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Polymer materials based on ED-20 epoxy oligomer and carbon nanotubes for repair of gas production complex equipment

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Abstract

The scientific paper presents the technological aspects of modifying the ED-20 epoxy oligomer with carbon-containing additives to improve the thermophysical characteristics of nanocomposite materials and functional protective coatings based on them. The dynamics of the dependence of carbon nanotube content on the thermophysical properties of nanocomposites has been studied. Materials with improved thermal conductivity values are proposed for the formation of adhesives or functional coatings for the repair of gas equipment. The developed nanocomposites containing carbon nanotubes with the content of q = 0.075–0.100 pts.wt. per 100 pts.wt. of ED-20 epoxy oligomer are characterized by improved thermal conductivity λ = 0.40–0.58 W/m·K. An additional comparison of the structure of the developed nanocomposites and the calculated value of the activation energy allows us to state that a 2.0–2.7 times improvement in the thermophysical characteristics is associated with the resistance of the physicochemical bonds to the effects of temperature due to the active chemical and physical effects of the nanoadditive.

Keywords: *activation energy, carbon nanotubes, electron microscopy, epoxy matrix, thermophysical properties.*

Polymers are widely used in many industries, including the gas production complex for the repair of metal structures (main pipelines, valves) and highly specialized equipment (tubing, separation equipment, gas treatment units). The improved complex of adhesive and mechanical properties of polymeric materials based on epoxy binders makes it possible to use them in the development of sealing materials, coatings for various functional purposes, and adhesives. The ability to control the characteristics of thermoplastic polymers by rational selection of the "polymer-filler" system allows us to change their properties over a wide range, and therefore, expand the area of their use [1–6].

To ensure the efficiency and reliability of equipment and valve operation of the gas production complex, it is important to use polymeric materials filled with nano-additives. One of the promising nanoadditives that improve adhesive [7] and physico-mechanical [8] properties are carbon nanotubes. Despite high mechanical strength, CNTs are characterized by high thermal conductivity (1000–4000 W/m·K) and are also resistant to critical deformations of bending, tension, and compression. A characteristic property of CNTs is their ability to absorb liquid or gaseous substances. Therefore, it is promising to use such materials to provide improved thermal properties and their subsequent use in the repair and development of new equipment for the gas production complex.

The aim of the research is to determine the content of carbon nanotubes in an epoxy binder to improve the thermophysical characteristics of nanocomposites intended for the repair of process equipment and fittings.

Materials and research methods

ED-20 epoxy resin was used to form epoxy nanocomposites. For cross-linking the epoxy binder, there was used cold-hardening polyethylene polyamine (PEPA).

As a filler for experimental studies, there were used carbon nanotubes with a dispersion of 5 nm. The content of the nanofiller was changed within q = 0.010–0.500 pts.wt.

The technology for the formation of epoxy nanocomposites was carried out in a certain sequence indicated in scientific papers [9–11].

Thermal conductivity, polymer structure, and activation energy were studied in the course of the research.

The thermal conductivity was researched on an IT-λ-400 device, which is designed to study the temperature dependence of the thermal conductivity of solid materials in the monotonous heating mode based on the dynamic calorimeter method.

