Polymer composites for improving the resource of pipeline transport

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Abstract

Epoxy-composite protective coatings filled with anti-agglomerating additive have been investigated using IR-spectral analysis. The presence of O-H and C-H bonds in the range of wave numbers $v = 2848$–2922 cm^{-1}, C-C in the range of wave numbers $v = 1112$–1541 cm^{-1} and the amino groups in the range of wave numbers $v = 623$–667 cm^{-1}, indicating the catalytic activity of the additive. It has been established that it is expedient to use an additive for the contents of $q = 20$ pts.wt. for the formation of the adhesive layer of coating, while there was observed the maximum growth of adhesion strength. Then, as for the formation of a coating with high cohesive strength, it is advisable to use an additive containing $q = 10$–20 pts.wt., which provides both elastic properties and moderate stiffness of the epoxy composite material. By the method of optical microscopy there is analyzed the structure of epoxy composites and determined the optimum content of the filler with the ordered structure, without defects, which provides high indicators of cohesive strength of materials.

Keywords: *activity of the filler, adhesion strength, cohesive strength, fracture structure, IR-spectral analysis, optical microscopy.*

The oil and gas industry is important for a country's economic development, security and energy independence. Gas and oil are the main types of fuel, while up to 80 % of it is consumed by many enterprises of various industries in Ukraine, such as ship-, auto-, aircraft building, chemical and metallurgical, power engineering, which ensure the development of the country's economy. At the same time, given the significant consumption of raw materials, more and more attention is paid to the reliability and service life of pipeline transport. The length of gas pipelines within Ukraine is about 35 thousand km, oil pipelines – 2.5 thousand km, oil product pipelines – about 3 thousand km. Thus, a gradual decrease in strength, deformation and corrosion damage to the main oil and gas pipelines is an urgent problem of our time. One of the main directions of increasing the service life of pipeline transportation, in particular oil and gas pipelines, is the use of protective coatings [1–4].

Analysis of research results [1–3, 11], allows us to state that to ensure the service life of pipeline transport, it is advisable to use protective coatings based on epoxy binders. Slight shrinkage (up to 2 %) of coatings based on epoxy binder ensures manufacturability when applied on long surfaces of a complex profile, which is relevant in the oil and gas industry. At the same time, one of the ways to improve the properties of protective coatings is the use of anti-agglomerative additives. Such additives are evenly distributed throughout the volume

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of the binder, which ensures uniformity of the coating layer during application, and, consequently, increased performance characteristics. Particularly relevant is the use of anti-agglomerate additives in the development of multicomponent polymer systems, where fibrous constituents are additionally used. Such polymeric materials can be used for the restoration of pipeline transport elements. Considering the above, it is relevant to develop new materials that increase the service life of pipe transport.

Materials and research methods

The main component for the binder in the formation of CM was chosen the epoxy dyanoic oligomer of the mark ED-20 (GOST 10587–84), which is characterized by a complex of improved properties compared to other known thermosets [1], namely high strength of adhesion compounds in the metal base, the possibility of hardening at low temperatures, low shrinkage, lack of release of volatile substances during the formation of the product, adaptability when applied to parts with a complex surface profile, developed raw materials base.

For cross-linking epoxy compositions there was used polyethylenepolyamine (PEPA) hardener (TU 6-05-241-202–78), which allows cross-linking materials at room temperature. It is known that PEPA is a low molecular weight substance, which consists of the following structural monomeric units $[-CH_2-CH_2-NH-]_n$. Different stages of crosslinking were modeled and investigated with the introduction of the hardener into the composition according to the stoichiometric ratio of the components (10 pts.wt. per 100 pts.wt. of ED-20 epoxy oligomer).

Hydropho biervnsmittel (HDBS) was used as a filler. It is a white powder made in Germany. Hydropho

biervnsmittel is used as an anti-agglomerating agent for building mixtures. Additionally HDBS provides weather resistance, frost resistance and vapor permeability of building mixtures. The particle size is 8–12 microns.

