Submitted: August 7, 2023 Revised: September 20, 2023 Accepted: October 27, 2023

Evaluation of the efficiency of anti-corrosive protective coating based on epoxy polymers for protecting pipelines and metal structures

T.A. Grigoryeva [1]✉, **E.A. Khabarov** [1], **Z.V. Khabarova** [2],

[1] Ukhta State Technical University, Russia, Ukhta

[2] Engineering and technical center of OOO Gazprom transgaz Ukhta, Ukhta, Russia

✉ grigorjeva.tan@gmail.com

ABSTRACT
Studies have been carried out to assess the effectiveness of a protective anticorrosive internal coating for pipelines and metal structures, made on the basis of an epoxy polymer material modified with nanoparticles of aluminum oxide. The proposed protective coating has been checked for compliance with the specified characteristics: high corrosion resistance and abrasion resistance, resistance to icing, high adhesion to the protected material, processability of application.

KEYWORDS
protective coating • corrosion resistance • icing • composite material • epoxy polymers • edge angle • adhesion

Citation: Grigoryeva TA, Khabarov EA, Khabarova ZV. Evaluation of the efficiency of anti-corrosive protective coating based on epoxy polymers for protecting pipelines and metal structures. *Materials Physics and Mechanics*. 2024;52(1): 150–155.
http://dx.doi.org/10.18149/MPM.5212024_15

Introduction

To ensure reliable and long-term operation of metal structures and pipelines, it is necessary to take into account all the factors influencing the change in the properties of the materials from which they are made, as well as to take the necessary measures to reduce or eliminate the negative influence of the external environment on them.

Pipelines and metal structures operating in the oil and gas industry are influenced by a number of external factors: relative air humidity, time of periodic moistening of the steel surface, atmospheric pollution with aggressive gases (CO_2, SO_2, SO_3, NO_2, H_2S, etc.); dustiness (presence of small mineral particles in the air), changes in air temperature; presence of spores of fungi and bacteria in the air, etc [1,2]. In addition, the processed and transported raw materials and products are themselves corrosive compounds: gas condensate, oil and oil products, formation water.

A promising way to increase the resource and reliability of oil and gas equipment and pipelines is to modify their surfaces by applying protective coatings that meet a number of requirements: high corrosion resistance, resistance to icing, high adhesion, crack resistance, etc.

Technologies for applying coatings on pipes and metal structures based on epoxy resins have been used for a long time. The experience of their application accumulated during this time shows that the use of these coatings is promising for reducing energy consumption during the operation of pipelines, and various structures when working with aggressive media [3–7].

The properties of epoxy polymers can be easily controlled both by selecting the epoxy oligomer - hardener system and by introducing active (modifying) fillers. The use of oxide surfaces with different acidity or basicity allows you to control the adhesion of the matrix epoxy polymer on various surfaces, the method of application, resistance to external influences and other characteristics [8–12]. The effectiveness of aluminum oxide as a modifying component that improves performance characteristics has been shown in a number of studies [13-15].

The purpose of the study: to evaluate the effectiveness of protective anticorrosive internal coating of pipelines and metal structures, made on the basis of epoxy-polymer material modified with aluminum oxide nanoparticles. In order to achieve the set goal the tasks are defined:

1. to carry out studies of corrosion resistance and abrasion and icing resistance;
2. research adhesion of the applied material to steel substrate.

Materials and Method

In this work, we used an epoxy oligomer brand ED-20 (GOST 10587-84), iso-methyltetrahydrophthalic anhydride brand iso-MTHFA (TU 6-09-3321-73) as a hardener and a catalyst: 2,4,6, -tris (dimethylaminomethyl) phenol grade alcofen (TU 6-09-4136-75), nanodispersed aluminum oxide (99.6%) from Nanox was selected as a modifying component. This oxide was chosen based on previous experiments [11,14].

Steel grade ASTM A694 F65 was determined as a substrate. For the research, an epoxy-polymer matrix was selected with the composition: oligomer - epoxy resin ED-20 + hardener i-MTHFA, in a ratio of 100: 80 mass parts.

Mixing of ED-20 epoxy resin with filler was carried out on a stirrer at a speed of 500 rpm at a given temperature (80 °C) for 45 minutes, then the mixture was stirred for another 60 minutes. The aluminum oxide concentration was 1 % by weight of the epoxy resin weight. The choice of the conditions for the experiment and the concentration of the filler is based on the literature data and the results of previous studies.

