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INVESTIGATION OF THE MODIFIER 2-BENZOFURAN-1,3-DIONE CONTENT EFFECT ON THE HEAT RESISTANCE OF EPOXY COMPOSITES

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Summary. *The technological aspects of modification of epoxy oligomer DER – 331 to provide improvement of thermophysical characteristics of composite materials and protective coatings based on them are presented. Cold-cured triethylenetetramine TETA hardener was used to crosslink the epoxy binder ($q = 10$ parts by weight per 100 parts by weight of DER-331 epoxy resin). Thermogravimetric (TGA) and differential thermal (DTA) analysis was performed to study modified composites under the influence of elevated temperatures. A mathematical calculation of the values of the activation energy of thermal destruction to determine the resistance to destruction of chemical bonds under the influence of temperature factor.*

Key words: *epoxy binder, modifier, hardener, heat resistance, destruction, activation energy.*

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Problem statement. Nowadays, the development of new metal-energy saving technologies to improve the performance reliability of machines and mechanisms has been paid great attention to. The polymer composites' development and use are quite promising in this direction. The use of nonmetal composites for functional purposes will allow us to refuse from applying the traditional metals and alloys and simultaneously will provide the reliability of metal structures, parts and mechanisms of transport. In this case, it is possible to increase their service life under temperature impact conditions due to adding some modified substances to the epoxy matrix to provide the higher degree of cross-linking. Thus, the binder chemical modification will allow us to obtain the material with improved thermal – physical properties.

Analysis of the known results of the research. The considerable attention of scientists has been paid to the study and improvement of thermal – physical properties of epoxy binders-based composite materials [1–4]. The analysis of the authors' papers [5–8] has allowed us to state that the application of some small content of modified substances to the thermo-reactive binder is necessary to improve the properties of composite materials. The results of the study of heat conductive and fire-resistant properties of the epoxy matrix during its cross-linking with the modified fractions have been described in the papers [9–11]. It is shown [9], that the composition containing some epoxy resin ED-20 (100 wt %), hardener polyethylene polyamine (10 wt %),

plasticizer trichloroethylphosphate (10 wt %), chloramine fractions Б (2...4 wt %) is characterized by not only higher indices of heat resistance ($T = 369$ K), but thermal resistance as well. The obtained value of exoeffect temperature peak was equal to $T_{max} = 570$ K has proved their thermal stability under thermal field impact conditions. On the contrary, reactoplastic binder 9,9% and 4,0% disperse additives application provides an increase of composites' heat conductivity [11]. Taking into account all the above mentioned, we have considered the carrying out of the study of the modifier nature and content impact on the dynamics of thermal – physical properties of composite materials to be of great importance.

The aim of the paper is to study the impact of modifier 2-benzofuran-1,3-dione on thermal- physical properties of epoxy composites.

Materials and technique of the study. To form some polymer materials the epoxy binder DER – 331 (CAS No. 25085-99-8) made by «Dow Chemical Comp» (Germany) was used. For cross-linking of epoxy binder, the hardener of cold hardening triethylenetetramine TETA (CAS No. 112-24-3) was used whose content was equal to $q = 10$ wt % (it is given per 100 wt % of epoxy resin DER – 331). The structural formulae of the components are given on fig. 1 and fig. 2 respectively.

To improve the composites structure and properties the modifier 2-benzofuran-1,3-dione – phthalic anhydride (PhA) (CAS No. 112-24-3) was used, which was added to the binder of the content from $q = 0,10...3,00$ wt % (here and further in the text wt % means 100 wt % of epoxy oligomer DER – 331). The molecular formula of this modifier – $C_8H_4O_3$.

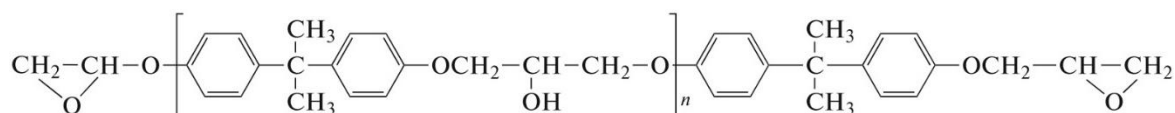


Figure 1. General structural formula of the epoxy oligomer DER - 331

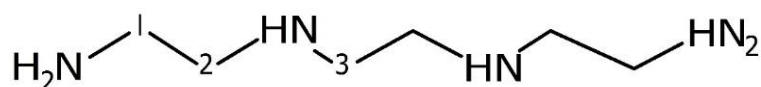


Figure 2. Fragment of the structural formula of TETA

The formation of modified epoxy matrix in the following sequence:

- preliminary preparation and dosing of ingredients;
- heating of epoxy resin DER – 331 up to the temperature $T = 373 \pm 2$ K and holding within the specified time period $\tau = 20 \pm 0,1$ min;
- mechanical matching of ingredients (epoxy binder + modifier) during $\tau = 1,5 \pm 0,1$ min;
- ultrasonic treatment (UST) of the composition during $\tau = 1,5 \pm 0,1$ min;

- cooling of the composition to room temperature $T = 273 \pm 2$ K during $\tau = 60 \pm 5$ min;
 - adding the hardener TETA and mixing the composition during $\tau = 5 \pm 0,1$ min;
 - applying the composition either by mechanic method or by pneumatic spraying.
- The materials were hardened according to the mode set by experiment:
- formation of patterns and their holding within time $t = 12,0 \pm 0,1$ hour at temperature $T = 293 \pm 2$ K;
 - heating with the speed $v = 3$ K/min up to the temperature $T = 393 \pm 2$ K;
 - the patterns were held at the given temperature during $t = 120 \pm 5$ min;
 - slow cooling to the temperature $T = 293 \pm 2$ K.