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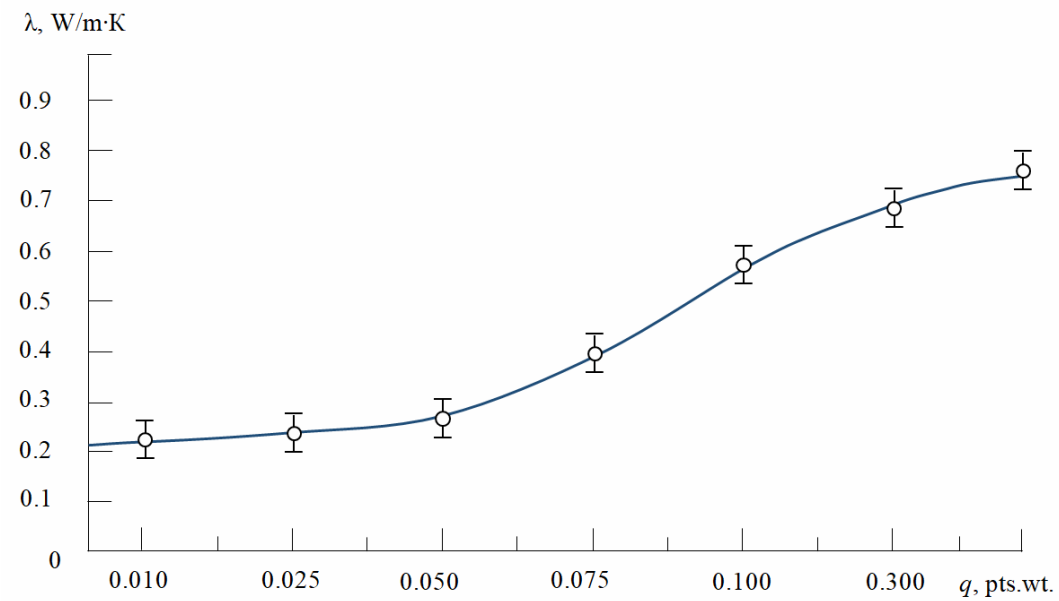


Figure 1 – Dependence of the thermal conductivity of composites on the content of carbon nanotubes

The study of the structure and microrelief of the polymer nanocomposite surfaces was carried out using the method of LEO EVO 50 scanning electron microscope (Zeiss, Germany).

The activation energy was calculated by mathematical processing of the TGA curve (thermogravimetric analysis) according to the Broido method [12–14]. The study was carried out in the temperature range ΔT = 323–873 K, using quartz crucibles for samples with a volume of V = 0.5 cm^3. In the course of the study, the rate of temperature rise was υ = 5 K/min, while Al_2O_3 (m = 0.5 g) was used as a reference substance, and the weight of the test sample was – m = 0.3 g. The error in determining the temperature was ΔT = ±1 K. The accuracy in determining thermal effects was 3 J/h. The accuracy of determining the change in sample weight was Δm = 0.02 g.

The condition for applying the Broido method is the first order of the decomposition reaction, which applies to both thermoset and thermoplastic polymers. The loss of matter mass is the 1st order process (n = 1) if there is observed the linear dependence of ln (100/(100 – Δm)) on the reciprocal temperature 10^3/T, K^{-1}. According to this technique, it is necessary to determine the mass loss (Δm) of the composite at a given temperature T and graphically draw a line in which E must be expressed by the tangent of the inclination angle of the logarithmic dependence of Δm on the reciprocal temperature T. Then the value of the activation energy of thermal destruction (kJ/mol) can be found from the Formula:

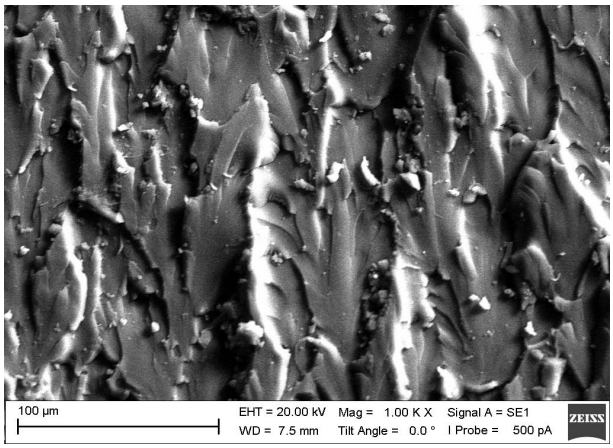
$$E_a = - R \operatorname{tg}(\varphi). \quad (1)$$

Results of the study and their discussion

Thermoplastic polymer materials can be used as thermal insulation materials due to their low thermal conductivity. In such materials, heat transfer depends on the degree of crosslinking, which directly affects the intramolecular mobility of the kinetic elements of the polymer. At the same time, such materials can be used as adhesives for the repair of heat exchangers for various functional purposes. Therefore, the dependence of the thermal conductivity of epoxy nanocomposites on the CNT content has been preliminary considered. The thermal conductivity of an unfilled polymer matrix has been determined to be λ = 0.22 W/m·K (Fig. 1).