The assessment of the adhesive properties of the coating under study was carried out according to the values of the contact angle of wetting. The contact angle was measured using an OSA-15EC DataPhysics Instruments GmbH optical device using the lying drop method. The prepared mixture in a heated state was applied to the surface of the studied substrate using a syringe with a thin needle (d = 0.6 mm), and the dynamic tracking function was simultaneously turned on.

Further measurements of the contact angle were carried out at room temperature in the course of dynamic tracking with fixing the readings every 10 seconds for an hour for each sample.

Steel samples treated in accordance with GOST 9.506-87 were coated and cured in a drying cabinet at a constant temperature (180 °C) for 3 hours, and then dried at room temperature. Area of steel plates (average) - 10 cm^3, coating area 5 cm^3.

These methods for evaluating the effectiveness of coatings have been tested on the development of similar materials, are quite representative [16–18].

Determination of corrosion resistance of coated steel plates in aggressive media was carried out on the basis of the methods described in GOST 9.308 Unified Corrosion and Aging Protection System. Metallic and non-metallic inorganic coatings. Methods of accelerated corrosion tests and GOST 9.506-87 GOST 9.506-87 Unified Corrosion and Aging Protection System. Metal corrosion inhibitors in water-oil media. Methods for determining protective capacity.

The prepared samples were located on the corresponding Wednesday, and were maintained in case of a water-oil emulsion at a temperature of + 55 °C within 24 hours, when hashing on the magnetic mixer with a speed of 1800 rpm.

The main principle of the gravimetric method of determination corrosion resistance is in evaluation of the mass loss of the test items after keeping them in corrosive medium in conditions close to the industrial [8].

Table 1. Physico-chemical properties of produced water (model)

Indicator	Value
Density at 20 °C, kg/m^3	1002.1
pH	6.72
Suspended solids, mg/dm^3	9.56
Eotal dissolved, mg/dm^3	219.5

Table 2. Physico-chemical properties of oil emulsion

Indicator	Value
Density at 20 °C, kg/m^3	865.5
Mass. % water	2.4
Chloride salts, mg/dm^3	22.1
Mass. % sulfur	1.24
Mass. % mechanical impurities	0.0092
Mass. % paraffin	7.2
Mass. % resins	15.66
Mass. % asphaltenes	3.81
Fractional composition at 200° C, %	19.4
Fractional composition at 300° C, %	37.4

Table 3. Properties of corrosive structure

pH	1.2
Mass. % mechanical impurities	5.4

Since while the evaluation of the quality of cover its omnitude is important, research of corrosion resistance has been conducted in three media: 1 - the model of produced water with total dissolved solids 250 mg/dm^3; 2 - water-oil emulsion of North Savinoborsk origin with 12 % watering and the contents of mechanical impurities 0.95 %; 3 - fresh water, acidated with commercial hydrochloric acid solution to the indicator pH = 3.0 (aggressive substances). Properties of environments are shown in Tables 1-3.

All studies were carried out for three samples: an initial steel sample without a coating, a sample coated with an epoxy polymer without the addition of a modifier, and a sample with a modified coating. For the same samples, studies were additionally carried out to determine the resistance to icing by the gravimetric method.

The ice resistance of the coating was determined by the edge angle of wetting using the lying drop method. The suitably prepared coated and uncoated steel samples were dosed with fresh and salty water and the angle values recorded at the initial moment and after 10 minutes. The values of the edge angle Θ more 100° indicate the superhydrophobicity of the coating.

Results and Discussion

Evaluation of adhesive ability of coating

Epoxy polymers can contain OH groups, electronegative atoms, such as oxygen, chlorine and others, which can interreact with functional groups on the initial substance surface, providing high bond strength.

Injection of modifying component – aluminium oxide leads to formation of additional active sites, that leads to adhesion build and change of mechanical characteristics of epoxypolymeric materials. Usage of oxide surface with different acidity or basicity allows to control adhesion of matrix epoxy polymer on different surfaces. Acid-basic type of substrate was found out by free surface energy determination (FCE). It consists of the following components: dispersive, associated with intermolecular interaction of instantaneous dipoles and acid-basic type, associated with all other non-dispersive reasons (measurement according to the method of van Oss-Chodery-Good) [19].