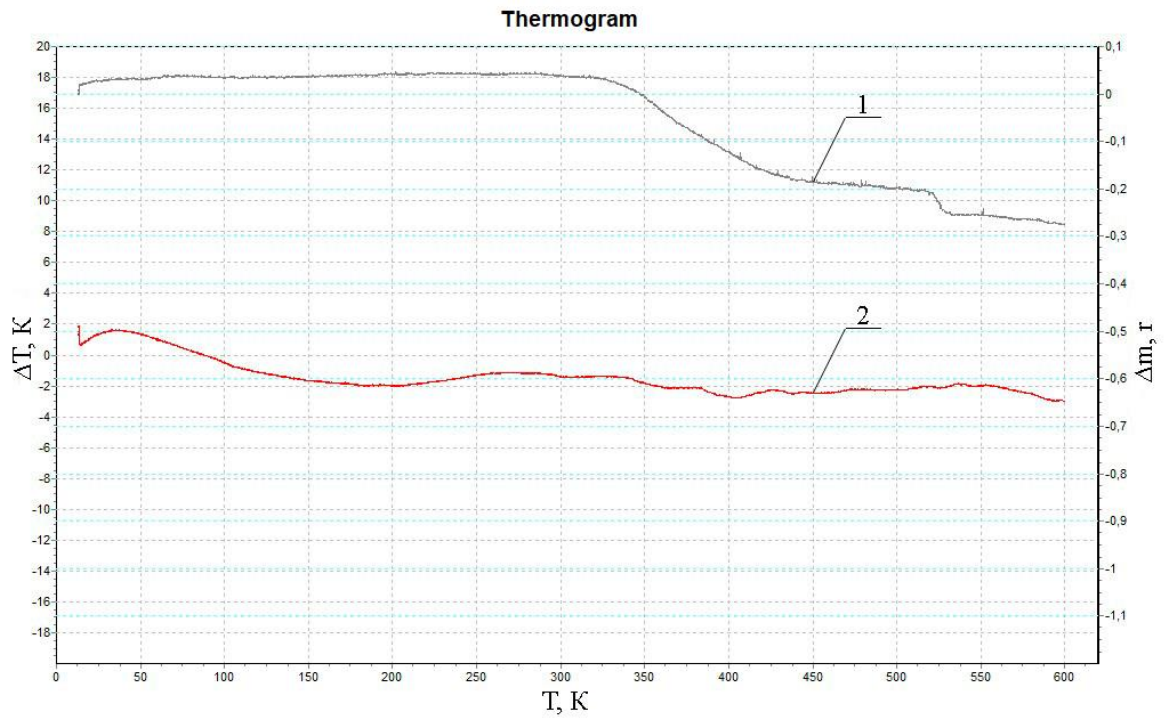
To stabilize the structural processes in the matrix the patterns were held during $t = 24$ hours in the open air at temperature $T = 293 \pm 2$ K with the further conducting of experimental tests.

We have studied in the paper: thermal resistance by method of thermogravimetric (TGA) and differential-thermal (DTA) analysis, activation energy.

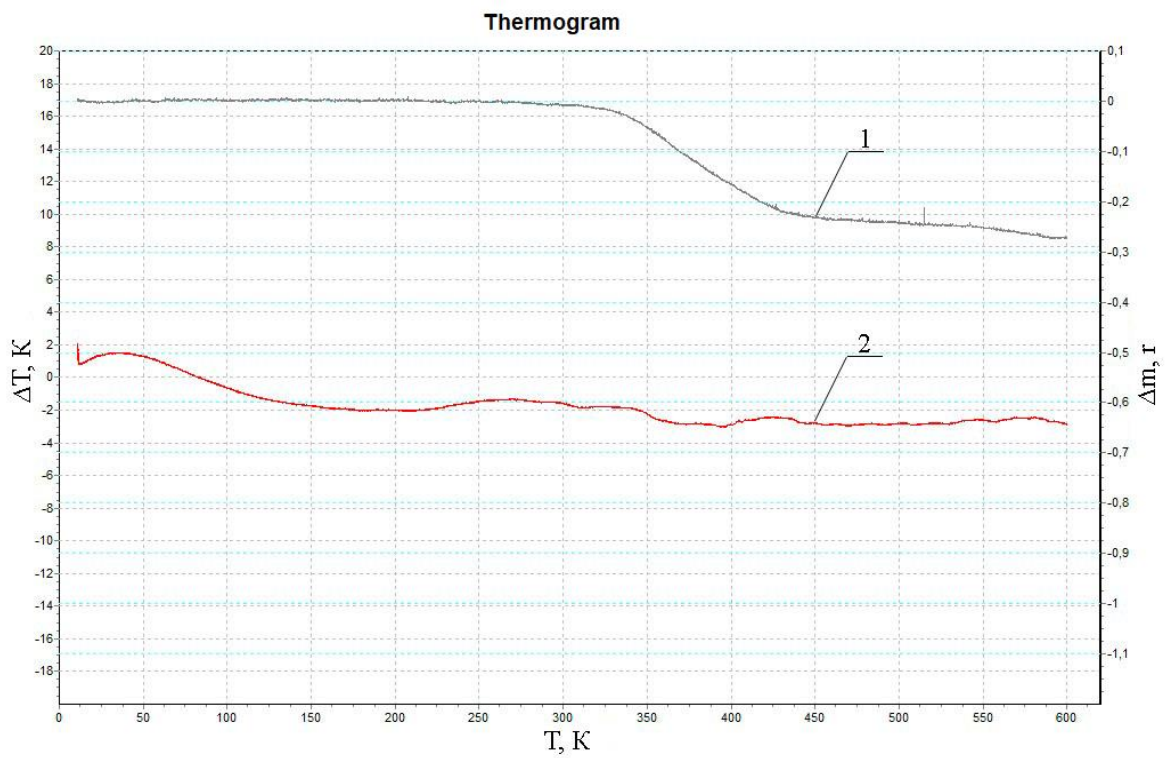
To study the impact of nanofiller nature on the thermal transformations of composites the method of thermogravimetric (TGA) and differential-thermal (DTA) analysis was applied using the derivatograph «Thermoscan-2». The study was conducted within the temperature range $\Delta T = 298 \dots 873$ K using quartz crucibles for the specimen of volume $V = 0,5$ cm³. During the study the speed of temperature rising was $v = 5$ K/min, and Al₂O₃ ($m = 0,5$ g) was used as a reference substance, the weight of the specimen under study was $m = 0,3$ g. The temperature measurement error was $\Delta T = \pm 1$ K. The accuracy of thermal effects determination is 3 J/g. The accuracy of the specimen weight change determination is $\Delta m = 0,02$ g.

