UKRAINIAN JOURNAL OF MECHANICAL ENGINEERING AND MATERIALS SCIENCE
Vol. 5, No. 2, 2019

Petro Savchuk [1], Dmytro Matrunchyk [2], Vitalii Kashytskyi [3],
Oksana Sadova [4], Iryna Moroz [5]

1. Department of Material Science, Lutsk National Technical University, Ukraine, Lutsk, Lvivska street 75, E-mail: savchuk71@gmail.com
2. Department of Material Science, Lutsk National Technical University, Ukraine, Lutsk, Lvivska street 75, E-mail: patrikk0708@gmail.com
3. Department of Material Science, Lutsk National Technical University, Ukraine, Lutsk, Lvivska street 75, E-mail: v.kashitskyi@lntu.edu.ua
4. Department of Material Science, Lutsk National Technical University, Ukraine, Lutsk, Lvivska street 75, E-mail: sadova111oksana@gmail.com
5. Department of Material Science, Lutsk National Technical University, Ukraine, Lutsk, Lvivska street 75, E-mail: moroz.iryna1@gmail.com

THE INFLUENCE OF METAL OXIDE POWDERS ON THE PHYSICAL AND MECHANICAL PROPERTIES OF EPOXY COMPOSITES FOR THE PROTECTION OF CONSTRUCTIONS MADE OF ALUMINUM ALLOYS

Received: July 20, 2019 / Revised: August 28, 2019 / Accepted: August 30, 2019

Abstract. Protection of designs of vehicles made of aluminum alloys is an urgent application problem because these alloys are being extensively destroyed under the influence of aggressive environments, climatic factors, cyclic changes of temperature, the influence of the flow of abrasive particles. The protective coating increases significantly duration of operation of the construction and reduce the number of overhaul operations associated with restoring the surface of the product. However, there is a problem associated with the complexity of the coating technology on the constructions made of aluminum alloys, because these surfaces are inert due to the presence of oxide films. To ensure reliable protection of the surface of the construction, it is necessary to provide high adhesion strength of coating with substrate, cohesive strength and corrosion resistance of the coatings. An effective solution to this problem is the use of polymer coatings based on epoxy resins, characterized by high adaptability, specific strength, high operated properties. The use of epoxy oligomers as a polymeric matrix allows you to meet the requirements, however, it requires the development of composition of epoxy composite material and coatings technology. The purpose of the work is determination of the influence of highly dispersed powders of metal oxides on the structuring process and mechanical characteristics of epoxy composites, and optimization of the composition for the formation of protective coatings of construction made of aluminum alloys. The classical methods of research of physical and mechanical characteristics of epoxy composites are used in the work: the gel fraction content, adhesion strength, compressive strength, impact energy. The optimum content of titanium oxide powder is found to be 8 wt % because these epoxy composites have the highest impact energy compared to composites having a different stoichiometric ratio of components. Considerable increase in impact energy of epoxy composites take place as a result of treatment of the composition at the mixing stage of the components with ultrasound, which ensures high uniformity of the composition and the lyophilicity of the powder particles. The developed coatings have increased adhesion strength, impact energy and compressive strength, which ensures their use as coatings of designs of vehicles made of aluminum alloys for protection against climatic conditions, abrasive wear and corrosion. A promising area of research is the introduction of modifying additives into the epoxy composites developed to increase their resistance to cyclic change of temperature and the application of treatment of the compositions in physical fields to ensure the high uniformity of the composition and increase the lyophilicity of the powder particles.

Keywords: adhesive strength, impact energy, dispersed filler, titanium oxide.

Introduction

Increasing the life of the structural elements of vehicle bodies made of aluminum alloys, is an actual problem of modern technology, because the surface layers of these alloys are destroyed by aggressive environments. This requires a solution, associated with the cost of replacing the construction elements or restoration the corroded surfaces. The application of corrosion-resistant coatings based on polymers can solve this problem for constructions that are operated under normal conditions. There are problems associated with the operation of vehicles in difficult conditions in the presence of simultaneous effects of cyclic changes in temperature, humidity, abrasive particles and corrosive environments. One solves to this problem is to use polymeric materials that are amenable to structural or chemical modification with using additives which are capable of transforming the structure of the macromolecules of the polymer. Among the wide range of polymers effective in terms of ability to modify are epoxy resins that have satisfactory rheological characteristics and high compatibility with other polymers.

Problem Statement

The introduction into the composition of the epoxy polymer matrix of the dispersed fillers causes the heterogeneity of the structure of the composite due to the uneven distribution of the particles of the filler and the lack of wettability of the surface of the particles by the polymeric matrix. Therefore, it is necessary to use finely dispersed fillers with an optimum degree of dispersion and ability to form the structure of epoxy composite with additional chemical bonds to obtain coatings characterized by high density, adhesion strength and cohesion strength, resistance to dynamic and cyclic mechanical or thermal loads.

