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Polymeric materials based on epoxy oligomer DER-331 and hardeners of different physical and chemical nature for repairing of gas production equipment

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Abstract

The optimal content of PEPA and TETA hardeners and polymerization temperature during matrix formation on the basis of epoxy oligomer DER-331 were determined. The dynamics of dependence of hardener content on physical and mechanical properties of epoxy matrix was investigated. According to the results of the study, materials with the optimal content of hardener and temperature range of polymerization for the formation of a composition with high physical and mechanical properties and its further use for the repair of gas equipment are proposed. Developed polymeric materials containing the hardener TETA with a content of q = 8–10 weight parts per 100 weight parts of epoxy oligomer DER-331 are characterized by high physical and mechanical properties, in particular: the fracture stresses during the flexion are σ_{fl} = 80.0–95.1 MPa, the modulus of elasticity E = 2.8–2.9 GPa, impact strength W = 7.9–13.5 kJ/m^2. The fracture structure of such composites is characterized by less deep branched chip lines with relatively uniform transitions, which makes it possible to state a slight stress state of the polymer, and hence its increased resistance to fracture.

Keywords: *epoxy matrix, gas industry, hardener, physical and mechanical properties.*

Introduction

Today, the gas production complex is an important component of Ukraine's resource supply. Analysis of the state of existing gas and oil fields shows rather difficult operating conditions of machinery and equipment. During operation, equipment failures occur due to physical and moral deterioration, which in its turn leads to interruptions and their unstable operation, and subsequently – shutdowns of the gas production complex. Therefore, one of the main directions for the scientific and technical development of the gas production complex is the effective use of new technologies and polymeric materials to ensure the functioning of facilities and specialized equipment (tubing, fittings). At the same time special attention is paid to the elimination of inter column gas kicks. This in its turn makes it possible to use polymers as sealing materials. Polymers based on epoxy resins are characterized by increased both adhesive and cohesive properties. Therefore, it is important to use them in the formation of protective coatings, adhesives, sealing compounds in many fields of industry, including gas industry [1–6].

Today it is important to develop new polymeric materials that can perform both highly specialized and general functions. The analysis of scientific works [7] allows to state that for formation of polymers liquid epoxy resin DER-331, produced by "Dow Chemical Comp" (Germany) is widely used. For crosslinking the compositions with the above resin, a significant number of hardeners are available, the choice of which is made depending on the operating conditions of the polymers, which allows to change the properties of the materials in a wide range. Therefore, it is important to compare the effect of two hardeners of different physical and chemical nature (polyethylene polyamine PEPA and triethylenetetramine TETA) on the properties of the epoxy matrix for use in the gas production complex.

The aim of the work is to determine the optimal content of hardeners of triethylenetetramine and polyethylene polyamine in the epoxy binder based on the oligomer DER-331 to improve the physical and mechanical properties of the functional matrix.

Materials and methods of research

Epoxy resin DER-331 was used to form the epoxy matrix. Cold curing hardeners polyethylene polyamine (PEPA) (TU 6-05-241-202–78) and triethylenetetramine TETA (TU 6-02-1099–83) were used to crosslink the epoxy binder. Their content varied within q = 8–14 pts. wt. (indicated per 100 parts by weight of epoxy resin DER-331). Note that the introduction of an insufficient amount of hardener in the binder or vice versa – its excess adversely affects the properties of the resulting material (low strength, wear resistance, heat resistance).

