Increasing the reliability of the equipment of oil and gas transportation industry due to polymeric nanocomposites

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Abstract

On the basis of the performed tests of the thermophysical properties of epoxy composites filled with nanoparticles, using modern research methods, the permissible temperature ranges have been set, at which it is possible to use the developed materials. The thermal coefficient of linear expansion (α) and heat resistance (T) of epoxy composites have been investigated. The absolute values of the thermal coefficient of linear expansion of materials, which can be used in different temperature ranges, have been defined. It has been proved that for the formation of composite materials with enhanced thermophysical properties, it is advisable to use a nano filler in the amount of $q = 0.5$ %. This material is characterized by the highest activation energy, resistance to structural change at the highest temperatures and intense interaction of functional groups of the filler and epoxy oligomer during the formation at the molecular level among all investigated materials.

Keywords: *destruction, epoxy composite, exoeffect, heat resistance, thermal resistance.*

Operational life of the equipment of the oil and gas transportation industry depends to a large extent on the conditions of their operation and quality of used materials. Taking into account external factors (aggressive environment, temperature changes, mechanical loads, etc.) that affect the surface of the equipment of the oil and gas industry, there is a rapid destruction of them. Therefore, an urgent task for this direction is an in-depth study of materials degradation taking into account structural heterogeneity, the influence of operational factors on the origin and development of material damage, with the aim of developing new nanocomposites and coatings on their basis, which provide for increasing their operational characteristics. To ensure reliable operation, as well as long service life of the equipment of the oil and gas industry, it is expedient to use epoxy nanocomposites and coatings based on them with a complex of improved adhesion, physical and mechanical, thermophysical, anticorrosive properties, wear resistance. Providing the above-mentioned will ensure resistance to corrosion damage and wear of surfaces during operation, and thus increase the life of their work. In this regard, the research and development of polymeric nanocomposites by introducing new technological methods for the formation and optimization of ingredients is a promising direction of the present.

It is known [1–3] that it is possible to improve the cohesive and, in particular, the thermophysical properties of polymer composites as a result of their modification, plasticization or introduction of nano additives for homeopathic contents. The use of dispersed nanofillers, which is beneficial from an economic and environmental point of view, is relevant. The authors [1–6] show that the introduction of dispersed nanoparticles into a polymer binder for insignificant content (0.05–0.15 %) provides an increase in cohesive characteristics of protective coatings in 2.2–2.8 times.

Thus, we can indicate that the development of new technologies for obtaining polymer nanocomposites and protective coatings on their basis to increase the operational life of oil and gas equipment is an urgent task. At the same time, it is important to create environmentally friendly and economically profitable materials for renovation work. In this context, the use of nanoaditives in a small amount in polymeric composites is rather promising from a scientific and practical point of view.

The aim of the work is to develop measures to explore the possibility of using epoxy nanocomposites to improve the thermophysical properties of the equipment of the oil and gas transportation industry.

Materials and research methods

The epoxy dyanoic oligomer of the mark ED-20 (GOST 10587–84), which is characterized by high adhesion and cohesive durability, 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 composites.

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For cross-linking of epoxy compositions, a polyethylene polyamine hardening agent PEPA (TU 6-05-241-202–78) has been used, which allows the materials to be hardened at room temperatures. It is known [1] that PEPA is a low molecular weight substance consisting of such interconnected components as: $[-CH_2-CH_2-NH-]_n$. Composite material was cross-linked by introducing the hardening agent into the composition at a stoichiometric ratio of components per content (mass fraction) – ED-20: PEPA – 100 : 10.

As a filler, particles of nanopowders were used. The grains of the particles are d = 5–7 nm. The content of the filler was changed within q = 0.01–1.00 pbw per 100 pbw epoxy binder.

In this paper, the following properties of composite materials were investigated: the thermal coefficient of linear expansion and heat resistance.

Heat resistance (by Martens) of composites was determined in accordance with GOST 21341–75. The research methodology is to determine the temperature at which the sample under study is heated at a speed of υ = 3 K/min under the impact of a constant bending load F = 5 ± 0.5 MPa, which results in deformation to a given value (h = 6 mm).

