

## Temperature impact upon structural and thermal physical properties of epoxy composites modified with 4,4-sulfonyl bis (4,1-phenylene) bis (n,n-diethyldithiocarbamate)

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### Abstract

The effect of the 4,4-sulfonylbis (4,1-phenylene) bis (n,n-diethyldithiocarbamate) ( $C_{22}H_{28}N_2O_2S_5$ ) modifier on the thermal properties of the epoxy bisphenol oligomer ED-20 within the temperature range  $\Delta T = 303\text{--}873$  K has been defined. The heat resistance by Martens, thermal expansion coefficient, glass transition temperature and shrinkage have been studied. As the result of the acquired data analysis, the optimum concentration of the  $C_{22}H_{28}N_2O_2S_5$  modifier, significantly improving the thermal properties of epoxy composite, has been set. It has been demonstrated that in order to get a composite material (CM) or a protective coating with enhanced thermal properties, it is necessary to introduce the optimum amount of modifier into the epoxy binder ( $q = 0.10\text{--}0.25$  mass parts out of 100 % ED-20 resin). In this case, the composite is formed with the heat resistance value by Martens of  $T = 362$  K.

On the basis of experimental studies of thermal properties using modern research methods such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) the allowable temperature limits at which it is possible to use modified epoxy composites have been set. CM with the entered modifier of  $q = 0.75$  mass parts and  $T_0 = 601.8$  K is characterized by the biggest destruction temperature value if compared with the matrix ( $T_0 = 600.1$  K). The difference between the minimum and the maximum value is only  $\Delta T_0 = 1.7$  K, which indicates insignificant positive impact of modifier upon the initial destruction temperature.

Using DTA curves exothermic effects when exposed to the thermal field within the temperature range of CM  $\Delta T = 591.3\text{--}683.7$  K have been defined. It has been found out that the maximum values of exothermic peak, if compared with the matrix ( $T_{max} = 618.3$  K) are  $T_{max} = 626.6\text{--}641.0$  K, and they are characteristic for CM, filled with the  $C_{22}H_{28}N_2O_2S_5$  modifier in an amount of  $q = 0.50\text{--}0.75$  mass parts. The difference between the minimum (matrix component) and the maximum value is  $\Delta T_{max} = 22.7$  K, which (within experimental error) shows a significant positive impact of the modifier upon the maximum exoeffect value. It is said to increase the thermal stability of CM, which in its turn, is due to the stability of physical and chemical bonds in the material, providing improved physical and mechanical properties of materials under the impact of rising temperatures.

Keywords: epoxy composite modifier, heat resistance, glass transition temperature, shrinkage.

One of the promising areas of materials science is the development of new polymer composite materials by modifying them with various filling agents. First of all in the course of modifying useful properties of the material must be kept, while new properties must be added or undesirable properties must be eliminated. With the help of modification it is possible to control the structure of polymeric binders, eliminate its inherent disadvantages and improve the strength properties of the materials, etc. [1]. Modifiers can be solid, liquid, organic, inorganic or with low molecular weight [2, 3], etc. These compounds have been found interesting for a long time due to the fact that the introduction of a modifier in a polymeric binder, and further mixing of the individual compositions can help to create new

materials with improved properties as compared to the original components. The addition of a modifier effects the formation of supramolecular composite structure and allows obtaining materials with valuable properties, without creating new expensive chemical technology to produce a new polymer with the required parameters. Meanwhile combination of ingredients of different nature to obtain a complex of improved properties, modified epoxy composites, including thermal, allows to extend the temperature range of use of such materials.

Thus, currently the modification of existing polymers and obtaining of new materials on their basis is one of the most important areas of polymer chemistry.

In this regard, the formation and application of composites based on epoxy binder is rather promising. Epoxy resins are a class of thermosetting plastics and similar materials such as phenols and polyesters. A number of improved properties of epoxy composites leads to their widespread use in the industry, including oil and gas industry. Failures are often associated with explosions, fire, emission of hydrocarbons, causing considerable economic and environmental damage, and in some cases accompanied by the loss of human life.

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One of the main reasons for such failures as the failure of the oil and gas equipment production facilities, training, transport, processing and storage of oil, is the corrosion of metal. The inner surface of the oil and gas equipment is most susceptible to corrosion due to constant contact with oil, produced water, gas-oil ratio (industrial pipelines, oil treatment, reservoirs).

The main way to improve the safety and service life of oil industry equipment, tanks for oil storage and preparation, pipelines, is the use of high-quality and relatively expensive insulating coatings.

One of the most effective solutions is the use of the modified anti-corrosion epoxy composite materials. Such protective coatings have a complex of properties required for oil industry equipment: good adhesion to metal and non-metallic surfaces, hardness, good chemical resistance (to oils and solvents, water resistance in fresh and marine waters, gas impermeability), high abrasion resistance, higher rates of dielectric properties, as well as low shrinkage and significant hardening rate [4–7].

Thus, one can make a conclusion that epoxy composites are of a general purpose and can be applied in many fields of industry. Therefore, to expand the range and possibilities of industrial application of epoxy composites it is necessary to study the thermal properties of the modified materials that allows to predict their reliability in various temperature ranges of operation.

The purpose of this study is to investigate the impact of 4,4-sulfonilbis (4,1-phenylene) bis (n,n-diethyl-dithiocarbamate) modifier upon structural properties in epoxy composites under the thermal field impact.

#### Materials and methods of research

On the basis of the above mentioned information, epoxy diene oligomer ED-20 (GOST 10587–84) has been selected as the main component for the binder in the formation of CM. It is characterized by high adhesion and cohesion strength, low shrinkage and manufacturability when applied to the surface of a complex profile.

4,4-sulfonil bis (4,1-phenylene) bis (n,n-diethyl-dithiocarbamate) has been selected as a modifier. It is characterized by reactivity to interaction with molecules of epoxy oligomer due to a significant number of active groups. The modifier was introduced in the amount of from 0.10 to 2.00 mass parts for 100 mass parts of epoxy oligomer ED-20 (hereinafter mass parts are referred to as per 100 mass parts of epoxy oligomer ED-20). The formula of the 4,4-sulfonilbis (4,1-phenylene) bis (n,n-diethyl-dithiocarbamate) modifier is as follows:  $C_{22}H_{28}N_2O_2S_5$ .

For the cross-linking of epoxy compositions, the polyethylene polyamine PEPA (TU 6-05-241-202–78) hardener is used, which makes it possible to form materials at room temperatures. It is known that PEPA is a low-molecular substance that consists of the following monomeric units:  $[-CH_2-CH_2-NH-]_n$  [4, 8]. The curing agent was added to the composition in an amount of 10 mass parts per 100 mass parts of epoxy oligomer ED-20. Characteristics of epoxy diene oligomer, modifier and hardener are given in Table 1.

**Table 1 – Characteristics of epoxy binder components**

Characteristics	Epoxy-oligomer ED-20	The $C_{22}H_{28}N_2O_2S_5$ modifier	PEPA hardener
Molar mass	340	512.8	215–258
Epoxy group content, %	20.0–22.5	–	–
Hydroxyl content, %	1.25	–	–
Hydrogen content (H), %	–	5.50	–
Nitrogen content (N), %	–	5.46	19.5–22.0
Carbon content (C), %	–	51.53	–
Oxygen content (O), %	–	6.24	–
Sulfur content (S), %	–	31.26	–
Viscosity $\eta$ , Pa·s	13–20	–	0.9
Density $\rho$ , g/cm <sup>3</sup>	1.16	6.08	1.05

Epoxy CM was formed according to the following technology: component dosing, hydrodynamic mixing of the modifier and ED-20 epoxy-dian resin to obtain a homogeneous mixture and then complete dissolving of the additive for a time  $\tau = 2 \pm 0.1$  min at room temperature  $T = 298 \pm 2$  K, the introduction of a filler of a predetermined content, the ultrasonic treatment of the composition for a time  $\tau = 1.5 \pm 0.1$  min, the introduction of a PEPA hardener and hydrodynamic alignment of the components for a time  $\tau = 2 \pm 0.1$  min, curing the composition. The validation of the CM was carried out according to the experimentally established regimes: the formation of samples and their holding for a time  $\tau = 12.0 \pm 0.1$  h at a temperature of  $T = 298 \pm 2$  K, heating with a velocity  $v = 3$  K/min to the cross-linking temperature  $T = 413 \pm 2$  K, holding the samples at a given temperature for a time  $\tau = 2.0 \pm 0.05$  h, slow cooling to a temperature  $T = 298 \pm 2$  K. In order to stabilize the structural processes in the matrix, the samples were held for a time  $\tau = 24$  h in air at a temperature  $T = 298 \pm 2$  K with the subsequent experimental studies.