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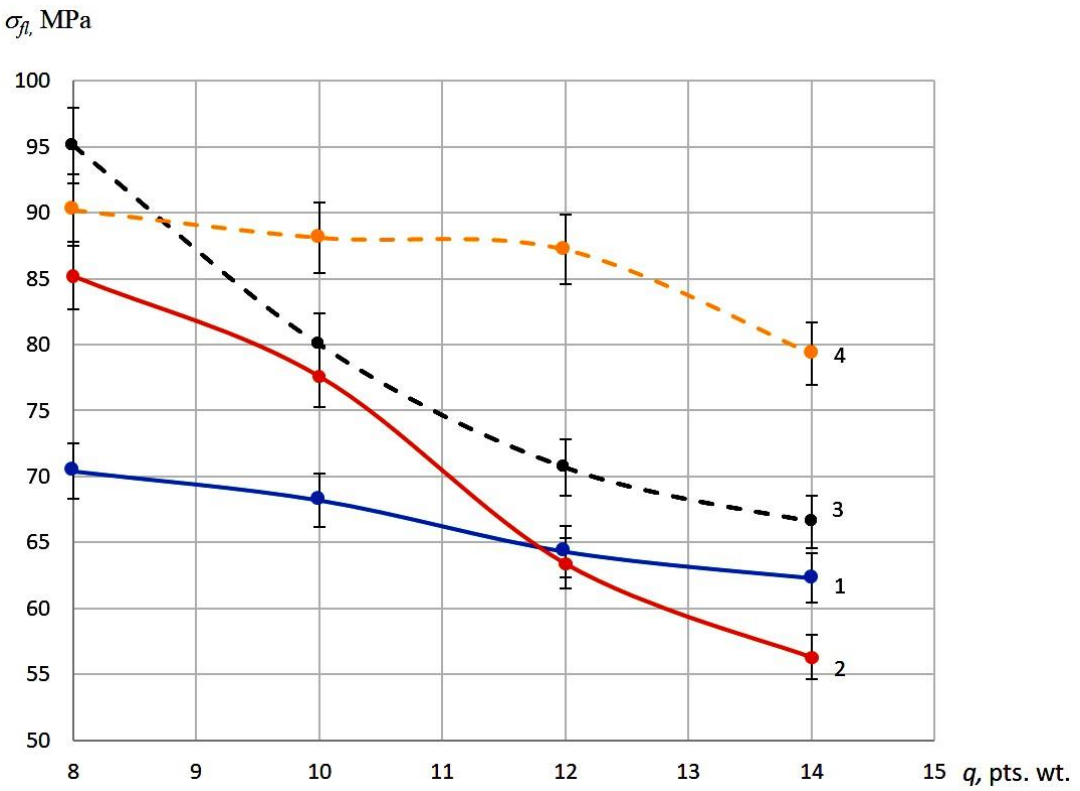


(1) T = 393 ± 2 K and (2) T = 413 ± 2 K; fracture stresses during the flexion (σ_{fl}) of the polymer matrix, hardened at a temperature: (3) T = 393 ± 2 K and (4) T = 413 ± 2 K

Figure 1 – The dependence of physical and mechanical properties on the content of the PEPA hardener (curve 1,2) and TETA hardener (curve 3,4) and the determined temperature conditions: fracture stresses during the flexion (σ_{fl}) of the polymer matrix, hardened at a temperature

The formation of the epoxy matrix was performed in the following sequence: heating the resin to a temperature of T = 353 ± 2 K and keeping at this temperature for a time τ = 20 ± 0.1 min; ultrasound composition over time τ = 1.5 ± 0.1 min; cooling the composition to room temperature over time τ = 60 ± 5 min; the introduction of the hardener and stirring the composition for a time τ = 5 ± 0.1 min.

Materials were hardened according to the experimentally established mode: the formation of samples and their aging over time t = 12.0 ± 0.1 h at a temperature T = 293 ± 2 K, heating at a rate of υ = 3 K/min to a temperature of T = (393–413) ± 2 K, keeping the specimens at a given temperature for a time t = 2.0 ± 0.05 h, slow cooling to a temperature T = 293 ± 2 K. In order to stabilize the structural processes in the matrix, the specimens were kept for a time t = 24 h in air at temperature T = 293 ± 2 K, followed by experimental tests. Regulation of temperature and time modes of formation of polymeric materials primarily refers to traditional methods of influencing their performance characteristics and makes it possible to change the structure and, consequently, the properties of polymers.

The study investigated: the destructive stresses and modulus of elasticity during the flexion, resilient modulus, the structure of the epoxy matrix by optical microscopy.

The destructive stress and modulus of elasticity during the flexion were determined in accordance with GOST 4648–71 and GOST 9550–81 correspondingly. Specimen parameters: length l = 120 ± 2 mm, width b = 15 ± 0.5 mm, height h = 10 ± 0.5 mm.