Review of Modern Information Sources on the Subject of the Paper

Aluminum alloys are widely used for the manufacture of constructions in automotive, aircraft and shipbuilding due to their high specific strength [1]. It is often necessary to give a decorative appearance to constructions that are elements of the exterior of the vehicle body, or to protect these alloys from climatic influences and aggressive environments [2], leading to their rapid destruction. The classic solution to these problems is application of multilayer polymer coatings [3] on the construction surface, which are a barrier to penetration of the corrosive environment. Polymer coatings are characterized by high manufacturability, high corrosion resistance, modification ability [4]. Tthis allows you to change the structure of the polymer and improve the coating properties. It is necessary to ensure a high density of the coating material, to prevent the penetration of the corrosive substance into the substrate and to provide a high adhesive strength of the coating to the substrate to prevent delamination of the coating [5].

Much work is devoted to the study of the processes of passivation of the aluminum surface, which will provide additional protection of the aluminum surface of the constructions in case of destruction of the polymer coating. Before applying the polymer coating, the surfaces are treated using chromium-based compounds or anodized. Much work is devoted to the study of the processes of passivation of the aluminum surface, which will provide additional protection of the aluminum surface of the constructions in case of destruction of the polymer coating. Before applying the polymer coating, the surfaces are treated using chromium-based compounds or anodized. Chromium-based compounds are toxic, which limits the widespread use of this technology [6], and the synthesis of the anode coating leads to the formation of a fragile highly porous layer of material [7].

A simpler and more effective method of protecting constructions from corrosion is to use high-tech epoxy resins with high adhesion to many materials. However, polymers based on epoxy resins have high brittleness, low thermal resistance and resistance to cyclic change of temperature [8]. This limits their use to protect the elements of constructions which are exposed climate influence. The introduction into the epoxy polymer matrix of dispersed mineral fillers, which are resistant to corrosive environments, will allow to obtain composite protective coatings [9–11], provided that the filler particles are capable of chemical interaction with the macromolecules of the epoxy matrix [12]. The use of metal oxides powders ensures the formation of a dense structure of epoxy composites due to the intermolecular and interphase interaction of the components [13–15]. However, due to the high surface energy, particle agglomeration occurs [16] or the formation of a non-uniform structure. This requires the selection of fillers that can provide high technological characteristics of the composition at the stage of composite formation, as well as high physical, mechanical and operational characteristics of the material due to the optimum degree of dispersion of the filler [17], its lyophilicity and uniform distribution of particles.

Objectives and Problems of Research

The purpose of the work is determination of influence of highly dispersed powders of metal oxides on the structuring process and mechanical characteristics of epoxy composites, and optimization of the composition for the formation of protective coatings of construction made of aluminum alloys.

Research objectives:

- to investigate the influence of dispersed metal oxides powders on the physical and mechanical characteristics of epoxy composites;
- determine the optimum content of the dispersed filler.

Main Material Presentation

To investigate the physical and mechanical characteristics of epoxy composites, samples containing components in stoichiometric ratio were formed. As the polymeric matrix used epoxy resin ED-20, structured by the introduction of polyethylenepolyamine (PEPA). PEPA is a cold action hardener. The optimum content of the hardener is 12 wt % per 100 wt % epoxy resin that provides the optimum degree of the structuring system with low residual stresses. The components were dosed, followed by mechanical mixing. The composition was placed in form for a pre-structuring for 24 h at room temperature. To complete the structuring process, a stepwise heat treatment was performed: 1 h at 50 °C, 1 h at 100 °C, 4 h at 140 °C.

The adhesion strength was determined by the method of normal rupture of the glue connection of cylindrical specimens with a conical projection at the point of capture for self-centering. The compressive strength was determined on cylindrical specimens with a diameter of 10 mm and a height of 15 mm by applying a static compressive load. The impact energy was determined on specimens with a square section (10×10 mm) and a length of 60 mm on Charpy machine. The gel fraction content was determined by weight method using a Soxklet extractor, which worked in an automatic mode for 8 h.

For epoxy composites containing 6 wt % of the highly dispersed titanium oxide powder, increases the adhesive strength of the glue connection by 12…15% (Fig. 1). This is due to the formation of additional intermolecular bonds between the reactive groups on the particle surface and the hydroxyl groups of the epoxy resin. Increasing the content of titanium oxide powder from 6 wt % up to 16 wt % leads to a decrease of this characteristic by 8…12%. This is due to the uneven distribution of the powder particles in the epoxy matrix and the decrease in its lyophilicity due to the high dispersion of particles and the formation of agglomerates.

With a powder content of chromium oxide 2…6 wt % the adhesive strength of the epoxy composite material to the substrate surface compared to the unfilled system decreases by 2.1…2.3 times. This is due to the blocking of the formation process of covalent bonds between the epoxy end groups and the amine groups of polyethylenepolyamine due to the low specific surface area of the particles of chromium oxide powder.