Thermophysical properties of CM have been studied, such as heat resistance by Martens, thermal coefficient of linear expansion, thermal stability (DTA and TGA analysis).

Heat resistance of CM by Martens was determined according to GOST 21341–75. The method of investigation consists of determining the temperature at which the sample was heated at a speed of  $v = 3$  K/min under the impact of a constant bending load  $F = 5 \pm 0.5$  MPa, as a result of which it has been deformed by a predetermined value ( $h = 6$  mm).

The thermal coefficient of linear expansion of materials was calculated on the basis of the graphical dependence of the relative strain on temperature, approximating this dependence by the exponential function. The relative deformation was determined from the change in the length of the sample with increasing temperature under steady-state conditions (GOST 15173–70). The dimensions of the samples for the study were  $65 \times 7 \times 7$  mm, the nonparallelism of the polished ends was not more than 0.02 mm. Before the test, the length of the sample was measured with the accuracy of up to  $\pm 0.01$  mm. The rate of temperature increase was  $v = 2$  K/min.

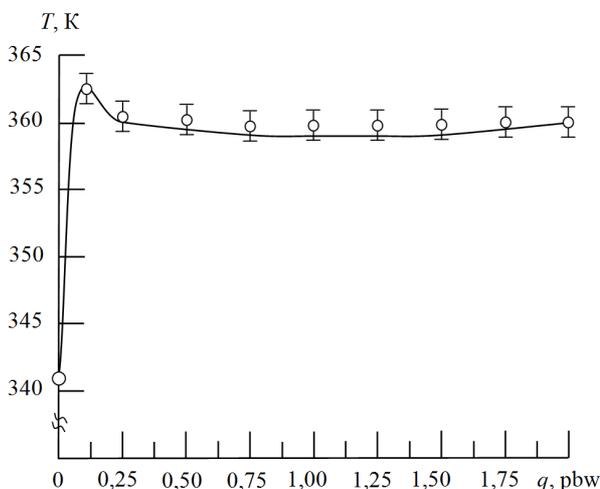
The deviation of values in the study of the parameters of the thermophysical properties of CM (heat resistance by Martens, thermal coefficient of linear expansion) was 4–6% of the nominal value.

To study the effect of the amount of filler on thermal transformations in composites, the TGA and DTA analysis was used using the Thermoscan-2 derivatograph. The investigations were carried out in the temperature range  $\Delta T = 298\text{--}873$  K, using quartz crucibles for samples with a volume of  $V = 0.5$  cm<sup>3</sup>. During the studies, the rate of temperature rise was  $v = 10$  K/min, while Al<sub>2</sub>O<sub>3</sub> ( $m = 0.5$  g) was used as a reference substance, the weight of the sample under investigation was  $m = 0.3$  g. The error in determining the temperature was  $\Delta T = \pm 1$  K. Accuracy of determination of thermal effects was 3 J/g. The accuracy of determination of the change in the mass of the sample is  $\Delta m = 0.02$  g.

### The results of the research and their discussion

When materials are used in production and operation in various technological processes, it is important to study structural changes when CM is heated, allowing us to estimate the temperature range of use of new materials. Therefore, we first studied the heat resistance (according to Martens) of CM, modified by the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier. At the same time, the filler content was varied within the range of  $q = 0.10\text{--}2.00$  mass parts.

It has been established [6–8] that the heat resistance of a modified epoxy matrix is  $T = 341$  K (Fig. 1). Introduction to the binder, the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier in the amount  $q = 0.10$  mass parts leads to a significant increase in heat resistance relative to the matrix, resulting in a maximum on the curve of the  $T$ – $q$  curve, which is  $T = 362$  K. This indicates an active physical and chemical interaction of the modifier with the epoxy binder and indicates the formation of a spatial polymer network in which the dissolved modifier is uniformly distributed throughout the volume, which is an important factor in the structure formation of the



**Figure 1 – The dependence of the thermal resistance by Martens ( $T$ ) of CM upon the content of the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier ( $q$ , pbw)**

composition and indicates a homogeneous polymerization of CM.

The introduction of the modifier in an amount of  $q = 0.25$  mass parts leads to the insignificant decrease in the heat resistance to  $T = 360$  K. The subsequent increase in the amount of the modifier to  $q = 0.50\text{--}2.00$  mass parts also insignificantly affects the heat resistance of the CM and within the experimental error makes up an analogous value of  $T = 360$  K. On the basis of the above mentioned experimental data, it can be concluded that the introduction of the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier in an amount exceeding  $q = 0.10$  mass parts practically does not affect the parameters of heat resistance of CM and remains within the limits of the constant.

One of the important and basic characteristics of polymers is the glass transition temperature. It is associated with the decrease in the mobility of the polymer units. Below the glass transition temperature ( $T_c$ ), the supply of kinetic energy in macromolecules is insufficient to move the segments of the chain as a whole, which leads only to minor oscillations of atoms relative to their centers of gravity. The structure of the polymers under these conditions is solid, in a sufficiently brittle state, their macromolecules have an elongated shape and are characterized by only a slight elastic deformation. With an increase in temperature exceeding the threshold  $T_c$ , polymers with an increase in the thermal energy reserve become highly elastic and become capable of highly elastic deformations, in other words, they remain in a plastic form. When the temperature is raised, the transition of the polymer into a viscous-flowing state is noticeable, and deformations during the action of critical temperatures prove to be irreversible, which leads to the destruction of the coating and the impossibility of its further operation. Therefore, we conducted an analysis of the behavior of CM under the influence of a thermal field, investigated the glass transition temperature and shrinkage in the cross-linking of the developed CM.

It has been experimentally established [6–8] (Table 2, Fig. 2, Fig. 3) that the glass transition temperature of the modified RCD epoxy matrix is  $T_c = 327$  K. The introduction of the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier in the amount of  $q = 0.10$  mass parts leads to a significant increase in the glass transition temperature and amounts to  $T_c = 334$  K. It should be noted that the obtained values correlate with the values of the CM heat resistance indexes, which are also maximal for the given composite. The subsequent increase in the concentration of the modifier in the range from  $q = 0.25$  to  $q = 0.50$  mass parts reduces the glass transition temperature of the matrix to  $T_c = 323\text{--}324$  K. It is established that on the contrary the addition of an additive in an amount of  $q = 0.75$  mass parts substantially increases  $T_c$  to 343 K, which is the largest value obtained in the course of the experiment. This, in its turn, is consistent with the obtained thermal resistance data, which are described below. Further increase in the amount of filler in the binder ( $q = 1.00\text{--}2.00$  mass parts) led to a significant decrease in the glass transition temperature relative to the matrix to  $T_c = 322\text{--}307$  K.

Table 2 – Thermophysical properties of CM

Properties	Content of the C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> S <sub>5</sub> modifier <i>q</i> , pbw									
	matrix	0.10	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Glass transition temperature <i>T<sub>g</sub></i> , K	327	338	323	324	343	322	304	306	313	307
Shrinkage $\delta$ , %	0.32	0.25	0.19	0.19	0.22	0.16	0.032	0.074	0.069	0.042

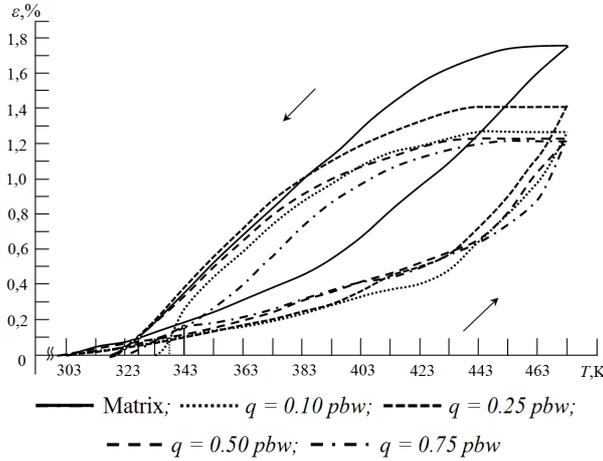


Figure 2 – The dilatometric curves of epoxy matrix and CM with different content of the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier, *q*, pbw

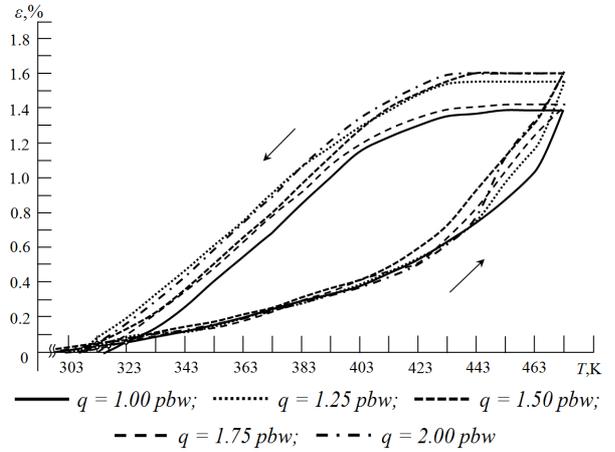


Figure 3 – The dilatometric curves of CM with different content of the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier, *q*, pbw