Amounts of this components was estimated by the measuring of water contact angle of substrate surfaces by test matters: Lewis acids (phenol and glycerine) and bases – aniline and formaldehyde. According to the result of the researches free surface energy of the substrate under discussion (steel 17G1S) 24.90 MJ/m^2, dispersion component of FSE is 20.29 MJ/m^2, polar – 4.61 MJ/m^2.

As it has been said before, there are acid and base sites on the surface of aluminium oxide, used as the filler, so it is likely that in support of absorption theory of adhesion this modifying component is sure to influence the adhesive attributes of the epoxy materials respectively to the substrate with the basic nature [20,21].

The effect from loafing of filler can be considered positive providing derating of water contact angle of promoted epoxy polymer in comparison with the initial, because smaller amounts of water contact angle mean better wettability of the substrate by the adhesive. The work of adhesion was calculated by Young – Dupre equation (Table 4).

Table 4. Adhesion characteristics of the coating

Sample material	Cos*Θ*	*Wa*/*Wk*	*Wa*, mJ/m^2
Unmodified resin coating	0.4384	0.7192	56.1
Coating with aluminium oxide	0.8192	0.9096	65.5

The method of measuring of water contact angle showed, that injection of nanodispersed aluminium oxide in polymeric matrix under chosen optimal conditions improves wettability of epoxy binder to steel substrate.

The interaction between nanoparticles of aluminium oxide and epoxy matrix depend on physicochemical properties of particle surfaces and affects fundamentally on further processes, that run on while separation of the adhesive from the substrate, aced-base interaction between which determine the adhesive strength.

Evaluation of corrosive resistance of the sample materials

For assessment of corrosion resistance of metals and alloys with anticorrosive protection and without her use various criteria:
1. change of appearance of a sample during test;
2. time which passed before emergence of the first center of corrosion of base metal or a covering;
3. quantity and distribution of corrosion defects;
4. change of the weight (GOST P 9.907);
5. change of the sizes (especially thickness).

The results of the research show, that coating provides good corrosion resistance to steel article of interest in high aggressive substances: corrosion rate decreases in more than two times in comparison to raw sample. Level of protection increases while injection of modifying component in epoxypolymeric matrix. This effect can be explained, as it has been said before, by formation of interfacial additional sites, that provide firmer adhesion and more continual and homogemnous application (Table 5).

Table 5. Evaluation of corrosion resistance of the surface

Sample	Media	Speed of corrosion, mm/yr	Appearance
Without coating	1	0.221	All surface area has scratches and compression marks with the dimeter of 1 mm
	2	0.198	
	3	0.265	
Bare coating	1	0.112	No changes
	2	0.104	Slight scratches
	3	0.131	No changed
Coating with filler	1	0.088	No changes
	2	0.092	Slight scratches
	3	0.082	No changes

Conclusion

The obtained results allow to state that protective coating on the base of epoxypolimeric matrix, modified by particles of fumed alumina is expected to increase the safety of steelworks, used in conditions of Extreme North, the Arctic and shelf sea, described by low temperatures of environment, humidity and aggressive corrosion attack.

Interaction between nanoparticles of aluminium oxide and epoxy matrix depends on physicochemical characteristics on the surface of the particles and influences on the further processes while separation of the adhesive from the substrate, acid-base interaction of which results in adhesive strength, high workability of application, that provide continual application and high security level in corrosive medium.

References

1. Wasim M, Milos BD. External corrosion of oil and gas pipelines: A review of failure mechanisms and predictive preventions. *Journal of Natural Gas Science and Engineering*. 2022;100: 104467.
2. Dong B, Zeng D, Yu Z, Cai L, Yu H, Shi SZ, Tian G, Yi Y. Major corrosion influence factors analysis in the production well of CO_2 flooding and the optimization of relative anti-corrosion measures. *Journal of Petroleum Science and Engineering*. 2021;200: 108052.