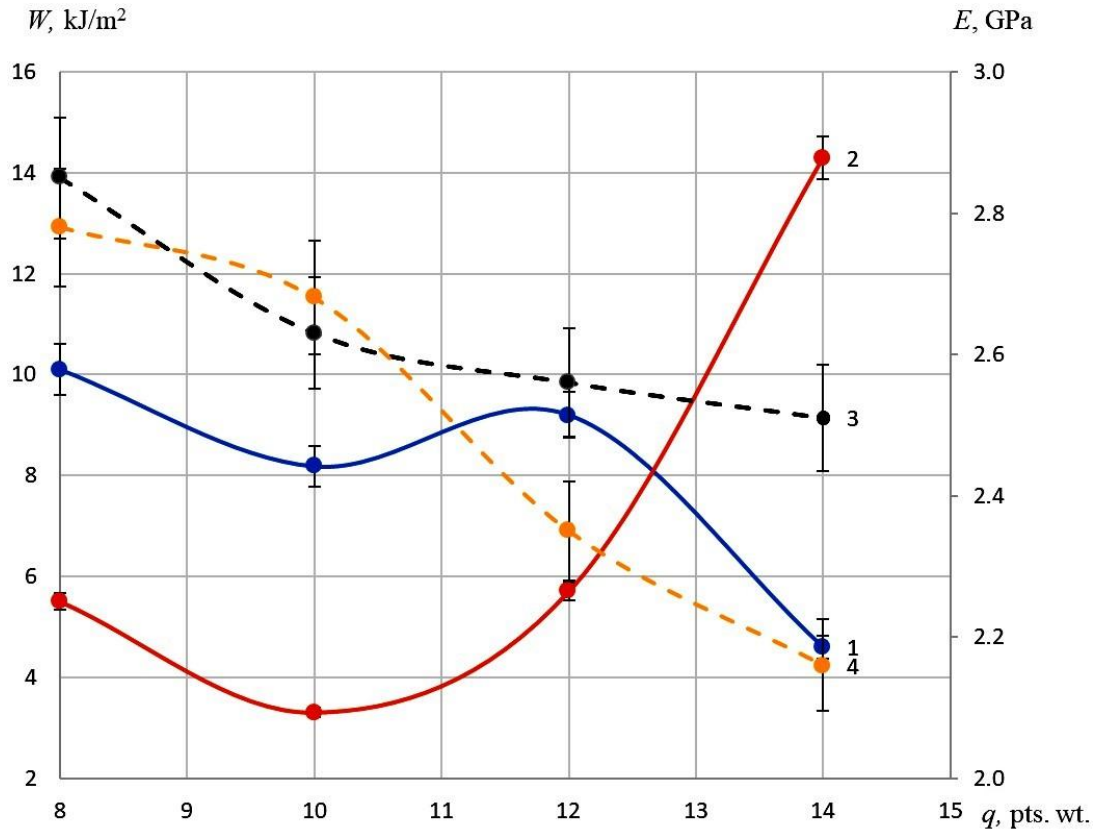
Impact strength was determined by the method according to GOST 4647–80 on a pendulum dill MK-30 at a temperature of T = 298 ± 2 K and relative humidity d = 50 ± 5%. Specimens with a size (63.5 × 12.7 × 12.7) ± 0.5 mm were used.

Additionally, the structure of the developed materials was investigated on a metallographic microscope model XJL-17AT, which is equipped with a camera 130 UMD (1.3 megapixels). Image magnification range from ×100 to ×1600 times. In this work, the samples were examined at a magnification of × 250 times.

Research results and their discussion

At the first stage, the influence of the optimal content of polyethylene polyamine hardener (PEPA) in the epoxy oligomer DER-331 on the physical and mechanical properties of the epoxy matrix was investigated. The influence of PEPA hardener on: destructive stresses (σ_{fl}, MPa), flexural modulus (E, GPa) and impact strength (W, kJ/m^2) was investigated.

It has been found out that (Fig. 1, curve 1) that when the hardener PEPA with a content of q = 8 weight parts is introduced into the epoxy oligomer and the



(1) T = 393 ± 2 K and (2) T = 413 ± 2 K – the modulus of elasticity during the flexion (E) of the polymer matrix, hardened at a temperature: (3) T = 393 ± 2 K and (4) T = 413 ± 2 K

