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Epoxy composite modifications influence on the energy activation's of thermal destruction

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Values of the activation energy of the thermal-oxidative breakdown (E) of modified epoxy composite materials were calculated based on thermogravimetric analysis and using the Broido method. It is established that the composites with the SFEK modifier in an amount of $q = 0.10$ pts·wt. are characterized by the highest values of activation energy ($E = 144.5$ kJ/mol) and composites with the modifier in an amount of $q = 1.75$ pts·wt. are characterized by the activation energy which is equal to $E = 175.0$ kJ/mol. This indicates a significant effect of the modifier on the epoxy composites activation energy. The results of the experiments point to the formation of relatively thermally stable intra- and intermolecular bonds, which proves the compaction of the macromolecule cross-linking in the epoxy composites. The latter, in turn, leads to an increase of thermal stability and, as a consequence, the durability of materials.

Keywords: activation energy, thermogravimetry, Broido method, modifier, epoxy composite, properties.

На основе термогравиметрического анализа и с помощью методики Бройдо были рассчитаны значения энергии активации термоокислительной деструкции (E) модифицированных эпоксикомпозитных материалов. Установлено, что наибольшими значениями энергии активации ($E = 144{,}5$ кДж/моль) характеризуются композиты с модификатором СФЭК в количестве $q = 0{,}10$ масс·ч., а также композиты с модификатором в количестве $q = 1{,}75$ масс·ч., энергия активации которых равняется $E = 175{,}0$ кДж/моль. Это свидетельствует о значительном влиянии модификатора на энергию активации эпоксидных композитов. Результаты эксперимента также указывают на формирование относительно термоустойчивых внутри- и межмолекулярных связей, что свидетельствует об уплотнении сшивки макромолекул эпоксикомпозитов, что приводит к увеличению термостойкости и, как следствие, долговечности материалов.

Вплив модифікації епоксикомпозитів на енергію активації їх термічної деструкції. *А.В.Букетов, С.А.Сметанкін, А.В.Акімов, А.Г.Кулініч.*

На основі термогравіметричного аналізу та за допомогою методики Бройдо були розраховані значення енергії активації термоокислюючої деструкції (E) модифікованих епоксикомпозитних матеріалів. Встановлено, що найбільшими значеннями енергії активації ($E = 144{,}5$ кДж/моль) характеризуються композити з модифікатором СФЕК в кількості $q = 0{,}10$ мас·ч., а також композити з модифікатором в кількості $q = 1{,}75$ мас·ч., енергія активації яких дорівнює $E = 175{,}0$ кДж/моль. Це свідчить про значний вплив модифікатора на енергію активації епоксидних композитів. Результати експерименту також вказують на формування відносно термостій ких внутрішньо- і міжмолекулярних зв'язків, що свідчить про ущільнення з шивання макромолекул епоксикомпозитів. Останнє що призводить до збільшення термостійкості і, як наслідок, довговічності матеріалів.

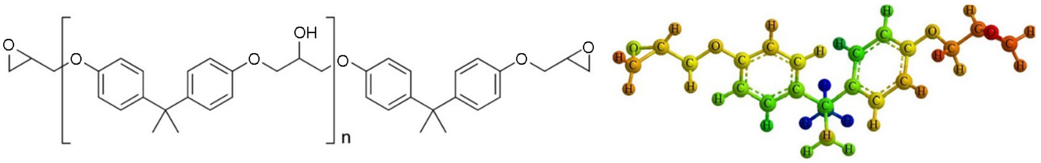

Fig. 1. Structural formula of epoxy diane oligomer ED-20.

1. Introduction

At present, under conditions of increasing competition, the main task of polymer materials producers is the constant improvement of their quality and, consequently, the durability of the products. Polymer products should possess not only high physical and mechanical characteristics, but also such important properties as thermal stability and durability. These characteristics acquire special significance based on the operating conditions of ship and engineering machinery in various climatic regions. The currently created polymer composite materials (CM) are heterogeneous systems consisting of components of different nature. Various fillers are used that give a complex of properties to the materials and stabilizers which reduce the negative impact of environmental factors on the materials. Such studies are very relevant, since the use of their results is necessary to create a scientifically based approach during selecting components and technology for producing CM.

In this regard, it is promising to form and use composites based on an epoxy binder consisting of epoxy-diane resin ED-20 and a hardener of polyethylene polyamine (PEPA) [1–3]. To improve matrix properties, additional modifiers of various natures in small amounts are added to the binder.

2. Materials and research technique

The composites based on epoxy-diane resin ED-20 (GOST 10587-93) (Fig. 1) with a molecular weight of 360...470, containing 21.5 % of epoxy groups are studied. For binding the epoxy oligomer (TU 6-05-241-202-78), a low-molecular-weight hardener — polyethylene polyamine (PEPA) was used (Fig. 2), which allows hardening the materials at room temperatures. The chemical formula of the PEPA is H2N(CH2CH2NH)nH, where n = 1...4, and the dynamic viscosity is 0.9 Pa·s.