The results of the study. An important aspect in protective coatings application is their possible operation under different temperature ranges conditions enabling us to broaden the use boundaries of polymer materials and coatings based on them considerably. Thus, some research of the behavior of the developed composite materials under high temperature conditions was carried out by method of thermogravimetric (TGA) and differential-thermal (DTA) analysis (fig. 3, a-e). To study the complete process of bonds decomposition in the polymer the speed of temperature rising 5 K/min was chosen. The modifier content was varied within $q = 0,10 \dots 3,00$ wt %.

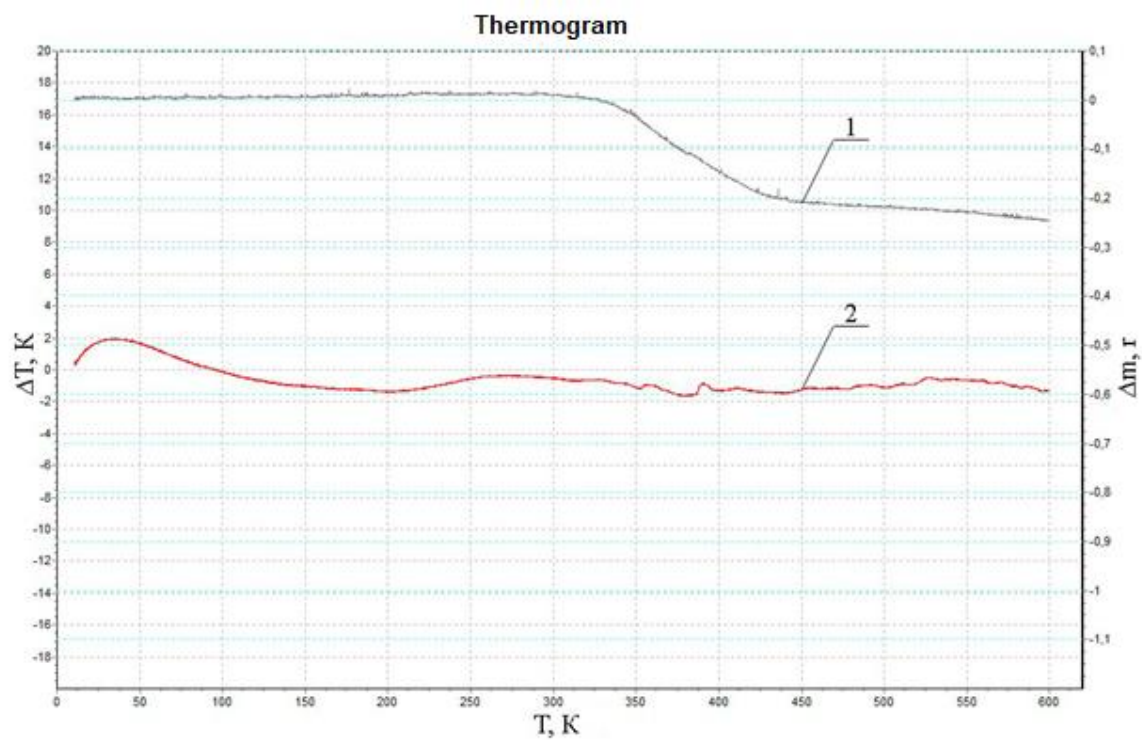
Analysis of TGA-curve allows us to state that there is no loss of materials mass within the temperature range $\Delta T = 303 \dots 622$ K (fig. 3, curve 1, table 1). Herewith, the comparison of the mass loss initial temperature (table 1) with the thermo reactive composites filled with antipyrine (tris-(2-monochloroethyl) phosphate, chloramine B, sovelite powder, calcium carbonate, dichloroisocyanuratenatrium), where the indices vary within $T_n = 456 \dots 581$ K, has proved inhibition action of the modifier. Thus, we can state, that the modifier is able to decelerate the thermal destruction, and some additional application of antipyrine will allow us to provide the coating fire resistance. It should be mentioned, that epoxy binder DER – 331 is characterized by higher initial temperature of the mass loss ($\Delta T_n = 18 \dots 23$ K higher) comparing with the binder EД-20 [2, 3, 9, 12]. Whereas, phthalic anhydride injection into the epoxy binder of the content $q = 0,10 \dots 0,25$ wt % provides $\Delta T_n = 29,7 \dots 33,3$ K shift (against matrix) of the mass loss initial temperature in the areas of high temperatures ($T_n = 618 \dots 622$ K). The end of the destruction process of the developed composites was observed within the temperature range $T_\kappa = 709,2 \dots 726,7$ K. Herewith, relative loss of such materials mass is $\varepsilon_m = 57,7 \dots 72,7\%$.



