

Influence of physical fields upon adhesive strength of epoxy composite protective coatings in oil and gas sector

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Abstract

The article investigates the influence of ultrasonic treatment and electromagnetic radiation on the adhesive strength of epoxy composite coatings in oil and gas sector, containing fine-particles. The results of research have been analyzed, optimal composition and type of treatment of epoxy polymer composition on the stage of formation have been selected. The introduction of high particle content ensures optimal significant improvement of study characteristics that indicate the future of research in this area and the feasibility of formation of high quality protective epoxy composite coatings.

Keywords: *electromagnetic radiation, epoxy composite material, fine powder, ultrasonic processing.*

Problem formulation. Polymer composites are considered to be perspective materials that can be used as protective coatings to protect oil and gas process equipment from corrosive environments, variable temperatures and dynamic loads. This can significantly increase the durability, reliability and performance of machine parts and steel structures of oil and gas equipment. A key role in ensuring the reliability of the materials is played by an adhesive bond between the polymer and the substrate because its strength and stability stipulate physical, mechanical and performance characteristics of coatings. The strength of the adhesive connection with the substrate polymer matrix is determined by the intensity of molecular and chemical interactions in the point of contact of polymercomposite material with the metal base. Adhesive strength of coatings depends on the nature of the polymer, substrate and the state of its surface.

Polymer composite materials based on epoxy binders, containing superfine fillers, have high adhesive strength. These materials are characterized by high adaptability when applied on parts with complex surface profile and are characterized by high performance in terms of aggressive environments impact [1]. The efficiency of modification of thermosetting polymers by fine particles depends on the following characteristics of the filler, such as: particle size and shape, the bulk of its content, particle size distribution, uniform distribution of filler in the polymer matrix [2].

Due to the high surface energy fine particles are characterized by a tendency to form agglomerates and sedimentation, which complicates their uniform distribution in the polymer. Compositions are irradiated by external energy fields at the stage of formation to guarantee uniformity of structure and high stability of phase composition [3]. Application of these fields enables us to customize a supramolecular structure, density as well as mechanical properties of epoxycomposite materials. Treatment of polymer composites with electromagnetic field or ultrasound is rather perspective in this regard, it helps to promote equal distribution of structural components, enhance interaction at the interface and reduce defects in the system [4].

Thus, the development of technology of treatment of epoxy composites with external physical fields at the stage of heterogeneous structure formation, which allows to reduce the degree of aggregation of particles and ensure uniformity of the system is an actual scientific and practical problem.

Materials and research methods. In this work epoxy composite materials based on epoxy resin of ED-20 brand (GOST 10587-84), which is a liquid reactive oligomeric product based on diglycidyl ether of diphenyl propane, have been investigated. Coatings based on ED-20 resin are characterized by high adhesion to metal, glass, ceramics, high hardness, elasticity, high dielectric properties, resistance to aggressive environments. Compositions have been solidified, using polyetylen poliamin (TU 6-02-594-70), characterized by a high rate of interaction of primary and secondary amino groups with epoxy groups at room temperature.

Superfine powder of iron PZHR-3, carbonyl iron R-20 and teflon 4PN-20 have been used as fillers. Maximum filler content was 40 pts. wt. for 100 pts. wt. of oligomer.

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Iron powder PZHR 3 (GOST 9849–86) contains not less than 97% of metallic iron, dispersion of particles is 300...500 mc. The powder is obtained by spraying molten steel with water under high pressure.

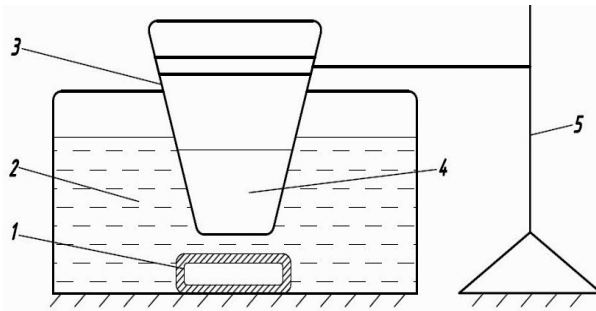
Carbonyl iron of P-20 brand (GOST 13610–79) is fine powder of pure iron, produced by thermal decomposition of iron pentacarbonyl. The powder contains spherical particles without sharp protrusions of layered structure, the average diameter of particles is 2.5–3.5 mc.