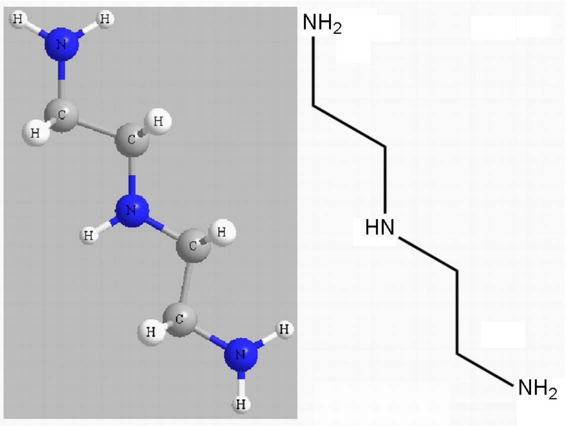

Fig. 2. Structural formula of hardener PEPA.

As a modifier, 4.4 — sulfonylbis (4.1-phenylene)bis(N, N-dietyldithiocarbamate) is used (Fig. 3), characterized by reactivity capacity to interaction with epoxide oligomer molecules due to a significant number of active groups.

The modifier is added in an amount of 0.10 to 2.00 pts·wt. per 100 pts·wt. of the epoxy oligomer ED-20 (hereinafter parts by weight are given per 100 parts by weight of the epoxy oligomer ED-20). The formula of the 4.4-sulfoylbis(4.1-phenylene)bis(N, N-dietyldithiocarbamate) modifier has the following form: $C_{22}H_{28}N_2O_2S_5$.

The epoxy CM is formed using the following technology: dosing of components, hydrodynamic mixing of a modifier and the epoxy-diane resin ED-20 to obtain a homogeneous mixture and subsequent complete decomposition of the additive for a time $\tau = 2\pm0.1$ min at room temperature $T = 298\pm2$ K; introduction of a filler of a predetermined content, ultrasonic treatment of the composition for a time $\tau = 2\pm0.1$ min; addition of the PEPA hardener and hydrodynamic mixing of the components for a time $\tau = 2\pm0.1$ min, and hardening of the composition. The validation of the CM is carried out according to the experimentally established regimes: formation of samples and holding them at a temperature $T = 298\pm2$ K for $\tau = 12.0\pm0.1$ h; heating with a rate $\upsilon = 3$ K/min up to the cross-linking temperature $T = 413\pm2$ K; holding the samples at this

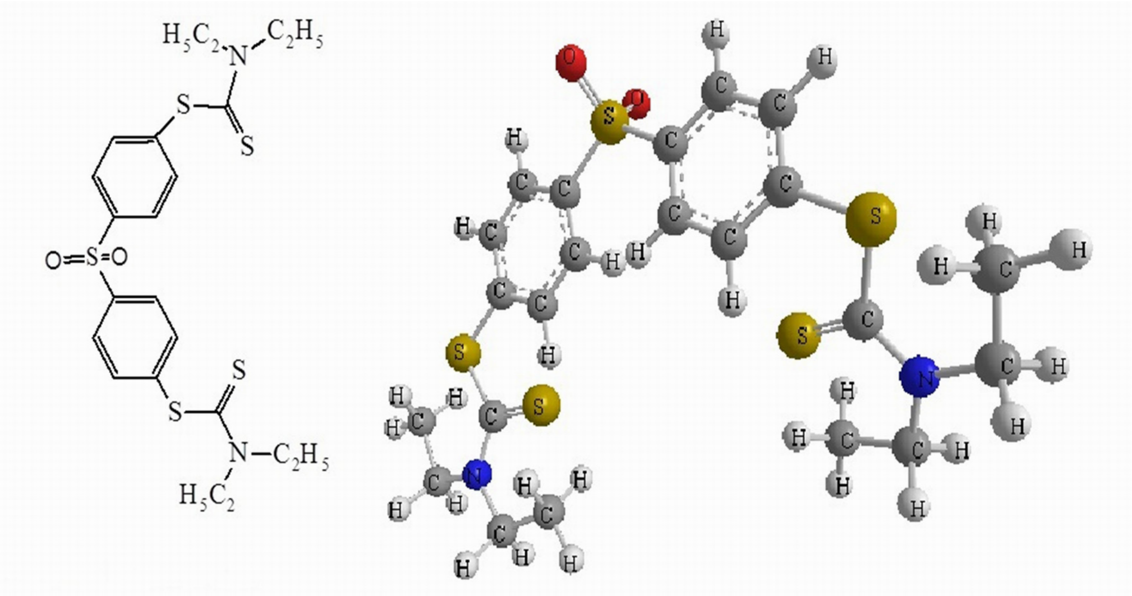

Fig. 3. Structural formula of modifier 4,4-sulfoylbis(4,1-phenylene)bis(N, N-dietyldithiocarbamate).

temperature for $\tau = 2.0\pm0.05$ h, and slow cooling to the temperature $T = 298\pm2$ K. In order to stabilize the structural processes in matrix, the samples are held at a temperature $T = 298\pm2$ K for $\tau = 24$ h in air; then experimental studies follow.