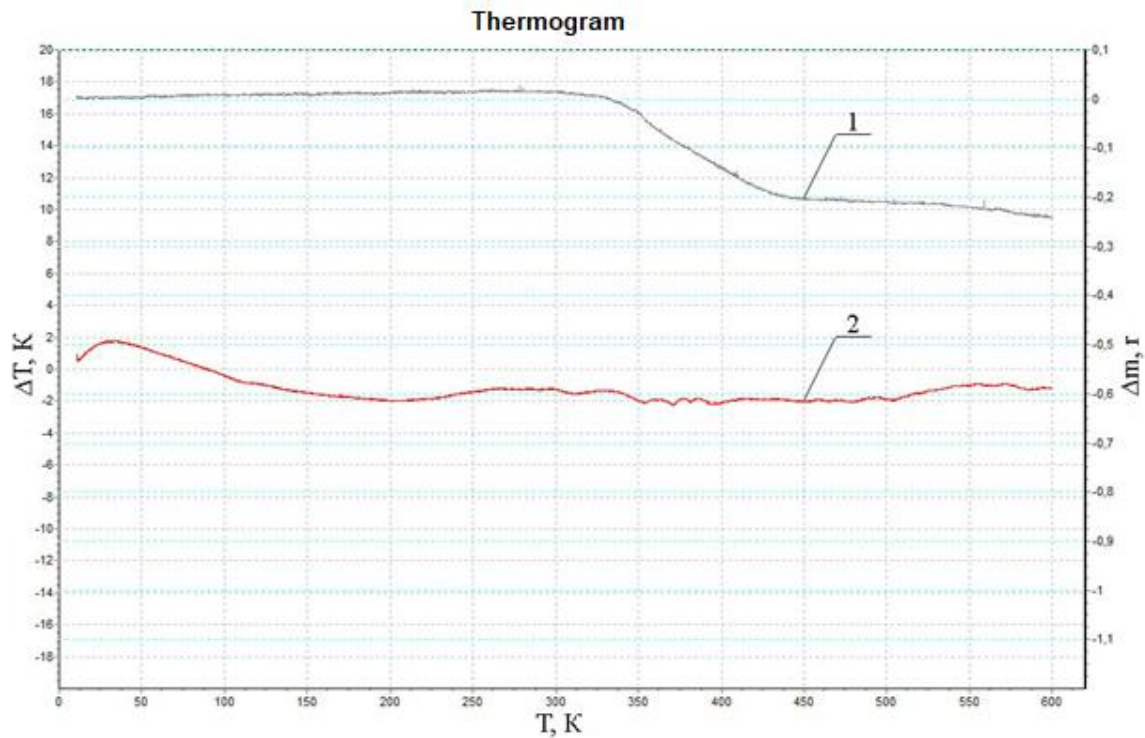
a)



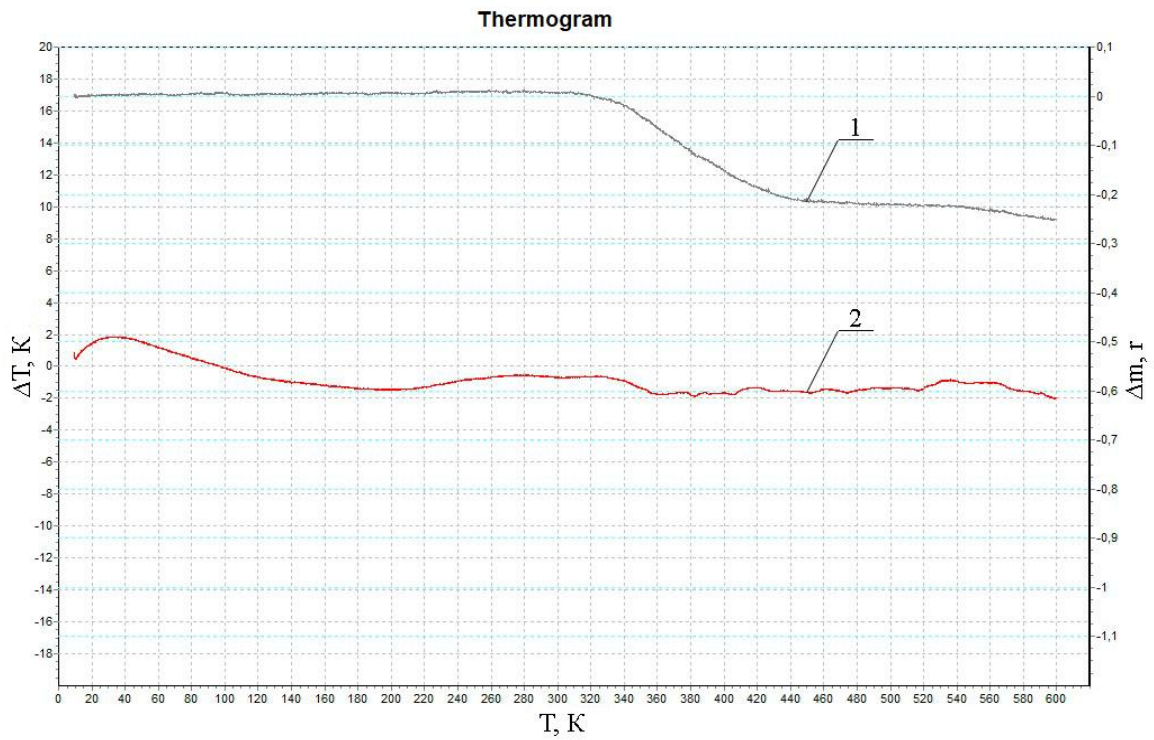
b)