3. Parhizkar N, Ramezanzadeh B, Shahrabi T. Corrosion protection and adhesion properties of the epoxy coating applied on the steel substrate pre-treated by a sol-gel based silane coating filled with amino and isocyanate silane functionalized graphene oxide nanosheets. *Applied Surface Science*. 2018;439: 45–59.
4. Deyab NA, Ouarsa R, Al-Sabagh AM, Lachkar M, El Bali B. Enhancement of corrosion protection performance of epoxy coating by introducing new hydrogenphosphate compound. *Progress in Organic Coatings*. 2017;10: 37–42.
5. Boomadevi Janaki G, Xavier JR. Evaluation of Mechanical Properties and Corrosion Protection Performance of Surface Modified Nano-alumina Encapsulated Epoxy Coated Mild Steel. *J Bio Tribo Corros*. 2020;6: 20.
6. Caldona EB, Wipf DO, Smith Jr DW. Characterization of a tetrafunctional epoxy-amine coating for corrosion protection of mild steel. *Progress in Organic Coatings*. 2021;151: 106045.
7. Zhang J, Zhang W, Wei L, Pu L, Liu J, Liu H, Li Y, Fan J, Ding T, Guo Z. Alternating multilayer structural epoxy composite coating for corrosion protection of steel. *Macromolecular Materials and Engineering*. 2019;304(12): 1900374.
8. Mallakpour S, Khadem E. Recent development in the synthesis of polymer nanocomposites based on nano-alumina. *Progress in Polymer Science*. 2015;51: 74–93.
9. Jin FL, Li X, Park SJ. Synthesis and application of epoxy resins: A review. *Journal of Industrial and Engineering Chemistry*. 2015;29: 1–11.
10. Chowaniec A, Sadowski Ł, ŻA. The chemical and microstructural analysis of the adhesive properties of epoxy resin coatings modified using waste glass powder. *Applied Surface Science*. 2020;504: 144373.
11. Sitnikov PA, Ryabkov YI, Belykh AG, Vaseneva IN, Kuchin AV. Physicochemical laws of the creation of new hybrid epoxy-polymer nanocomposites with increased strength characteristics. *Proceedings of the Komi Science Centre of the Ural Division of the Russian Academy Of Sciences*. 2016;25: 18–22. (In Russian)
12. Chebotareva EG, Ogrel LY. Modern trends in modification of epoxy polymers. *Fundamental Research*. 2008;4: 102–104. (In Russian)
13. Zolotareva VV, Popova OS. Evaluation of the physical and mechanical characteristics of epoxy polymers filled with dispersed fillers. *Fundamental and Applied Research of the Cooperative Sector of the Economy*. 2015(3): 135–142. (In Russian)
14. Faghihi M. Properties of alumina nanoparticle-filled nitrile-butadiene-rubber/phenolic-resin blend prepared by melt mixing. *Polymer Composites*. 2009;30(9): 1290–1298.
15. Kaybal HB. Effects of alumina nanoparticles on dynamic impact responses of carbon fiber reinforced epoxy matrix nanocomposites. *Engineering Science and Technology, an International Journal*. 2018;21(3): 399–407.
16. Khabarova, ZV. Evaluation of the effectiveness of the developed protective coating for metal structures with increased corrosion resistance and resistance to icing. *Equipment and Technologies for the Oil and Gas Complex*. 2021;4(124): 70–74. (In Russian)
17. Khabarova ZV. *Protective composite coating with increased corrosion resistance and resistance to leaking*. 2020. (In-Russian)
18. Morozova ZV. Development of composite coating with corrosion resistance and resistance to icing for the protection of pipelines and reservoirs. In: *Salnikov. Bulatovskie readings: materials of the I International Scientific and Practical conference (March 31, 2017)*. Krasnodar; Publishing House-Yug; 2017. p.64–68. (In Russian)
19. Van Oss CJ. Use of the combined Lifshitz–van der Waals and Lewis acid–base approaches in determining the apolar and polar contributions to surface and interfacial tensions and free energie. *Journal of Adhesion Science and Technology*. 2002;16(6): 669–677.
20. Starostina IA, Burdova EV, Sechko EK, Huzahanov RM, Stoyanov OV. Influence of acid-base properties of metals, polymers and polymer composite materials on adhesion interaction in metal-polymer systems. *Bulletin of Kazan Technological University*. 2009;3: 85–95. (In Russian)
21. Starostina IA, Makhrova NV, Stoyanov OV, Aristov IV. Assessment of acid and basic parameters of free surface energy using polymer surfaces. *Bulletin of Kazan Technological University*. 2011;14: 150–157. (In Russian)

About Authors

Tatyana A. Grigoryeva
Assistant Professor (Ukhta State Technical University, Russia, Ukhta)

Egor A. Khabarov
PhD Student (Ukhta State Technical University, Russia, Ukhta)

Zoya V. Khabarova
Engineer (Engineering and technical center of OOO Gazprom transgaz Ukhta, Ukhta, Russia)