The increase in the content of chromium oxide powder to 12 wt % increases the adhesive strength because the amount the powder particles of chromium oxide in the epoxy composite increases and the total number of hydroxyl groups on the surface of the particles. In this case, the adhesive strength of the epoxy composites with the content of chromium oxide powder does not exceed the value of the adhesive strength of epoxy polymers without fillers. This indicates that the high content of this filler (8…12 wt %) provides an increase in the adhesive strength of the binder to the filler compared to the low powder content (2…6 wt %). Therefore, the dominant factor in determining the adhesive strength is the cohesive strength of the epoxy composite material. Therefore, it can be argued that the increase in the adhesive strength of epoxy composites filled with chromium oxide powder to the substrate surface does not occur.

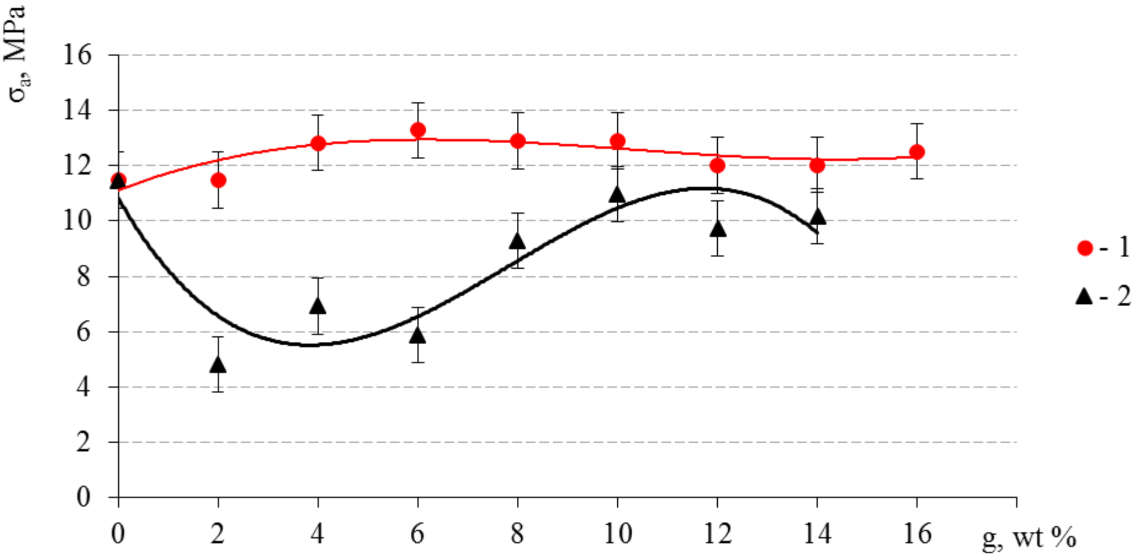


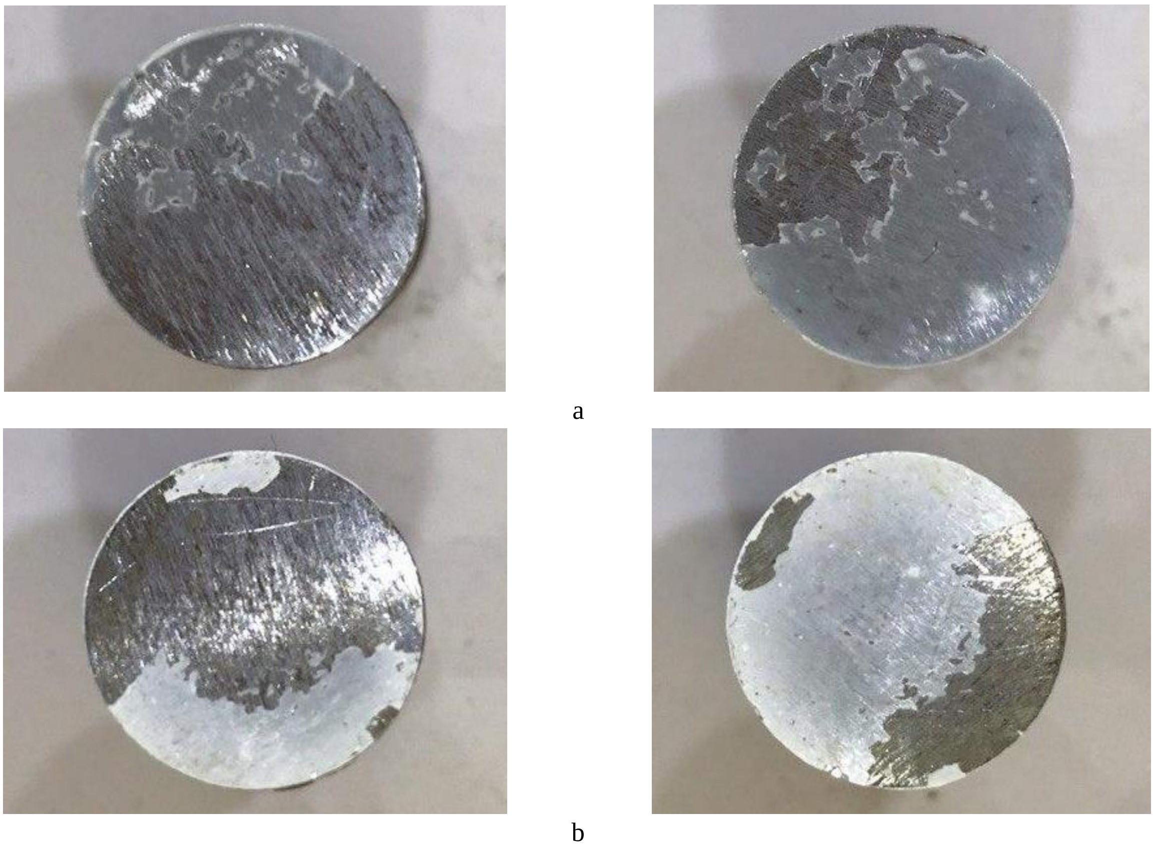
Fig. 1. The dependence of the adhesive strength of epoxy composites on the powder content: 1 – titanium oxide; 2 – chromium oxide