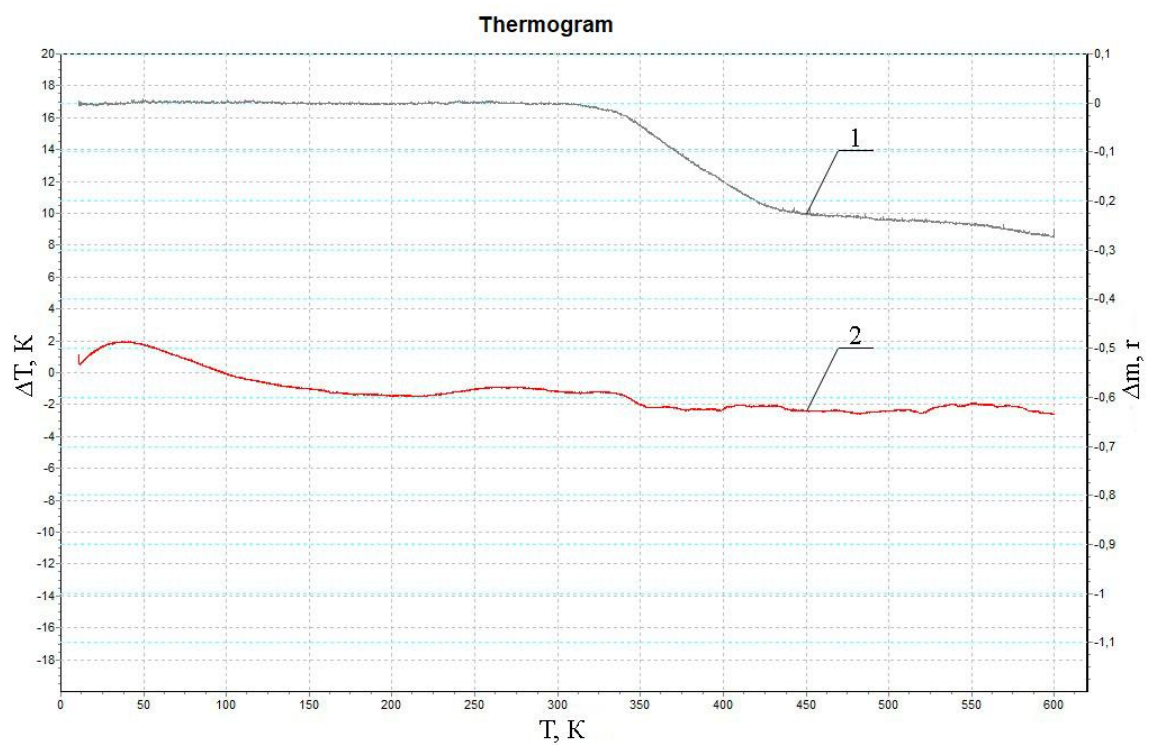
c)



d)



e)



f)

Figure 3. The results of thermogravimetric (1) and differential thermal (2) analysis of composites modified with 2-Benzofuran-1,3-dione: a) 0.10 wt %; b) 0.25 wt %; c) 0.50 wt %; d) 1.00 wt %; e) 2.00 wt %; e) 3.00 wt %

Table 1

Heat resistance of composites modified with 2-Benzofuran-1,3-dione

Content of modifier, q , wt %	T_0 , K	T_5 , K	T_{10} , K	T_{20} , K	T_{κ} , K	ε_m , %
0	589,1	607,5	618,4	623,5	695,6	73,3
0,10	622,4	628,0	632,6	643,3	709,2	57,7
0,25	618,8	624,9	628,3	638,8	706,1	61,0
0,50	605,3	614,1	623,5	634,2	708,5	68,0
1,00	608,1	618,3	624,8	636,3	710,2	64,7
2,00	596,5	613,0	619,9	632,3	726,7	70,0
3,00	585,5	607,7	616,9	630,5	715,2	72,7

Note: T_0 – temperature of the mass loss start (start of the material destruction); T_5 , T_{10} , T_{20} – temperatures of the mass loss (5 %, 10 %, 20 %); T_{κ} – final temperatures of the mass loss (finish of the material destruction); ε_m – relative loss of mass.

Simultaneously, DTA-curve was analyzed (fig. 3, curve 2) within the temperature range $\Delta T = 303,0 \dots 600,0$ K. It was found, that composites with the modifier content $q = 0,10 \dots 0,25$ wt % were characterized by the highest initial temperature of exoeffect (fig. 3, curve 2, table 2). The obtained values ($T_n = 479,4 \dots 499,4$ K) allow us to state about decrease of mobility, deformation of macromolecules and segments of polymer (comparing with CM filled with $q = 0,50 \dots 3,00$ wt %), and due to this, increased thermal resistance.