Table 3 – Thermal coefficient of linear expansion of CM within various testing temperature ranges

Content of the C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> S <sub>5</sub> modifier, <i>q</i> , pbw	Thermal coefficient of linear expansion $\alpha \cdot 10^5$ , K <sup>-1</sup>			
	Testing temperature ranges $\Delta T$ , K			
	303–323	303–373	303–423	303–473
matrix	6.30	6.81	9.92	10.91
0.10	3.11	2.74	3.29	7.41
0.25	2.89	2.77	4.16	7.25
0.50	2.63	3.24	4.48	7.26
0.75	3.65	3.57	4.21	7.16
1.00	2.87	3.35	4.43	8.25
1.25	4.65	3.60	4.60	9.11
1.50	3.02	3.53	4.86	9.42
1.75	3.03	3.39	4.48	9.38
2.00	3.40	3.21	4.09	9.38

To study and analyze the structural processes occurring in the samples under the influence of the thermal field, the thermal coefficient of linear expansion of the materials was investigated. On the basis of dilatometric curves (Fig. 2, Fig. 3) of deformation versus temperature dependences the thermal coefficient of linear expansion of CM was calculated within the temperature range of  $\Delta T = 303\text{--}473$  K. The results of calculating of thermal coefficient of linear expansion in predetermined temperature ranges are given in Table 3.

It was found that with increasing temperature at different temperature sections of the study, the thermal coefficient of linear expansion of the samples increases. According to the obtained experimental data, it is established that the minimum value of thermal coefficient of linear expansion in the thermal range  $\Delta T = 303\text{--}373$  K is characterized by materials with an amount of modifier  $q = 0.10\text{--}0.25$  mass parts (Table 3). At the same time, the value of thermal coefficient of

linear expansion fluctuates within the limits  $\alpha = (2.74\text{--}2.77) \cdot 10^{-5}$  K<sup>-1</sup>. Also, special attention should be paid to the behavior of CM at higher temperatures, in our case in the temperature range  $\Delta T = 303\text{--}473$  K. It is proved that the smallest thermal coefficient of linear expansion in the above temperature range of tests is characterized by materials with a modifier content in the amount of ( $q = 0.10\text{--}0.25$  mass parts). Thermal coefficient of linear expansion of such materials is  $\alpha = (7.25\text{--}7.41) \cdot 10^{-5}$  K<sup>-1</sup>. It is worth noting that the results of the investigation of modified matrices with the above-described additive concentrations are in good agreement with each other in different temperature exposure ranges, since the lowest values of thermal coefficient of linear expansion correlate with data on heat resistance, glass transition.

Thus, it can be argued that in the formation of CM with improved thermophysical properties, it is advisable to introduce the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier with a

Table 4 – Temperature resistance of the CM filled with  $C_{22}H_{28}N_2O_2S_5$  modifier

The content of $C_{22}H_{28}N_2O_2S_5$ modifier, $q$ , pbw	$T_0$ , K	$T_5$ , K	$T_{10}$ , K	$T_{20}$ , K	$T_{fin}$ , K	$\varepsilon_m$ , %
matrix	600.1	619.3	626.4	645.8	734.0	73.3
0.10	594.1	621.2	630.8	641.7	737.5	75.3
0.25	596.2	619.5	630.0	641.9	778.1	78.6
0.50	600.8	624.0	633.8	646.5	760.3	77.3
0.75	601.8	626.0	635.6	648.8	731.3	74.3
1.00	601.8	622.6	632.4	643.4	747.9	76.3
1.25	598.6	620.2	630.7	642.1	749.7	77.0
1.50	598.5	622.8	630.2	640.4	750.1	78.3
1.75	591.1	616.8	627.6	639.1	741.0	75.0
2.00	591.5	617.4	628.9	640.3	752.9	75.0

Note:  $T_0$  – the initial temperature of mass losses (beginning of the destruction);

$T_5, T_{10}, T_{20}$  – the temperatures of mass losses (5, 10, 20 %);

$T_{fin}$  – the final temperature of mass losses (completion of destruction);  $\varepsilon_m$  – relative mass losses

concentration of  $q = 0.10$ – $0.25$  mass parts. It was believed that in such materials, with the optimum amount of additive, the physicochemical processes of interaction of the modifier with the binder are activated. In our opinion, this is due to a high content of carbon in the modifier (Table 1), which is uniformly distributed over the volume of the spatial grid and leads, due to the ability to form various types of bonds with many chemical elements, to increase the interfacial interaction when the modified matrix is cross linked. Thus, a stable, cross linked polymer structure is formed with increased resistance to deformation (linear or volumetric) upon exposure to a temperature factor (at a maximum temperature value of  $\Delta T = 303$ – $473$  K). At the same time, the modifier also contains sulfur, the amount of which is 31.26 % (Table 1). This content of sulfur atoms, on the contrary, negatively affects the polymerization processes, especially under conditions of increasing temperatures, forming in them an increased content of sol-fraction, which accordingly leads to a deterioration of the thermophysical properties of the modified matrices. This is confirmed by the experimental data obtained above, which indicate a decrease in the thermophysical properties of materials with an increase in the amount of the modifier (and hence the amount of sulfur) in them.

The process of polymeric materials combustion is a complex physico-chemical process, which encompasses, among other things, the chemical reactions of destruction. During the process of material's heating to the critical temperature and its further destruction, the structure of the CM undergoes changes. Therefore, as the temperature rises, its physical, in particular, thermophysical properties change, affecting the conditions of diffusion, heat transfer, leading to a viscous-flowing, highly elastic state of the polymer. Consequently, the state of the epoxy-composite coating structure changes, and there is observed the formation and development of micropores and microcracks in particular. This leads to a deterioration of functional (physical and mechanical, electrically conductive, etc.) characteristics and affects the operational and technological properties of

materials. In this regard, it is important to apply a comprehensive approach to optimizing the composition of epoxy-composite materials and protective coatings on their basis.

On this basis, the behavior of epoxy composites at elevated temperatures (thermal stability) was studied and analyzed by the thermogravimetric (TGA) and differential thermal (DTA) analysis (Fig. 4) in the temperature range  $\Delta T$  from 298 to 873 K. The analysis was carried out in the air. During the study of the destruction process of physico-chemical bonds in the initial and modified matrices, the rate of temperature rise of the samples was  $v = 10$  K/min. Thus, at this stage of work, the thermal stability of the matrix and the CM, filled with  $C_{22}H_{28}N_2O_2S_5$  modifier, was investigated. In the course of experimental studies, it has been found that there is no loss of mass (Fig. 4–6, Table 4) for the investigated CM in the temperature range from  $\Delta T = 303.0$  K to  $T_0 = 591.1$ – $601.8$  K. This indicates the absence of significant structural transformations during the process of heating in the CM, and it indirectly indicates insignificant moisture content in the samples, being studied.

At the same time, on the basis of the TGA curve, we have determined the temperature at which the initial and modified matrices begin to degrade ( $T_0 = 600.1$ – $601.8$  K), and the process ends at  $T_{fin} = 734.0$ – $778.1$  K due to the losses of the samples masses relative to the standard. Relative mass losses for all modified samples, as well as the initial matrix are  $\varepsilon_m = 73.3$ – $78.6$  % (Table 4), where the difference between the minimum and maximum value is only  $\Delta\varepsilon_m = 5.3$  %. In our opinion, this indicates a uniform mechanism of the behaviour of destructive processes, associated primarily with the destruction of chemical bonds of the "epoxy matrix – modifier" system components. It is worth emphasizing that the relative mass losses, as well as the final destruction temperature, are not decisive factors when choosing the optimum performance characteristics of the developed materials, since their maximum destruction occurs at ( $T_{fin}$ ). Since the initial destruction temperature ( $T_0$ ) is characterized by the initial stage of destruction of the intra-chemical bonds of materials, this