An epoxy composite filled with HDBS particles was formed according to the following technology: pre-dosing of ED-20 epoxy resin, heating the resin to a temperature of $T = 353\pm2$ K and keeping it at this temperature for a time $\tau = 20\pm0.1$ min; dispensing the dispersed filler and its further introduction into the epoxy binder; hydrodynamic combination of ED-20 oligomer and dispersed filler over time $\tau = 1\pm0.1$ min; ultrasonic treatment (UST) of the composition during the time $\tau = 1.5\pm0.1$ min; cooling the composition to room temperature for a time $\tau = 60\pm5$ min; the introduction of PEPA hardener and mixing the composition for a time $\tau = 5\pm0.1$ min. Later, CM was approved according to the experimentally established mode: sample formation and holding for a time $\tau = 12.0\pm0.1$ h at a temperature $T = 293\pm2$ K, heating with a speed $\upsilon = 3$ K/min to a temperature $T = 393\pm2$ K, holding the CM for a time $\tau = 2.0\pm0.05$ h, slow cooling to a temperature $T = 293\pm2$ K. In order to stabilize the structural processes in the matrix, the samples were kept for a time $\tau = 24$ h in air at a temperature $T = 293\pm2$ k followed by conducting experimental trials.

The following properties of the developed epoxy composite coatings were investigated: adhesive and shear strength, residual stresses, destructive stresses and elasticity modulus, impact strength, structure of composite materials by means of the optical microscopy. To study the activity of the additives there was used IR spectral analysis.

The adhesive strength of the matrix to the metal base was studied by measuring the breaking stress with a uniform separation of a pair of glued samples according to GOST 14760–69. The study of adhesion shear strength was carried out according to GOST 14759–69, similarly measuring the force of detachment of adhesive joints of steel specimens on an UM-5 automated tensile machine at a loading rate $\upsilon = 10$ N/s. The diameter of the working part of the steel samples at separation was d = 25 mm. It should be noted that the area of bonding of the samples, which were investigated at separation and shear, was the same.

The residual voltages in the matrix were determined by the console method [5]. The coating thickness $\delta = 0.3$–0.5 mm was formed on a steel base. Base parameters are as follows: the total length $l = 100$ mm; the working length $l_0 = 80$ mm, the thickness $\delta = 0.3$ mm.

Destructive stress and elasticity modulus were deter-mined according to GOST 4648–71 and GOST 9550–81, respectively. Sample parameters are the following: length $l = 120 \pm 2$ mm, width $b = 15 \pm 0.5$ mm, height $h = 10 \pm 0.5$ mm.

Impact toughness was determined by the Charpy method in accordance with GOST 4647–80 by means of a pendulum scraper MK-30 at a temperature of $T = 298 \pm 2$ K and relative humidity $d = 50 \pm 5$ %. The samples sized $l \times b \times h = (63.5 \times 12.7 \times 12.7) \pm 0.5$ mm

were used. The distance between the supports $l = 40 \pm 0.5$ mm.

The deviation of values in the study of indicators of physical and mechanical properties of CM was 4–6 % of the nominal one.

For the study of chemical bonds in the filler, IR spectral analysis was used. The IR spectra were recorded on a spectrophotometer "IRAffinity-1" (Japan) in the range of wave numbers $\nu = 400$–2400 cm^{-1} by a single beam method using reflected light. The sweep of the spectrum by wave numbers $\lambda^{-1} = \nu$ was carried out on a diagram within 225 mm in the range of the chosen frequencies. Wave numbers, transmission intensity, half-width, and absorption band area were determined using the IR solution software. The error in determining the wave number is $\nu = \pm 0.01$ cm^{-1}, and in determining the accuracy of the location of the peak $\nu = \pm 0.125$ cm^{-1}. The measurement accuracy was ± 0.2 % at software control of the slot and the integration time $t = 10$ s. The integration step $\Delta\lambda = 4$ cm^{-1}.

The study of the structure (topology) of the CM was performed on a metallographic microscope XJL-17AT equipped with the Levenhuk C310 NG Digital Camera (3.2 MegaPixels). The range of magnification of the image ranges from 100 to 1600 times. For processing digital images there was used Levenhuk ToupView software.

