1. Introduction

Epoxy oligomers are the most important engineering thermo-reactive materials with wide industrial applications in adhesive, electronic, aerospace, and other systems. High chemical resistance to the effects of aggressive environments and increased durability cause the widespread use of epoxy composite materials. At present, the composites based on the epoxy matrix are effectively used to protect technological equipment from corrosion and to improve the physical-mechanical and thermal-physical properties of machine parts in many industries. However, the operation of the technological equipment under aggressive conditions leads to an increase in the operational requirements to epoxy composite materi-
als. That is why creation of new materials with the improved complex of performance characteristics is one of the main tasks of the production of composite materials.

Among the techniques to improve the physical and mechanical properties of epoxy composite materials is to introduce the dispersed fillers, which are different in chemical nature, to the matrix. At the same time, filling of epoxy oligomers in order to improve the performance of materials at the relative ease of implementation is far from being universal and is suitable only for a limited number of dispersed fillers. Among a wide variety of heterogeneous polymer systems, metal-filled compositions have been studied insufficiently. It is worth noting that the addition of metal oxides makes it possible to obtain the materials with new characteristics, not typical of other filled polymers. At the same time, the functionality of epoxy composites makes it possible to significantly expand their applications when filling with metals of different structures and characteristics, as well as to create new methods for regulating their structure and properties.

Creation of metal-filled epoxy composite materials with the enhanced complex of resistance and operational properties is one of the pressing challenges. Solving the problems of disposal of wastes of metallurgical industries, such as dust and gas treatment sludge, which are generated in the industry is a significant amount, is also an urgent problem. For example, according to [1], at steel smelting, up to 20 % of the waste is finely dispersed dust and gas treatment sludge. The accumulation of such waste leads to an increase in the environmental risk of the areas surrounding steel works. Article [2] deals with the ways of treatment of wet gas purification drains of metallurgical enterprises, but the issues of sediment or dust disposal are not considered. That is why, the issues of the disposal of such waste and using it as valuable raw materials are of scientific interest.

2. Literature review and problem statement

Currently, the use of wastes from various industries as reinforcing fillers of composite materials is a common practice. For example, paper [3] shows the possibility of reusing the materials of recycling the printing plates in polypropylene composites. An increase in durability of composites by 1.3 times was established. The optimal amount of the filler, which was not more than 30 %, was found. Paper [4] considered the possibility of disposal of aluminia production waste, red sludge, as a filler of polymer composite material. The described composites with the red sludge filler content of 55–75 % by weight had the resistance over 17 MPa when compressed. However, these studies did not identify the dependences that make it possible to offer the optimal composition of the filler for other types of waste.

Paper [5] examined the polymer composites of high-density secondary polyethylene, filled with solid phase of the used drilling solution with the content of up to 30 % by weight. It was established that the optimal content of such wastes in polymer composites is only 20 % by weight. At this, the maximum values of impact viscosity and destruct stress at bending up to 63.3 kJ/m² and 207.4 MPa, respectively, are achieved. However, this work does not address other types of waste.

Thus, finely dispersed wastes are of a particular interest as fillers of composite materials.

Current studies of metal-filled epoxy composite materials are carried out in three main directions. These include obtaining composites with an increased set of resistance characteristics, development of various metal-filled epoxy nanocomposites, as well as obtaining materials with good dielectric and current conductive characteristics. For example, in study [6], the epoxy oligomer with the filler from the mixture of aluminum, brass and copper powders is used to obtain casting molds for the production of samples of mechanical testing of thermoplastic plastics for pressurized casting. The results of the studies showed that a casting mold from such composites has a higher fluidity limit at stretching equal to 36.3 MPa and impact resistance at the level of 18.23 MPa, compared to conventional metal casting molds, the characteristics of which are 33.8 MPa and 10.02 MPa. Articles [7–9] also describe the results of the study of filling epoxy oligomers with various metals in the dispersed form ensuring enhanced resistance properties of cured composites. However, the main drawbacks were the low limit content of metal fillers – not more than 30 %, and rather medium indicators of resistance and adhesion characteristics of composites. This restriction does not make it possible for wastes to be disposed of large quantities.