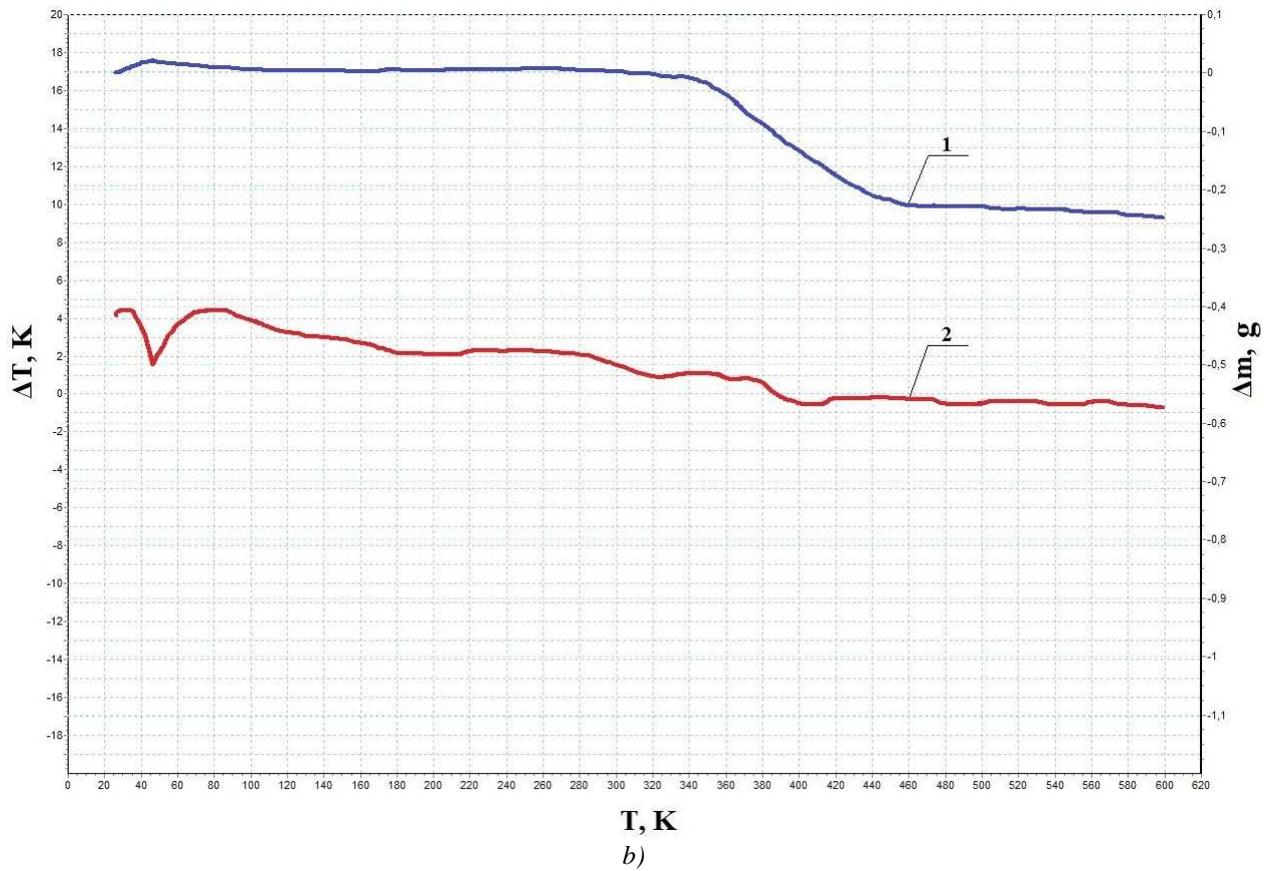
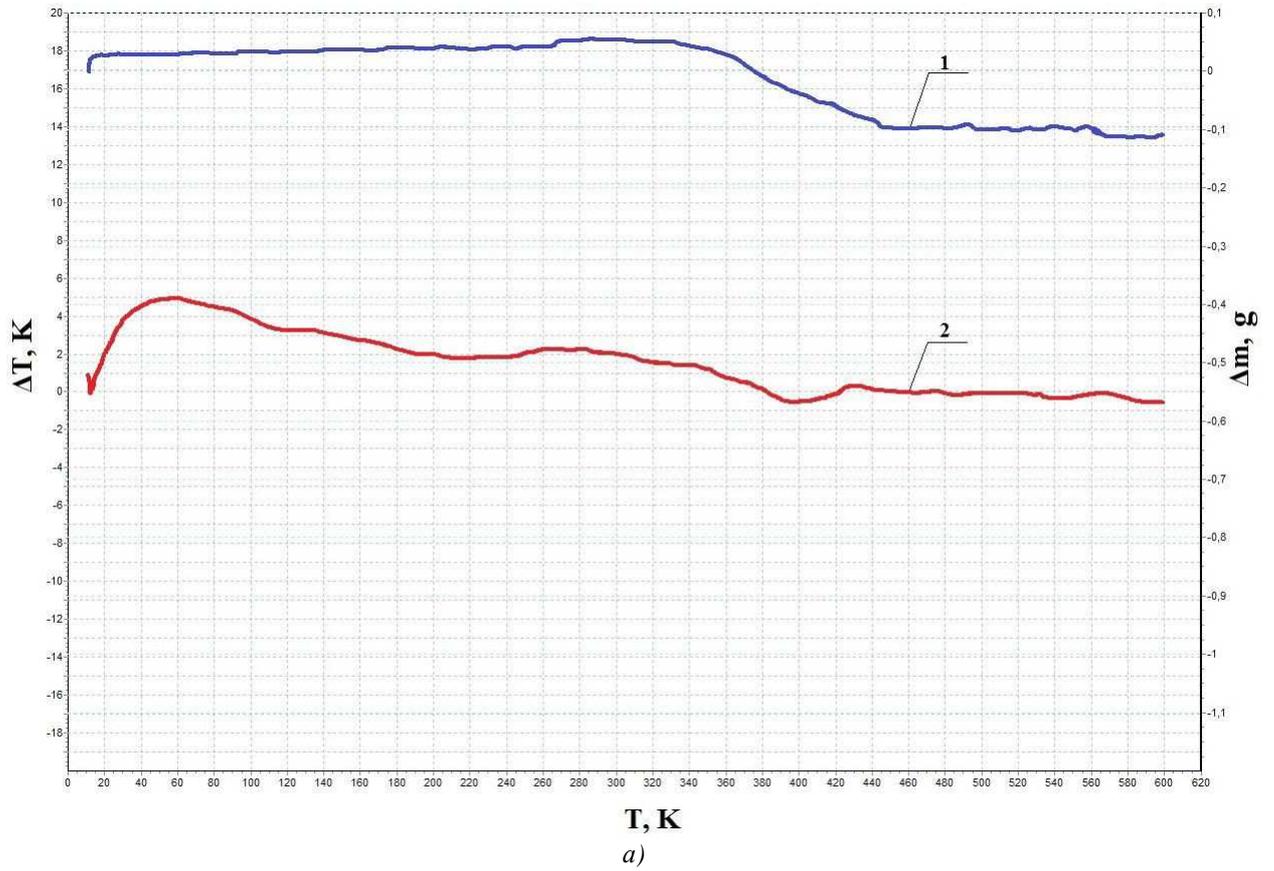


Figure 4 – The results of thermogravimetric (1) and differential thermal (2) analysis of the epoxy matrix and CM, containing the  $C_{22}H_{28}N_2O_2S_5$  modifier,  $q$ , pbw:  $a$  – the initial matrix;  $b$  – 0.10