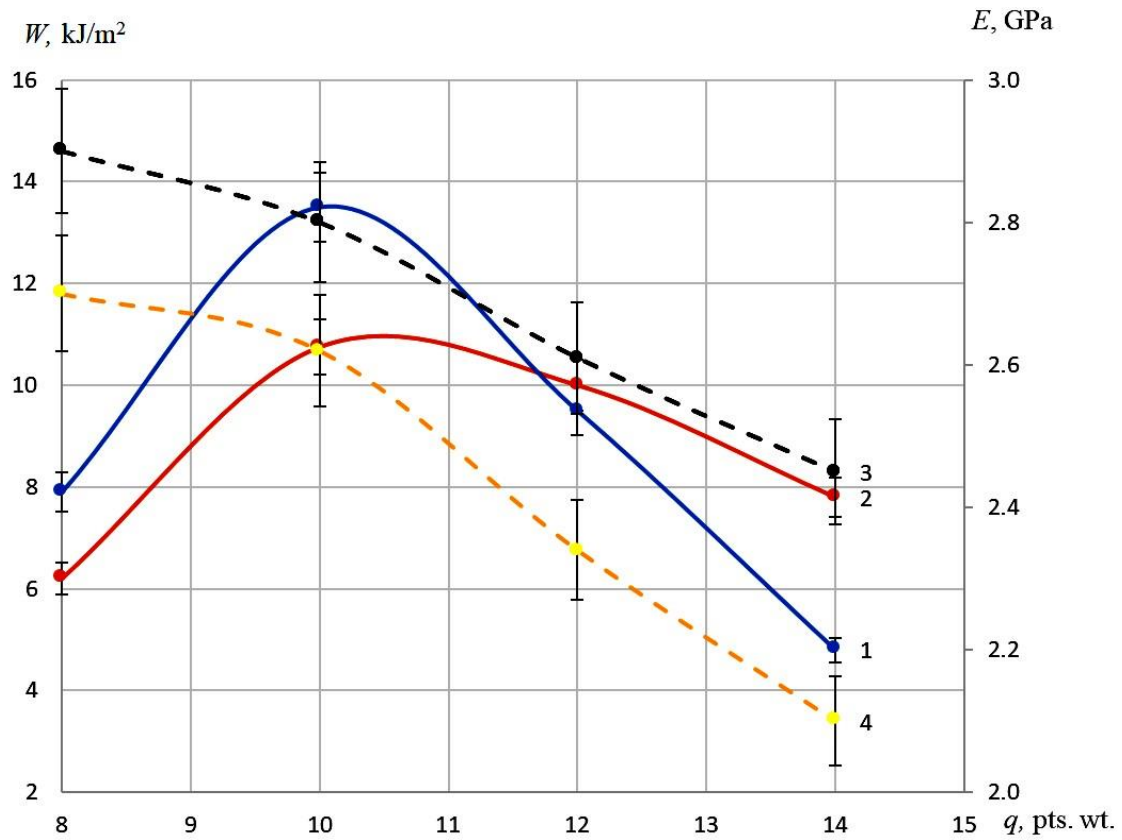
Figure 2 – The dependence of physical and mechanical properties on the content of the PEPA hardener and the temperature conditions: impact strength (*W*, kJ/m^2) of the polymer matrix, hardened at a temperature

crosslinking temperature is T = 393 ± 2 K, the value of the destructive stresses during the flexion is σ_{fl} = 70.04 MPa. Subsequently, the increase of the content of the hardener to q = 10–14 weight parts, leads to a decrease in the destructive stresses during the flexion, the value of which is σ_{fl} = 68.26–62.30 MPa. Concurrently, the obtained values of the modulus of elasticity were analyzed (Fig. 2, curve 3). It is shown that the maximum value of the modulus of elasticity during the flexion is E = 2.85 GPa, if the content of the PEPA hardener is q = 8 weight parts per 100 weight parts of epoxy oligomer DER-331. Subsequent introduction of the hardener at a content of q = 10–14 weight parts provides a decrease in the modulus of elasticity to E = 2.51–2.63 GPa. It was believed that the results of the study can be explained by a decrease in the intermolecular interaction of the components, due to the supersaturation of amino groups that disrupt the spatial bond of the corresponding elements in the epoxy matrix due to significant residual stresses [8–9].

The values of the impact strength of the epoxy matrix were additionally investigated, since this property characterizes the ability of the polymer to resist the influence of external loads. It was found that the maximum value of impact strength is W = 10.1 kJ/m^2 (Fig. 2, curve 1), with the introduction of PEPA hardener with a content of q = 8 weight parts. When the hardener was introduced within q = 10–14 weight parts, a decrease in impact strength W = 4.6–8.1 kJ/m^2 was obtained. Analyzing the results of the study, we can state their reliability, as in all three cases of studies of physical and mechanical properties of the matrix, the optimal content of the PEPA hardener is q = 8 weight parts.