To study the effect of the modifier amount on the thermal and chemical transformations in the composites, a thermogravimetric (TGA) analysis was used with a "Thermoscan-2" derivatograph. The change in the mass of the studied sample was continuously recorded graphically depending on temperature in the form of a characteristic thermogravimetric curve (TG curve).

The study was carried out in an air atmosphere in the temperature range $\Delta T = 298...873$ K using quartz crucibles for samples with volume $V = 0.5$ cm^3. During the studies, the samples were heated in a programmed mode, the rate of temperature rise was $\upsilon = 10$ K/min. In order to more accurately determine the temperature of the beginning of product decomposition in the derivatograms, along with the mass loss curve (TG), the temperature difference between the tested substance and the inert Al_2O_3 sample ($m = 0.5$ g) was analyzed. The weighted quantity of the tested sample was $m = 0.3$ g.

The error in determining the temperature was $\Delta T = \pm1$ K. The accuracy of determining the thermal effects was 3 J/g. The accuracy of determining the change in the mass of sample was $\Delta m = 0.02$ g.

3. Results and discussion

The activation energy is the excess energy necessary for destruction of the chemical bonds that form the main chain of the polymer under the influence of heat and oxygen in the air. This parameter makes it possible to evaluate the effectiveness of the stabilizing action, the degree of cross-linking of epoxy composites, and it is also a universal and fairly accurate criterion for the resistance of CM to thermal-oxidative destruction.

Generally, TG is the preferred technique for such determinations, since the relevant mass changes are easier to measure than the associated heat effects [5].

Therefore, the TGA method was used to fully characterize the stability of modified CMs to thermal-oxidative degradation.

Using the method of thermogravimetric analysis, the change in mass of the sample was recorded depending on the temperature. The experimentally obtained curve of the dependence of the mass change on temperature (thermogravimetric curve or thermogram) makes it possible to judge about thermal stability and the degree of destruction of the samples under the influence of a given temperature regime [5]. The activation energy of the thermal-oxidative degradation E (kJ/mol) is determined by means of TG-curves. The obtained values are processed by calculation using the Broido method in the temperature range from 573 to 713 K (Fig. 4).

As can be seen in Fig. 4, during the heating of the samples with increasing temperature from 273 to 573 K, moisture and vola-

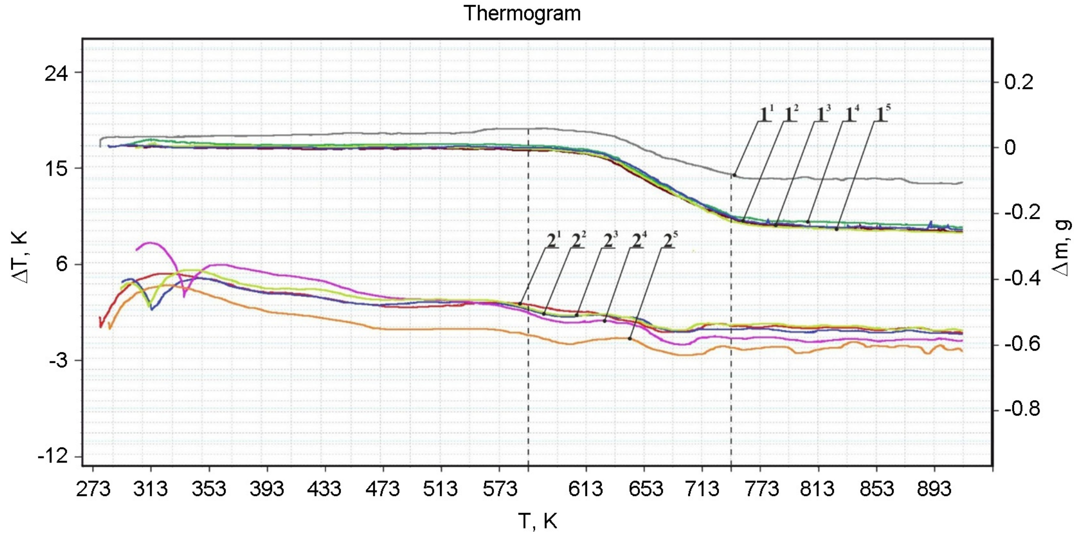

Fig. 4. The results of thermogravimetric (*1*) and differential-thermal (*2*) analysis of epoxy matrix and CM with different content of $C_{22}H_{28}N_2O_2S_5$ modifier (typical curves) *q*, pts·wt.: 1^1–2^1) initial matrix; 1^2–2^2) 0.10; 1^3–2^3) 0.25; 1^4–2^4) 0.50; 1^5–2^5) 0.75.