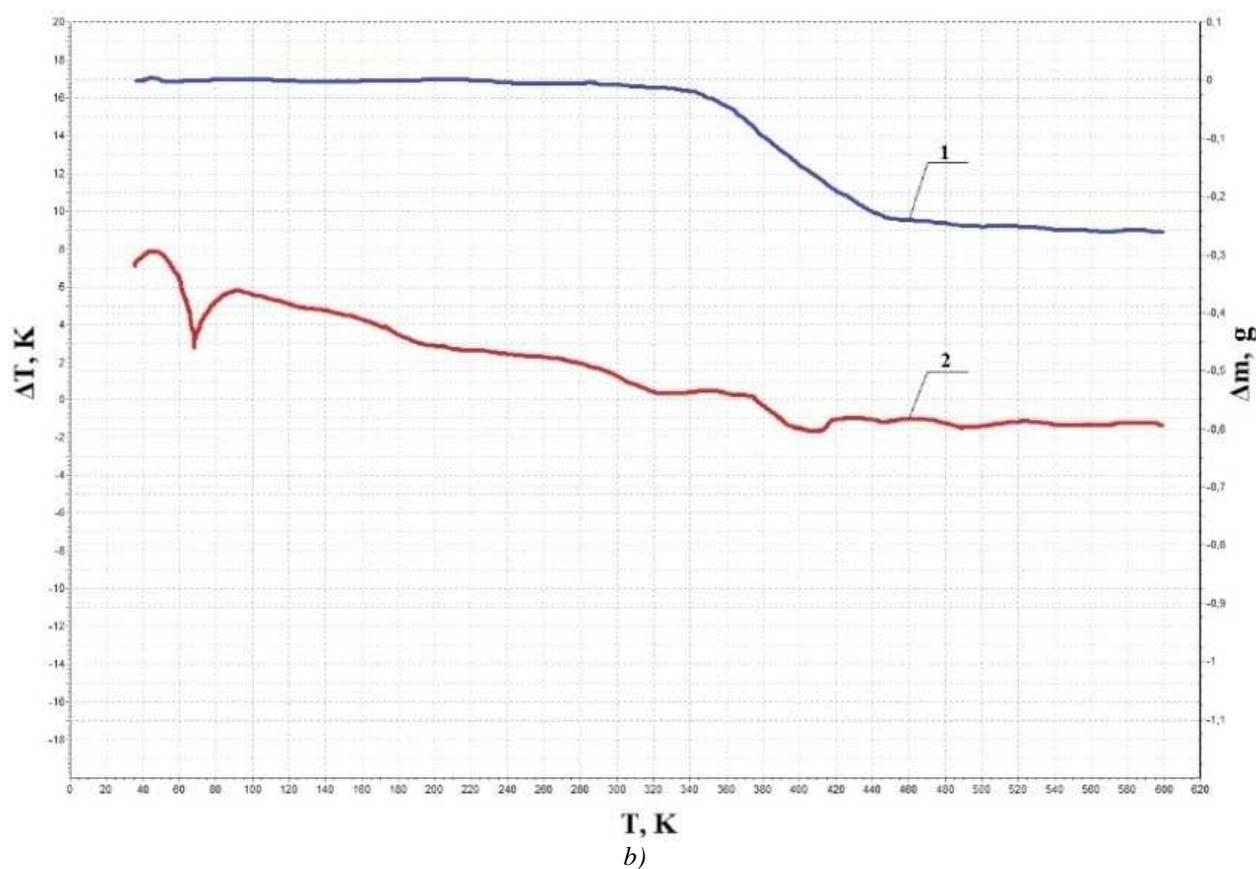
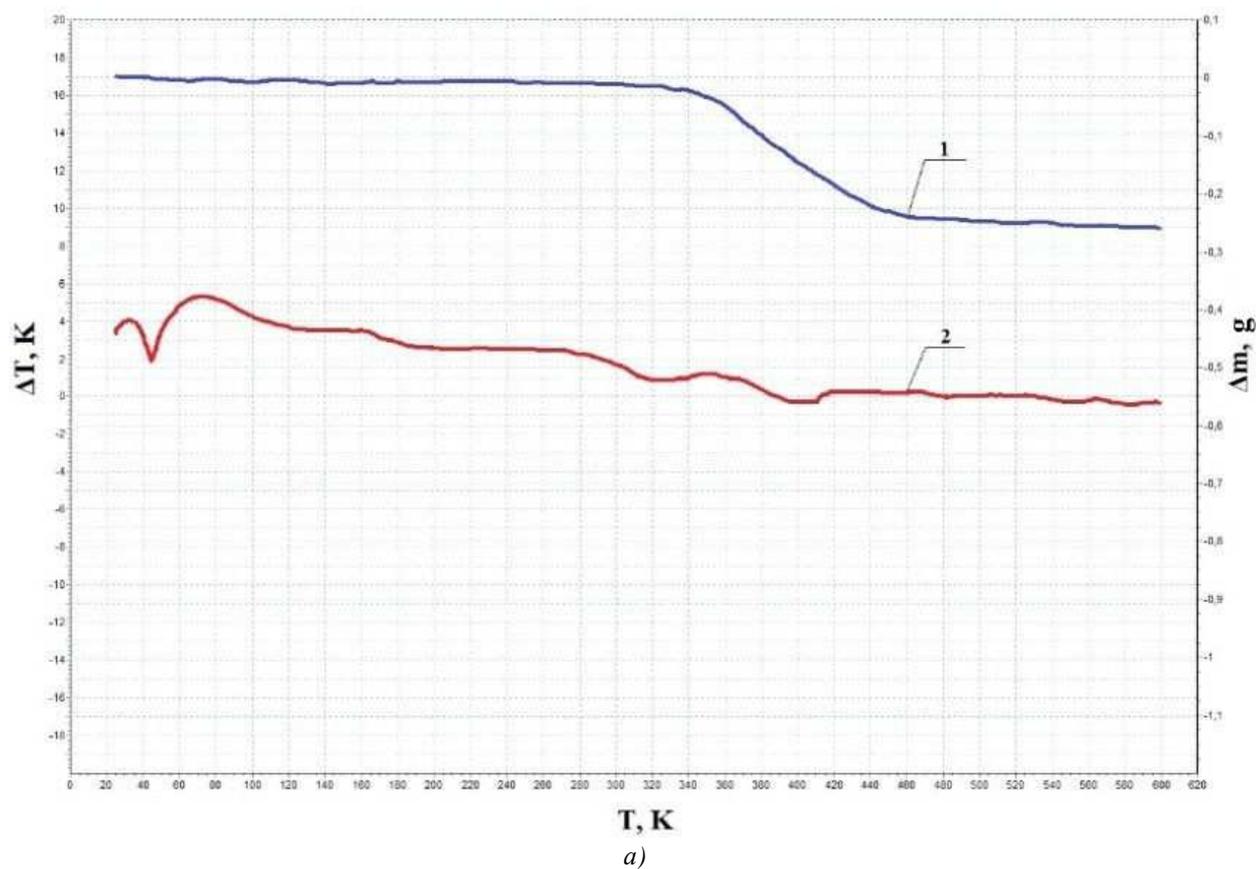


Figure 5 – Results of thermogravimetric (1) and differential thermal (2) analysis of CM, containing the  $C_{22}H_{28}N_2O_2S_5$  modifier,  $q$ , pbw:  $a - 0.25$ ;  $b - 0.50$