The introduction of CNTs according to the content q = 0.010–0.050 pts.wt. does not significantly affect the thermal conductivity since the thermal conductivity varies within $\Delta\lambda$ = 0.03 W/m·K. It is known [15] that the value of the thermal conductivity of CNTs significantly exceeds the corresponding value of the polymer matrix. At the same time, previous research works [8, 10] have shown that at such a content, the value of the complex of mechanical and thermophysical characteristics increases significantly. This is due to a significant adsorption interaction between the polymer and the filler when the interaction forces at the boundary of "polymer-nanoparticle" phase separation make it possible to unfold the polymer molecule, which provides resistance to bending and impact deformations. Therefore, it is believed that a slight increase in thermal conductivity is associated with a minimum contact between nanoparticles. The increase in the content of CNT to q = 0.075–0.100 pts.wt. provides a monotonous increase in the value of thermal conductivity by 2.0–2.7 times (λ = 0.40–0.58 W/m·K). These results are in good agreement with the main provisions of the classical theory of thermal conductivity of polymers [15]. If we consider a uniform distribution of nanoparticles in the bulk of the polymer, which provides an ordered structure (Fig. 2, *a*), then an increase in the amount of CNTs leads to a decrease in the distance between nanoparticles. This, in turn, ensures the formation of penetrating nanoclusters, which transfer thermal energy through the nanoparticle phase. That is, the formation of such clusters ensures the development of specific heat-conducting channels in the thermoplastic matrix, which

leads to a linear increase in thermal conductivity. While exceeding the limiting value of CNTs, that is, the introduction of more than q = 0.100 pts.wt., provides, on the one hand, an increase in thermal conductivity (λ = 0.70-0.85 W/m·K), it also causes the formation of structural defects (Fig. 2, *b*), which in turn reduces the mechanical strength of the polymer.



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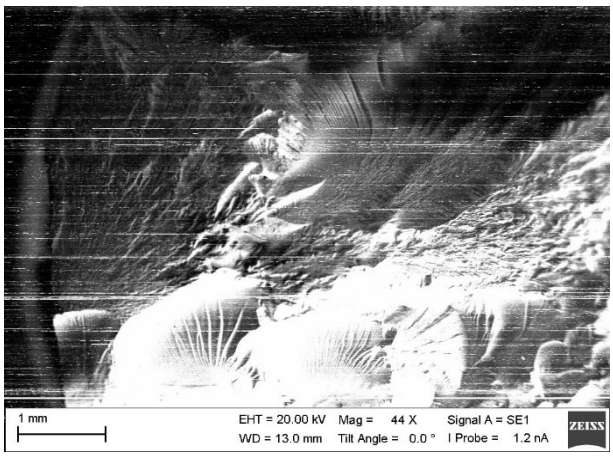


b)

q, pts. wt.: a) 0.100; b) 0.300

Figure 2 – Electron micrographs of the fracture of epoxy nanocomposites with different contents of carbon nanotubes

It should be noted that when developing nanocomposites, adhesives, or sealing materials, it is necessary to take into account the operating temperatures at which the technological equipment of the gas production complex will be operated. Therefore, additionally, based on the TGA analysis, the activation energy of the CNT-filled composites was calculated. We know [13] that the activation energy characterizes the overabundance of thermal energy necessary for the destruction of chemical bonds under conditions of thermal exposure. Therefore, the calculation of the activation energy will make it possible to determine the optimal content of the nanocomposite, which will be appropriate to use in the repair of process equipment.