The introduction of titanium oxide powder increases the cohesive strength, so the destruction occurs at the interface between the epoxy material layer and the substrate surface (Fig. 2). The adhesive nature of the destruction of the adhesive connection with variable relief (Fig. 2, a) is observed for materials with low powder content (2…4 wt %). This is due to the fact that part of the free hydroxyl groups of the epoxy resin, which have not formed bonds to the surface of the particles, participate in the formation of hydrogen bonds with the surface of the substrate. Due to the high content of titanium oxide powder (10…14 wt %), the number of hydroxyl groups of epoxy macromolecules decreases due to the intensive interaction with the reactive groups on the surface of the particles. Therefore, the destruction of the adhesive connection is also predominantly the adhesive nature with variable relief due to the reduced mobility of the macromolecule segments and the increase of resistance to the appearance of microcracks (Fig. 2, b).

Particles of chromium oxide powder at low content (2…6 part by weight) blocked the formation of the polymer mesh, so the adhesive bonding of these epoxy composites have the adhesive type of fracture (Fig. 3, a). In this case, the crack propagation occurs clearly along the epoxy composite-substrate interface. The introduction of chromium oxide powder in an amount of (8…12 part by weight) increases the adhesive strength, as it increases the resistance of the epoxy polymer mesh to deformation during static loading. Therefore, the destruction of the adhesive connection have adhesive type with variable relief (Fig. 3, b).

Introduction to the epoxy polymer system 4…6 wt % of highly disperse powder of chromium oxide increases the compressive strength by 19…21% (Fig. 4). The maximum value of compressive strength is 73.5 MPa, which is explained by the formation of a homogeneous structure with low internal stresses. Further increase in the content of the filler leads to a decrease the compressive strength by 15…18%. The minimum compression strength of 59.2 MPa obtained by powder content of 10…14 wt % of powder.