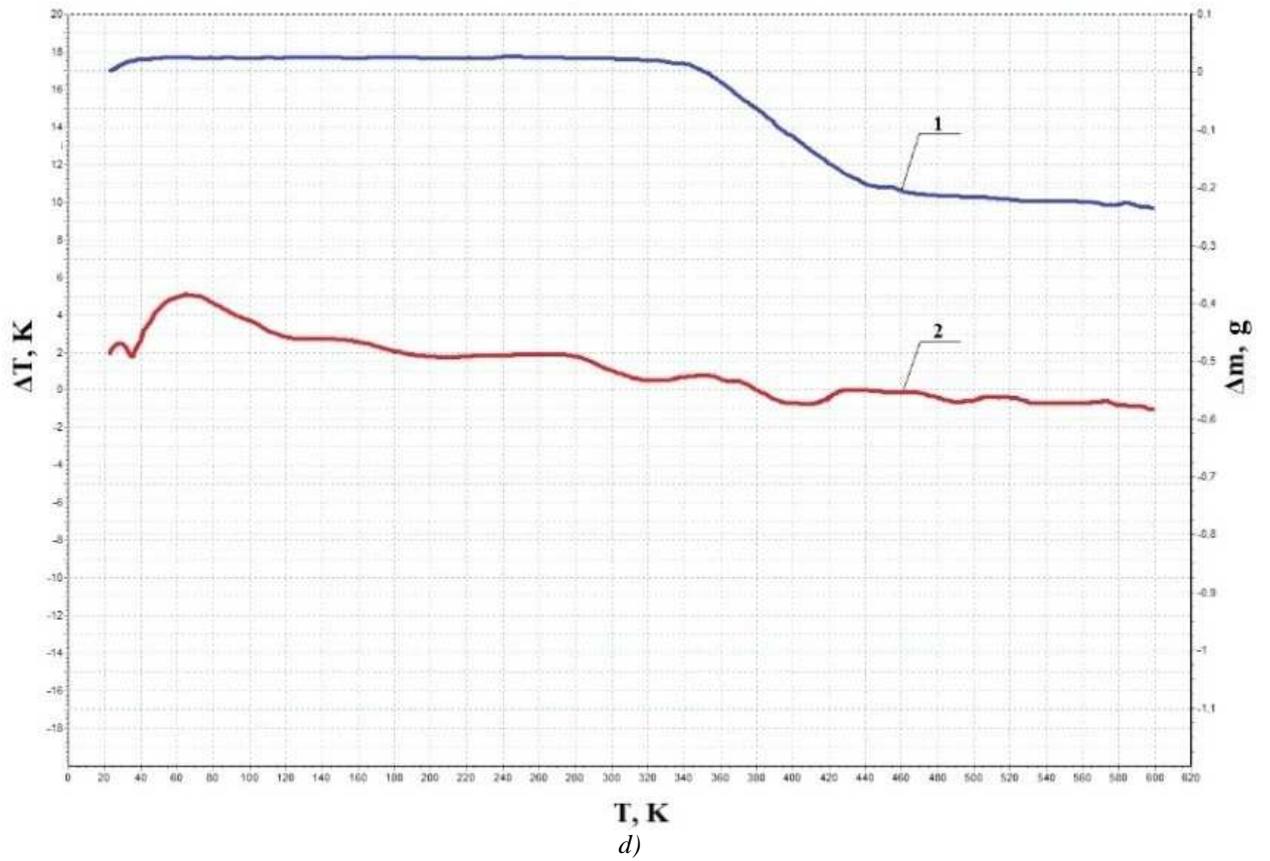
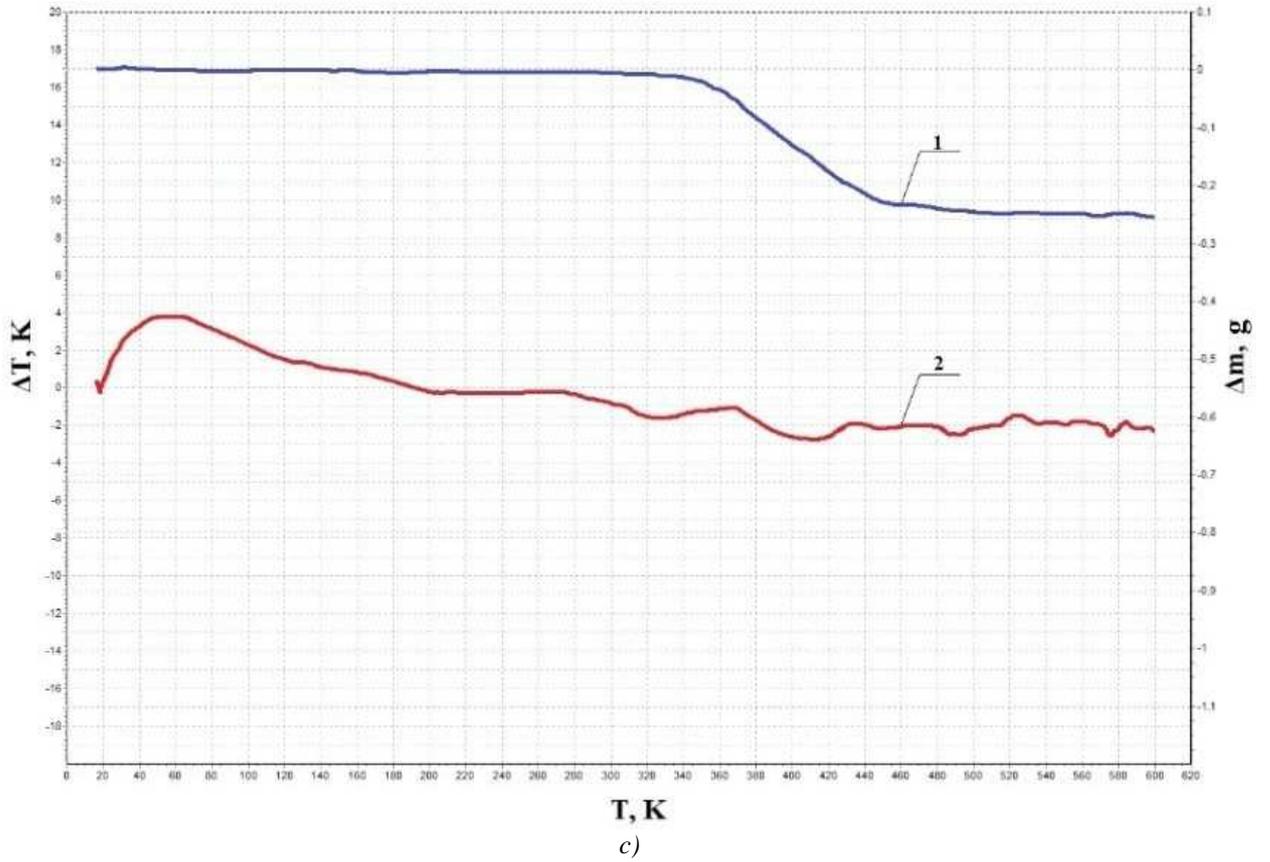


Figure 5 – Results of thermogravimetric (1) and differential thermal (2) analysis of CM, containing the  $C_{22}H_{28}N_2O_2S_5$  modifier,  $q$ , pbw:  $c - 0.75$ ;  $d - 1.00$

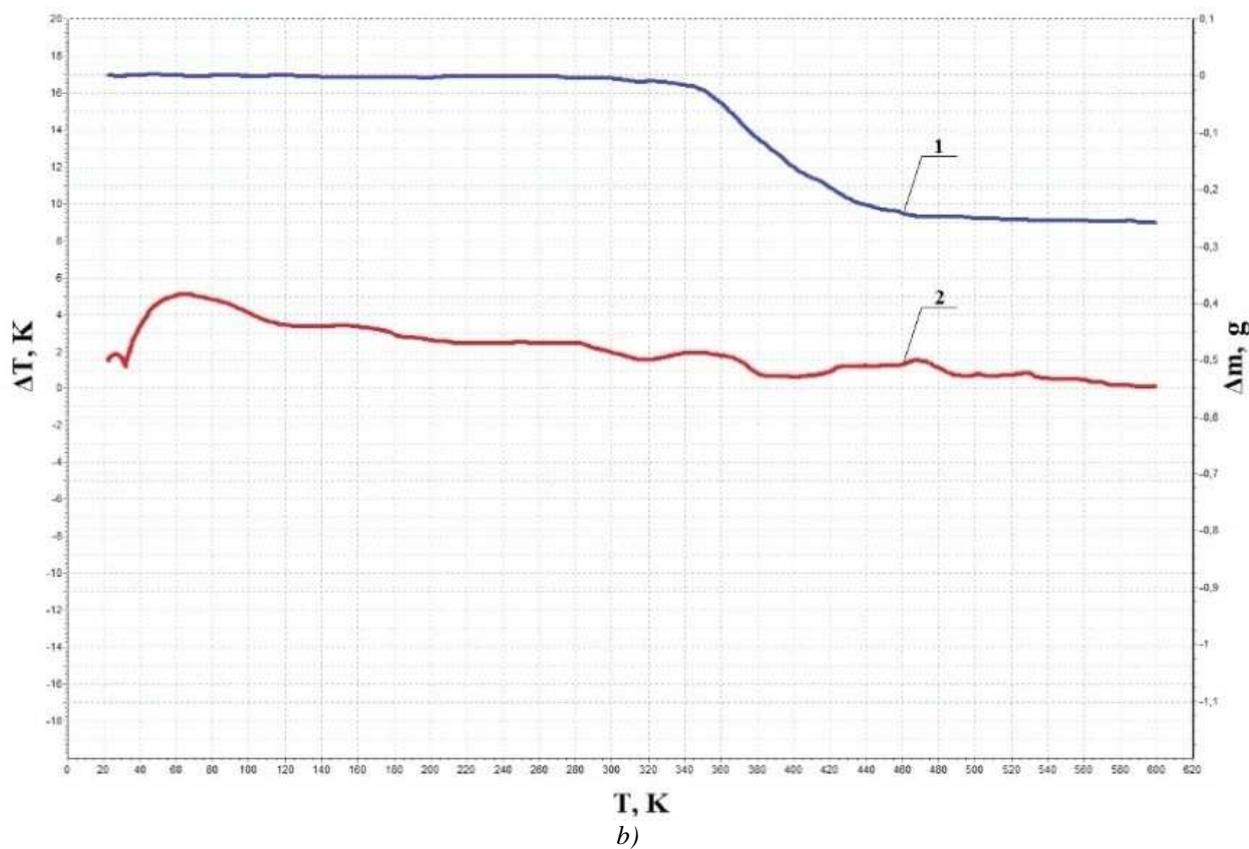
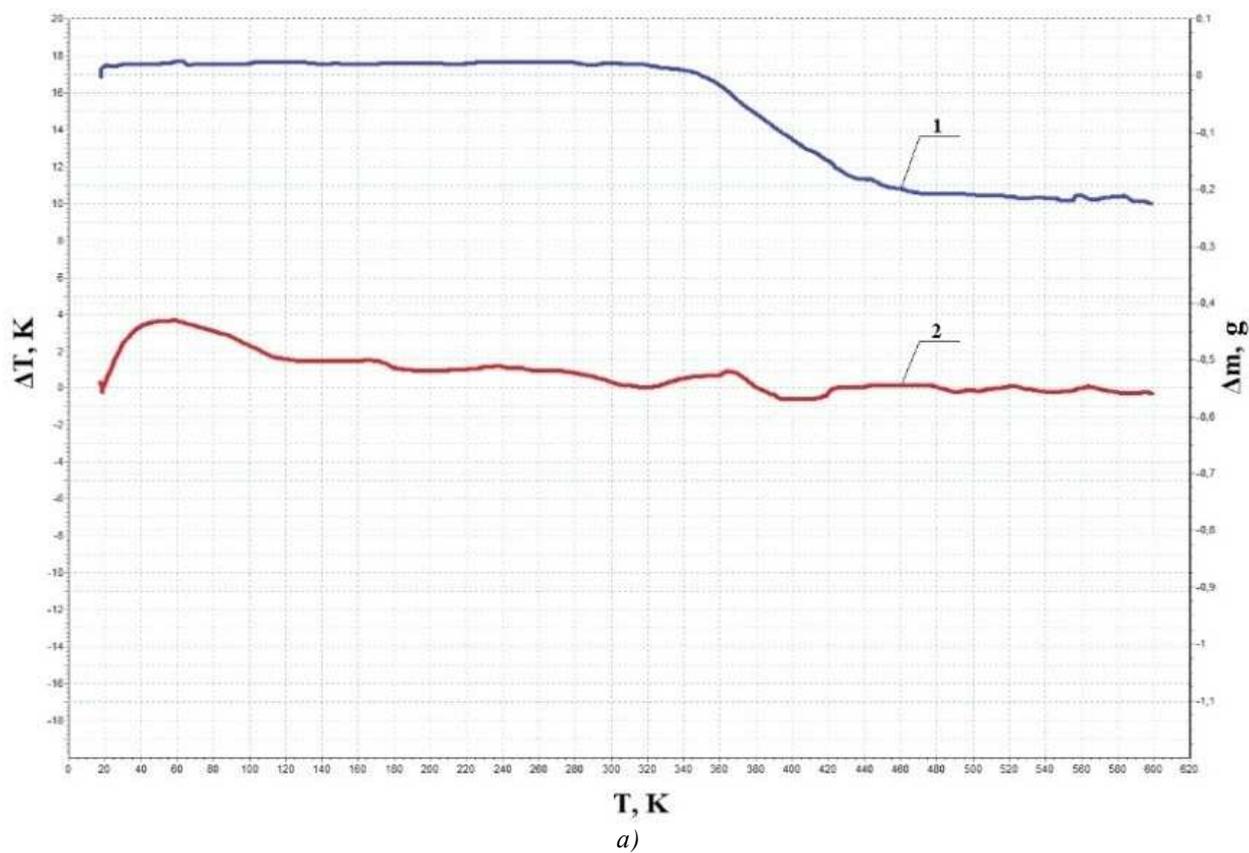