Article [10] summarizes scientific and practical research into the basic areas in the development and the use of epoxy nanocomposites. It was shown that modern multifunctional epoxy nanocomposites with magnetic, electrical, thermal conductive and fire-resistant properties are widely used in the aerospace industry, in car building, anti-corrosion coatings and high-voltage fields. In article [11], epoxy nanocomposites were obtained using recycled metal dust powder as the filler by altering the filler content. The filler has been shown to promote an increase in density and hardness of the cured epoxy nanocomposite. The study showed that metal waste powders have a good potential for being used as a nanofiller for thermo-reactive materials, such as epoxy oligomer. However, the small effective amount of metal fillers in epoxy nanocomposites (up to 5 % of weight) does not make it possible to significantly increase their complex of resistance and performance characteristics.

A series of current studies describe metal-filled epoxy composites with elevated levels of dielectric permeability. Thus, articles [12, 13] analyzed the dielectric properties of aluminum-filled epoxy composites, such as frequency function (1 kHz – 1 MHz), temperature (from room temperature up to 150 °C) and the volume fraction of aluminum filler. It was shown that the improvement of dielectric permeability was observed at an increase in the concentration of the filler. This is due to an increase in inter-phase polarization and the formation of filler clusters. An increase in dielectric permeability with the temperature for all samples was attributed to an increase in the mobility of segments due to the inclusion of metal in the polymer matrix. The authors of articles [14, 15] showed an increase in electrical conductivity of epoxy resin up to 10⁻³–10⁻⁴ Ohm-cm, when it is modified with nickel powder. Metal powders are introduced into polymers in order to obtain electrically conductive polymeric materials. Due to this filling, a system that is preserved after the polymer hardens is created in the magnetic field. Paper [16] dealt with the filled composites based on epoxy polymer and the fillers of ferromagnetic (red sludge), paramagnetic (B, C, TiC) and diamagnetic (Al₂O₃, SiC) nature. The fillers were treated with the high-frequency magnetic field with the frequency of 1–100 MHz.
The aim of this study is to identify the properties of metal-filled epoxy composites of cold curing by filling them with a solid disperse phase from the wastes of metallurgical enterprises. This will make it possible to find the optimal composition of epoxy composites, predicting its properties, as well as to determine the possibilities of recycling metal-containing waste as the filler.

To achieve the set aim, the following tasks have been solved:

- to explore the effect of the dispersed solid phase of metal wastes on the operational and resistance characteristics of metal-filling epoxy composites of cold curing;
- to reveal the optimal content of dispersed solid phase of metal wastes in metal-filled epoxy composites of cold curing.

4. Procedure for obtaining and studying the samples of composite materials

Finely dispersed dust of two operating foundries (Fig. 1) was used as a filler of the composite. Sample No. 1 (O1) was the dust of smelting black metals and metal wastes (Fig. 1, a) of the characteristic black color. Sample No. 2 (O2) was the dust of electric furnaces of doped steel of brown color, sticking together in lumps (Fig. 1, b).

The elemental composition of the samples was determined at the laboratory X-ray fluorescent spectrometer ElvaX made by company “Elvatex” (Ukraine).

![Fig. 1. Photographs of samples of the waste from metallurgical production (ruler division between the numbers is 1 mm): a — sample No. 1; b — sample No. 2](image_url)

The compositions based on epoxy dian resin of the ED-20 brand with the molecular weight of 360–470, containing 21.5 % of epoxy groups were studied. The hardener of the amino type – polyethylene polyamine (PEPA) (TU 6-02-594-85), capable of forming a three-dimensional mesh structure in the absence of heating, was used as the hardener of epoxy oligomer. The chemical formula of the PEPA is \( \text{H}_2\text{N(CH}_2\text{CH}_2\text{NH})\text{nH} \), where \( n = 1–4 \), dynamic viscosity is 0.9 Pa·s. A highly active modified amine hardener of epoxy oligomers was used as a catalyst.