Thermal coefficient of linear expansion of materials was calculated by the curve of the dependence of the relative deformation on temperature, approximating this dependence on the exponential function. Relative deformation was determined by changing the length of the sample with increasing temperature in stationary conditions (GOST 15173–70). The dimensions of the samples for research: 65 × 7 × 7 mm, the non-parallelism of the polished ends was not more than 0.02 mm. Before the study, the length of the sample was measured with an accuracy of ± 0.01 mm. The rate of raising the temperature was υ = 2 K/min.

The deviations of the values in the investigations of the parameters of the thermophysical properties of the composite materials (heat resistance by Martens, thermal coefficient of linear expansion) amounted to 4–6 % of the nominal value.

Research results and their discussion

It has been experimentally established (Fig. 1) that the heat resistance of the initial epoxy matrix treated with ultrasound is T = 341 K. It has been proved that the presence of nano disperse particles in epoxy systems significantly influences the process of cross-linking of materials, since the introduction of an additive in the selected range of research in the minimum amount is q = 0.10 pbw per 100 pbw the epoxy oligomer ED-20 (hereinafter referred to as the mass content of 100 pbw of the epoxy oligomer ED-20) provides an increase in the heat resistance values from T = 341 K (for an epoxy matrix) to T = 360 K The maximum (T = 365 K) on the dependence curve "T – q" was observed when the nanoscale was introduced into the polymer at a content of q = 0.25 pbw. Further increasing the content of the filler to q = 2.00 pbw does not lead to improvement of thermophysical properties of composites, since the value of heat resistance of the developed materials varies within the limits of the experimental error (ΔT = ± 1 K). Thus, it can be argued that the nanoparticles have a positive influence on the improvement of the heat resistance of epoxy composites, which, in our view, is ensured by the activation of physical and chemical interaction at the interface of the phases "nano-filler-epoxy oligomer". In this case, the critical content of nanoparticles (q = 0.25–0.50 pbw) in the epoxy binder is established. Formation of composites for such a content increases their heat resistance from T = 341 K (for an epoxy matrix) to T = 366 K.

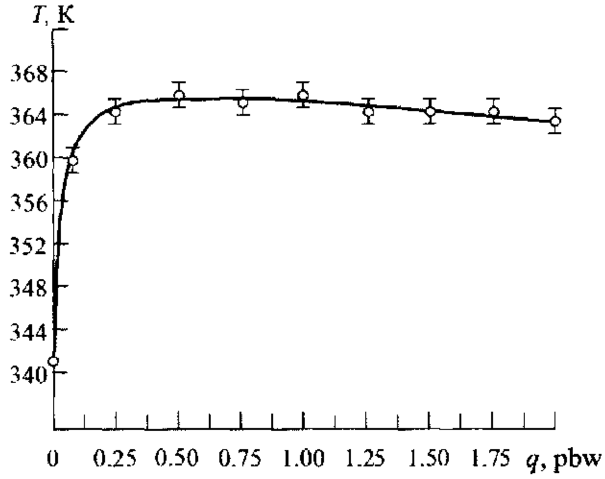
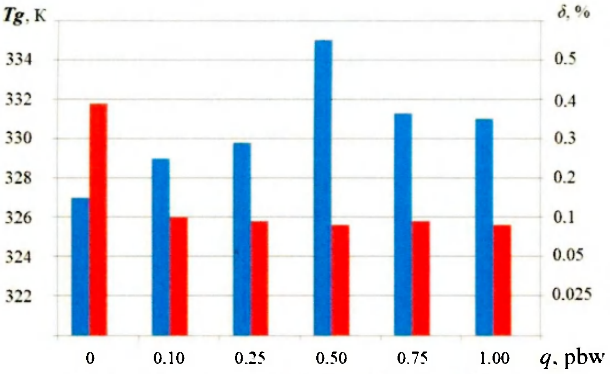


Figure 1 – Dependence of heat resistance of CM on the contents of the nano filler