Figure 6 – Results of thermogravimetric (1) and differential thermal (2) analysis of CM, containing the  $C_{22}H_{28}N_2O_2S_5$  modifier,  $q$ , pbw:  $a - 1.25$ ;  $b - 1.50$

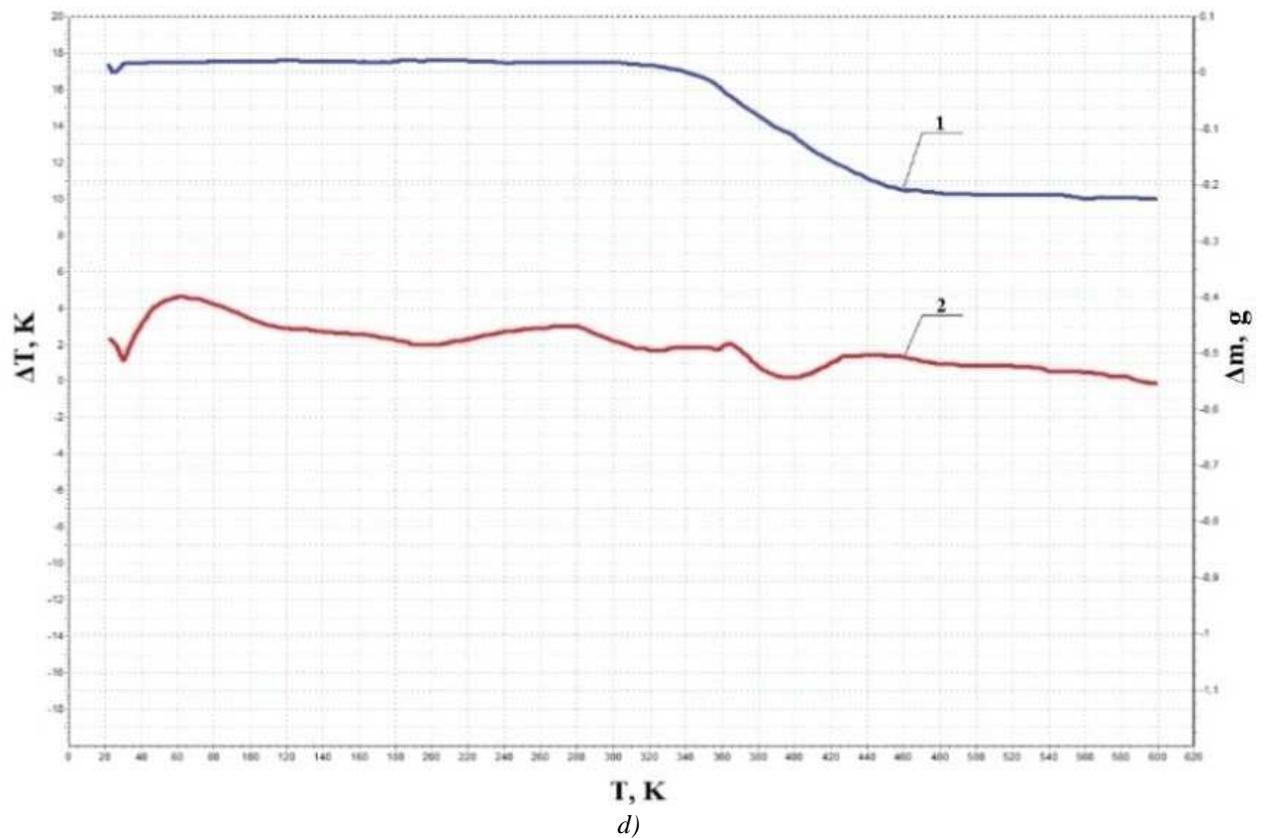
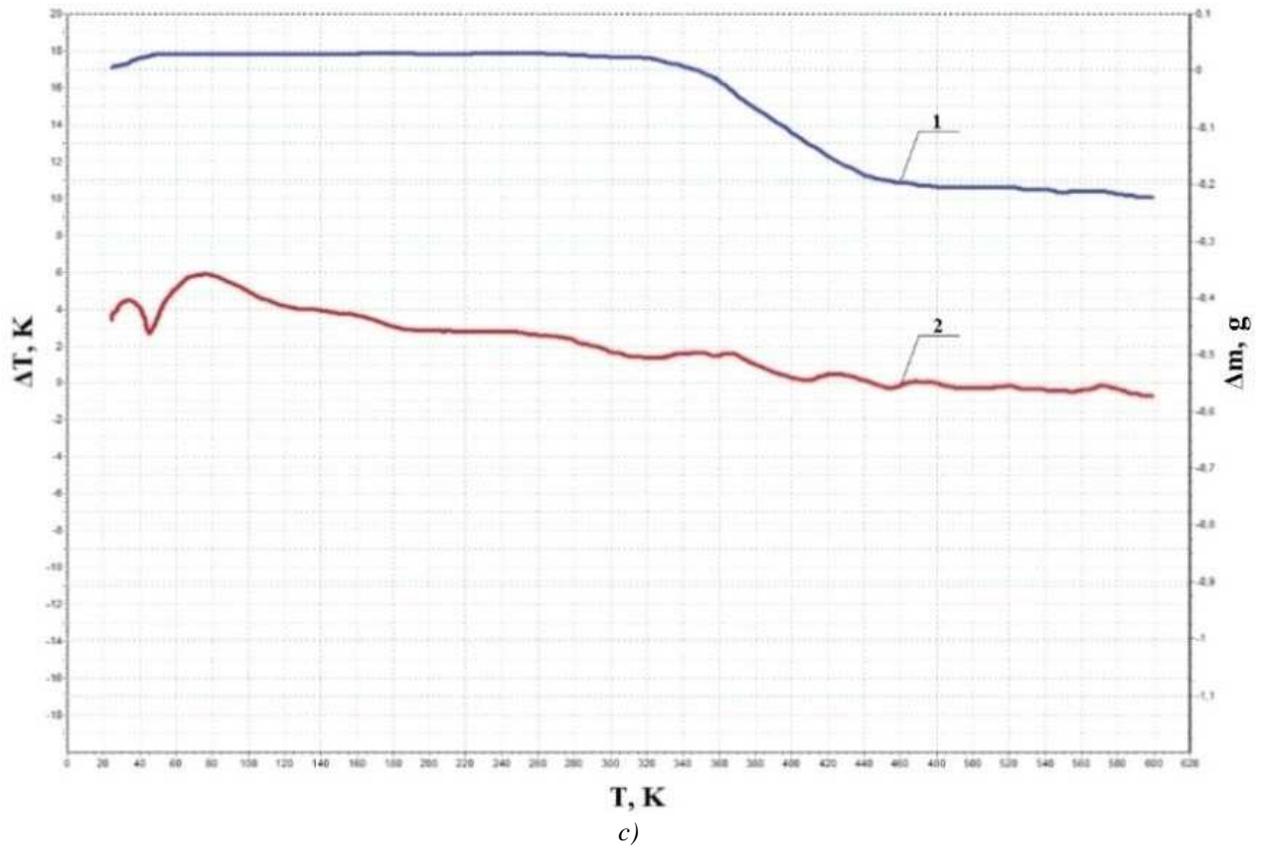