Table 2

Temperature intervals of exoeffects of modified composites 2-Benzofuran-1,3-dione

Content of modifier, q , wt %	Intervals of exoeffects temperatures				Maximum value of exoeffects, T_{max} , K
	T_n , K	T_{κ} , K	ΔT_1 , K	ΔT_2 , K	
0	476,7	735,6	177,6	1,81	523,1
0,10	479,4	679,6	200,2	1,65	542,7
0,25	499,4	670,3	171,3	1,68	542,9
0,50	482,5	620,4	137,9	0,62	548,3
1,00	491,1	622,1	131,0	0,69	557,7
2,00	484,1	632,7	148,6	0,38	558,0
3,00	491,8	627,8	136,0	1,29	546,6

Note: T_n – initial temperature of exoeffect; T_{κ} – final temperature of exoeffect; ΔT_1 – Intervals of exoeffect temperatures; ΔT_2 – difference intemperatures between the test specimen, where some structural transformations take place, and control specimen where there are no changes.

The analysis of maximum values of exoeffect peak temperature (T_{max} K) has allowed us to see a linear dependence. It means, that the higher content of the modifier in the epoxy binder was, the higher T_{max} was observed. As T_{max} characterizes the strength of physical-chemical bonds against their destruction under temperature impact conditions, and the linear dependence does not allow to make more accurate estimation of the modifier impact, we have also calculated the activation energy of thermal destruction.

The temperature of decomposition (table 1) and relative loss of mass at heating to 713 K (table 3) were found according to the obtained data of the TGA -curve of the modified composites, and on their basis activation energy was calculated (table 6).

The calculation of activation energy was carried out due to mathematical processing of the TGA-curve and the technique described in the papers [13, 14]:

Table 3

The results of studies of composites modified with 2-Benzofuran-1,3-dione

T, K	Change in the specimen mass, g						
	Content of modifier, q, wt %						
	0	0,10	0,25	0,50	1,00	2,00	3,00
573	0,331	0,34	0,30	0,31	0,32	0,31	0,30
583	0,330	0,34	0,30	0,31	0,31	0,31	0,30
593	0,325	0,34	0,29	0,30	0,31	0,30	0,29
603	0,318	0,33	0,28	0,30	0,30	0,29	0,29
613	0,302	0,31	0,27	0,28	0,29	0,28	0,28
623	0,281	0,29	0,25	0,27	0,27	0,26	0,26
633	0,254	0,27	0,23	0,24	0,24	0,24	0,23
643	0,231	0,24	0,20	0,22	0,22	0,21	0,21
653	0,207	0,22	0,18	0,19	0,20	0,19	0,18
663	0,188	0,20	0,15	0,18	0,18	0,17	0,16
673	0,167	0,18	0,13	0,16	0,16	0,15	0,14
683	0,151	0,16	0,12	0,14	0,14	0,13	0,12
693	0,133	0,14	0,10	0,12	0,12	0,11	0,10
703	0,122	0,13	0,08	0,11	0,11	0,10	0,09
713	0,115	0,12	0,07	0,10	0,10	0,09	0,08

The results of processing of the TGA-curve and parameters required for the activation energy calculation are given in table 4 and table 5.

Table 4

The results of TGA curve processing

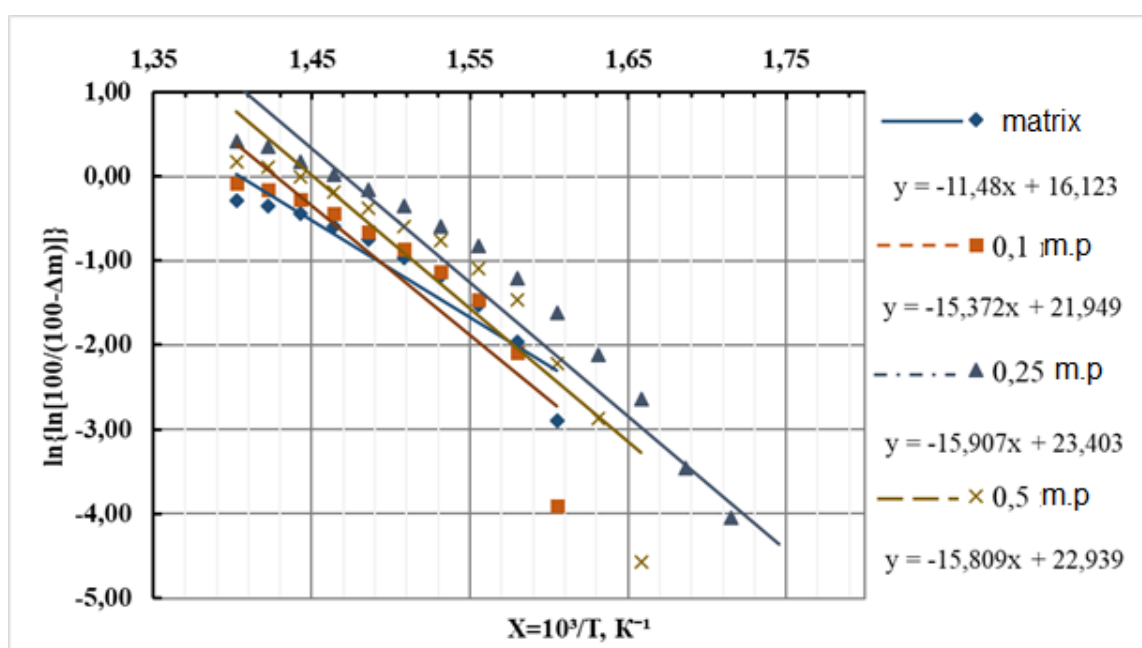
T, K	Change in the specimen mass (100- Δm), %						
	Modifier content, q, wt %						
	0	0,10	0,25	0,50	1,00	2,00	3,00
573	-8,81	-13,33	0,34	-3,45	-5,17	-2,19	0,63
583	-8,52	-12,00	1,72	-3,10	-4,48	-1,88	0,63
593	-7,10	-11,67	3,10	-1,38	-2,41	-0,31	2,50
603	-5,11	-8,67	6,90	1,03	-1,03	2,19	4,69
613	-0,57	-4,67	11,38	5,52	3,10	5,94	7,81
623	5,40	2,00	17,93	10,34	9,66	13,44	14,06
633	13,07	11,67	25,86	20,69	20,00	20,00	22,19
643	19,60	20,67	35,52	28,62	27,59	27,81	29,38
653	26,42	27,67	42,41	37,24	35,17	35,00	36,88
663	31,82	34,33	50,69	42,41	41,38	40,31	44,06
673	37,78	40,33	57,24	49,66	48,62	47,50	50,00
683	42,33	47,67	63,79	56,55	55,17	53,44	56,25
693	47,44	53,33	69,66	63,10	61,38	58,13	62,81
703	50,57	57,33	75,86	67,24	66,21	62,19	66,88
713	52,56	60,33	77,93	69,66	68,97	64,69	69,06