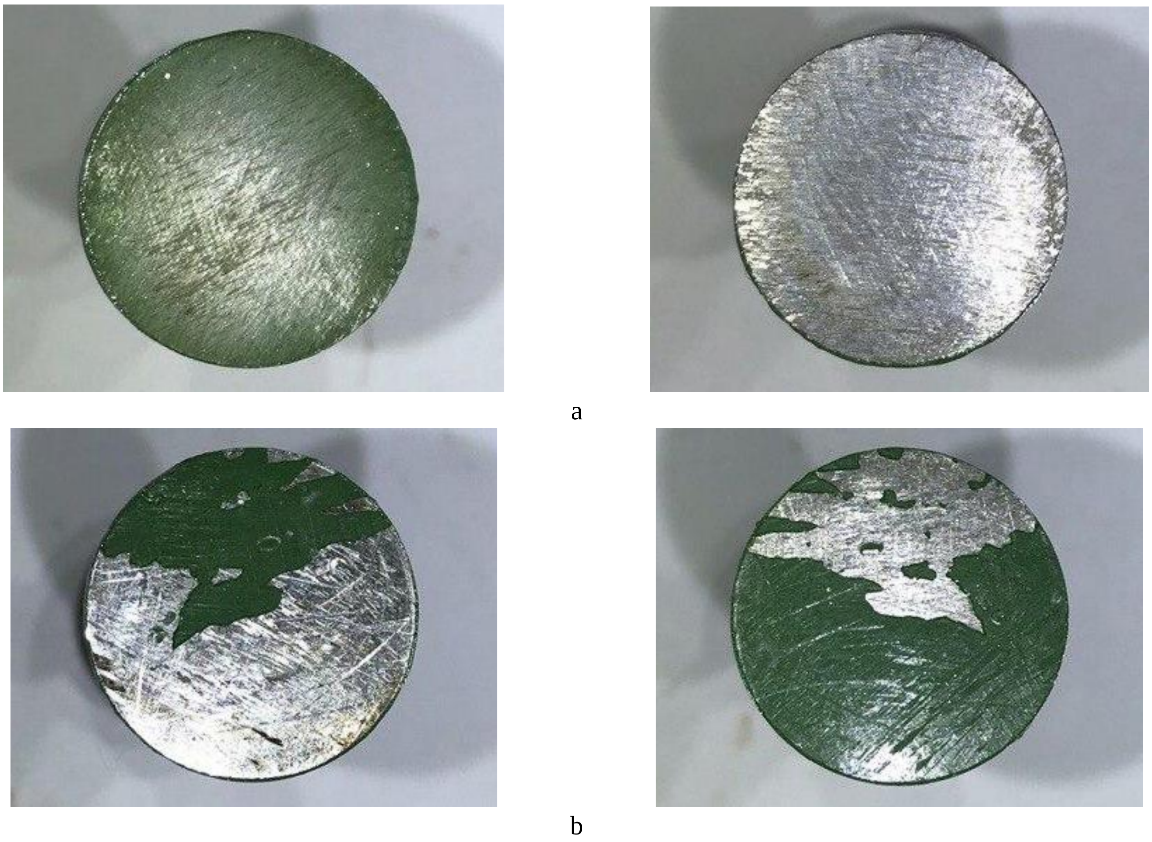
Increasing the compression strength of specimens with low content of chromium oxide powder is associated with the formation of an optimal structure of epoxy composite in which the filler particles perform a reinforcing function. These particles prevent the deformation of the polymeric grid of the matrix, resulting in increased resistance to static loading. With increasing content of filler, the number of bonds between the binder and the filler obviously growing, but the strength decreases due to the formation of the stress state of the system. This is due to the uneven location of the particles whose content is excess, resulting in the formation of a defective structure.



a

b

Fig. 2. View of the destroyed surface of glue connection of epoxy composites, filled with titanium oxide powder: a – 2 wt %; b – 10 wt %



a

b

Fig. 3. View of the destroyed surface of glue connection of epoxy composites, filled with chromium oxide powder: a – 2 wt %; b – 10 wt %

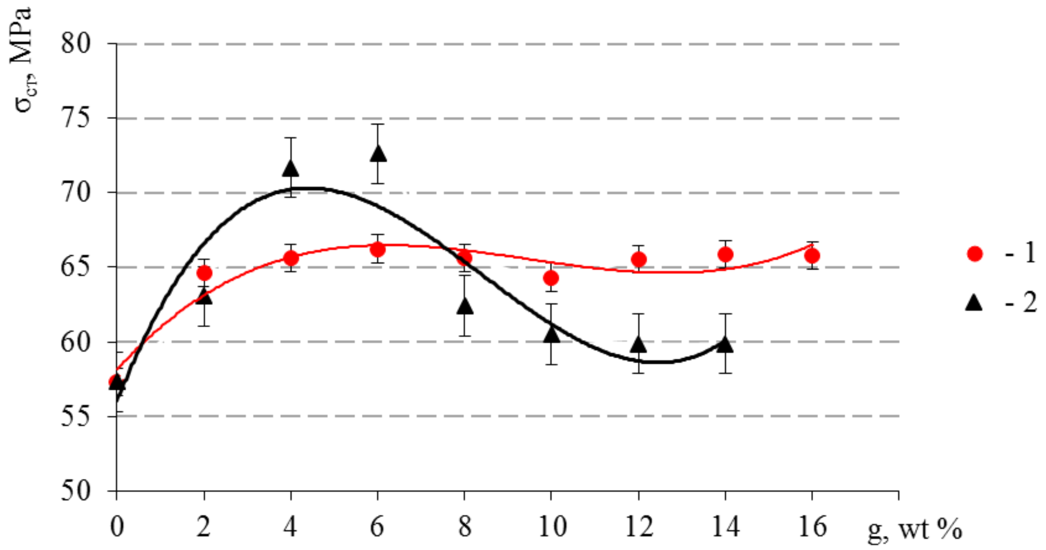


Fig. 4. The dependence of the compressive strength of epoxy composites on the powder content:
1 – titanium oxide; 2 – chromium oxide

The introduction of a highly disperse powder of titanium oxide increases the compressive strength of epoxy composites by 13…15 %, since these particles also perform a reinforcing function. The maximum value of compressive strength is 66.5 MPa with a content of 6 wt %, which can be explained by the optimal degree of structuring of the epoxy composite material. The compressive strength of epoxy composites filled with titanium oxide powder is lower than the strength of epoxy composites filled with chromium oxide powder due to the higher dispersion of titanium oxide powder. Particles of this powder are easier to move during loading than larger particles of chromium oxide powder. Further increase of the content of titanium oxide powder leads to stabilization of the values of the compressive strength which is due to the increase in the number of reinforcing elements. At a higher content of titanium oxide powder, the values of the compressive strength are higher compared to epoxy composites with a same degree of filling of the system by chromium oxide powder, which is associated with the formation of heterogeneous structure. Obviously, that with higher filler content the dominant influence has a homogeneous structure of the epoxy composite. Therefore, particles of higher dispersion powder are able to be placed more evenly in the polymeric binder than larger particles.

