# Influence of nanoparticles on the physical and mechanical properties of modified epoxy-composite coatings

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**Abstract**

In the work, to form a composite material with increased physical and mechanical properties, an epoxy diane oligomer ED-20, a hardener polyethylene polyamine PEPA and a modifier 2,4 diaminotoluene were used as a binder. The dependence of the nanoparticle content as a mixture of nanodispersed compounds on the physicomechanical properties of epoxy composites was studied. To form a protective coating with increased cohesive properties, the optimal content of nanoparticles is q = 0.5 pts.wt. by 100 parts by weight of epoxy oligomer ED-20, which provides an increase in the ability of the developed material to resist static, dynamic, and shock loads. The adsorption and catalytic activity of nanofillers has been proved by optical spectroscopy, which provides interaction with the side chains of the epoxy oligomer chain, as a result of which the cohesive strength of the materials increases.

Keywords: *epoxy composite, fracture stresses during the flexion, modulus of elasticity, nanoparticles, resilience.*

Nowadays the development of polymer nanocomposite materials is one of the ways of polymer technologies development. If we introduce inorganic nanodispersed fillers as components to a polymer binder, we can improve the properties of composite materials (CM), developed on their basis [1, 2]. Epoxy polymers are widely used in the oil and gas industry as matrices for such materials due to a wide range of their properties. These include: increased cohesive and adhesion strength, chemical resistance, workability, resistance to aggressive environments and relatively low cost [3–5]. Epoxy composites with a dense three-dimensional mesh structure have relatively high thermal stability and glass transition temperature. At the same time, such materials are susceptible to fragile destruction and have a low counteraction to the propagation of cracks when they are operated under critical conditions. This limits their use in the oil and gas industry to increase the stability of protective coatings. Therefore, increasing the cohesive strength of the CM without reducing the thermophysical properties is a prerequisite for the formation of materials that are exposed to stress.

The authors [6, 7] researched the properties of CM on the basis of epoxy diane resin for different contents of nano-fillers. The regularities of surface and bulk modification for obtaining polymer materials with increased performance parameters [8] have been established. The modes of ultrasonic treatment of epoxy compositions have been investigated in order to form disperse systems with uniform distribution of nanoparticles in volume [9]. This allows the formation of protective coatings and CM with improved cohesive properties. It is proved that the introduction of insignificant content of nano-fillers increases the ability of materials to resist static and dynamic (including shock) load [10]. In the papers of [11, 12] it is shown that for insignificant content of nano-dispersed fillers, the indexes of physical and mechanical properties of CM are increased. Therefore, the study of the effect of various nano-fillers on the properties of epoxy composites is an urgent task in creating materials with increased performance characteristics for the oil and gas industry.

The aim of the work is to study the influence of nanoparticles as a mixture of nanodispersed compounds (MNDC) on the cohesive properties of epoxy composites.

### Materials and methods of research

The epoxy diane oligomer ED-20 (GOST 10587–84), which is characterized by high adhesion and cohesive strength, slight shrinkage and technological efficiency when applied on the surface of a complex profile, is chosen as the main component of the binder during the formation of epoxy CM.

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2,4-diaminotoluene (DAT) is used as a modifier. The modifier was injected into the binder (1.00 mass parts for 100 mass parts of an epoxy oligomer ED-20) (hereafter mass parts referred to as for 100 mass parts of an epoxy oligomer ED-20). Molecular formula of the modifier is $C_7H_{10}N_2$. The molecular mass of 2,4-diaminotoluene is 122.1677. The melting point is 98 ºC. This substance is from a series of diamines of the phenylene series. The modifier is soluble in polar organic solvents, such as methanol, ethanol, acetone, ethyl acetate and is slightly soluble in water. It is used as a synthon for the synthesis of acridine dyes.

For cross-linking of epoxy compositions, a polyethylene polyamine PEPA (TU 6-05-241-202–78) hardener was used, which allows the materials to be cured at room temperatures. PEPA is a low molecular weight substance that consists of the following interconnected components: $[-CH_2-CH_2-NH-]_n$. CM was cross-linked, introducing the hardener into the composition at a stoichiometric ratio of components (mass parts) – ED-20 : PEPA – 100 : 10.

As a nanodispersed filler for experimental studies we used powders that are MNDC and are characterized by the following composition,%:

MNDC 1: $Si_3N_4$ – 59.5; $Al_2O_3$ – 24.4; AlN – 10.1; TiN – 6.0;

MNDC 2: $Si_3N_4$ – 85; $AlF_3$ – 5; IH – 5; ZrH – 5.