Discussion of research results

The chemical activity of HDBS particles was pre-determined, that is, the presence of active groups on the surface and in its structure (in the range of wave numbers $\nu = 487$–3408 cm^{-1}) by the IR spectral analysis (Fig. 1, Table 1) [6–8].

Further, the effect of HDBS content on adhesion strength at separation (σ_a), displacement (τ) and residual stresses (σ_{res}) in CM was investigated. It was established experimentally (Fig. 2), the introduction of HDBS fractions into an epoxy oligomer for a content of $q = 10$ pts.wt. leads to an increase in adhesion strength when CM is detached from 24.4 MPa HDBS (for epoxy matrix) to 34.0 MPa (Fig. 2, curve 1). The introduction of an additive at a content of $q = 20$–30 pts.wt. causes the formation of a material with a maximum value of adhesive strength at separation, which is $\sigma_a = 35.0$ MPa.

A significant effect of the additive on the adhesive strength of the coating can be explained by the increased adsorption and catalytic activity, expressed by a significant number of O-H bonds and C-H filler, found in the wave number range $\nu = 2848$-2922 cm^{-1} and C-C- in the wave number range $\nu = 1112$–1541 cm^{-1}. The introduction of HDBS particles in the binder more than $q = 40$ pts.wt. leads to a decrease in adhesive strength (Fig. 2, curve 1). It was believed that the reason for this could be the increase in residual stresses due to the supersaturation of the active anti-agglomeration agent [9–12].

The studies of the effect of HDBS on adhesion strength allowed us to state a similar relationship. This indicates the same mechanism of destruction expressed by the ability of adhesive macromolecules to deform in both longitudinal and transverse directions, ensuring the
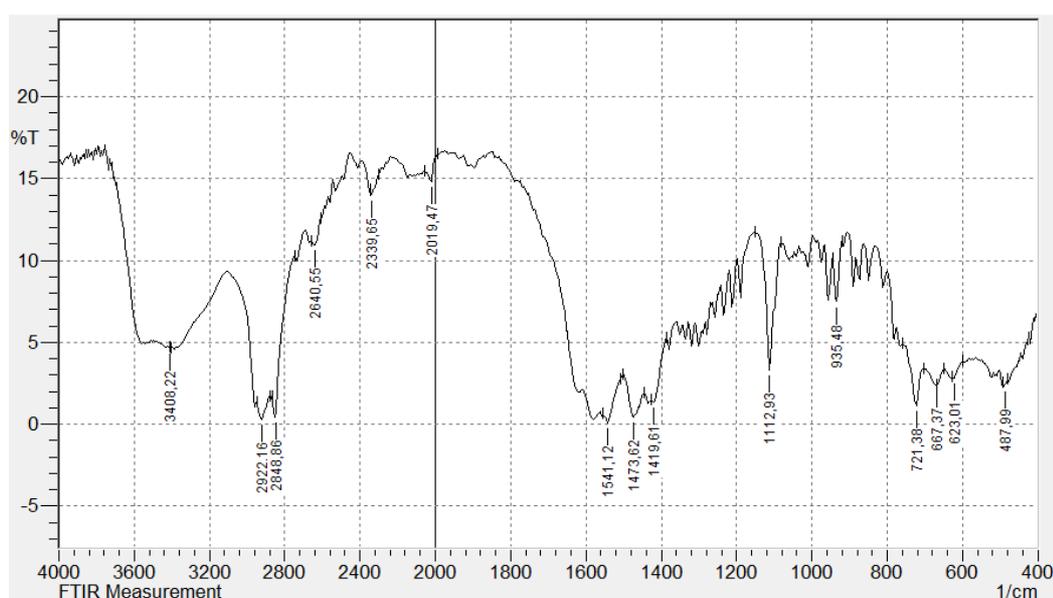
Figure 1 – IR-spectrum of the HDBS filler in the range of wave numbers $v = 487$–3408 cm^{-1}