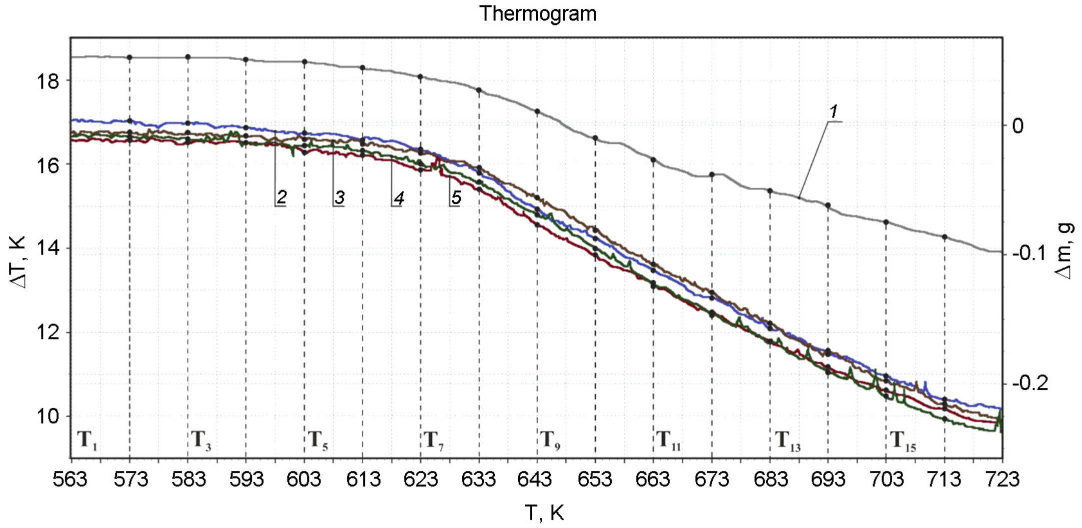

Fig. 5. The results of a thermogravimetric (TGA) analysis of an epoxy matrix and CM with a content of modifier $C_{22}H_{28}N_2O_2S_5$, *q*, pts·wt.: 1) initial matrix; 2) 0.10; 3) 0.25; 4) 0.50; 5) 0.75.

tile components are first released, then, the materials soften gradually, which is fixed in the form of characteristic exothermic peaks and bends on curves *1*. In this temperature range, polymer samples usually remain stable and are not subjected to thermal destruction. The processes of the thermal-oxidative destruction proceed at a noticeable rate in the range of higher temperatures. In our case, the most characteristic reactions of the thermal-oxidative destruction occur in the temperature range ΔT = 573...713 K; these are accompanied by a mass loss of samples in an amount of 10...50 %. On this basis, and also in accordance with the temperature interval of the location of exothermic peaks on curves 2, the range of analysis of TG-curves was chosen to calculate the activation energy of the ther mal-oxidative destruction of the CM under study [6–9].

The specified section of the diagram with TG curves showing a characteristic bend was used to calculate the sample mass loss depending on the temperature. For this purpose, the mass losses of the samples were analyzed in the chosen temperature range of the TG curves with an interval of ΔT = 10 K (Fig. 5 and Fig. 6 (indicated by dots)). First, the mass of the sample in each temperature range on the TG curves was deter-

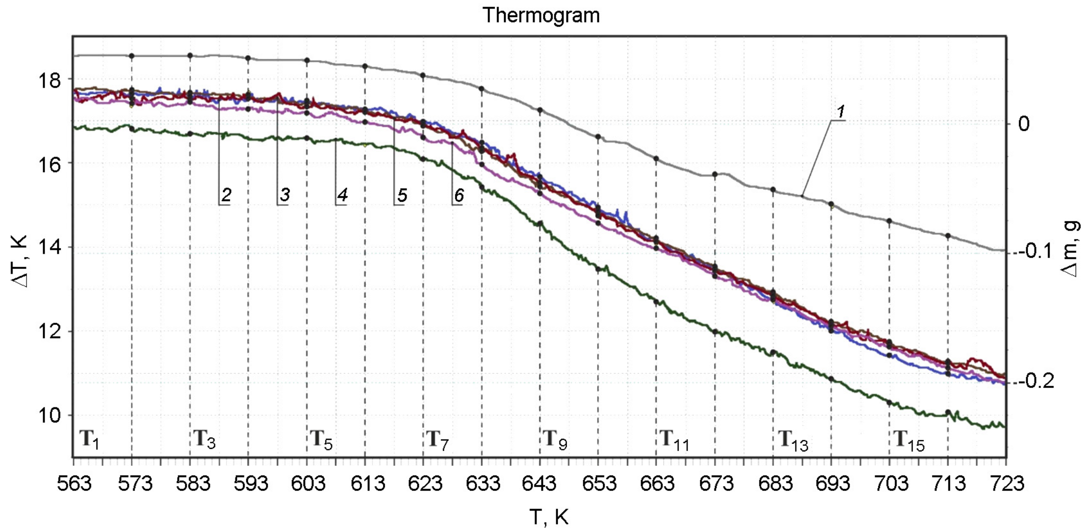

Fig. 6. The results of a thermogravimetric (TGA) analysis of an epoxy matrix and CM with a content of modifier $C_{22}H_{28}N_2O_2S_5$, q, pts·wt.: 1) initial matrix; 2) 1.00; 3) 1.25; 4) 1.50 5) 1.75; 6) 2.00.

mined and converted into percentages using the formula (1) [10]:

$$(100-\Delta m)\% = (100 - \left(\frac{m_H+\Delta m}{\Delta m}\cdot 100\right))\%, \quad (1)$$

where m_H is an initial sample mass at the initial tested temperature T_1 = 573 K (m_H = $const$), g; Δm is the sample mass loss, g.