Fluorocarbon of 4PN-20 brand (GOST 10007–80) is tetrafluoroethylene polymer powder with the dispersion of 6...20 mc. High bonding strength of fluorine and carbon atoms causes high chemical and physical properties. The powder is heat-resistant, resistant to corrosive media, has high mechanical, insulating, anti-friction properties and the ability to maintain the above mentioned properties in a wide range of operating temperatures and pressures.

The adhesion strength research method have been used in order to define tailored composition and technology of formation of epoxy composites filled with fine particles (GOST 14759–69). In accordance with the above mentioned method the study material was applied on the front surface of the rod with a conical projection in place for self-centering grips. After epoxy composite layer structuring, research was conducted on tensile machine of UMM-5 brand at the lower traverse velocity of 2 mm/min.

Building of prototypes involved obtaining a homogeneous composition, containing necessary components with mechanical mixing of components at every stage to ensure high uniformity of the system. Obtained composition was applied to the prepared surface. Surface was previously treated with an abrasive to achieve the desired roughness and degreased with acetone.

Ultrasonic treatment has been performed in a laboratory ultrasonic unit (Fig. 1) in the medium of water at a frequency of 20 kHz. The resulting polymer composition in the vessel was placed at a distance of 10 mm from the source of ultrasonic waves. The optimal duration of treatment was 15 min.



1 – the source of radiation; 2 – medium (water); 3 – container; 4 – composition; 5 – tripod

Figure 1 – The layout of ultrasonic treatment of composition

To study the magnetic field impact electromagnetic mixer has been used. The treatment was performed in the air medium at a frequency of 50 MHz. The resulting composition was placed above the source of electromagnetic waves.

Material solidification was held by the following modes: shutter for 24 h at 18 °C; 1 hour of exposure at 70 °C, 1 hour at 100 °C, 4 h at 130 °C.

Discussion of results. As a result of conducted research it has been found out (Fig. 2) that with the introduction of ultrafine PTFE powder (6 pts. wt.) into the polymer matrix adhesive bond is rapidly increased 2.5 times and has a maximum value ($\sigma_a = 43.22$ MPa) as compared to unfilled system ($\sigma_a = 17.3$ MPa). PTFE powder promotes the formation of a strong adhesive bond between the filler surface and polymer matrix due to its high capacity for wetting and homogeneous polymer composition.

It has been established that the range of critical content of dispersed PTFE powder particles in a matrix is 6–10 pts. wt., at this value the adhesive strength of epoxy composites materials reaches the maximum value.

Increase of powder content in the composition in the range of 20–40 pts. wt. leads to a smooth decrease in values of adhesion due to the presence of agglomerates that have been formed due to incomplete wetting of

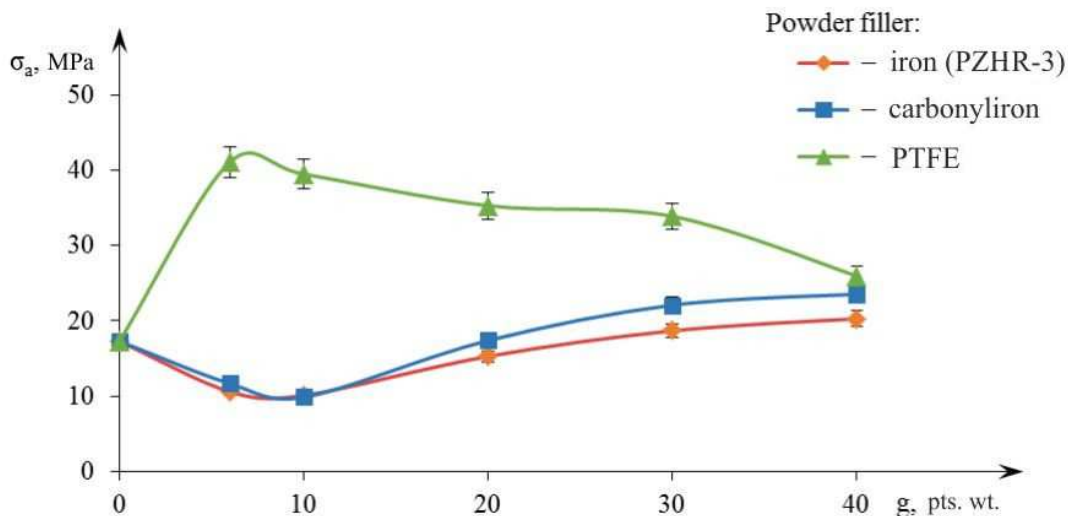


Figure 2 – Dependence of adhesive strength of epoxy composites upon filler content