Table 1 – Characteristic absorption bands according to the IR spectrum of HDBS particles

| No.	Wave number, v, cm^{-1}	Intensity, T, %	Relative peak area, S, %	Groups corresponding to characteristic absorption bands
1	487	2.3	15.4	-C-H- bending vibrations of the aliphatic chain
2	623	2.7	20.1	primary amines: $-NH_2$; CH_2-NH_2
3	667	2.4	29.9	
4	721	1.1	43.4	C-O-O
5	935	7.4	26.1	C-H- bending vibrations
6	1112	3.3	75.7	C-C- bond of the aromatic ring
7	1419	1.3	14.4	C-C- bond of the aromatic ring
8	1473	0.4	106.5	C-C- bond of the aromatic ring
9	1541	0.1	32.7	C-C- bond of the aromatic ring
10	2019	14.7	2.6	C=O- stretching vibrations
11	2339	13.9	35.6	$-C\equiv N-$ stretching vibrations
12	2640	10.9	39.1	C-H
13	2848	0.4	166.9	C-H
14	2922	0.2	142.9	O-H
15	3408	4.6	–	-NH- stretching vibrations

formation of the same magnitude of tangential and normal shear and shear stresses. In this case, the maximum value of shear strength is $\tau = 9.5$–9.7 MPa. Therefore, the introduction of HDBS particles in a binder with a content of q = 20–30 pts.wt. provides the formation of a material with a maximum value of shear and the peel strength.

At the same time, it is advisable to take into account the value of the residual adhesive stress for long-term use of the coating. Therefore, the dependence of residual stresses on the content of HDBS particles was additionally analyzed. It is shown that the minimum values of residual stresses ($\sigma_{res} = 2.0$–2.5 MPa) are with the introduction of the additive with a content of q = 10–30 pts.wt. Interconnections with relatively low absolute values of residual stresses and adhesive strength indicate the possibility of long-term operation of the coating. At the same time, it should be noted that the introduction of HDBS particles into the binder more

than q = 40 pts.wt. leads to the maximum growth of residual stresses ($\sigma_{res} = 2.6$–3.1 MPa) and coating delamination with time (Fig. 3).

During the operation of CM, not only the adhesion strength indicators, but also the physical and mechanical properties are significant. Therefore, the physico-mechanical properties of CM, filled with HDBS particles, were further investigated. It was established that the introduction of HDBS filler into the epoxy binder for a content of $q = 10$–20 pts.wt. leads to a maximum increase in destructive stresses when CM is bent relative to the matrix (Fig. 4, curve 1). The destructive flexural stresses of such materials are $\sigma_{ben} = 60.0$–64.0 MPa. Considering the results of IR spectral analysis (Table 1), it can be assumed that the increase in σ_{ben} is associated with crosslinking of the epoxy groups of ED-20 oligomer with the participation of O–H groups of the additive and amino acid groups of the hardener. Due to this, the material is characterized by
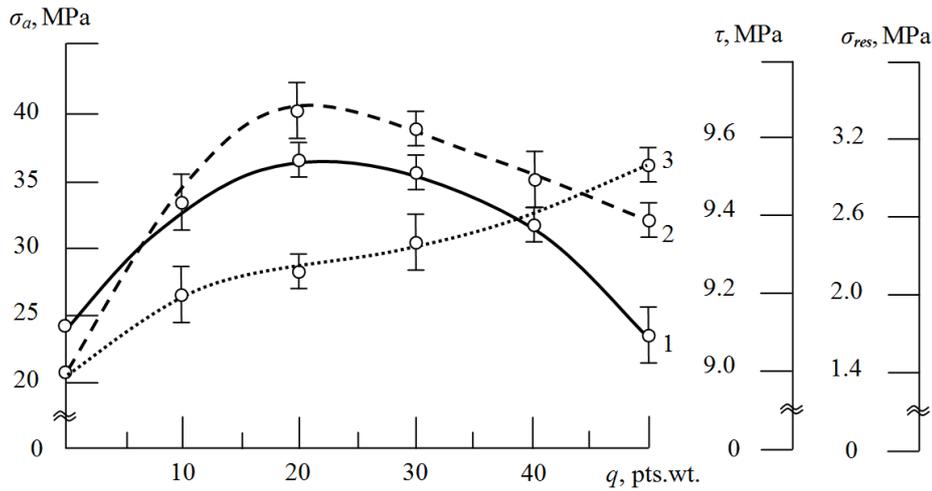
1 – adhesive strength in isolation (σ_a); 2 – adhesive strength in shear (τ); 3 – residual stresses (σ_res)
**Figure 2 – Dependence of adhesion strength (σ_a, τ) and residual stresses (σ_res)
of CM on the content of the HDBS filler**