The introduction of chromium oxide powder leads to an increase in the content of the gel fraction of epoxy composites in the filling range of the system 2…4 wt %. (Fig. 5). It was found that epoxy composites with the content of 2 wt % of chromium oxide powder have the highest degree of structuring (84.35 %). In the filling range of 6…14 wt % there is a decrease in the content of the gel fraction, which is related to excess filler content. The optimum content of this filler promotes the formation of intermolecular bonds with the epoxypolymer matrix. In the case of increasing the content of the powder, new ligaments are not formed, which is limited by the small number of active groups on the surface of the particles.

For epoxy composites containing titanium oxide powder in the range of 2…8 wt %, there is an increase in the content of the gel fraction, due to the formation of additional bonds between the components of the system. The maximum value of the degree of structuring is 84.33 % for filling the system 6 wt %. By increasing the content of titanium oxide powder to 14 wt % there is a significant decrease in the degree of structuring, which can be explained by the agglomeration of the powder particles.

The maximum values of the degree of structuring of epoxy composites filled with titanium oxide powder are obtained with a higher powder content, which is ensured by the formation of the maximum number of intermolecular bonds with the macromolecules of the binder. This is determined by the greater number of hydroxyl groups on the surface of the titanium oxide particles compared to the chromium oxide powder.

The minimum values of impact energy 5.1 kJ/m^2 (Fig. 6) were obtained for unfilled epoxy polymer systems. The introduction 2…6 wt. % of titanium oxide powder increases the impact energy of epoxy composites by 20…30 %, which is explained by the formation of additional intermolecular bonds between the polymer matrix and the powder particles. With the introduction of powder more than 8 wt. % the impact energy of epoxy composites decreases sharply, due to the presence of agglomerated particles whose concentration is higher in the polymer matrix. Agglomerated particles form complexes due a high specific surface area which does not provide complete wetting of each particle by binder. These complexes are stress concentrators. During the distribution of the shock wave, they act as a source of microcracks.

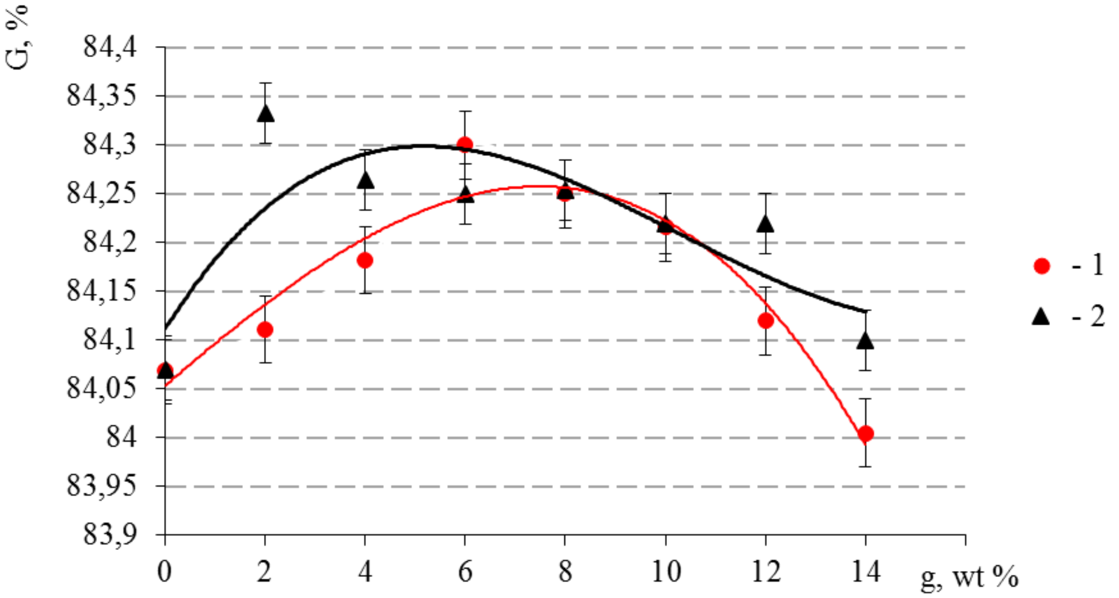


Fig. 5. The dependence of the gel fraction content of epoxy composites on the powder content:
1 – titanium oxide; 2 – chromium oxide