Further, we studied the effect of PEPA hardener on the complex of physical and mechanical properties of the epoxy matrix at the polymerization temperature T = 413 K. It is shown (Fig. 1, curve 2) that the values of destructive stresses increase by 15.1 MPa compared to the matrix set at T = 393 ± 2 K. Thus, the introduction of the hardener PEPA with a content of q = 8 pts. wt. provides the formation of a polymer matrix with values of destructive stresses during the flexion, which are σ_{fl} = 85.2 MPa. With a further increase in the content of the hardener, a monotonic decrease in the values of σзг was observed, which is σ_{fl} = 56.3–77.6MPa. At the same time, analyzing the value of the modulus of elasticity in bending (Fig. 2, curve 4), we observed a similar dependence, ie in this case the maximum value of the modulus of elasticity is E = 2.78 GPa.

Analysis of the results of the impact strength study of the polymer matrix set at a temperature of T = 413 K (Fig. 2, curve 2), allowed to establish the opposite relationship. Thus, at the maximum content of hardener q = 14 weight parts, the obtained results of impact strength of the polymer matrix is W = 14.3 kJ/m^2, which



(1) T = 393 ± 2 K and (2) T = 413 ± 2 K – the modulus of elasticity during the flexion (E) of the polymer matrix, hardened at a temperature: (3) T = 393 ± 2 K and (4) T = 413 ± 2 K

Figure 3 – The dependence of physical and mechanical properties on the content of the TETA hardener and the temperature conditions: impact strength (*W*, kJ/m^2) of the polymer matrix, hardened at a temperature

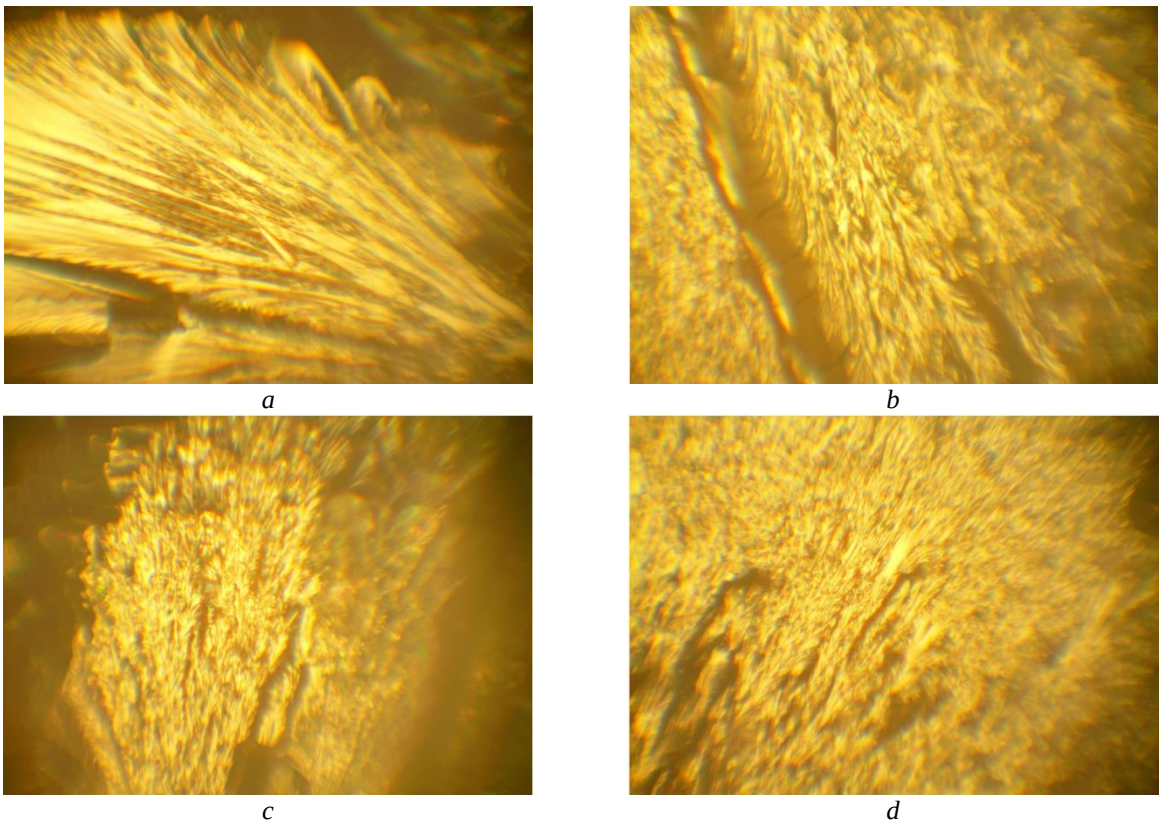
in turn is the maximum value at a given crosslinking temperature.