The granularity of the particles is as follows:

1. MNDC 1 – *d* = 20–80 nm.
2. MNDC 2 – *d* = 30–40 nm.

The characteristics of nano-fillers are given in Table 1.

**Table 1 – The characteristics of nano-fillers**

| Characteristics | $Si_3N_4$ | $Al_2O_3$ | AlN | TiN |
|---|---|---|---|---|
| Specific surface area S, $m^2/g$ | 44 | 44 | 39 | 48 |
| Particle size by heat adsorption method *d*, nm | 41 | 41 | 47 | 23 |
| Particle size by electron microscopy *d*, nm | 39 | 76 | 26 | 43 |

Epoxy composites were formed according to the following technology: warming the resin to a temperature $T$ = 353 ± 2 K and curing it at the given temperature during the time $t$ = 20 ± 0.1 min; hydrodynamic combination of oligomer, modifier and filler particles during the time $t$ = 10 ± 0.1 min; ultrasound processing of the composition during the time $t$ = 1.5 ± 0.1 min; cooling the composition to room temperature during the time $t$ = 60 ± 5 min; introduction of the hardener and mixing of the composition during the time $t$ = 5 ± 0.1 min. CM was cured according to the mode: the formation of specimens and their curing during the time $t$ = 12.0 ± 0.1 h at a temperature $T$ = 293 ± 2 K, heating at a speed of $\upsilon$ = 3 K/min to a temperature $T$ = 393 ± 2 K, curing during the time $t$ = 2.0 ± 0.05 h, slow cooling to a temperature of $T$ = 293 ± 2 K. In order to stabilize the structural processes in the composite, the samples were kept at a temperature of $T$ = 293 ± 2 K for $t$ = 24 h in air. This was followed by experimental testing.

In this study the following properties of CM were investigated: destructive stresses and elasticity modulus at bending, impact strength, the structure of the formed composites was investigated by optical microscopy.

Destructive stresses and elastic modulus at bending were determined according to GOST 4648–71 and GOST 9550–81 respectively. Parameters of samples: length $l$ = 120 ± 2 mm, width $b$ = 15 ± 0.5 mm, height $h$ = 10 ± 0.5 mm.

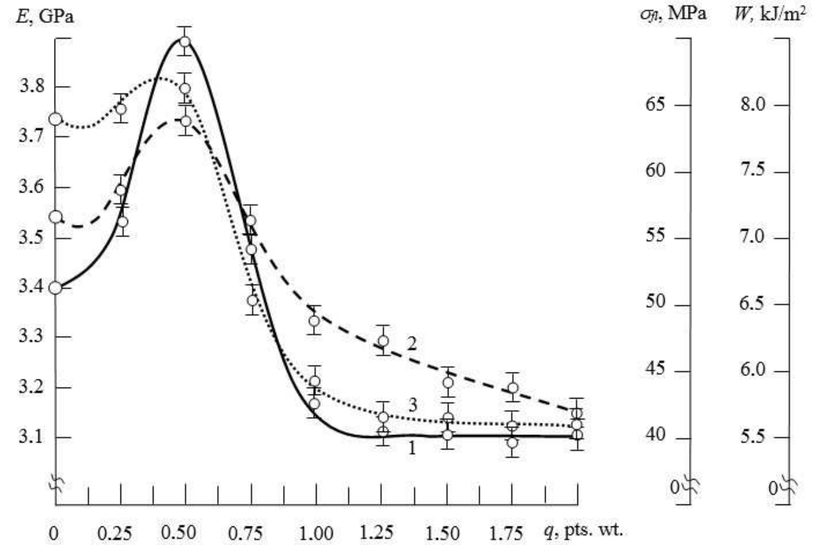
Impact viscosity was determined by the Charpy impact test according to GOST 4647–80 at the MK-30 pendulum spear at a temperature $T$ = 298 ± 2 K and a relative humidity $d$ = 50 ± 5 %. Samples with the following parameters were used: (63.5×12.7×12.7) ± 0.5 mm. The distance between the supports is 40 ± 0.5 mm.

Deviations of the values in the studies of the adhesion and physical and mechanical properties of the CM were 4–6 % of the nominal.

**Results and discussion**

The influence of nanodispersed particles on the physical and mechanical properties of CM is investigated in this paper. The developed epoxy matrix based on the oligomer ED-20 (100 mass parts) was previously modified with 2,4-diaminotoluene (1 mass part) and treated with ultrasound (before the introduction of the hardener). After cooling the composition to room temperature, a polyethylenepolyamine hardener was injected into the binder (10 mass parts).