The activation energy was determined using the TGA curve (Fig. 3) according to the Broido method [12–14]. The most intense course of the thermal destruction reaction for filled CMs takes place in the temperature range ΔT = 597–735 K (Fig. 3), which corresponds to the weight loss $T_{0...90}$ %, K [10]. Therefore, the choice of the temperature range for studying TGA curves is relevant for research, where the onset and significant structural changes of the nanocomposite were observed: ΔT = 573–713 K. In the specified temperature range, the mass loss of materials was determined with an interval of ΔT = 10 K and an interval of ΔT = 50 K; in fact, it was determined with an interval of ΔT = 10 K (Fig. 3) for NCM filled with CNT at a content of q = 0.050 pts.wt. Similarly, studies were carried out for NCM filled with CNT at the content of q = 0.100–0.300 pts.wt.

The value of the mass of the studied composite material was calculated as a percentage using Formula 1 [12].

$$\Delta m = \left(100 - \frac{m_{in} + \Delta m}{\Delta m} \cdot 100\right)\%, \qquad (2)$$

where m_n is the initial mass of the material at the initial test temperature, T_1 = 573 K (m_n = const), g; Δm is the mass loss of the material, g.

The mass of nanocomposites at the initial temperature was taken as 100 %. Table 1 and Table 2 show the results of processing the TGA curve and the parameters required to calculate the energy activation of nanocomposites.

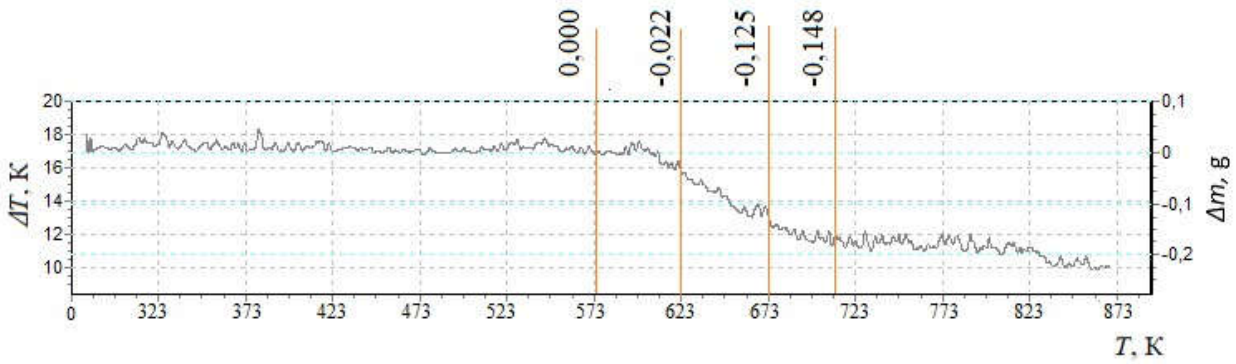


Figure 3 – Mass loss of a composite material filled with carbon nanotubes (the content of q = 0.050 pts.wt.), with an interval in the temperature range – ΔT = 573-713 K

Table 1 – Results of nanocomposites studies with different carbon nanotube contents

T, K	Change in mass of samples, g					
	Content of carbon nanotubes, *q* (pts.wt.)					
	0.010	0.025	0.050	0.075	0.100	0.300
573	0.36	0.32	0.30	0.33	0.26	0.29
583	0.36	0.32	0.30	0.33	0.26	0.29
593	0.36	0.31	0.30	0.32	0.25	0.29
603	0.35	0.31	0.29	0.32	0.25	0.28
613	0.34	0.30	0.28	0.31	0.24	0.27
623	0.32	0.28	0.26	0.29	0.23	0.25
633	0.30	0.25	0.24	0.27	0.22	0.23
643	0.28	0.23	0.22	0.24	0.21	0.21
653	0.26	0.21	0.20	0.22	0.18	0.19
663	0.23	0.19	0.18	0.20	0.15	0.17
673	0.22	0.17	0.17	0.18	0.12	0.16
683	0.20	0.16	0.15	0.16	0.11	0.13
693	0.19	0.15	0.13	0.15	0.09	0.12
703	0.18	0.14	0.12	0.14	0.07	0.11
713	0.17	0.14	0.12	0.13	0.07	0.10