Therefore, it can be stated that the increase of physical and mechanical properties of the epoxy matrix polymerized by PEPA hardener can be provided by increasing the crosslinking temperature to T = 413 K [4].

At the second stage, the impact of the optimal content of triethylenetetramine hardener (TETA) in the epoxy oligomer DER-331 on the physical and mechanical properties of the epoxy matrix was investigated. As before, the influence of TETA hardener on: destructive stresses during the flexion (σ_{fl}, MPa), modulus of elasticity in bending (E, GPa) and impact strength (W, kJ/m^2) was studied. A characteristic feature of this hardener is the ability to polymerize at higher temperatures and as a result of forming a material with a wider range of performance characteristics.

Analysis of the obtained results allows us to state (Fig. 1, curve 3) that at the polymerization temperature of the epoxy matrix T = 393 ± 2 K and the content of the hardener TETA q = 8 weight parts the value of the destructive stresses during the flexion is σ_{fl} = 95.1 MPa. Further, when increasing the content of the hardener to q = 10–14 weight parts, observed a decrease in the property to σ_{fl} = 66.58 MPa. It should be noted that σ_{fl} remains higher than for the matrix of PEPA at the same content of components and the temperature of the polymerization. Despite the fact that the hardeners used in the work have a very similar molecular structure, they are characterized by certain features, namely, the presence of impurities. In the case of PEPA: the hardener in its pure form is 25–35 %, the other 65–75 % residue – impurities that remain in the epoxy matrix. Whereas for TETA: the hardener in its pure form is 90–95 %, the other 5–10 % residue. Therefore, a certain ratio of the components of the hardener TETA and epoxy binder DER-331, at the established temperature-time modes of polymerization, provides the formation of a homogeneous polymer matrix with high mechanical strength. It was believed that the explanation of the above is associated with an increase in the rate of physicochemical processes, due to the small amount of impurities, which affects the processes of increasing the gel fraction of the polymer and consequently provides a high degree of crosslinking [2–5].

Analysis of the dependence of the modulus of elasticity while bending on the content of the hardener TETA allows us to state that the obtained values are similar in nature to the hardener PEPA. When introducing the hardener TETA with a content of q = 8 weight parts (Fig. 3, curve 3) the modulus of elasticity is E = 2.9 GPa. Increasing the content of the hardener leads to a decrease in the modulus of elasticity, the minimum value of which is E = 2.45 GPa. The impact strength of the matrix set by the TETA hardener (Fig. 3, curve 1) is also characterized by higher values compared to the PEPA hardener. But it should be noted that the optimal content of the hardener is q = 10 weight



a) 8 weight parts, b) 10 weight parts, c) 12 weight parts, d) 14 weight parts

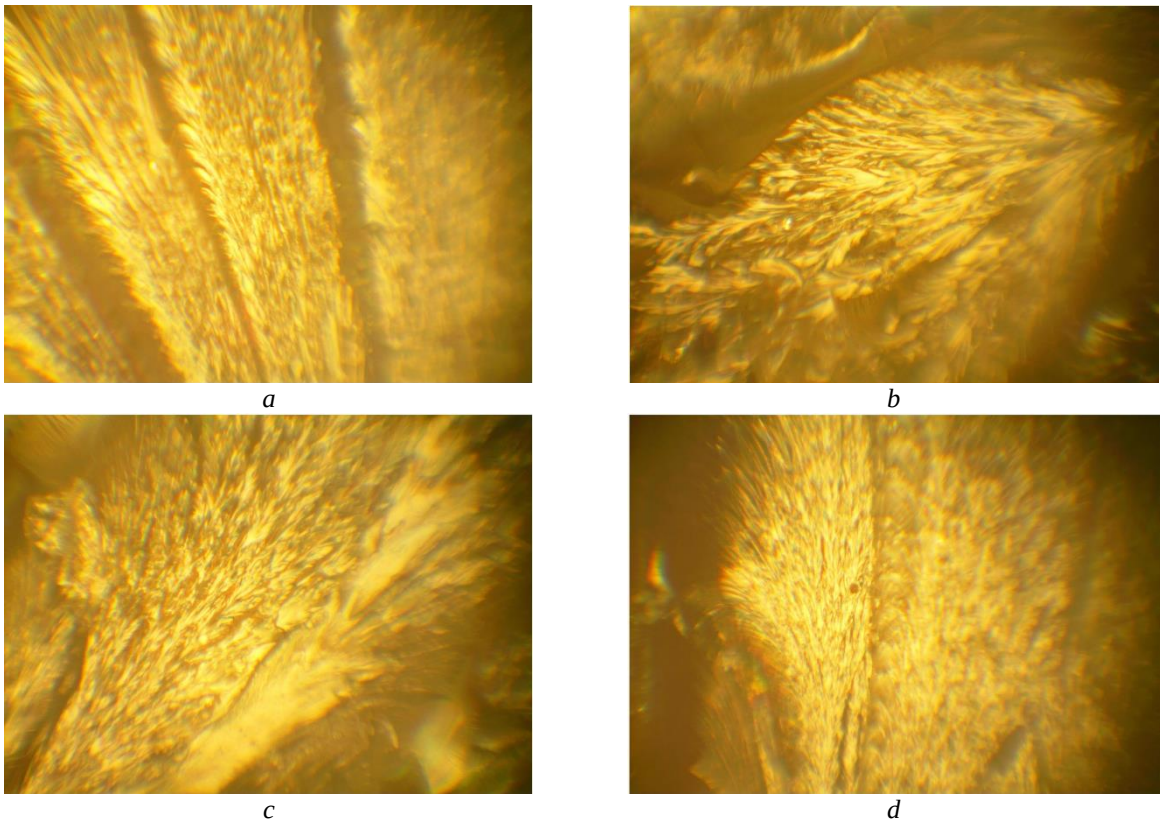
Figure 4 – Fracture pattern of the polymer matrix hardened at a temperature T = 413 ± 2 K with usage of PEPA hardener