According to the recommendations of the method, the sample mass at the initial temperature, is taken as 100 %.

Obtained data are given in Table 1 and Table 2.

The calculation of E is based on the mathematical processing of the thermal analysis curve using the Broido double-logarithm method, which is quite accurate for polymers, and is performed by the formula (2) [10]:

$$\ln(\ln\frac{100}{100 = \Delta m}) = \frac{E}{R}\cdot\frac{1}{T} + const, \qquad (2)$$

where Δm is the mass loss of the sample, %, at each of the temperatures within the interval of the substance destruction; R = $8.31\cdot 10^3$ kJ/(mol·K) is the universal gas constant.

The results of the double-logarithm calculations of the sample mass changes are given in Table 3.

The condition for the applicability of the Broido method is the first-order destruction reaction, which is true for many polymers [10, 11]. The mass loss of a substance is the first-order process (n = 1) if the ln(100/(100 – Δm) dependence on the reciprocal temperature 1000/T, K^{-1} is linear.

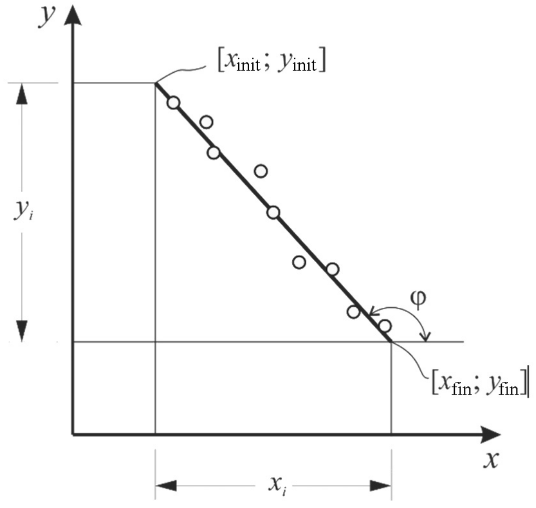

Fig. 7. To graphically determination of the activation energy.

With the known the mass loss (Δm) of the sample at temperature T, a straight line was plotted in which E was expressed by the tangent of the slope angle of the logarithmic dependence of Δm on the reciprocal temperature T [10, 11]. Then the activatio n energy of destruction in kJ/mol was found by formula (3):

$$E = -R\cdot \mathrm{tg}\varphi. \qquad (3)$$

To determine the activation energy, the graph should be a straight line; the activation energy E is calculated from the slope angle (Fig. 7):

$$-\mathrm{tg}\{\varphi) = y_i/x_i, \qquad (4)$$

Table 1. The results of derivatograms processing (Fig. 5, Fig. 6) of the original matrix and CM filled with SFEK modifier

T, K	Mass of samples, g									
	Concentration of the modifier, q, pts·wt.									
	Matrix	0.10	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
573	0.352	0.30	0.29	0.29	0.29	0.32	0.32	0.30	0.33	0,32
583	0.353	0.30	0.29	0.29	0.29	0.32	0.32	0.29	0.32	0.32
593	0.351	0.30	0.29	0.29	0.29	0.32	0.32	0.29	0.32	0.31
603	0.349	0.29	0.28	0.28	0.29	0.32	0.31	0.29	0.32	0.31
613	0.344	0.29	0.28	0.28	0.29	0.31	0.31	0.28	0.31	0.30
623	0.337	0.28	0.27	0.27	0.28	0.30	0.30	0.27	0.30	0.29
633	0.327	0.26	0.25	0.26	0.27	0.28	0.28	0.25	0.28	0.27
643	0.310	0.23	0.22	0.23	0.24	0.26	0.26	0.22	0.25	0.25
653	0.290	0.21	0.20	0.21	0.22	0.24	0.23	0.19	0.23	0.22
663	0.273	0.19	0.18	0.18	0.19	0.21	0.21	0.16	0.21	0.20
673	0.261	0.17	0.16	0.16	0.17	0.19	0.19	0.14	0.19	0.18
683	0.249	0.14	0.13	0.13	0.15	0.16	0.17	0.12	0.17	0.16
693	0.237	0.12	0.11	0.11	0.12	0.14	0.15	0.10	0.15	0.14
703	0.225	0.11	0.10	0.09	0.10	0.12	0.13	0.09	0.13	0.13
713	0.213	0.09	0.08	0.07	0.08	0.11	0.12	0.07	0.12	0.11

Table 2. Results of studies of the initial matrix and CM filled with SFEK modifier