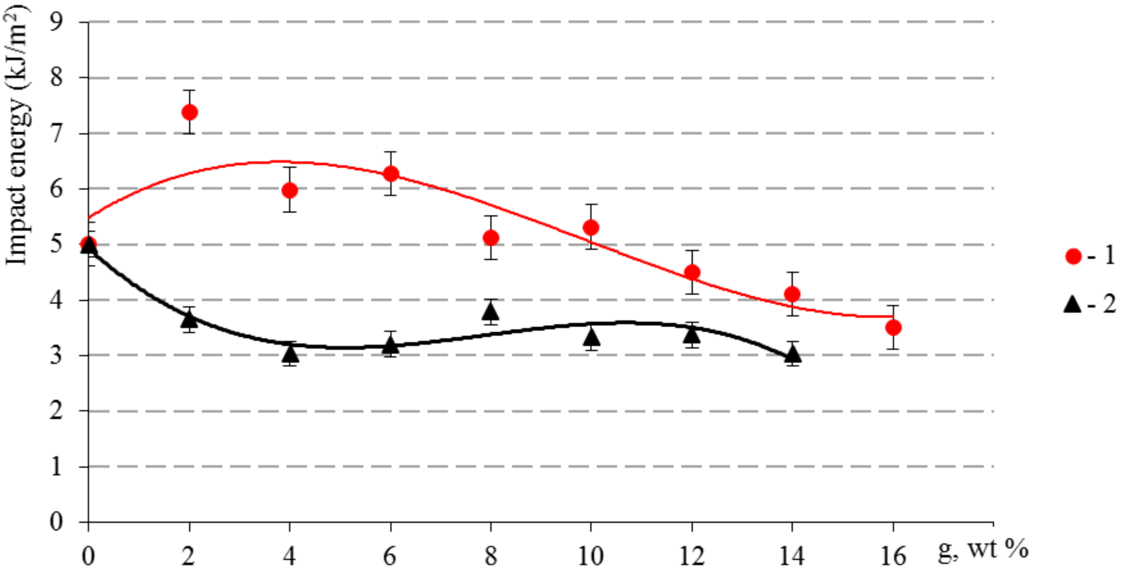


Fig. 6. The dependence of the impact energy of epoxy composites on the powder content:
1 – titanium oxide; 2 – chromium oxide

The introduction of chromium oxide powder reduces the impact energy of epoxy composites by 25…40% for any degree of filling the system from the test range. This powder does not have on the surface of the particles the required number of reactive groups for the formation of new intermolecular bonds and the formation of a stable structure to the influence of dynamic loads.

Conclusions

It was found that the introduction of titanium oxide powder into the epoxy polymer matrix is more expedient than that of chromium oxide powder, since there is an increase of mechanical characteristics by

15…30%. This is due to the ability of particles of titanium oxide powder to form additional intermolecular bonds with macromolecules of the epoxy matrix.

The optimum content of titanium oxide powder in the epoxy polymer matrix is 6 wt. %, resulting in the formation of epoxy composite material with high adhesive strength, compressive strength, impact energy and degree of structuring in the studied range of degrees of filling. Epoxy composites with a lower content of this powder do not provide the formation of a sufficient number of chemical bonds. With the use of higher content is the agglomeration of particles, which leads to the formation of a defective structure.

When forming epoxy composites with a low content of chromium oxide powder, a significant increase in mechanical properties compared to epoxy composites filled with titanium oxide powder does not occur, because on the surface of the powder particles of chromium oxide there is a smaller number of hydroxyl groups involved in the formation of chemical bonds. In the case of the formation of epoxy composites with a higher content of chromium oxide powder, the cohesive strength is reduced, which is due to the uneven distribution of particles in the polymer matrix and the formation of non-uniform structure.

References

[1] Y. Ota, T. Kojima, "Surface treatment technologies of aluminum alloy for automobiles", *Kobelco Technology Review*, no. 35, pp. 61–64, June, 2017.

[2] M. M. Bratychak, M. M. Bratychak, N. V. Chopyk, "Zahysni polimerni plivky na osnovi epoksy-oligoesternykh kompozytsij" ["Protective polymer films based on epoxy-oligoester compositions"], *Budivelni materialy, vyroby ta sanitarna tekhnika [Construction materials, products and sanitary ware]*, vol. 42, pp. 67–71, 2011. [in Ukrainian].

[3] H. D. Johansen, C. M. A. Brett, A. J. Motheo, "Corrosion protection of aluminium alloy by cerium conversion and conducting polymer duplex coatings", *Corrosion Science*, vol. 63, pp. 342–350, 2012.

[4] A. Stankiewicz, M. B. Barker, "Development of Self-healing Coatings for Corrosion Protection on Metallic Structures", *Smart Materials and Structures*, vol. 25, no. 8, 084013, 2016.