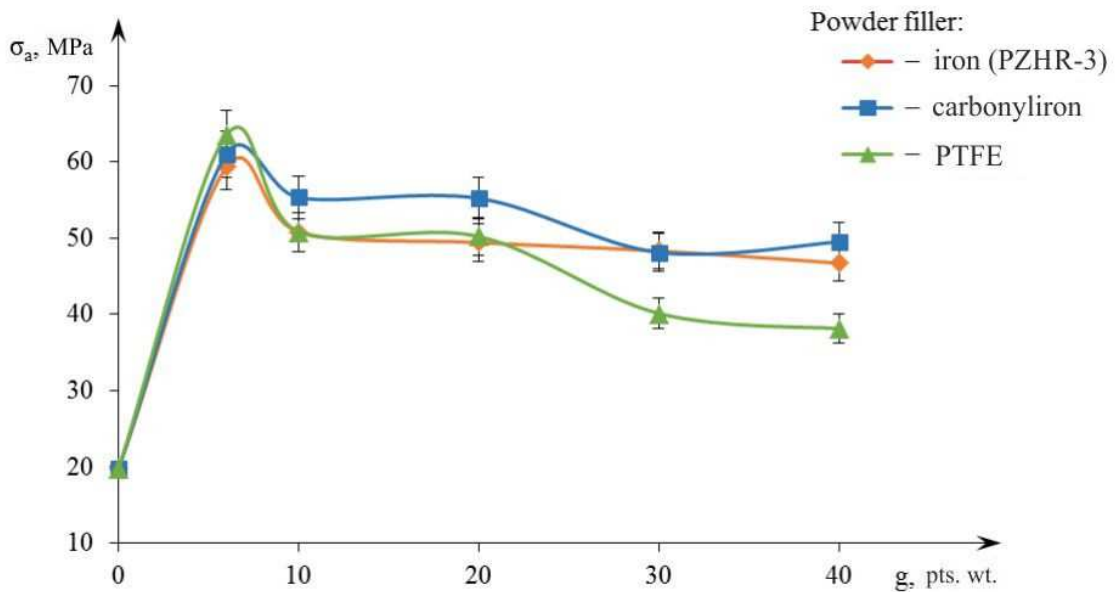


Figure 3 – Dependence of adhesive strength of epoxy composites, modified by electromagnetic field, upon filler content

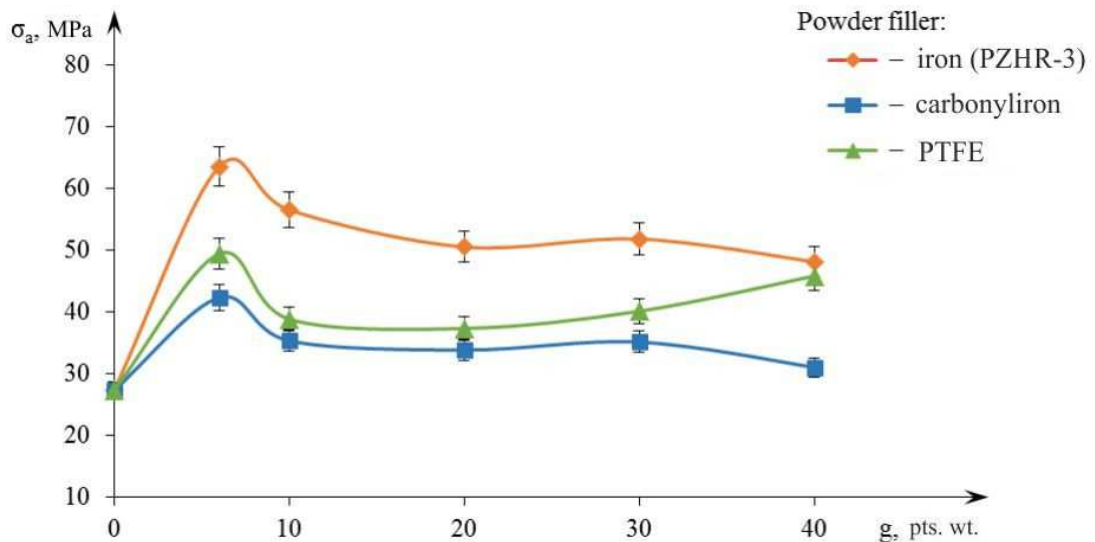


Figure 4 – Dependence of adhesive strength of epoxy composites, modified by ultrasound upon filler content

particles with polymer, resulting in uneven distribution of filler in the volume matrix.