Table 2 – Results of TGA-curve processing

T, K	Change in mass of samples (100-Δm)					
	Content of carbon nanotubes, *q* (pts.wt.)					
	0.010	0.025	0.050	0.075	0.100	0.300
573	-19.00	-7.24	-0.34	-10.00	11.88	4.06
583	-21.33	-6.21	0.34	-9.31	12.50	4.06
593	-18.33	-4.14	1.03	-7.93	14.38	4.38
603	-15.67	-2.41	2.41	-6.21	14.69	7.50
613	-12.00	0.69	7.93	-3.10	20.00	10.31
623	-6.33	5.86	12.41	2.07	21.56	15.94
633	-1.33	18.62	21.38	10.34	25.63	22.19
643	7.67	25.17	26.55	21.38	29.38	29.06
653	14.00	31.03	33.45	27.59	39.06	35.00
663	23.33	37.24	42.76	34.83	46.56	39.69
673	26.67	43.45	44.83	41.03	55.00	45.00
683	34.33	48.62	52.76	47.93	59.69	52.19
693	35.67	52.76	59.66	52.76	67.19	55.31
703	41.33	55.17	61.38	56.90	70.63	60.94
713	44.00	55.86	62.41	59.66	72.81	63.44

The calculation of the activation energy is based on the mathematically processed TGA curve using the dependence [12-14]:

$$ln\left(ln\frac{100}{100-\Delta m}\right)=-\frac{E}{R}\cdot\frac{1}{T}+const, \qquad (3)$$

where Δm is the mass loss of the sample, g; E is the activation energy, kJ/mol; R is the universal gas constant, R = 8.31 J/(mol·K); T is temperature, K.

The results of calculating the value of the double logarithm of the change in the samples` mass are presented in Table 3.

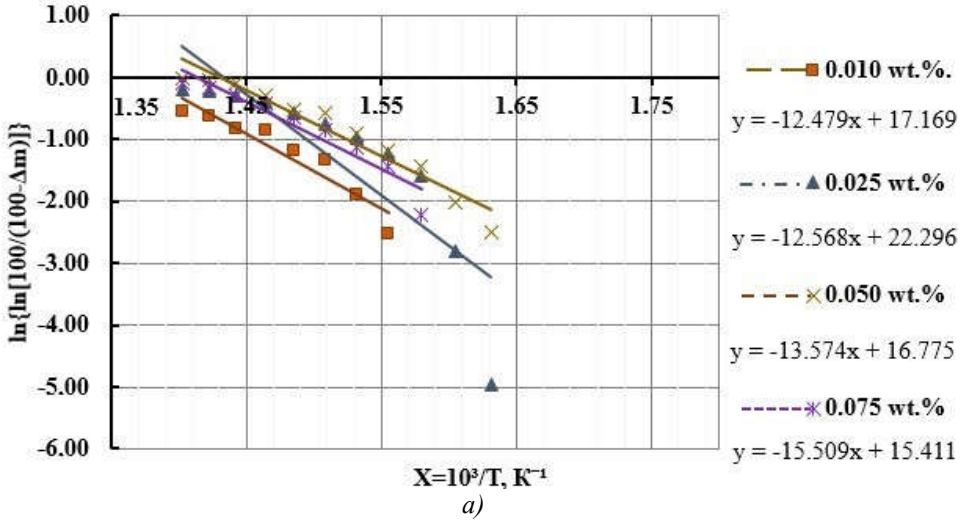
If we know the mass loss (Δm) of the composites filled with CNT at temperature T, a straight line was plotted graphically, in which E was determined from the tangent of the inclination angle of the logarithmic dependence of Δm on the reciprocal temperature T. The value of the destruction activation energy in kJ/mol was found using Formula (1). Fig. 4 shows the graphical dependence of the rate of destruction on the reverse temperature, and Table 4 shows the analytical results of the graphical determination of the activation energy of the developed NCMs.

It has been experimentally proven that the thermal decomposition of the developed composite filled with CNT with a content of q = 0.075 pts.wt. requires the highest activation energy (E_a = 132.2 kJ/mol) among the studied materials.

The calculated values of the activation energy indicate the stability of physicochemical bonds at elevated temperatures due to the maximum compaction of particles in the polymer volume, which ensures a decrease in the segmental mobility of the structural elements of the nanocomposite.