The technology of making metal-filled epoxy composites of cold curing was the following. The metal filler (waste sample O1 or O2) was introduced to epoxy oligomer heated up to 60–70 °C at intensive stirring until the homogeneous mass was obtained. Then the hardener polyethylene polyamine (PEPA) and the curing catalyst – manganese triacetate (Etal-12) – were mixed, still being stirred. The adhesive composition prepared in this way was applied by a thin even layer on a preliminarily degreased metal surface and kept for 1.5–6 hours at the temperature of 20–25 °C, depending on the composition. The composition of the studied epoxy composites of cold curing is given in Table 1.

| Composition | Epoxy Resin | Hardener | Curing Catalyst |
|-------------|-------------|----------|-----------------|
| O1          | ED-20       | PEPA     | Manganese triacetate |
| O2          | ED-20       | PEPA     | Manganese triacetate |
The results of the study of the elemental composition of the waste samples are given in Table 2.

Analysis of the data in Table 2 shows that the metal part of sample No. 1 is mainly represented by iron and calcium compounds, and the metal part of sample No. 2 – by iron, zinc, calcium, and manganese. Thus, these types of waste are of interest as fillers for metal-filled composites.

Table 2 gives data about the physical, resistance and operational characteristics of the studied metal-filled epoxy composites of cold curing, filled with wastes of metallurgical productions.

5. Results of studying the properties of composites at the introduction of metallurgy wastes

5.1. The effect of the dispersed solid phase of metal wastes on the operational and resistance characteristics

The results of the study of the elemental composition of the waste samples are given in Table 2.

Fig. 3 shows the dependence of impact resistance on the content of waste in composites. Analysis of Fig. 3 shows that the introduction in the composite of wastes in the amount of 45–65 % increases their impact resistance up to 42 MPa for O1 and 48 MPa for O2. An increase in the content of waste of more than 55 % for both samples leads to a gradual decrease in resistance. Filling over 65 % significantly increases the fragility of the samples. In addition, the resistance of the composites filled with sample O2 is slightly higher than those filled with waste O1.

As a result of statistical treatment of the experimental data, the equations of approximating curves were derived, which made it possible to calculate the values of impact resistance $a$ (MPa) depending on the amount of the filler from wastes $x$ (% by weight), introduced to the composite:

$$a_{O1}=333.2331-21.8565x+0.4892x^2-0.0034x^3; \quad (1)$$

$$a_{O2}=949.6941+51.6221x-0.8719x^2+0.0048x^3. \quad (2)$$

Fig. 4 shows that for the data on the composition formulations, a maximum heat resistance by Vicat is observed: 190 °C and 170 °C for composite samples filled with waste O1 and O2, respectively. At the same time, the results shown in Fig. 4 indicate that composites filled with waste No. 2...
have a lower softening temperature. That is why, depending on the purpose of application of this composite and the necessary properties (better impact resistance or a higher softening temperature), it is possible to recommend the application of waste O1 or O2.

![Fig. 3. Dependence of impact resistance on the share of wastes in composites: 1 — sample No. 1; 2 — sample No. 2](image)

As a result of statistical treatment of the experimental data, the equations of approximating curves were derived, which made it possible to calculate the values of softening temperature $T$ (°C), depending on the amount of the filler from wastes $x$ (% by weight), introduced in the composite:

$$T_{O1} = 1469.2929 - 84.7309 \cdot x + 1.7775 \cdot x^2 - 0.012 \cdot x^3;$$ (3)

$$T_{O2} = -72.8578 + 5.5278 \cdot x + 0.041 \cdot x^2 - 0.0011 \cdot x^3.$$ (4)

5. 2. Analysis of optimal content of the dispersed solid phase of metal waste

The results of the study of the dependence of cross-linking degree on the content of waste in the composite are presented in Fig. 5. It is important to note that at an increase in the degree of filling the composite with waste, there is a proportional dependence of an increase in cross-linking degree. If the content of the filler in the composite is less than 45 %, cross-linking degree is less than 90 %, which can be the cause of low values of impact resistance and softening temperature of the obtained samples. Despite an increase in the cross-linking degree at an increase in the share of the filler, a decrease in these properties of composites at the content of the filler of more than 65 % can be associated with the formation of a heterogeneous structure of the filler.