**Figure 3 – Defects of the coating caused
by high residual stresses**

its ability to resist deformation. The structure of such composites is characterized by homogeneity, where blocks of the same absolute size prevail (Fig. 5, *b*, *c*). Comparing fractographic patterns of the epoxy matrix fracture (Fig. 5, *a*) and the composite material with HDBS particles with the content of $q = 10$–20 pts.wt. (Fig. 5, *b*, *c*) it is found that the CM is characterized by the absence of wide splitting lines. This indicates the uniform distribution of residual stresses by volume and ensures the formation of a material with high mechanical strength.

Further introduction of HDBS particles with the content of $q = 30$–50 pts.wt. leads to a decrease in destructive stresses when bending $\sigma_{ben} = 50.0$–55.0 MPa. Despite the fact that the particles of hydropho biervnsmittel is an anti-agglomeration additive, the CM structure is characterized by the appearance of agglomerates, the onset of which was observed when HDBS was introduced for a content of $q = 30$ pts.wt. (Fig. 5, *b*). It is assumed to be due to the dispersion of particles ($d = 5$–10 μm) and their supersaturation in the binder, which causes an increase in the viscosity of the polymer system. This, in its turn, leads to incomplete wetting of particles, and with further introduction ($q = 40$–50 pts.wt) it ensures the formation of a significant amount of agglomerates (Fig. 5, *d*, *e*) in the polymer volume, and, consequently, a significant decrease of mechanical strength of materials.

Additionally, we analyzed the dependence of the elastic modulus upon bending on the HDBS content (Fig. 4, curve 2). It is established that the growth dynamics of the elastic modulus is similar to the flexural stress. However, the maximum value of the elastic modulus ($E = 4.2$ GPa) was observed with the introduction of HDBS for the content of $q = 20$ pts.wt, characterizing the elastic properties of the developed materials with the critical amount of filler.

It has been established (Fig. 4, curves 1 and 3) the correlation relationship between the physical and mechanical properties of the indicators (σ_{ben} and W) with the introduction of HDBS particles with the content of $q = 10$–20 pts.wt. Such materials are characterized by impact toughness, which is $W = 9.0$–9.5 kJ/m^2 (Fig. 4, curve 3). Moreover, the further introduction of HDBS particles leads to a decrease in toughness of $W = 7.5$ kJ/m^2, which is characteristic of CM with a defective structure. The results of the toughness study are additionally coordinated with optical microscopy, confirming the reliability of the results obtained.

Based on the results of the study of the cohesive strength of epoxy composites, it is found that to obtain materials with a complex of improved physical and mechanical properties, it is advisable to inject an HDBS filler within $q = 10$–20 into epoxy binder; (up to $\sigma_{ben} = 60.0$–64.0 MPa), elasticity modulus ($E = 3.5$–4.2 GPa), impact toughness ($W = 9.0$–9.5 kJ/m^2).

Conclusions

1. The surface of hydropho biervnsmittel particles was studied by IR spectral analysis. The activity of the anti-agglomeration additive was established, expressed by a significant number of O–H and C–H bonds in the range of wave numbers ν = 2848–2922 cm^{-1}, C–C in the range of wave numbers ν=1112–1541 cm^{-1} and amino groups – in the wave number range ν = 623–667 cm^{-1}.