For systems filled with powder of iron PZHR-3 and carbonyl iron P-20 (for filler content of 6–10 pts. wt.) adhesive strength is 1.7–2.8 times decreased, apparently due to lack of formation of chemical bonds between macromolecules of polymer matrix and reinforcing particles, as evidenced by research degree structure, which is characterized by low content of gel fraction in the system.

At higher levels of system filling with powders PZHR-3 and 4PN-20 (20–40 pts. wt.) adhesive strength of polymer composites is increased by a factor of 3.5–4.5. This indicates a growing degree of cross-linking of the matrix in the outer surface layers around the filler, which increases the physical and mechanical properties of these polymer composite coatings.

It has been defined that epoxy composition with fine fillers (Fig. 3) is more sensitive to the influence of

the electromagnetic field, compared to the polymer matrix, as a slight increase of adhesive strength of epoxy polymers by a factor of 1.3 is recorded after processing of the composition in an electromagnetic field as compared to untreated epoxy polymer.

It has been experimentally defined that electromagnetic field treatment leads to a sharp increase of characteristic under investigation (1.5–12 times) at low degrees of system filling (6–10 pts. wt.) with fine of different chemical composition compared to untreated system. Additional treatment of investigated materials, filled with fine particles with electromagnetic field enhances the adhesive strength of epoxy composites due to improvement of polymerization conditions. On the surface of particulate filler particles centers are activated as a result of the external field impact, which in the process of epoxy composites formation intensify structuring processes, resulting in increase of the number of links between the binder and the surface of

dispersed particles. This reduces the molecular mobility in the intermediate boundary layers and increases the degree of material cross-linking.

Adhesive strength of epoxy polymers in the course of ultrasound treatment (Fig. 4) increases by 1.7 times compared to the untreated polymer matrix and 1.5 times compared with electromagnetic field treatment of epoxy polymer composition. Ultrasonic treatment provides a higher degree of homogeneity of epoxy composites as a result of the intensification of interaction between the components of the system and reduction of system defects in general.

Ultrasound treatment facilitates the increase of adhesion strength of epoxy composites at low degrees of system filling (6–10 pts. wt.): 1.2 times for PTFE, 3 times for carbonyl iron and 12.6 times for iron of PZR-3 mark. Increased adhesion as a result of ultrasound treatment can be explained by appearance of active sites on the reinforcing elements surface and free radicals in the polymer basis macro molecules, accompanied by formation of hydrogen bonds between resin carbonyl groups and particulate filler surface.

Conclusions

The introduction of fine fillers allows to increase the adhesive strength of the polymer matrix, so epoxy composites with fine fillers are highly promising materials in terms of their use for formation of process equipment protective coatings. However, the introduction of fine fillers of the epoxy resin results in the formation of defects (cavities, pores) and the uneven distribution of particles in a polymer matrix, which is mainly due to the formation of agglomerates of particles. Low values of adhesive strength of polycomposite systems can be explained by increased viscosity of the solution. As a result the solution doesn't fill the asperities of the substrate completely.

To improve the uniformity of distribution of reinforcing elements and phase stability, epoxy polymer composition must be irradiated with the external physical fields. Application of these fields enables you to customize a supramolecular structure and mechanical properties of epoxy composite materials.

Treatment of compositions with external physical fields improves the interaction of components and promotes uniform distribution in the bulk composition through improved mobility and stream lining of the filler particles in the polymer matrix. Additional processing of epoxy composite coatings, developed at low degrees of system filling 6–10 (pts. wt.) increases the adhesion strength (1.5–12 times) when exposed to electromagnetic fields. Mean while ultrasound treatment promotes the increase of characteristic under investigation (1.2–12.6 times), enhancing feasibility indicators of developed epoxy composite protective coatings.

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Вплив фізичних полів на адгезійну міцність епоксидних композитних захисних покриттів в нафтогазовій галузі

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Наведено результати досліджень впливу ультразвукової обробки та електромагнітного випромінювання на адгезійну міцність епоксидних композитних покриттів нафтогазового комплексу, що містять високодисперсні частинки. Проаналізовано результати досліджень, вибрано оптимальний склад та вид обробки епоксиолімерної композиції на стадії формування. Введення високодисперсних частинок за оптимального вмісту забезпечує значне покращення досліджуваної характеристики, що вказує на перспективність даного напрямку досліджень та доцільність створення високоякісних захисних епоксидних композитних покриттів.

Ключові слова: *високодисперсний порошок, електромагнітне випромінювання, епоксидний композитний матеріал, ультразвукова обробка.*