It has been proved (Fig. 2) that the glass transition temperature increases with the increase of the amount of the nano filler to its critical content in the epoxy matrix, which is q = 0.50 pbw. When adding an additive for this content, the glass transition temperature increases from T_g = 327 K (for the epoxy matrix) to T_g = 334 K. Further, the increase in the content of the filler leads to deterioration of the properties of the materials, because for CM with the number of particles q = 0.75–1.00 pbw the glass transition temperature is T_g = 330–332 K. It is obvious that the critical content of the nanoparticles in the epoxy KM is q = 0.50 pbw, which is consistent with the results of the study of the heat resistance of the materials. In our opinion, the excessive number of nanoparticles leads to the formation of thermodynamically unbalanced systems, which implies the deterioration of their thermophysical properties. The active particles of the filler during gel formation interact with the lateral groups and segments of the macromolecules of the epoxy oligomer. This speeds up the processes of structuring the composites. However, the excessive amount of structural remnants involves the formation of systems with defective structure, which contributes to the deterioration of cohesive properties of materials. In our opinion, this is the main reason for decreasing the glass transition temperature for CM, where the content of nanoparticles is higher than the critical content (q = 0.50 pbw). At the same time, this hypothesis is planned to be tested by the authors in the future using the methods of infrared spectroscopy and electron microscopy.



1 – matrix; 2 – q = 10 pbw; 3 – q = 20 pbw; 4 – q = 30 pbw; 5 – q = pbw; 6 – q = 50 pbw

– glass transition temperature (T_g)

– shrinkage (δ)

Figure 2 – Dependence of the glass transition temperature (T_g) and shrinkage (δ) of CM on the content of the nano filler

The shrinkage test confirmed the results of the above tests. It is shown (Fig. 2) that the shrinkage of the initial matrix (in the study in the temperature range ΔT = 303–473 K) is δ = 0.32 %. The introduction of the nano-filler results in a decrease in the shrinkage of the CM to values δ = 0.07–0.09 %, which indicates the significant effect of the additive on the content of the gel fraction in the CM, and, consequently, on the indices of their cohesive, including thermophysical properties.

In order to confirm the above mentioned results, at the next stage, the thermal coefficient of linear expansion of CM with nanodispersed particles was investigated. It was experimentally established (Table 1), that in the temperature range of ΔT = 303–323 K, the introduction of nanoparticles provides a 2.0–2.2 times decrease in the thermal coefficient of linear expansion of CM (from $\alpha = 6.3 \cdot 10^{-5}$ K^{-1} (for the polymer matrix) to $\alpha = (2.15–3.15) \cdot 10^{-5}$ K^{-1}. It is interesting to analyze the difference in the thermal coefficient of linear expansion between the matrix and the CM in the temperature range of ΔT = 303–423 K. In this field of influence of the thermal field, the greatest difference was observed in the values of the thermal coefficient of linear expansion between the matrix and the materials developed. It has been proved (Table 1) that the introduction of disperse particles ensures a 2.9–3.2 times decrease in the values of thermal coefficient of linear expansion of composites compared to the polymer matrix (from $\alpha = 9.92 \cdot 10^{-5}$ K^{-1} (for a polymer matrix) to $\alpha = (3.37–3.48) \cdot 10^{-5}$ K^{-1}. It should be noted that throughout the studied range of temperatures (ΔT = 303–473 K), composites containing nanoparticles in the amount of q = 0.50 pbw are characterized by the lowest values of the thermal coefficient of linear expansion ($\alpha = 8.24 \cdot 10^{-5}$ K^{-1}), which is in good agreement with the results of previous studies. Thus, it can be stated that the formation of protective coatings on the basis of epoxy composite containing q = 0.50 pbw of nano-filler will significantly increase the life of the equipment of the oil and gas transportation industry.

Table 1 – Thermal coefficient of linear expansion of CM at various temperature ranges of the study

Filler content *q*, pbw	Thermal coefficient of linear expansion $\alpha \cdot 10^5$, K^{-1}			
	Temperature ranges of the study *ΔT*, K			
	303–323	303–373	303–423	303–473
Matrix	6.30	6.81	9.92	10.91
0.10	3.00	2.40	3.37	8.36
0.50	2.15	2.35	3.42	8.24
0.75	2.34	2.48	3.45	8.62
1.00	3.15	2.53	3.48	8.65

Conclusions

The critical content of nanoparticles (q = 0.25–0.50 pbw) in an epoxy binder was experimentally determined. Formation of composites for such a content increases their heat resistance from T = 341 K (for an epoxy matrix) to T = 366 K.