parts. At this content, the value of impact strength is W = 13.5 kJ/m^2. Further increase of the hardener content in the epoxy oligomer to q = 12–14 weight parts, leads to a decrease in impact strength and is W = 4.8–9.5 kJ/m^2.

As at the previous stages, specified content of TETA hardener in the epoxy oligomer at elevated polymerization temperature T = 413 K was studied. It was found that with increasing polymerization temperature of the epoxy matrix, a decrease in physical and mechanical properties compared to a similar matrix [1] was observed. It is shown (Fig. 2, curve 4) that the maximum values of the destructive stresses while bending are σ_{fl} = 90.2 MPa, when the hardener is introduced at a content of q = 8 weight parts. The value of the modulus of elasticity while bending (Fig. 3, curve 4) is E = 2.7 GPa. Increasing of the content of the hardener to q = 10–14 weight parts provides a monotonous reduction of the physical and mechanical properties of the epoxy matrix to σ_{fl} = 79.3–88.1MPa and E = 2.10–2.62 GPa, respectively. The impact strength in this case is characterized by the maximum values for the content of the hardener q = 10 weight parts (Fig. 3, curve 2) and is W = 10.75 kJ/m^2.

To confirm the above results of the physical and mechanical properties of polymer matrices, the fracture surface was additionally investigated at different content of hardeners by optical microscopy. The magnification range of the fracture surface image was × 250 times. Analysis of fracture fractures of epoxy matrices allows to obtain a characteristic of the formed material in terms of homogeneity, the presence of structural defects, the nature of the destruction. Thus, complex studies of the properties and structure of the formed matrices allow to form certain ideas about the technological mode of formation of the polymer matrix with high indicators of physical and mechanical properties. It was considered appropriate to compare the material, which is characterized by high physical and mechanical properties, i.e. polymer matrix with PEPA hardener set at a temperature of T = 413 K and polymer matrix with TETA hardener set at a temperature of T = 393 K. Analysis of the obtained fractograms states that the structure of the fracture surface at first glance is quite similar. However, in a more detailed analysis of the structure of the matrices observed a change in the stress state of the material when the content of hardeners.

Epoxy matrix with PEPA hardener with a content of q = 8 weight parts, which is set at a temperature of T = 413 K (Fig. 4, *a*) is characterized by a significant stress state, which is expressed by the presence of depressions and cracks of chaotic nature, which are directed in different directions. the starting point of the chip. This type of fracture of the studied samples is characteristic of the material with high residual stresses, which is consistent with the results of the study presented in the previous work [10]. Subsequently, the amount of hardener was increased to q = 10 weight parts (Fig. 4, *b*) leads to a decrease in the stress state of the polymer on the surface of which we observe a smaller number of recesses and their insignificant recess.



a *b* *c* *d*

a) 8 weight parts, b) 10 weight parts, c) 12 weight parts, d) 14 weight parts

Figure 5 – Fracture pattern of the polymer matrix hardened at a temperature T = 393 ± 2 K with usage of TETA hardener

Additionally, it was observed that the structure of the material with the content of PEPA hardener in the range from q = 12–14 weight parts (Fig. 4, *c*, *d*). The surface of the studied materials is characterized by a relief with small craters on the surface.