2. For the formation of coatings that provide high rates of adhesion strength at separation and shear, it is advisable to use composites containing particles of
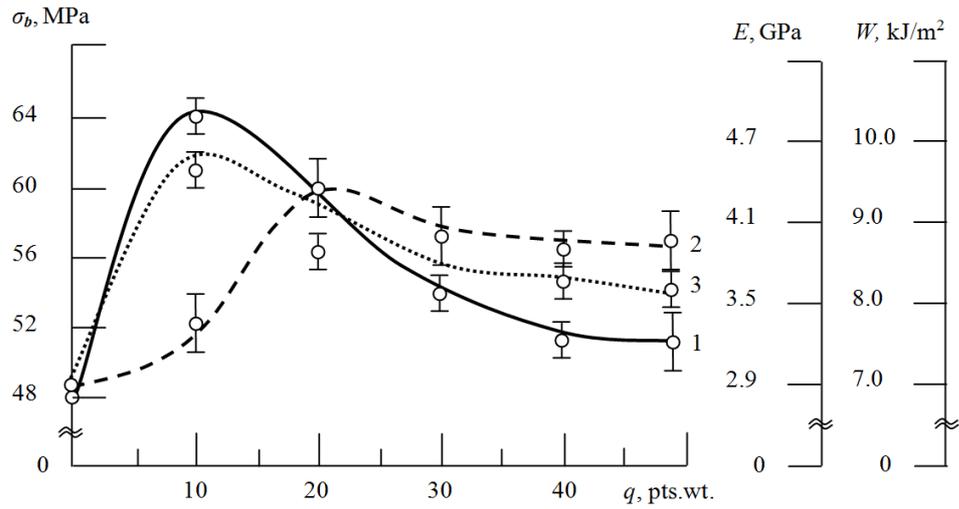
1 – bending strength (σ$_b$); 2 – elasticity modulus (E); 3 – impact toughness(W)

Figure 4 – Dependence of the bending strength (σ$_b$), elasticity modulus (E) and impact toughness (W) of the CM on the content of the HDBS filler

a) ×400

b) ×400

c) ×400

d) ×400

e) ×400

f) ×400
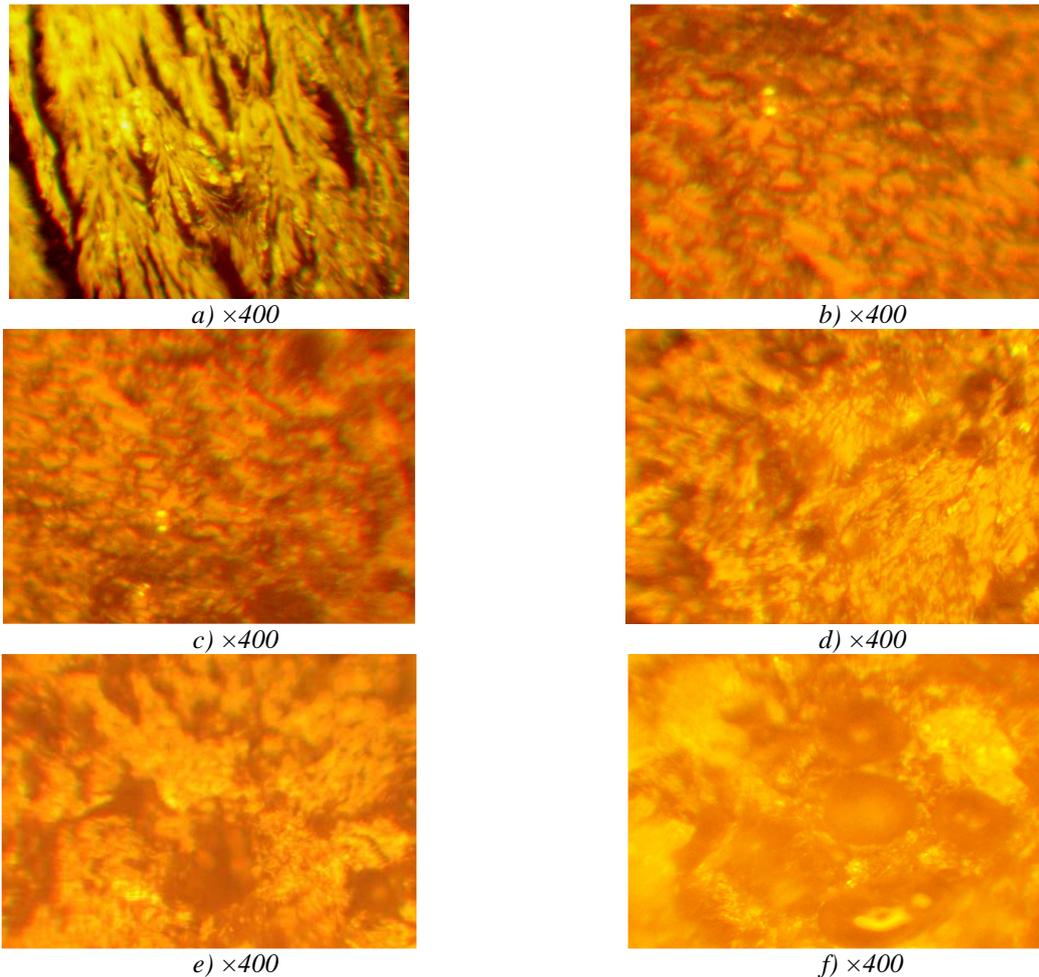
a) matrix; b) 10 pts. wt.; c) 20 pts. wt.; d) 30 pts. wt.; e) 40 pts. wt.; e) 50 pts. wt.