[5] J. T. Boerstler, "Corrosion Degradation of Coated Aluminum Alloy Systems through Galvanic Interactions", Ph.D. dissertation, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, 2018.

[6] F. Pearlstein, V. S. Agarwala, "Trivalent Chromium Solutions For Applying Chemical Conversion Coatings To Aluminum Alloys or for Sealing Anodized Aluminum", *Plating and Surface Finishing*, no. 81, pp. 50–55, July, 1994.

[7] Bonding to Aluminum. Epoxy Technology Inc., 2013. [Online]. Available: http://www.epotek.com/site/files/Techtips/pdfs/Tech_Tip_24_-_Bonding_to_AL.pdf. Accessed on: June 10, 2019.

[8] M. Zoriany, A. Nashaat, Y. El-Shaer, M. Gobara, "Anti-Corrosion Silica-Based Hybrid Coatings for the Protection of AA2024 Alloy", in *Proc. 17th Int. Conf. on Aerospace Sciences & Aviation Technology, ASAT–17,* Military Technical College, Kobry Elkobbah, Cairo, Egypt, April 11–13, 2017, pp. 1–17.

[9] Yu. M. Danchenko, O. V. Strumskas, T. M. Obizhenko, T. I. Umanska, "Epoksydni polimerni materialy z pidvyshhenoyu stijkistyu do vodnykh rozchyniv dlya restavraciyi naturalnogo kamenyu" ["Epoxy polymeric materials with improved resistance to water solutions for restoration of natural stone"], *Problemy nadzvychaynykh sytuatsiy [Problems of Emergency Situations]*, no. 1 (29), pp. 100–112, 2019. [in Ukrainian].

[10] O. I. Redko, "Doslidzhennya struktury epoksykompozytiv z mineralnymy chastkamy metodom infrachervonoyi spektroskopiyi" ["Investigation of the structure of epoxy composites with mineral particles by infrared spectroscopy"], *Naukovyj visnyk Khersons'koho derzhavnoho mors'koho instytutu [Scientific Bulletin of the Kherson State Maritime Institute]*, no. 1 (4), pp. 245–252, 2011. [in Ukrainian].

[11] P. D. Stukhlyak, A. V. Buketov, O. I. Redko, "Zalezhnist gidroabrazyvnoyi znosostijkosti epoksykompozytiv vid pryrody i vmistu dvokomponentnogo napovnyuvacha" ["Dependence of water jet durability of epoxycomposites of the nature and content of two-component filler"], *Problemy tertya ta znoshuvannya [Problems of friction and wear]*, vol. 53, pp. 159–174, 2010. [in Ukrainian].

[12] G. V. Martynyuk, "Vplyv napovnyuvachiv na protses polimeryzatsiynoho otrymannya epoksydnykh kompozytiv" ["Influence of fillers on the process of polymerization production of epoxy composites"], *Pervyy nezavisimyy nauchnyy vestnik [First Independent Scientific Herald]*, no. 1, pp. 36–39, 2015. [in Ukrainian].

[13] Yu. Danchenko, V. Andronov, E. Barabash, T. Obigenko, E. Rybka, R. Meleshchenko, A. Romin, "Research of the intramolecular interactions and structure in epoxyamine composites with dispersed oxides", *Eastern-European Journal of Enterprise Technologies*, vol. 6, no. 12 (90), pp. 4–12, 2017.

[14] Yu. Danchenko, V. Andronov, M. Teslenko, V. Permiakov, E. Rybka, R. Meleshchenko, A. Kosse, "Study of the free surface energy of epoxy composites using an automated measurement system", *Eastern-European Journal of Enterprise Technologies*, vol. 1, no. 12 (91), pp. 9–17, 2018.

[15] P. D. Stukhlyak, K. M. Moroz, "Vplyv porystosti u systemi epoksydna matrycya – polivinilovyj spyrt-dyspersnyj napovnyuvach na udarnu vyazkist" ["Influence of porosity in epoxy matrix – polyvinyl alcohol – disperse filler system on impact viscosity"], *Fizyko-khimichna mekhanika materialiv [Physicochemical Mechanics of Materials]*, vol. 46, no. 4, pp. 27–34, 2010.

[16] V. Kashytskyi, P. Savchuk, V. Malets, Y. Herasymiuk, S. Shchehlov, "Examining the effect of physical fields on the adhesive strength of protective epoxy composite coatings", *Eastern-European Journal of Enterprise Technologies*, vol. 3, no. 12 (87), pp. 16–22, 2017.

[17] V. M. Malets, I. V. Shvets, V. P. Kashytskyi, P. P. Savchuk, "Optymizatsiya skladu epoksykompozytnykh pokryttiv napovnenykh dyspersnym poroshkom tsyrkoniyu" ["Optimization of the composition of epoxy composite coatings filled by dispersed powders of zirconium"], *Naukovi notatky [Scientific Notes]*, vol. 50, pp. 118–122, 2015.