![Fig. 4. Dependence of softening temperature on waste share in composites: 1 — sample No. 1; 2 — sample No. 2](image)

The values of cross-linking degree $j$ (%), depending on the amount of the filler of the studied waste samples $x$ (% by weight), introduced in the composite, is described by the following linear dependences:

$$j_{O1} = 77.3752 + 0.2773 \cdot x;$$ (5)

$$j_{O2} = 75.1838 + 0.3318 \cdot x.$$ (6)

As the data in Table 1 and Fig. 7 demonstrate, at an increase in the content of the hardener and the catalyst, the time of curing of metal-filled epoxy composites decreases from 6 to 1.5–1.4 hours. However, the use of the curing catalyst by more than 2 % accelerates the process insignificantly, although it can lead to an increase in the fragility of the compositions.

Thus, at the introduction of the filler of more than 65 % by weight, resistance decreases due to an increase in the fragility of the compositions at an excess of the amount of the filler and curing catalyst. At the waste content of less than 45 %, there is a decrease in impact resistance due to a drop in the degree of cross-linking of the oligomer part of the composites.

![Fig. 5. Dependence of the cross-linking degree on the content of waste in composites: 1 — sample No. 1; 2 — sample No. 2](image)

The photographs of samples (Fig. 6) of epoxy composite No. 3 with the best properties after curing show that the filler in these samples is evenly distributed and there are no heterogeneous clusters of it.

![Fig. 6. Photographs of metal-filled epoxy composites No. 3 of cold curing: a — the surface of the fault of sample O1; b — the surface of the fault of sample O2](image)
It was established that the proposed compositions allow reducing the curing time at 20–25 °C up to 2–4 hours in comparison, for example, with a well-known composition, which gets cured within 26 hours [17]. The rejected compositions have a higher limit of resistance at the impact of up to 48 MPa and a higher heat resistance of not less than 160 °C with the known composites [17, 18]. This is achieved by optimizing the degree of cross-linking the compositions while ensuring their quite quick curing within 2 hours. At the same time, compositions No. 3, which are characterized by maximum resistance characteristics and curing time of about 2 hours, were chosen as optimal.

The advantage of this study is the possibility of disposal of finely dispersed dust and sludge, for example, those of gas treatment of metallurgical productions in epoxy composites of cold curing. The obtained and described dependences can be used to calculate the optimal composition or to predict the properties of the composite, depending on the degree of filling with waste.

However, this study is limited only to the dust wastes from foundries. However, the described procedure of studying the samples and obtaining dependences of performance characteristics can be adapted to any filler of composites.

The search for the ways to dispose of other industrial waste as reinforced fillers of composites opens up the prospects for further research into spheres of applications of anthropogenic waste.

6. Discussion of results of studying the properties of metal-filled epoxy composites

As a result of our research, the possibility to dispose of the dust of foundries was established. It was proposed to solve this problem by introducing dust as a metal-containing filler of epoxy composites of cold curing. This decision allowed the improvement in the performance of the obtained samples of composites.

According to the experimental data given in Table 3, Fig. 3, 4, the optimal content of the filler for metal-filled epoxy composites is 45–60 % by weight. Both an increase, and a decrease in the proportion of the filler leads to a decrease in impact resistance (Fig. 3) and softening temperature (Fig. 4) of the composition in all the studied compositions. This is due to the fact that impact resistance of the studied metal-filled epoxy composites is influenced by two main factors: the content of the filler and the amount of introduced hardener and catalyst. In fact, in the compositions with the highest resistance and performance characteristics, there is an optimized content of the filler and the catalyst.

7. Conclusions

1. The study into the effects of dispersed solid phase of metal wastes on the operational and resistance characteristics of metal-filled epoxy composites of cold curing was carried out. It was established that the disposal of finely dispersed dust of foundries as a filler leads to reinforcement of cured samples up to 40–50 MPa at the waste content of 55 %.

2. It was established that the optimal content of the filler for the studied metal-filled epoxy composites is 45–60 % by weight. At the content of the filler of less than 45 %, there is some deterioration in the performance of the composite due to a decrease in cross-linking degree. At the content of wastes of more than 60 %, the impact resistance of the compositions decreases due to an increase in fragility at the excess of the filler and the catalyst.

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