It is established (Fig. 1) that the values of destructive stress and elastic modulus at bending of the modified epoxy matrix are respectively $\sigma_{ben}$ = 57.2 MPa and $E$ = 3.4 GPa, and the impact strength is $W$ = 7.9 kJ/m$^2$. In the first stage, regularities of the influence of the filler of MNDC 1 on the physical and mechanical characteristics of the CM were established. Results of experimental tests of CM for the contents of a nano-filler in the range of $q$ = 0.10–2.00 mass parts are presented in Fig. 1. It was established that with insignificant introduction of the additive in the quantity of $q$ = 0.10 mass parts, the cohesive properties of the material are almost unchanged. Indicators of destructive stress and elastic modulus at bending have the following values: $\sigma_{ben}$ = 57.0 MPa, $E$ = 3.5 GPa, impact strength – $W$ = 7.7 kJ/m$^2$. As the content of the filler increases to $q$ = 0.50 mass parts, an increase in the indexes of the properties of studied CM is observed. Correspondingly, the parameters of the destructive stresses at bending increase from $\sigma_{ben}$ = 57.2 MPa (for a modified epoxy matrix) to $\sigma_{ben}$ = 63.7 MPa (Fig. 1, curve 1), the elastic modulus for bending increases from $E$ = 3.4 GPa to $E$ = 3.9 GPa (rice 1, curve 2), and indicators of impact strength – from $W$ = 7.9 kJ/m$^2$ to $W$ = 8.1 kJ/m$^2$ (Fig. 1, curve 3). It is obvious that for the given content of MNDC 1, compounds that make it up have a positive effect on the physical and mechanical properties of the materials under study. With a further increase in the content of nano-dispersed filler ($q$ = 1.00–2.00 ppm), a




*1 – the modulus of elasticity at bending (E); 2 – fracture stresses at bending ($\sigma_{fl}$); 3 – impact viscosity (W, kJ/m$^2$)*

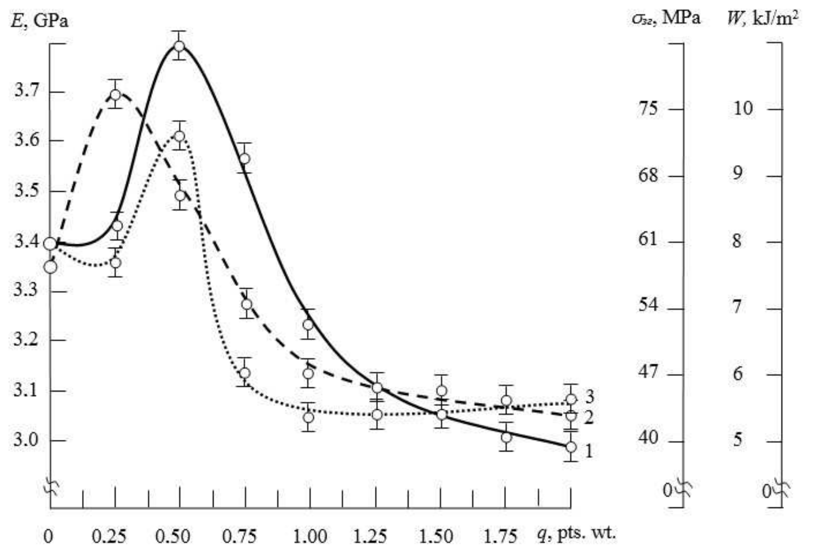
**Figure 1 – Dependence of physical and mechanical properties and impact viscosity of the CM on the content of the filler MNDC 1**

decrease in the values of destructive stresses at bending and toughness was observed up to $\sigma_{ben}$ = 41.2–47.6 MPa and W = 5.4–5.6 kJ/m$^2$. By increasing the content of the filler over q = 1.00 mass parts, the parameters of the elastic modulus at bending almost do not change and make *E* = 3.1 GPa (Fig. 1, curve 2). Thus, it has been experimentally established that when introducing into the modified epoxy matrix of a nano-dispersed additive such as a MNDC 1 (d = 20–80 nm) (0.50 mass parts), the destructive stresses at bending, the elasticity at bending and impact strength are maximally raised to $\sigma_{ben}$ = 63.7 MPa, *E* = 3.9 GPa and *W* = 8.1 kJ/m$^2$ respectively. To obtain a CM with improved performance, it is appropriate to use a material with the following composition: epoxy resin ED-20 (100 mass parts), 2,4-diaminotoluene modifier (1 mass part), PEPA hardener (10 mass parts), nanodispersed filler MNDC 1 (0.50 mass parts). In the formation of such a composite, the destructive stresses at bending of a relatively modified epoxy matrix increase 1.1 times, the modulus of elasticity at bending – 1.2 times, the index of impact strength practically does not change.