It has been proved that the glass transition temperature increases with an increase in the amount of the nano filler to its critical content in the epoxy matrix, which is q = 0.50 pbw. When adding an additive for this content, the glass transition temperature increases from T_g = 327 K (for the epoxy matrix) to T_g = 334 K. The results of the above tests confirmed the shrinkage. It has been proved that the shrinkage of the initial matrix (in the study in the temperature range ΔT = 303–473 K) is δ = 0.32 %. The introduction of the nano-filler results in a reduction in the shrinkage of the composites to values δ = 0,07–0,09 %, which indicates the significant effect of the additive on the content of the gel fraction in the CM, and, consequently, on the indicators of their cohesive and thermophysical properties.

It has been justified that throughout the studied range of temperatures (ΔT = 303–473 K), composites containing nanoparticles in the amount of q = 0.50 pbw are characterized by the lowest values of the thermal coefficient of linear expansion ($\alpha = 8.24 \cdot 10^{-5}$ K^{-1}), which is in good agreement with the results of previous studies. Consequently, it can be stated that the formation of protective coatings on the basis of an epoxy composite containing q = 0.50 pbw of filler for 100 pbw of epoxy oligomer ED-20 will significantly increase operational life of oil and gas transport equipment.

References

[1] Buketov, AV, Zinchenko DO & Smetankin, SO 2017, 'Nanomodified dispersed particles- and synthetic fibers-filled epohy composite materials for the metal-polymer tribosystems of transport vehicles', *Nanomechanics Science and Technology: An International Journal*, vol. 8, pp. 41–54.

[2] Buketov, A, Maruschak, P, Sapronov O, Zinchenko D & Jatsjuk, V 2016, 'Enhancing performance characteristics of equipment of sea and river transport by using epoxy composites', *Transport*, vol. 31(3), pp. 333–342.

[3] Chernyn, NE 1982, *Epoxyde materials in composition*, Moscow, Chemistry. [in Russian]

[4] Buketov, AV, Sapronov, OO, Zinchenko, DO & Jatsjuk, VM 2015, 'The thermophisical properties of epoxy composites filled with silver carbonate microdisperse particles', *Bulletin of Kherson National Technical University*, no. 4(55), pp. 192–195. [in Ukrainian]

[5] Buketov, AV, Sapronov, AA, Akymov, AV, Braylo NV & Zynchenko, DA 2016, 'Improvement of heat and physical properties of CM on the basis of plastic properties of an epoxy matrix by introduction of heat-resistant microdisperced fillers of different physical nature', *Mechanics of composite materials in construction*, no. 2, pp. 254–268. [in Russian]

[6] Hodakovs'kyj, OV, Amelin, MJu, Smetankin, SO, Akimov, OV & Jacjuk, VM 2016, 'Investigation of the effect of paraaminoazobenzene on the adhesion properties of epoxy matrix for protective coatings of vehicles', *Bulletin of NTU «HPI»*, no. 50 (1222), pp. 42–46. [in Ukrainian]

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Підвищення надійності устаткування нафтової та газотранспортної промисловості за рахунок полімерних нанокомпозитів

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На основі вивчення теплофізичних властивостей епоксикомпозитів, наповнених наночастками, за допомогою сучасних методів дослідження встановлено допустимі межі температури, при яких можна їх використовувати. Досліджено термічний коефіцієнт лінійного розширення (α) і теплостійкість (Т) епоксикомпозитів. Встановлено абсолютні значення термічного коефіцієнту лінійного розширення матеріалів, які можна застосовувати у різних температурних діапазонах. Виявлено, що для формування композитних матеріалів з підвищеними показниками теплофізичних властивостей доцільно використовувати нанонаповнювач у кількості q = 0,5 мас.ч. Такий матеріал характеризуються найбільшою енергією активації, стійкістю до структурних перетворень при максимальних температурах та інтенсивною взаємодією функціональних груп наповнювача та епоксидного олігомеру під час структуроутворення на молекулярному рівні серед усіх досліджуваних матеріалів.

Ключові слова: *деструкція, екзоефект, епоксидний композит, теплостійкість, термостійкість.*