Figure 5 – Fractograms of the CM fracture, filled with HDBS particles

hydropho biervnsmittel for the content of q = 20–30 pts.wt. per 100 pts.wt. of ED-20 epoxy oligomer and 10 pts.wt. of PEPA hardener. Introduction of antiagglomerate additives at optimum content ensures the maximum growth of adhesion strength at separation of σ_a = 33.0–35.0 MPa, shift τ = 9.4–9.7 MPa and slight residual stresses σ_{res} = 2.0–2.5 MPa, which is due to the increased adsorption and catalytic activity.

3. For the formation of coatings that provide high rates of cohesive strength, it is advisable to use composites containing particles of hydropho biervnsmittel for the content of $q = 10–20$ pts.wt. per 100 pts.wt. of ED-20 epoxy oligomer and 10 pts.wt. of PEPA hardener. The addition of the additive at the optimum content ensures the maximum growth of cohesive strength (compared with the matrix: $\sigma_{ben} = 48.0$ MPa, $E = 2.9$ GPa, $W = 7.0$ kJ/m^2), namely: destructive bending stresses $\sigma_{res} = 60.0–64.0$ MPa, elasticity modulus $E = 3.5–4.2$ GPa, impact strength $W = 9.0–9.5$ kJ / m^2.

4. The results obtained by the method of optical microscopy are consistent with the results of the study of the cohesive strength of materials. It is established that composite materials, filled with particles of hydropho biervnsmittel for the content of $q = 10–20$ pts.wt., are characterized by a homogeneous structure that ensures a uniform distribution of residual stresses by volume and growth of the mechanical strength of the material.

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Полімерні композити для підвищення ресурсу роботи трубопровідного транспорту

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Методом ІЧ-спектрального аналізу досліджено поверхні епоксикомпозитного захисного покриття, наповненого антиагломеруючою добавкою. Встановлено присутність зв'язків О-Н і С-Н у діапазоні хвильових чисел $\nu = 2848–2922$ см$^{-1}$, С-С – у діапазоні $\nu = 1112–1541$ см$^{-1}$ та аміногруп – у діапазоні $\nu = 623–667$ см$^{-1}$, що вказує на каталітичну активність добавки. Встановлено, що для формування адгезійного шару покриття доцільно використовувати добавку за вмісту $q = 20$ мас. ч., при цьому спостерігається максимальне зростання адгезійної міцності. Для формування покриття з високими показниками когезійної міцності доцільно використовувати добавку з $q = 10–20$ мас. ч., що забезпечує як пружні властивості, так і помірну жорсткість епоксикомпозитного матеріалу. Методом оптичної мікроскопії проаналізовано структуру епоксидних композитів і визначено оптимальний вміст наповнювача, при якому характерна впорядкована і без дефектів структура із високими показниками когезійної міцності матеріалів.

Ключові слова: *адгезійна міцність, активність наповнювача, ІЧ-спектральний аналіз, когезійна міцність, оптична мікроскопія, структура злому.*