The fractures of the polymer matrix set by the TETA hardener at a temperature of T = 393 K were similarly studied. The analysis of the obtained fractograms showed that the fracture surface as in the previous case is characterized by both straight and branched chip lines. This in its turn makes it possible to argue about the nature of the influence of the hardener TETA on the formation of the epoxy matrix. Thus, when the content of the hardener in the polymer matrix with a content of q = 8 weight parts formed material with noticeable moderate depressions, chip lines (Fig. 5, *a*) which are tightly located over the entire surface of the test material. This indicates the structure of the developed material with a slight stress state. When increasing the content of the hardener to q = 10 weight parts we observed a surface with branched chipping lines, which are smoothly and gradually connected to each other (Fig. 5, *b*). The presented results of the study also indicate a decrease in the stress state of the matrix, and therefore, such materials are characterized by increased resistance to failure. Analysis of the fracture surface of materials with the content of the hardener TETA q = 12–14 weight parts characterized by inhomogeneous transitions during destruction. This indicates a significant residual stress in the polymer structure (Fig. 5, *c*, *d*). The obtained results correlate with the results of the study of the physical and mechanical properties of the epoxy matrix, which indicates the reliability of the obtained results.

Conclusions

On the basis of the conducted researches the dynamics of influence of PEPA and TETA hardeners in epoxy binder on physical and mechanical properties of polymer matrix is established.

1. It is proved that for the repair of gas production equipment as a sealing solution it is possible to use polymers based on epoxy oligomer DER-331 and hardeners TETA and PEPA, respectively. It is established that for the formation of a matrix with improved physical and mechanical properties it is necessary to introduce PEPA hardener with a content of q = 8 weight parts and the polymerization temperature T = 413 K. In this case, a material is formed with the following properties: destructive bending stresses σ_{fl} = 85.2 MPa, modulus of elasticity E = 2.78 GPa. At the same time, it was considered appropriate to use TETA hardener, as at the polymerization temperature T = 393 K obtained physical and mechanical properties that are higher than with PEPA. Namely, when using the hardener TETA in the amount of q = 8–10 weight parts the following values of physical and mechanical properties were obtained: destructive stresses during the flexion are σ_{fl} = 80–95.1 MPa, modulus of elasticity E = 2.8–2.9 GPa, impact strength W = 7.9–13.5 kJ/m^2.

2. The fracture surface of epoxy matrices was investigated by optical microscopy. Analysis of fracture fractures of epoxy matrices suggests that the fracture surface is characterized not only by straight chip lines, but also branched. It is shown that the pronounced fracture lines of the polymer matrices correspond to the stress state. In both cases, at a concentration of hardeners q = 8–10 weight parts we observed less branched chipping lines with relatively uniform transitions. This in its turn makes it possible to state the reduction of the stress state of the polymer, and hence its increased resistance to fracture.

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Полімерні матеріали на основі епоксидного олігомеру DER-331 і твердників різної фізико-хімічної природи для ремонту устаткування газовидобувного комплексу

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Визначено оптимальний вміст твердників поліетиленполіамін (ПЕПА) і триетилентетрамін (ТЕТА) та температури полімеризації при формуванні матриці на основі епоксидного олігомеру DER-331. Досліджено динаміку залежності вмісту твердника на фізико-механічні властивості епоксидної матриці. Згідно отриманих результатів дослідження запропоновано матеріали з оптимальним вмістом твердника та температурного режиму полімеризації для формування композиції з підвищеними фізико-механічними властивостями і її подальшого використання для ремонту газопромислового обладнання. Розроблені полімерні матеріали, що містять твердник ТЕТА за вмісту q = 8–10 мас. ч. на 100 мас. ч. епоксидного олігомеру DER-331, мають високі показники фізико-механічних властивостей, зокрема: руйнівні напруження при згинанні σ_{bend} = 95.1–80.0 МПа, модуль пружності при згинанні E = 2.8–2.9 ГПа, ударну в'язкість W = 7.9–13.5 кДж/м^2. Структура зламу таких композитів характеризується менш глибокими розгалуженими лініями сколу з відносно рівномірними переходами, що дає можливість констатувати про незначний напружений стан полімеру, а отже, і його підвищену стійкість до руйнування.

Ключові слова: *газова промисловість, епоксидна матриця, твердник, фізико-механічні властивості.*