Table 3 – Calculated value of the logarithm of the composites mass change filled with carbon nanotubes using a double logarithm

T, K	ln{ln[100/(100-Δm)]}					
	Content of CNTs, *q* (pts.wt.)					
	0.010	0.025	0.050	0.075	0.100	0.300
573	–	–	–	–	-2.068	-3.183
583	–	–	-5.668	–	-2.013	-3.183
593	–	–	-4.566	–	-1.863	-3.107
603	–	–	-3.712	–	-1.840	-2.552
613	–	-4.973	-2.493	–	-1.500	-2.218
623	–	-2.807	-2.021	-3.868	-1.415	-1.751
633	–	-1.580	-1.425	-2.215	-1.217	-1.383
643	-2.529	-1.238	-1.176	-1.425	-1.056	-1.069
653	-1.892	-0.990	-0.898	-1.131	-0.703	-0.842
663	-1.325	-0.764	-0.584	-0.848	-0.467	-0.682
673	-1.171	-0.562	-0.520	-0.638	-0.225	-0.514
683	-0.866	-0.407	-0.288	-0.427	-0.096	-0.304
693	-0.819	-0.288	-0.097	-0.288	0.108	-0.216
703	-0.629	-0.220	-0.050	-0.172	0.203	-0.062
713	-0.545	-0.201	-0.022	-0.097	0.264	0.006



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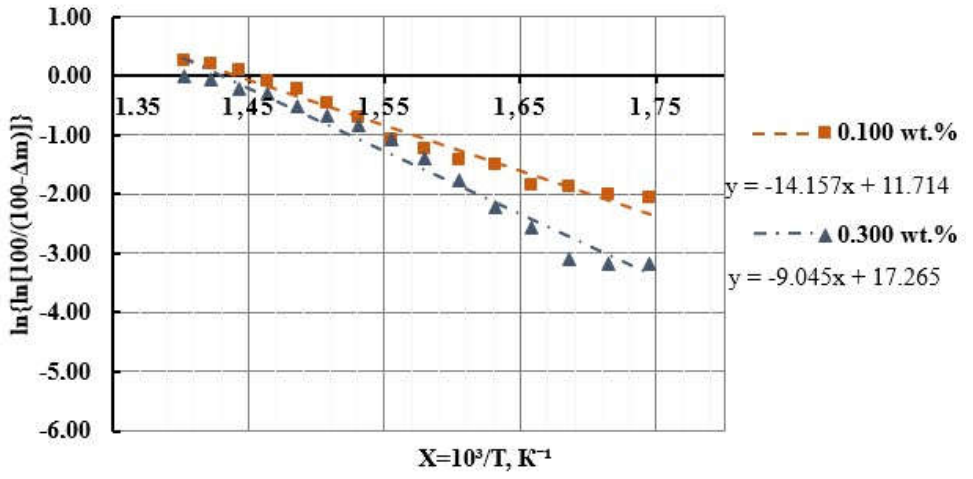

b)

Figure 4 – Graphical dependence of the degradation rate of composites filled with carbon nanotubes on the reciprocal temperature

Table 4 – Calculated value of the activation energy of thermal destruction of composites filled with carbon nanotubes

Content of carbon nanotubes q, % (pts.wt.)	X_{st}	X_{fin}	X_i	Y_{st}	Y_{fin}	Y_i	$tq_{(\varphi)}$	Activation energy E_a, J/mol
0.010	1.555	1.403	0.152	1.403	1.155	1.897	12.479	103.7
0.025	1.631	1.403	0.228	1.403	1.631	2.866	12.568	104.4
0.050	1.715	1.403	0.312	1.403	1.715	4.235	13.574	112.8
0.075	1.605	1.403	0.202	1.403	1.605	3.214	15.909	132.2
0.100	1.745	1.403	0.342	1.403	1.745	4.842	14.157	117.7
0.300	1.745	1.403	0.342	1.403	1.745	3.093	9.042	75.2

Conclusions

It has been established that at the ratio of such components as epoxy oligomer → solid polyethylene polyamine → carbon nanotubes: 100 → 10 → 0.075–0.100 pts.wt. the thermal conductivity of materials increases by 2.0–2.7 times compared to an unfilled matrix. The thermal conductivity values of such nanocomposites are λ = 0.40–0.58 W/m·K.