Table 5

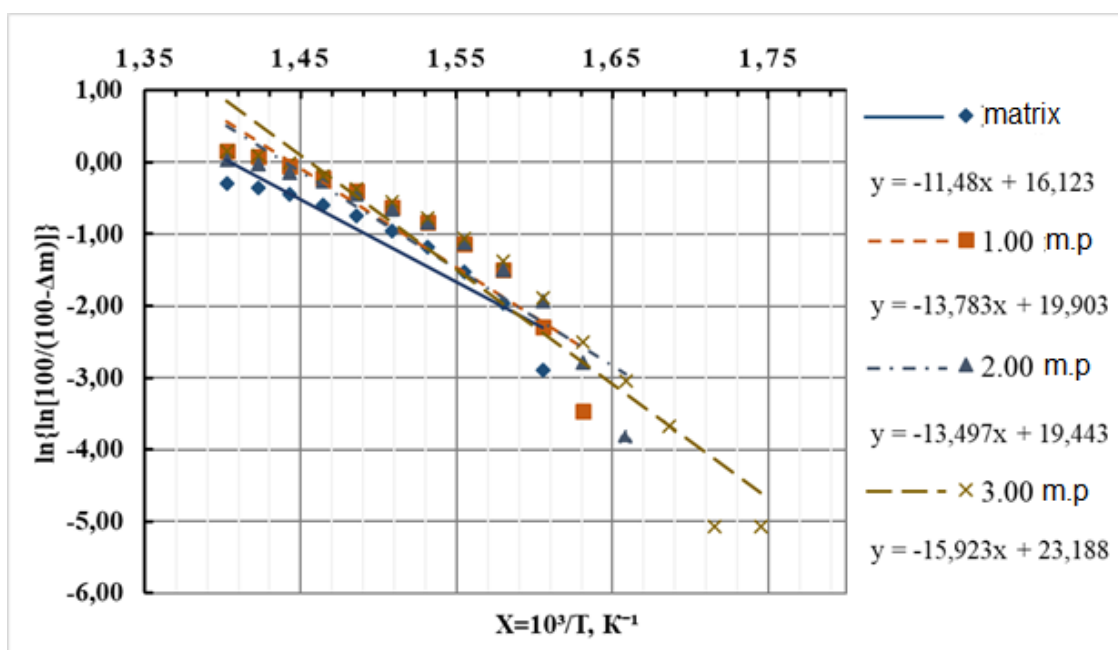
Estimated values of the logarithm of the change in the mass of the samples using the double logarithm

T, K	$\ln\{\ln[100/(100-\Delta m)]\}$						
	Modifier content, q wt %						
	0	0,10	0,25	0,50	1,00	2,00	3,00
573	-	-	-5,67	-	-	-	-5,07
583	-	-	-4,05	-	-	-	-5,07
593	-	-	-3,46	-	-	-	-3,68
603	-	-	-2,64	-4,57	-	-3,81	-3,04
613	-	-	-2,11	-2,87	-3,46	-2,79	-2,51
623	-2,89	-3,90	-1,62	-2,21	-2,29	-1,94	-1,89
633	-1,97	-2,09	-1,21	-1,46	-1,50	-1,50	-1,38
643	-1,52	-1,46	-0,82	-1,09	-1,13	-1,12	-1,06
653	-1,18	-1,13	-0,59	-0,76	-0,84	-0,84	-0,78
663	-0,96	-0,87	-0,35	-0,59	-0,63	-0,66	-0,54
673	-0,75	-0,66	-0,16	-0,38	-0,41	-0,44	-0,37
683	-0,60	-0,43	0,02	-0,18	-0,22	-0,27	-0,19
693	-0,44	-0,27	0,18	0,00	-0,05	-0,14	-0,01
703	-0,35	-0,16	0,35	0,11	0,08	-0,03	0,10
713	-0,29	-0,08	0,41	0,18	0,16	0,04	0,16

The graphic dependences of the rate of destruction of modified composites on the inverse temperature are shown on figures 4 a) and b).



a)



b)

Figure 4. Graphic dependence of the rate of destruction of modified composites on the inverse temperature

Due to the obtained results and conducted mathematical calculations (fig. 4, a, b, table 6) it is found, that the increased activation energy of thermal destruction provides the decrease of constant of destruction reaction rate. It means, that the composite materials of the phthalic anhydride $q = 0,10...0,50$ wt % are characterized by the biggest activation energy of thermal destruction.