At the next stage, physical and mechanical properties of modified epoxy CMs, containing nanodispersed filler MNDC 2 were studied. The dynamics of the parameters of the studied characteristics for the content of the additive *q* = 0.10–2.00 mass. parts is shown in Fig. 2. It was established that the introduction of the filler into an epoxy binder in the amount of 0.10 mass parts leads to a significant increase in the indexes of destructive stresses at bending from $\sigma_{ben}$ = 57.2 MPa to $\sigma_{ben}$ = 76.6 MPa (Fig. 2, curve 1). At the same time, CM is characterized by a modulus of elastisity, having similar characteristics as the modified polymer matrix – *E* = 3.4 GPa, and the impact strength of this material is reduced from *W* = 7.9 kJ/m$^2$ to *W* = 7.6 kJ/m$^2$ (Fig. 2, curves 2, 3). At the content of nanofiller of *q* = 0.50 mass parts, we observed an increase in the indexes of all investigated properties. The values of destructive stresses at bending increase from $\sigma_{ben}$ = 57.2 MPa (for a modified epoxy matrix) to $\sigma_{ben}$ = 65.2 MPa, elastic modulus at – from *E* = 3.4 GPa to *E* = 3.8 GPa, and impact strength – from *W* = 7.9 kJ/m$^2$ to *W* = 9.6 kJ/m$^2$. With the introduction of MNDC 2 in a binder in the amount of 1.00 mass parts, physical and mechanical properties of the CM were decreased to $\sigma_{ben}$ = 48.4 MPa, *E* = 3.3 GPa and *W* = 5.2 kJ/m$^2$ respectively. Subsequently, the nano filler was injected into an epoxy binder in an amount of *q* = 2.00 mass parts. It is determined that the physical and mechanical properties of CM for such contents of particles considerably deteriorate and make respectively $\sigma_{ben}$ = 44.6 MPa, *E* = 2.9 GPa and *W* = 5.8 kJ/m$^2$.

On the basis of the results of the study, the critical content of the MNDC 2 nanoparticles was established in the modified epoxy CM. It has been experimentally proved that the introduction of a nanodispersed filler MNDC 2 in the amount of *q* = 0.50 mass parts provides formation of CM with maximum (in complex) indicators of physical and mechanical properties: destructive stresses at bending – $\sigma_{ben}$ = 65.2 MPa, elasticity modulus – *E* = 3.8 GPa, impact strength – *W* = 9.6 kJ/m$^2$. It is proved that at the content of the additive in the amount of 0.10 mass parts the destructive stresses at bending are maximum for the investigated range of concentrations ($\sigma_{ben}$ = 76.6 MPa). However, the value of the elasticity modulus at bending and impact strength, as compared with the critical content of the additive (*q* = 0.50 mass parts ), is 1.12 and respectively 1.26 times lower. Since these characteristics have a decisive influence on the performance of materials, it is appropriate to form a CM of the following composition: epoxy resin ED-20 (100 mass parts), 2,4-diamino-toluene modifier (1 mass part), PEPA hardener (10 mass parts), nanodispersed filler MNDC 2 (0.50 mass parts).

To prove the results of the study of physical and mechanical properties, an analysis of the fracture surfaces of the CM with the help of optical microscopy was performed. In Fig. 3 there are microimages of the fracture surfaces of the CM, filled with nano-filler MNDC 1. The photos of the fracture surfaces at the




*1 – the modulus of elasticity at bending (E); 2 – fracture stresses at bending ($\sigma_{fl}$); 3 – impact viscosity (W, kJ/m$^2$)*

**Figure 2 – Dependence of physical and mechanical properties and impact viscosity of the CM on the content of the filler MNDC 2**

content of particles of $q$ = 0.25 mass parts (Fig. 3, *b*) do not differ significantly from the photos of the control sample (modified epoxy matrix) (Fig. 3, *a*). The fracture surfaces of the samples are characterized by uneven lines of shaking, due to the presence of residual stresses in the CM. The dynamics of the parameters of the elasticity modulus at bending and impact strength (Fig. 1, curves 2, 3) is confirmed by the analysis of the fracture surfaces. In particular, for the contents of the filler in the amount $q$ = 0.50 mass parts (Fig. 3, *c*) a material with a flat fracture surface is formed. It can be argued that there are insignificant residual stresses in this composite, which implies its reliability during operation. Obviously, this is due to the adsorption activity of the particles of the nano-filler in the polymer binder when structuring the material. In this case, the dispersed particles during the cross-linking of CM are interphase interaction catalysts. The macromolecules of the binder are adsorbed on the catalytic surface of the filler, which ensures its interaction with the side groups of the epoxy oligomer and modifier chains. This leads to an increase in the strength of the material. The above assumptions correlate and coincide well with the results of studies on the physical and mechanical properties of the CM (Fig. 1). With further increase of MNDC 1 content ($q$ = 0.75–2.00 mass parts) in a polymer binder we observed the formation of inhomogeneous lines of shaking and increased fragility of the investigated CM (Fig. 3, *f*–*i*). It was envisioned that, at the cross-linking of such materials, local temperature stresses in polymer significantly increase, which leads to a decrease in the cohesion strength of the composites (Fig. 3, *h*, *i*).