T, K	Change in mass of samples (100 – Δm), %									
	Concentration of the modifier, q, pts·wt.									
	Matrix	0.10	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
573	–14.77	–1.00	3.79	3.10	2.07	–7.50	–6.25	1.00	–7.88	–5.31
583	–15.06	–0.33	4.83	3.45	2.41	–6.88	–6.56	2.67	–6.97	–5.00
593	–14.49	0.67	4.83	4.14	2.76	–5.94	–6.25	3.33	–6.36	–3.75
603	–13.92	2.33	6.55	5.52	3.45	–5.00	–4.38	4.00	–4.85	–2.50
613	–12.50	3.67	8.28	6.90	4.48	–3.75	–2.81	5.33	–3.03	–0.31
623	–10.51	6.33	11.72	10.00	7.24	–0.63	0.00	8.67	0.30	3.13
633	–7.67	12.33	17.24	15.17	11.72	5.00	5.63	16.00	6.36	10.00
643	–2.84	22.00	26.21	23.45	19.31	13.13	14.06	26.33	14.24	16.88
653	2.84	29.33	34.83	32.76	27.93	20.31	21.25	37.00	20.61	24.06
663	7.67	37.33	42.76	42.07	36.90	28.44	28.75	45.67	27.27	30.31
673	11.08	44.67	50.00	50.00	44.83	35.00	35.31	53.33	33.64	36.56
683	14.49	52.00	57.59	57.24	53.10	42.50	41.56	59.33	39.70	42.81
693	17.90	59.00	64.83	65.17	60.69	49.69	48.13	65.67	46.36	48.75
703	21.31	64.67	70.69	71.72	68.28	55.94	53.44	71.67	51.21	54.06
713	24.72	70.67	75.86	78.28	74.48	60.31	57.81	75.33	55.76	59.06

$$E = R \cdot y_i / x_i, \qquad (5)$$

where $x_i = x_b - x_e$ is the length of the line along the abscissa; $y_i = y_b - y_e$ is the length of the line along the ordinate; $[x_b; y_b]$ and $[x_e; y_e]$ are coordinates of the beginning and the end of the line, respectively.

In Table 3 the results of processing the derivatograms (TG-curves) and the parameters necessary for calculating the activation energy of CM filled with the SFEK modifier are given. The processing consists in performing a mathematical transformation presented in Excel. Below the Δm logarithmic plots are shown depending on the reciprocal temperature $1000/T$ (Fig. 8, Fig. 9).

Using the diagram and the obtained equations, the activation energy of the thermal oxidative destruction of the investigated composites were calculated. The results of the graphical determination of the activation energy are given in Table 4. For clarity, the plot of the activation energy E

Table 3. The results of calculating the value of double logarithm of the sample mass change

T, K	$10^3/T$, K	$\ln\{\ln[100/(100-\Delta m)]\}$									
		Concentration of the modifier, q, pts·wt									
		0	0.10	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
573	1.75	–	–	−3.25	−3.46	−3.87	–	–	−4.60	–	–
583	1.72	–	–	−3.01	−3.35	−3.71	–	–	−3.61	–	–
593	1,69	–	−5.01	−3.01	−3.16	−3.58	–	–	−3.38	–	–
603	1,66	–	−3.75	−2.69	−2.87	−3.35	–	–	−3.20	–	–
613	1,63	–	−3.29	−2.45	−2.64	−3.08	–	–	−2.90	–	–
623	1,61	–	−2.73	−2.08	−2.25	−2.59	–	–	−2.40	−5.80	−3.45
633	1.58	–	−2.03	−1.66	−1.80	−2.08	−2.97	−2.85	−1.75	−2.72	−2.25
643	1.56	–	−1.39	−1.19	−1.32	−1.54	−1.96	−1.89	−1.19	−1.87	−1.69
653	1.53	−3.55	−1.06	−0.85	−0.92	−1.12	−1.48	−1.43	−0.77	−1.47	−1.29
663	1.51	−2.53	−0.76	−0.58	−0.61	−0.78	−1.09	−1.08	−0.49	−1.14	−1.02
673	1.49	−2.14	−0.52	−0.37	−0.37	−0.52	−0.84	−0.83	−0.27	−0.89	−0.79
683	1,46	−1.85	−0.31	−0.15	−0.16	−0.28	−0.59	−0.62	−0.11	−0.68	−0.58
693	1.44	−1.62	−0.11	0.04	0.05	−0.07	−0.38	−0.42	0.07	−0.47	−0.40
703	1.42	−1.43	0.04	0.20	0.23	0.14	−0.20	−0.27	0.23	−0.33	−0.25
713	1,40	−1,26	0,20	0.35	0.42	0.31	−0.08	−0.15	0.34	−0.20	−0.,11