The structural features of the developed nanocomposites have been established by scanning electron microscopy. It is shown that although the thermal conductivity of the developed materials increases (relative to the polymer matrix) by a factor of 3.1–3.7 with the introduction of nanoparticles at a content of q = 0.300–0.500 pts.wt., the morphological features of the structure do not allow the use of such materials in the repair of a gas production complex. Polymeric materials containing CNT at a content of q = 0.075–0.100 pts.wt. are characterized by the homogeneity of the structure, and, consequently, improved thermophysical properties.

Using the method of thermogravimetric analysis, the mass loss (Δm) of composites was determined in the temperature range – ΔT = 573–713 K, on the basis of which the lines were plotted according to the tangent of the inclination angles φ of the logarithmic dependence. This makes it possible to determine the activation energy, and, consequently, the resistance of physicochemical bonds to the effects of temperature. It has been established that the maximum value of the excess thermal energy required to break chemical bonds under the influence of temperature is characterized by nanocomposites filled with carbon nanotubes at a content of q = 0.075–0.100 pts.wt. since the activation energy is the highest among the studied materials and is E_a = 117.7–132.2 kJ/mol.

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References

[1] Panda, A, Dyadyura, K, Valíček, J, Harničárová, M, Kušnerová, M, Ivakhniuk, T, Hrebenyk, L, Sapronov, O, Sotsenko, V, Vorobiov, P, Levytskyi, V, Buketov, A & Pandová, I 2022, 'Ecotoxicity Study of New Composite Materials Based on Epoxy Matrix DER-331 Filled with Biocides Used for Industrial Applications', *Polymers,* vol. 14(16):3275.

[2] Demchenko, VL, Kobylinskyi, SM, Riabov, SV, Shtompel VI, Iurzhenko, MV & Rybalchenko, NP 2020, 'Novel approach to the formation of silver-containing nanocomposites by thermochemical reduction of Ag+ ions in interpolyelectrolyte-metal complexes', *Applied Nanoscience (Switzerland)*, vol. 10(12), pp. 5409–5419.

[3] Kuzhir, P, Paddubskaya, A, Plyushch, A, Volynets, N, Maksimenko, S, Macutkevic, J, Kranauskaite, I, Banys, J, Ivanov, E, Kotsilkova, R, Celzard, A, Fierro, V, Zicans, J, Ivanova, T, Merijs, Meri, R, Bochkov, I, Cataldo, A, Micciulla F, Bellucci, S & Lambin, P 2013, 'Epoxy composites filled with high surface area-carbon fillers: Optimization of electromag-netic shielding, electrical, mechanical, and thermal properties', *Journal of Applied Physics*, vol. 114(16), 164304.

[4] Dunne, LJ, Sarkar, AK, Kroto, HW, Munn, J, Kathirgamanathan, P, Heinen, U, Fernandez J, Hare J, Reid DG & Clark, AD 1996, 'Electrical, magnetic and structural characterization of fullerene soots', *Journal of Physics: Condensed Matter*, vol. 8(13), pp. 2127–2141.

[5] Burya, A, Kuznetsova, O, Konchits, A & Redchuk, A 2011, 'The Influence of Nanocluster Carbon Materials on the Structure and Properties of Polyamide Nanocomposites', *Materials Science Forum*, vol. 674, pp. 189–193.

[6] Sapronov, O, Buketov, A, Sapronova, L & Vorobiov, P 2022, 'Development of epoxy composites resistant to impact loads. Advanced polymer materials and technologies: recent trends and current priorities: multi-authored monograph / edited by V. Levytskyi, V. Plavan, V. Skorokhoda, V. Khomenko, *Lviv: Lviv Polytechnic National University,* pp. 41–47.