Thus, the method of optical microscopy has established adsorption and catalytic activity of nano-fillers of MNDC 1 and MNDC 2, providing interaction with lateral groups of chains of an epoxy oligomer, as a result of which the cohesive strength of investigated materials increases. Experimental studies of physical and mechanical properties correlate with the results of the analysis of the microimages of fracture surfaces of CM.

**Conclusions**

The paper defines optimum content of nano-fillers for formation of materials and protective coatings with improved cohesive properties, which allows to provide long-term operation of surfaces and parts of technological equipment in the oil and gas industry. The following has been defined:

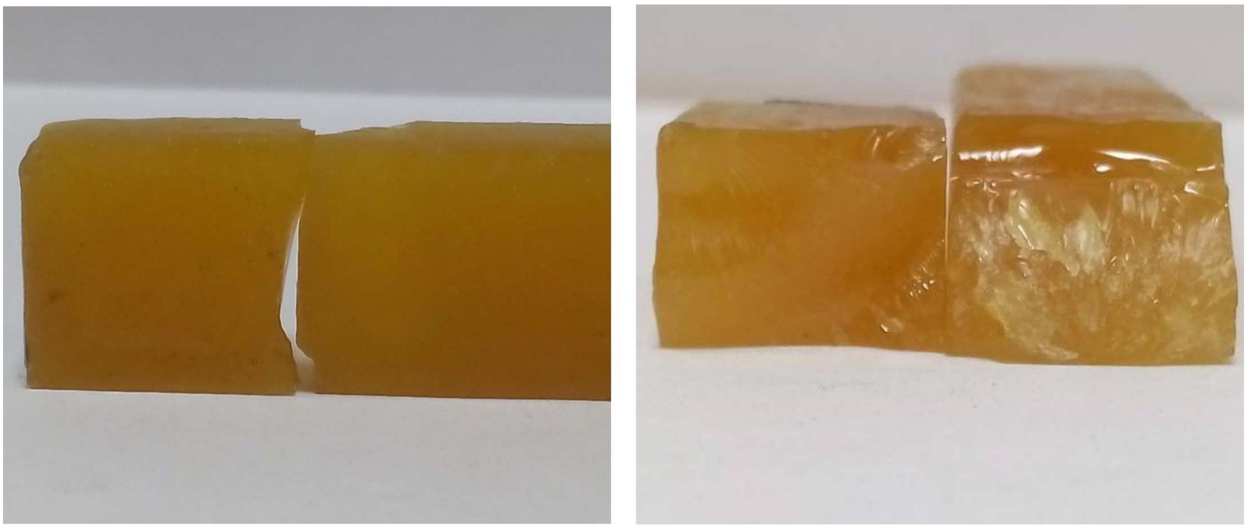
1) For the formation of coatings with improved physical and mechanical properties, it is expedient to use composites based on a polymer matrix containing an epoxy diane oligomer ED-20 (100 mass parts), a polyethylene polyamine PEPA (10 mass parts) and a 2.4-diaminotoluene modifier (1 mass part). Introduction of a nanodispersed filler into a binder ($d$ = 20–80 nm), which is a mixture of nanodispersed compounds: $Si_3N_4$ – 59.5 %; $Al_2O_3$ – 24.4 %; AlN – 10.1 %; TiN – 6.0 % provides the formation of a composite, in which the indices of cohesive properties compared to the modified matrix are increased as follows:

the modulus of elasticity at bending – from $E$ = 3.4 GPa to $E$ = 3.9 GPa;