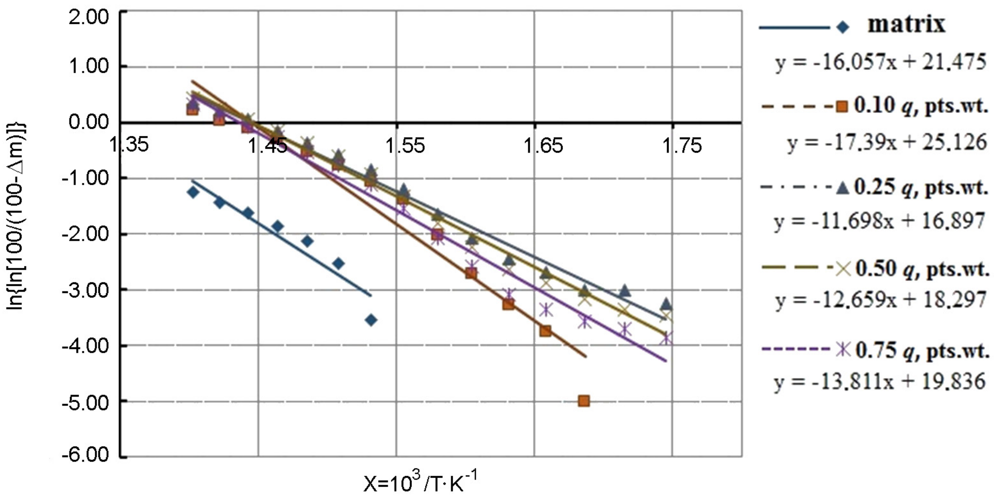

Fig. 8. The logarithmic dependence of Δm on the reciprocal temperature $10^3/T$, K^{-1} at thermal breakdown of CM with the SFEK modifier.

depending on the concentration of the modifier in the CM is shown below (Fig. 10).

The activation energy of the destruction processes of the epoxy matrix has been experimentally established as E = 133.4±0.2 kJ/mol. (Table 4, Fig. 10). The introduction of the SFEK modifier in an amount of q = 0.10 pts·wt. increased the activation energy of the thermal oxidative destruction to E = 144.5±0.2 kJ/mol.

The result obtained with the introduction of the modifier in a small amount can be explained by the initial interaction of the reactive modifier macromolecules and their partial cross-linking with the active groups of the ED-20 oligomer in the presence of the PEPA hardener. Further introduction of the modifier in an amount of q = 0.25 pts·wt. leads to a significant decrease of the activation energy to E = 97.3±0.2 kJ/mol, which is significantly lower than in the initial matrix. The subsequent introduction of the SFEK modifier at concentrations of q = 0.50...1.50 pts·wt. results in a monotonous increase of the activation energy to E = (105.3...123.6)±0.2 kJ/mol, which is also lower than the value characteristic of the initial matrix.

The maximum value of the activation energy (E = 175.1±0.2 kJ/mol) is established when the modifier was introduced into the

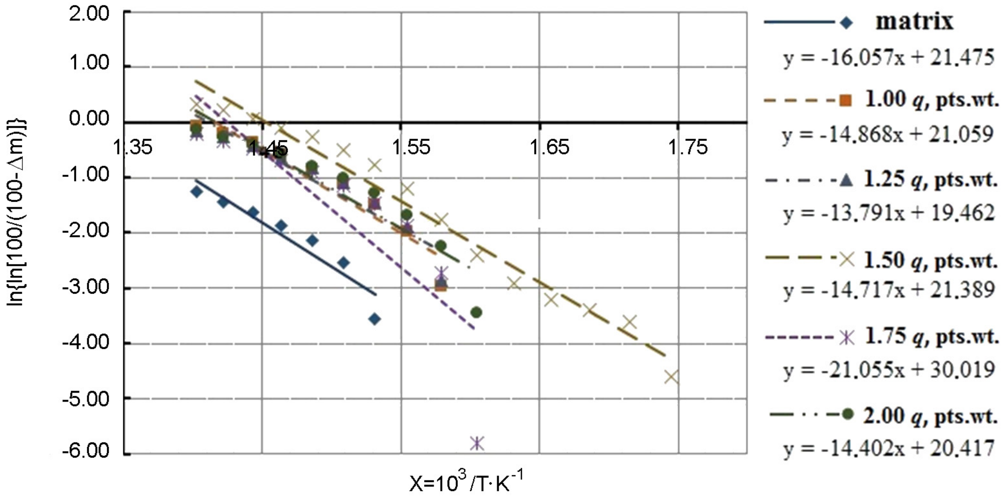

Fig. 9. The logarithmic dependence of Δm on the reciprocal temperature $10^3/T$, K^{-1} at thermal breakdown of CM with the SFEK modifier.

binder in an amount of $q = 1.75$ pts·wt; this indicates the active participation of the modifier in the physical-chemical processes of epoxy matrix structure formation. The modifier has a wide range of chemical elements, among which carbon (C) and sulfur (S) prevail in percentage (Fig. 3).

In our opinion, the introduction of the SFEK modifier in this amount led to the formation of stable covalent carbon bonds with elements of the additive, as well as with activated epoxy oligomer macromolecules during the processing of the USO. It should be added, that the interaction of sulfur with other elements of both the modifier and the epoxy binder, results in the formation of covalent polar bonds in macromolecules of polymers; these bonds significantly strengthen the three-dimensional PCM network as a whole. At the same time, activation of epoxy and carboxyl groups also leads to an improved interaction of both the oligomer ED-20 and the modifier with the hardener during polymerization. This in turn leads to a decrease in the segmental mobility of the polymer macromolecules. Consequently, it is possible to ascertain the increase in the heat resistance of the material, as well as the inhibitory effect of the modifier on the processes of thermal oxidative destruction of CM.