[7] Khun, NW, Troconis, BCR & Frankel, GS 2014, 'Effects of carbon nanotube content on adhesion strength and wear and corrosion resistance of epoxy composite coatings on AA2024-T3', *Progress in Organic Coatings*, vol. 77(1), pp. 72–80.

[8] Sapronov, OO, Buketov, AV, Maruschak, PO, Panin, SV, Brailo, MV., Yakushchenko, SV, Sapronova, AV, Leshchenko, OV & Menou, A 2019, 'Research of crack initiation and propagation under loading for providing impact resilience of protective coating', *Funct. Mater.*, vol. 26(1), pp. 114–120.

[9] Buketov, AV, Sapronov, OO, Brailo, MV, Maruschak, PO, Yakushchenko, SV, Panin, SV & Nigalatiy, VD 2020, 'Dynamics of destruction of epoxy composites filled with ultra-dispersed diamond under impact conditions', *Mechanics of Advanced Materials and Structures*, vol. 27, pp. 725–733.

[10] Buketov, A, Maruschak, P, Sapronov, O, Brailo, M, Leshchenko, O, Bencheikh, L & Menou A 2016, 'Investigation of thermophysical properties of epoxy Nanocomposites', *Crystals and Liquid Crystals*, vol. 628, pp. 167–179.

[11] Buketov, AV, Dolgov, NA, Sapronov, AA & Nigalatii, VD 2018, 'Adhesive pull and shear strength of epoxy nanocomposite coatings filled with ultradispersed diamond', *Strength of Materials*, vol. 50, no. 3, pp. 425–431.

[12] Broido, AA 1969, 'Simple sensitive graphical method of treating thermo gravimetric analyze data', *J. Polym. Sci.- Part A*, vol. 7, pp. 1761–1773.

[13] Yakushchenko, SV, Brailo, MV, Buketov, AV, Sapronov, OO, Popovych, V & Dulebova, L 2022, 'Investigation of the properties and structure of epoxy-polyester composites with two-component bidispersed filler', *Composites: Mechanics, Computations, Applications, An International Journal*, vol. 13(1), pp. 81–95.

[14] Buketov, AV, Smetankin, SA, Akimov, AV & Kulinich, AG 2019, 'Epoxy composite modifications influence on the energy activation's of thermal destruction', *Funct. Mater*., vol. 26, pp. 403–411.

[15] Wang, Z, Qi, R, Wang, J & Qi, S 2015, 'Thermal conductivity improvement of epoxy composite filled with expanded graphite', *Ceramics International,* vol. 41(10), pp. 13541–13546.

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Полімерні матеріали на основі епоксидного олігомеру ЕД-20 і вуглецевих нанотрубок для ремонту устаткування газовидобувного комплексу

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У роботі наведено технологічні аспекти модифікації вуглецевовмістними добавками епоксидного олігомеру ЕД-20 для поліпшення теплофізичних характеристик нанокомпозитних матеріалів і захисних покриттів на їх основі функціонального призначення. Досліджено динаміку залежності вмісту вуглецевих нанотрубок на теплофізичні властивості нанокомпозитів. Запропоновано матеріали з поліпшеними значеннями теплопровідності при формуванні адгезивів чи покриттів функціонального призначення для ремонту газопромислового обладнання. Розроблені нанокомпозити, що містять вуглецеві нанотрубки за вмісту q = 0.075–0.100 мас.ч. на 100 мас.ч. епоксидного олігомеру ЕД-20 характеризуються поліпшеними значенням теплопровідності λ = 0.40–0.58 Вт/м·К. Додаткове співставлення структури розроблених нанокомпозитів і розрахункового значення енергії активації дозволяють констатувати, що поліпшення у 2.0–2.7 рази теплофізичної характеристики пов'язано із стійкістю фізико-хімічних зав'язків до впливу температури, внаслідок активного хімічного і фізичного впливу нанодобавки.

Ключові слова: *вуглецеві нанотрубки, електронна мікроскопія, енергія активації, епоксидна матриця, теплофізичні властивості.*