Table 6

The calculated value of the activation energy during thermal destruction of modified composites

Modifier content, q , wt %	$X_{поч}$	$X_{кін}$	X_i	$Y_{поч}$	$Y_{кін}$	Y_i	$tq_{(q)}$	E_a , kJ/mol
Matrix	1,605	1,403	0,202	0,017	-2,302	2,319	11,480	95,4
0,10	1,605	1,403	0,202	0,382	-2,723	3,105	15,372	127,8
0,25	1,745	1,403	0,342	0,382	-4,355	5,440	15,907	132,2
0,50	1,658	1,403	0,255	0,759	-3,272	4,031	15,809	131,4
1,00	1,631	1,403	0,228	0,56545	-2,577	3,143	13,783	114,5
2,00	1,658	1,403	0,255	0,507	-2,935	3,442	13,497	112,2
3,00	1,745	1,403	0,342	0,84803	4,5976	5,446	15,923	132,3

The values of activation energy of the above-mentioned composites is $E_a = 127,8...132,2$ kJ/mol that is associated with the chemical bonds resistance to the temperature influence due to the restriction of mobility of macro chains and epoxy binder segments caused by the modifier bonds C-O, C=O strengthening.

Conclusions. It was found by the methods of thermogravimetric (TGA) and differential thermal (DTA) analysis that the materials containing the modifier phthalic anhydride (PhA) of the content $q = 0,10...0,25$ wt % per 100 wt % of epoxy oligomer DER – 331 within the range of temperature $\Delta T = 585,5...726,7$ K lose mass within $\varepsilon_m = 57,7...72,7$ % lost their mass within the boundaries $\varepsilon_m = 57,7...72,7$ %. Herewith, among the composites under study, the value of exoeffect peak temperature was equal to $T_{max} = 542,9$ K. $\Delta T = 19,8$ K displacement of the temperature value of the exoeffect peak into the area of high temperatures has proved the thermal stability under high temperature impact conditions. We can state, that the activation energy of the developed composites increased from $E_a = 95,4$ kJ/mol (matrix) to $E_a = 132,2$ kJ/mol under the modifier adding conditions of content $q = 0,10...0,25$ wt %, that has proved the restriction of mobility of the composite kinetic elements and provides thermal resistance of the modified composites.

The publication contains the results of research conducted in the framework of research and development of young scientists «Directional control of the formation of nanocarbon-containing polymer composites to improve the performance of transport» (0121U107610).

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ДОСЛІДЖЕННЯ ВПЛИВУ ВМІСТУ МОДИФІКАТОРА 2-БЕНЗОФУРАН-1,3-ДИОНУ НА ТЕРМОСТІЙКІСТЬ ЕПОКСИДНИХ КОМПОЗИТІВ

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Резюме. Наведено технологічні аспекти модифікації термореактивного зв'язувача для забезпечення поліпшення теплофізичних характеристик композитних матеріалів і захисних покриттів на їх основі. Для формування епоксикомпозитних матеріалів використовували епоксидний зв'язувач DER – 331 виробництва «Dow Chemical Corp» (Німеччина). Для зшивання епоксидного зв'язувача використано твердник холодного тверднення триетилентетрамін ТЕТА ($q = 10$ мас.ч. на 100 мас.ч. епоксидної смоли DER – 331). Для модифікування епоксидного олігомеру DER – 331 використовували модифікатор 2-Бензофуран-1,3-діон-фталевий ангідрид, який вводили у зв'язувач за вмісту від $q = 0,10 \dots 3,00$ мас.ч. Молекулярна формула даного модифікатора – $C_8H_4O_3$. Проведено комплексні дослідження теплофізичних властивостей, за результатами яких встановлено оптимальний вміст модифікатора фталевого ангідриду у реактопластичній матриці, який становить $q = 0,10 \dots 0,25$ мас.ч. на 100 мас.ч. олігомеру DER – 331. Дослідження модифікованих композитів в умовах впливу підвищених температур проводили з використанням термогравіметричного (ТГА) та диференційно-термічного (ДТА) аналізу. При цьому модифіковані композити характеризуються такими властивостями: температура початку втрати маси (початок деструкції матеріалу) – $T_n = 618 \dots 622$ К; кінцева температура втрати маси (завершення деструкції матеріалу) – $T_k = 706,1 \dots 709,2$ К; відносна втрата маси таких матеріалів становить $\varepsilon_m = 57,7 \dots 61,0\%$. Виконано математичний розрахунок значень енергії активації термічної деструкції для визначення стійкості до руйнування хімічних зв'язків при впливі температурного фактора. Доведено, що енергія активації розроблених композитів підвищується у 1,3–1,4 раза при введенні модифікатора за вмісту $q = 0,10 \dots 0,25$ мас.ч., що свідчить про термічну стійкість модифікованих композитів.

Ключові слова: епоксидний зв'язувач, модифікатор, твердник, термостійкість, деструкція, енергія активації.

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