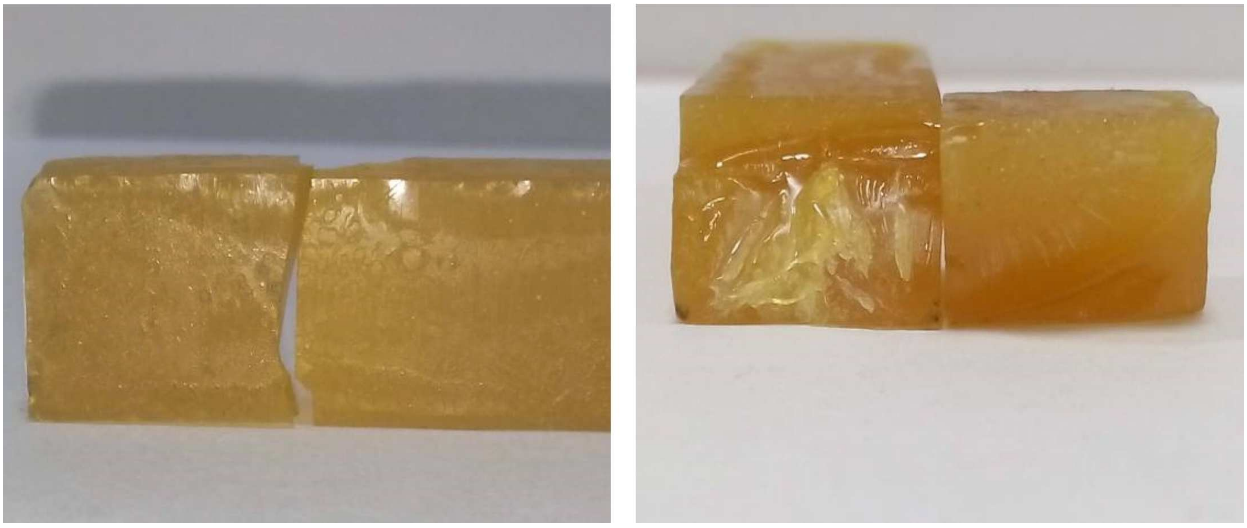
fracture stresses at bending – from $\sigma_{ben}$ = 57.2 MPa to $\sigma_{ben}$ = 63.7 MPa;

impact viscosity – from $W$ = 7.9 kJ/m$^2$ to $W$ = 8.1 kJ/m$^2$.

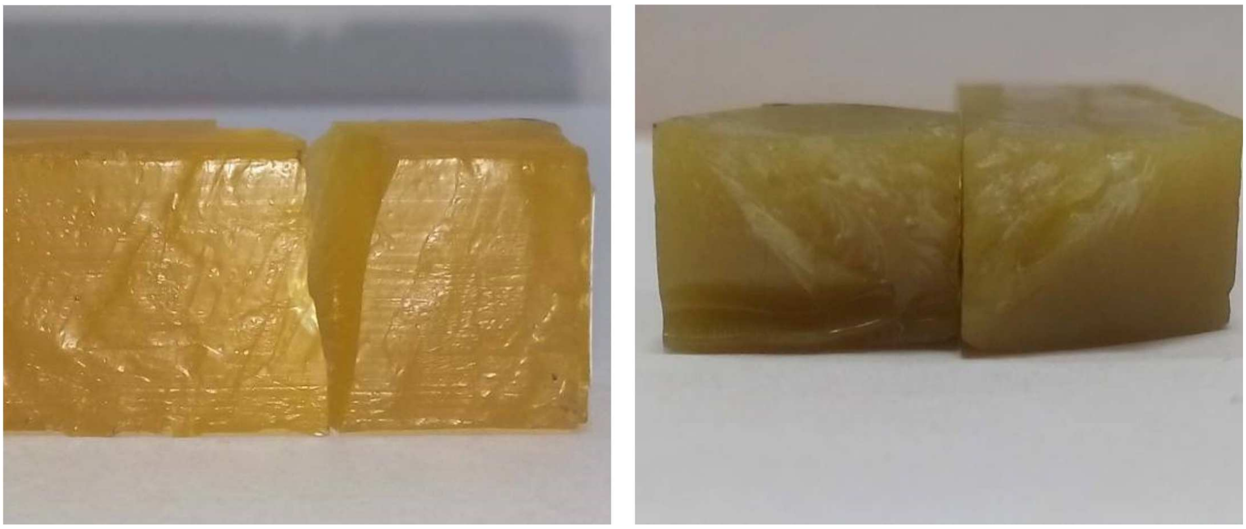
2) For the formation of coatings with improved physical and mechanical properties, it is expedient to use composites based on a polymer matrix containing an epoxy diane oligomer ED-20 (100 mass parts), a polyethylene polyamine PEPA (10 mass parts) and a 2.4-diaminotoluene modifier (1 mass part). Introduction of a nanodispersed binder ($d$ = 30–40 nm), which is a mixture of nanodispersed compounds: $Si_3N_4$ – 85 %; $AlF_3$ – 5 %; IH – 5 %; ZrH – 5 % provides the formation of a composite, in which the indices of cohesive properties compared to the modified matrix are increased as follows:



