of a binder;
- the density of the produced EHCM and its compliance with the calculated value.

The nature of the distribution of solid-phase components in the polymer fuel-binder was carried out at the stage of testing technological mixing modes. To do this, samples were taken periodically (at 5 minutes intervals) and their subsequent polymerization was carried out. The preparation of polymerized EHCM included a cross-sectional fracture and a conductive coating. The conductive layer on the surface of the samples was created by cathodic deposition of chromium in vacuum. The required coating thickness was made in 10 seconds of spraying. The morphology of the samples was studied using Mira high-resolution scanning electron microscope (Tescan, Czech Republic). The accelerating voltage during imaging was 15 keV. The results of the morphological analysis of the prepared mixture are shown in figure 3.

Figure 3. EHCM fracture surface morphology (a– after 5 minutes of stirring; b– after 10 minutes of stirring; c– after 15 minutes of stirring; d– after 20 minutes of stirring).

According to the results of morphological analysis, the appropriate mixing time of the EHCM components was determined and the required technological operating modes of the mixing equipment were chosen. The effectuality of the established operating modes was checked by the obtained value of
the EHCM density and the degree of its compliance with the calculated value based on the density of the EHCM components. Density was measured with a PZh-2 pycnometer. The degree of correspondence of the obtained EHCM density to its calculated value was determined as

$$\vartheta = \frac{\rho_r}{\rho_q}$$  \hspace{1cm} (3)

where $\vartheta$ – coefficient of compliance of EHCM density to the calculated value;

- $\rho_r$ – EHCM density obtained according to mixing results;
- $\rho_q$ – EHCM calculated density.

According to the results of studies it was found that with

$$0,97 \leq \vartheta \leq 1$$  \hspace{1cm} (4)

the EHKM product fully meets the requirements and can be used for its intended purpose. The obtained results were confirmed during testing of EHCM samples for compliance with physical and mechanical requirements, as well as homogeneity of the material after polymerization.

The criteria for assessing the physics-mechanical properties of EHCMs were formulated and justified for two options of use: inserted and a firmly bonded product and amounted to:

- tensile strength (inserted/firmly bonded) $\sigma_{\text{mef}} = 4$-10 MPa/ $\sigma_\varphi$ = up to 5 MPa;
- relative elongation (inserted/firmly bonded) $\varepsilon = 5$-10% / $\varepsilon \geq 11$%;
- compressive strength $\sigma_{\text{com}} = 10$-20 MPa (at $T = 50^\circ\text{C}$);
- specific impact viscosity $\alpha_k = 5$-10 kJ/m$^2$; (at $T = -50^\circ\text{C}$).

The results of the evaluation of physics-mechanical properties are described in [9].

The homogeneity of the structure resulted after polymerization for the presence of technological defects and the distribution of the substance density in the product was evaluated by the radiographic method. In the course of radiographic measurements of samples made of the EHCM, the effectuality of the criterion values proposed in (4) for evaluating the density of the resulted material was confirmed. For example, figure 4 shows the results of a radiographic study of the EHCM product. Its density was 0,97$\rho_q$.

![Figure 4. Results of radiographic control of the EHCM sample with a density of 0,97$\rho_q$.](image)

Deviations in the transmitted radiation intensity due to different densities over the entire cross section of the measured product were within normal limits. This confirmed the conclusion about the suitability of the resulted EHCM for operation as part of a technical system.
Studies of samples with $0.95 \leq \varnothing \leq 0.96(9)$ revealed two main groups of reasons for the deviation of the EHCM density from those established in (4), which are:

- lack of homogeneity and the presence of defects in the product made of EHCM;
- the presence of hidden defects in the EHCM structure.

The most typical examples for the listed defects are presented in figure 5.

**Figure 5.** Examples of the EHCM defects at density $0.95 \leq \varnothing \leq 0.96(9)$.

The presence of such defects in the EHCM is the main reason for the uncontrolled increase in its burning rate and pressure inside the combustion chamber during the operation of the technical system in which this material is operated. However, it has been practically confirmed that if there are 5 or more defects of the first group in the EHCM (figure 5 a), as well as if there are defects in the EHCM structure of the second group (figure 5 b), the operation of such a product is possible (where this characteristic is not important for operation of other systems), since insignificant jumps in the burning rate do not significantly affect the operation of the technical system as a whole.

If there are 1-3 defects of the first group in the EHCM product, observing the density requirements $0.95 \leq \varnothing \leq 0.96(9)$ in 50% of cases, combustion passes into detonation. Such products, as well as products with $\varnothing \leq 0.94(9)$, have to be disposed of in the manner prescribed for this class of material.
4. Conclusion

Thus, the use of the considered instrumental research methods makes it possible to develop technological modes of mixing polydispersed fractions in a liquid-phase medium and achieve uniform mixing of all components. It is the base for producing the EHCM with the required properties. The criteria values established by the experimental method for the density of the produced EHCM are the base for carrying out the output quality control of the final product that is simple in content and does not require large material costs.

The proposed methods and algorithms for their use, as well as criteria values after some adaptation, can be applicable to control the quality of the production of other composite materials made by mixing polydispersed solid-phase components in the medium of a polymeric material.

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