As a confirmation of the reliability of the data obtained, the thermal coefficient of linear expansion (TCLE) of the CM was investigated. The results of the TCLE calculation in the predetermined temperature ranges are given in Table 5.

As can be seen from the Table 5, the modified values of CM with an additive in the amount of $q = 0.10$ and 1.75 mass parts are optimal, which indicates the validity of the above results.

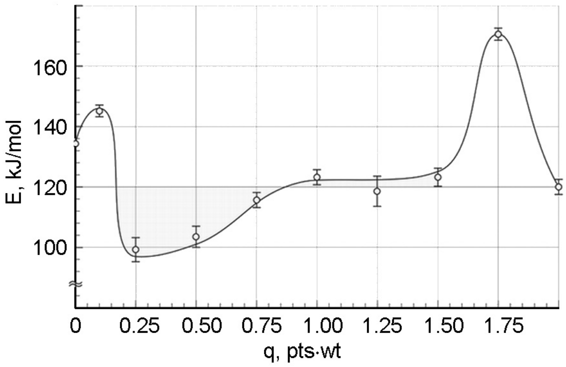

Fig. 10. Dependence of the activation energy E on the concentration of the modifier in the CM.

Further introduction of the modifier in the amount of $q = 2.00$ pts·wt. leads to a significant decrease in the activation energy to $E = 119.7 \pm 0.2$ kJ/mol) (Fig. 10). It was believed that such results were obtained due to the saturation of the CM with the active groups of the modifier, which led to deterioration in the degree of cross-linking of the macromolecules of the epoxy composite.

4. Conclusions

Based on the experimentally obtained thermogravimetric curves of the mass change depending on the temperature, and also using the Broido method of double logarithms, which was quite accurate for polymers, the activation energy of the thermal-oxidative destruction of the initial epoxy matrix and modified composite materials were calculated. It was established

Table 4. The results of the graphical determination of the activation energy E at the thermal oxidative breakdwon of CM with the SFEK modifier

q, pts·wt.	x_{HD}	x_k	x_i	y_H	y_k	y_i	tq(φ)	E, kJ/mol
0	1.531	1.403	0.128	−1.053	−3.108	2.055	16.057	133.5
0.10	1.686	1.403	0.283	0.728	−4.194	4.921	17.390	144.6
0.25	1.745	1.403	0.342	0.728	−3.516	4.001	11.698	97.3
0.50	1.745	1,403	0,342	0.536	−3.793	4.329	12.659	105.3
0.75	1.745	1.403	0.342	0.459	−4.264	4.723	13.811	114.8
1.00	1.580	1.403	0.177	0.197	−2.434	2.632	14.868	123.6
1.25	1.58	1.403	0.177	0.113	−2.3278	2.441	13.791	114.7
1.50	1,745	1,403	0.342	0,741	−4.292	5.033	14.717	122.4
1.75	1.605	1.403	0.202	0.478	−3.7743	4.253	21.055	175.1
2.00	1.605	1.403	0.202	0.211	−2.698	2.909	14.402	119.7

that the composites with the 4.4-sulfoylbis (4.1-phenylene) bis(N,N-dietyldithiocarbamate) modifier in the amount of q = 0.10 pts·wt. (E = 144.5±0.2 kJ/mol) and q = 1.75 pts·wt. (E = 175.1±0.2 kJ/mol) were characterized with the greatest values of the activation energy. This indicates a significant effect of the modifier on the cross-linking degree and the activation energy of the composites. This also indicates the formation of relatively thermally stable intra- and intermolecular bonds, which leads to an increase of thermal resistance and, at the same time, the durability of the developed materials. It has been proved, that the introduction of the SFEK modifier in the specified quantity results in formation of stable carbon covalent bonds with both the elements of the additive and the epoxy oligomer macromolecules activated during the USO processing.

In turn, the interaction between sulfur, which is also one of constituent elements of the modifier, and an epoxy binder results in the formation of covalent polar bonds in polymer macromolecules; this significantly strengthens the bulk polymer network as a whole. At the same time, the activation of epoxy and carboxyl groups leads to an improved interaction of both the oligomer ED-20 and the modifier with the hardener during polymerization.

Table 5. Thermal coefficient of linear expansion (TCLR) CM during different predetermined temperature ranges in testings

No.	SFEK modifiers content ($C_{22}H_{28}N_2O_2S_5$), q, pts·wt.	Thermal coefficient of linear expansion, $\alpha\times10^{-5}$, K^{-1}	
		Temperature ranges during testing, ΔT, K	
1	matrix	6.81	9.92
2	0.10	2.74	3.29
3	0.25	2.77	4.16
4	0.50	3.24	4.48
5	0.75	3.57	4.21
6	1.00	3.35	4.43
7	1.25	3.60	4.60
8	1.50	3.53	4.86
9	1.75	2.89	3.48
10	2.00	3.21	4.09

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