*a)*



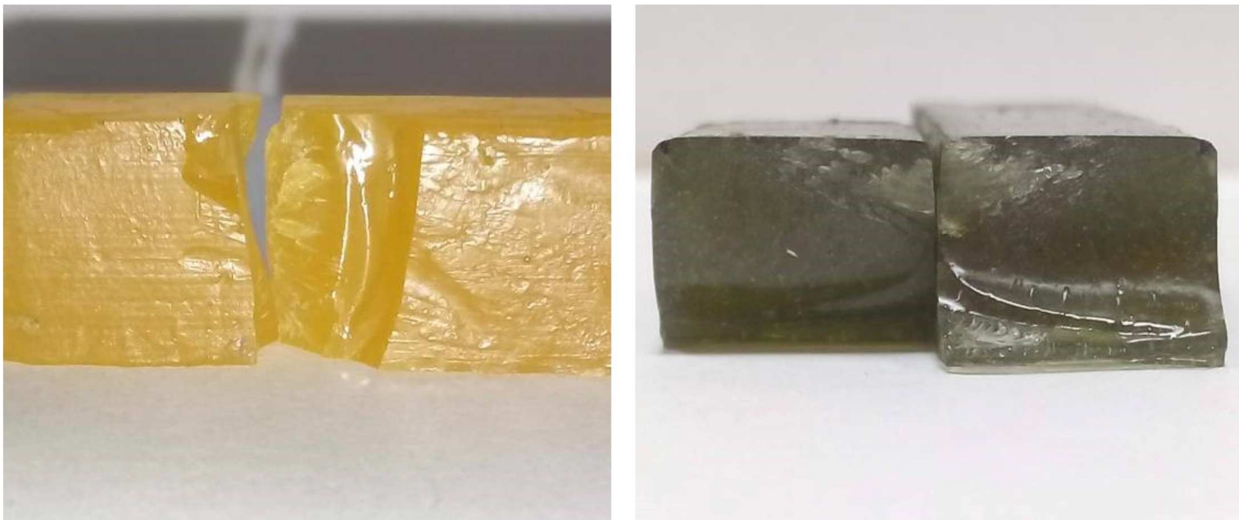
*b)*



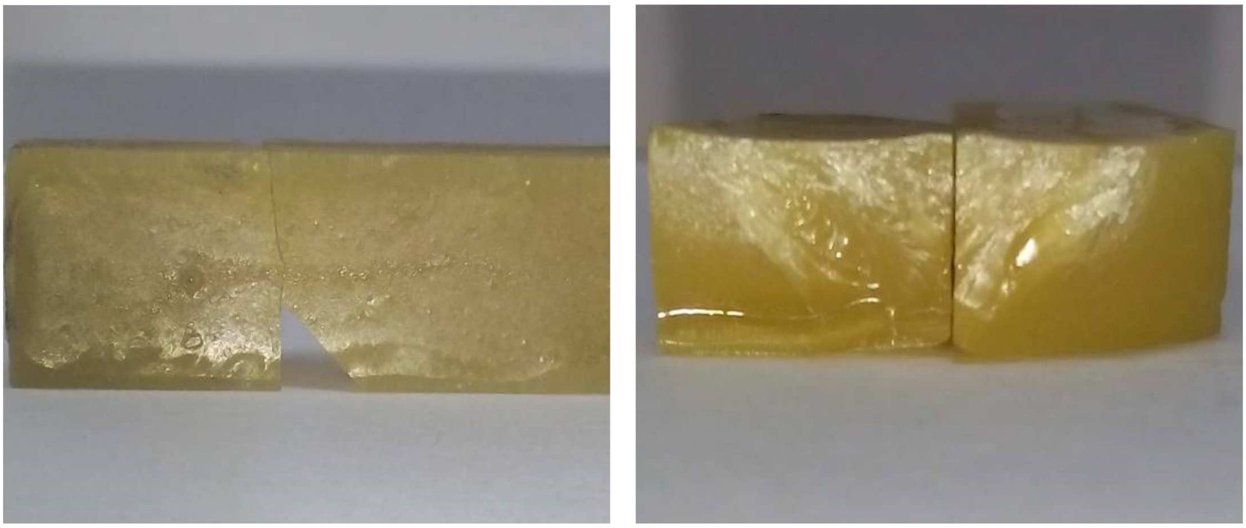
*c)*

*a) initial matrix (control specimen); b) 0.25; c) 0.50*

**Figure 3 (1) – Microimages of the fracture surface of the CM with nanofiller MNDC 1, *q*, mass parts (1×1)**



*d)*

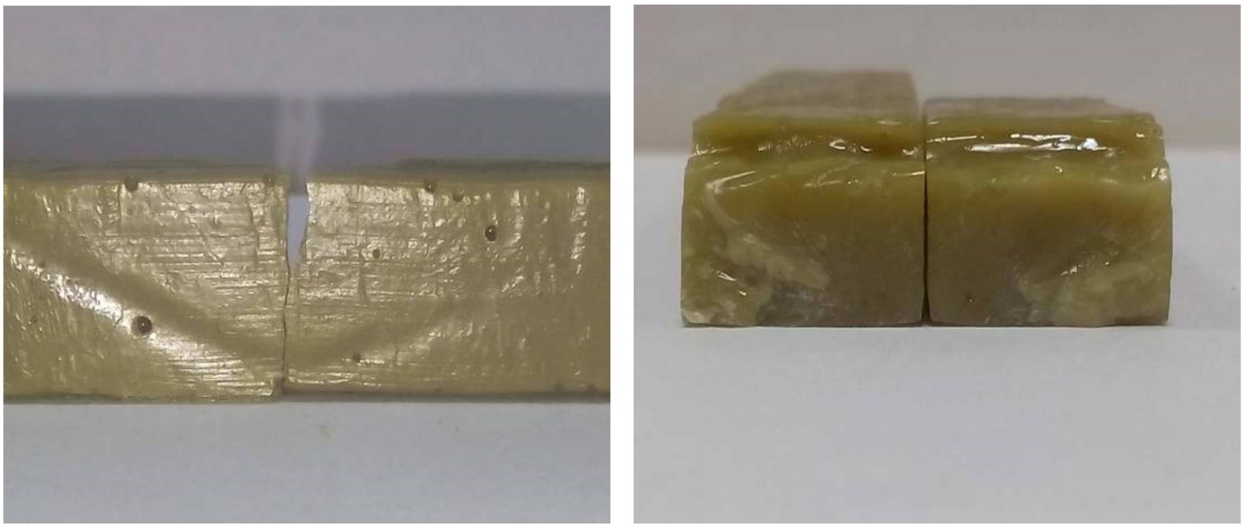


*e)*

*f)*

*d) 0.75; e) 1.00; f) 1.25*

**Figure 3 (2)**



*g)*

*h)*

*i)*

*g) 1.50; h) 1.75; i) 2.00*

**Figure 3 (3)**

the modulus of elasticity at bending – from $E = 3.4$ GPa to $E = 3.8$ GPa;

fracture stresses at bending – from $\sigma_{ben} = 57.2$ MPa to $\sigma_{ben} = 65.2$ MPa;

impact viscosity – from $W = 7.9$ kJ/m$^2$ to $W = 9.6$ kJ/m$^2$.

3) With the help of the optical microscopy method we investigated the fracture surface of samples, containing nanodispersed fillers. It has been confirmed that intorduction of additives (0.50 mass parts) leads to an increase in the coagulation strength of composite materials. The adsorption and catalytic activity of MNDC 1 and MNDC 2 nano fillers has been revealed, which provides the interaction of active centers on the surface of particles with side groups of the epoxy oligomer chains, which improves the physical and mechanical properties of the materials under study. The results of the study by the method of optical microscopy correlate with the results of testing of physical and mechanical properties of the developed materials.

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# Вплив наночасток на фізико-механічні властивості модифікованих епоксикомпозитних покриттів

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Для формування композитних матеріалів із підвищеними показниками фізико-механічних властивостей розглядається використання як зв'язувача епоксидного діанового олігомера ЕД-20, твердника поліетиленполіаміну ПЕПА і модифікатора 2,4-діамінотолуен. Досліджено залежність вмісту наночасток у вигляді суміші нанодисперсних сполук на фізико-механічні властивості епоксидних композитів. Для формування захисного покриття із поліпшеними когезійними властивостями оптимальний вміст наночасток становить q = 0.5 мас. ч. на 100 мас. ч. епоксидного олігомеру ЕД-20, що забезпечує підвищення здатності розробленого матеріалу чинити опір статичним і динамічним (в тому числі ударного характеру) навантаженням. Методом оптичної мікроскопії виявлено адсорбційну і каталітичну активність нанонаповнювачів, що забезпечує взаємодію з боковими групами ланцюга епоксидного олігомеру, внаслідок чого зростає когезійна міцність матеріалів.

Ключові слова: *епоксидний композит, модуль пружності, наночастки, руйнівні напруження при згинанні, ударна в'язкість.*