Figure 6 – Results of thermogravimetric (1) and differential thermal (2) analysis of CM, containing the  $C_{22}H_{28}N_2O_2S_5$  modifier,  $q$ , pbw:  $c - 1.75$ ;  $d - 2.00$

Table 5 – Temperature intervals of composites exoeffects according to DTA

Content of the C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> S <sub>5</sub> modifier, q, pbw	Temperature intervals of exoeffects				Maximum value of exo effects T <sub>max</sub> , K
	T <sub>in</sub> , K	T <sub>fin</sub> , K	ΔT <sub>1</sub> , K	ΔT <sub>2</sub> , K	
matrix	598.1	683.7	85.6	1.75	618.3
0.10	597.0	677.3	80.3	1.61	616.4
0.25	599.2	678.1	78.9	1.56	626.3
0.50	600.1	678.0	77.9	2.24	626.6
0.75	600.1	682.1	82.0	1.58	641.0
1.00	595.2	672.7	77.5	1.54	623.4
1.25	591.9	673.1	81.2	1.52	639.6
1.50	594.8	673.1	78.3	1.42	618.0
1.75	593.0	684.0	91.0	1.60	619.2
2.00	591.3	665.6	74.3	1.80	636.3

Note: T<sub>in</sub> – the initial temperature of the exoeffect; T<sub>fin</sub> – the final temperature of exoeffect; ΔT<sub>1</sub> – exoeffect temperature range; ΔT<sub>2</sub> – temperature difference between the sample with changes and a standard one, in which there are no changes

process was considered to be the defining parameter, which limits the operation of the developed CMs.

The highest temperature value of the destruction beginning in comparison with the original matrix (T<sub>0</sub> = 600.1 K) is the CM with the introduced modifier amount of q = 0.75 pbw and the exponent T<sub>0</sub> = 601.8 K. As can be seen from the results, the difference between the minimum and maximum values is only ΔT<sub>0</sub> = 1.7 K, which (within the experimental error) indicates an inessential positive effect of the modifier on increasing the initial destruction temperature. At the same time, the CM, filled with a minimum amount of a modifier (q = 0.10 pbw), is characterized by the highest value of the heat resistance (T = 362 K). For such a material, there was observed one of the lowest temperature values of the destruction beginning (T<sub>0</sub> = 594.1 K), where the difference between this value and the parameters of the original matrix is ΔT<sub>0</sub> = 6 K. Taking into account the error limits, this indicates the minimal effect of the C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub> modifier on the temperature value of the destruction beginning, and that is why it can be ignored during the operation of the coating.

Parallel analysis of the DTA curve (Fig. 4–6, curve 2) in the above-described temperature range (ΔT = 298–873 K) has additionally allowed us to establish exothermic effects. It should be noted that one of the most important parameters is the magnitude of exothermic effects (T<sub>in</sub>), which characterizes the beginning of deformation and structural transformations in epoxy-composite materials.

Exothermic effects are established by means of DTA curves under the influence of a thermal field upon the CM in the temperature range of ΔT = 591.3–683.7 K (Table 5). It should be emphasized that the displacement of the peak for the exothermic effect into the high temperature range provides for an increase in the thermal stability of materials under the influence of the thermal field. This is caused by the stability of physical and chemical bonds in the CM, leading to an improvement in the physical and mechanical properties of the material under the influence of the thermal field.

It is established that the maximum values of exoeffects, in comparison with the matrix (T<sub>max</sub> = 618.3 K),

which constitute T<sub>max</sub> = 626.6–641.0 K, are typical for CMs filled with the modifier in an amount of q = 0.50–0.75 pbw. As can be seen from the results, the difference between the minimum (matrix exponent) and the maximum value is ΔT<sub>max</sub> = 22.7 K, which (within the experimental error) indicates a significant positive effect of the modifier on the maximum value of the exoeffect. It should be emphasized that the obtained data are consistent with the previous results of the dilatometric curve analysis (glass transition point T<sub>c</sub> = 343 K), as well as the thermal stability of the CM, where a similar range of the introduced modifier (q = 0.50–0.75 pbw) leads to the formation of samples with maximum characteristics indices. This confirms the reliability of the studies conducted. However, the obtained data do not completely correlate with the tests results of the physical and mechanical properties of the CM. It was assumed that this was caused by the following fact. Since the destruction of physical intermolecular bonds depends on the load and temperature, then the effect of mechanic destruction also strongly depends on the effect and intensity of the thermal field upon the materials. At normal temperatures, under the influence of external mechanical forces upon the sample, physical and chemical bonds between macromolecules are strongly destroyed, while slippage of molecules with respect to each other in the field of mechanical stresses almost does not take place (with the exception of critical loads). With increasing temperature, this effect increases. In other words, mechanic destruction is more likely to occur in polymers in the glassy state, less in highly elastic, and even less in viscous flow. On the contrary, the thermal destruction occurs in a highly elastic, and even more in a viscous-flowing state. Such a distinct difference between these processes can fully explain the discrepancy between the results obtained in the study of the physicomaterial and thermophysical properties of the CM.

It is known [6–8] that the properties of the polymer CM are determined by the properties of the polymer matrix and the filler (in our case, the modifier), the distribution of the latter, the interaction at the "polymer-

filler" interface. A significant properties change of the filled polymers, especially rheological and physico-mechanical, is due not only to the effect of the additional boundary layer of the polymer on the structure and properties, but also to the interaction between the modifier macromolecules. The introduction of the modifier into the epoxy oligomer and their further hydrodynamic alignment led to the formation of a continuous network, formed as a result of the interaction of the modifier macromolecules with segments and side groups of the chain of the epoxy diene oligomer. In our opinion, such activity is associated with a wide range of chemical elements of the modifier and predominant carbon (C) 51.53 % and sulfur (S) 31.26 % (Table 1). As a result, with the increase in the amount of modifier and the high ability of its chemical elements (carbon and sulfur) to interact, due to stable covalent bonds, both with each other and with the binder, the density increases and the intermolecular distribution of the spatial grid of the matrix decreases. Thus, the physico-mechanical properties of CMs are significantly improved.

It was assumed that at room temperature (293–303 K) the S atoms are in the form of the most stable cyclic  $S_8$  molecules forming a rhombic ( $\alpha$ -sulfur) stable modification. The latter forms ring molecules with covalent bonds that are chemically active and capable of being combined with almost all elements during heating. This fact in its turn leads to the improvement in the physico-mechanical properties of the CM. However, as the temperature increases, the rhombic modification ( $\alpha$ -sulfur) transforms into monoclinic  $\beta$ -sulfur, which is stable at temperatures above  $T = 368$  K and melts at  $T = 392.3$  K. At  $T = 433$  K, the  $S_8$  molecules begin to break, open chains are formed, turning subsequently into plastic sulfur with an unstable chain structure. Further heating of materials to temperatures above  $T = 463$  K contributes to a decrease in the average chain length, respectively, the number and strength of covalent bonds also decreases. An increased content of sol-fraction is formed during the process, and this worsens the thermophysical properties of the materials. With a further increase in temperature, the mutual movement of the individual molecules rather than the links of the chain is accelerated. This in its turn leads to irreversible deformations in the material and further its complete destruction under the influence of the thermal field.

Thus, it follows from the above that the division of additives, including modifiers, into active (hardening, strengthening, heat-resistant) and inactive (inert) is to a certain extent conditional, since, while improving some characteristic of the system, the additive can worsen its other properties.

Based on the analysis of  $T_{in}$  and  $T_{fin}$  temperatures of the exoeffect beginning and end (Table 5), the following results are established: the best results of the initial exothermal temperature ( $T_{in} = 600.1$  K) of modified matrices are characteristic for samples with a modifier quantity of  $q = 0.50$  pbw and  $q = 0.75$  pbw. The final temperature of the exoeffect for the CM data is  $T_{fin} = 678.0$  and  $T_{fin} = 682.1$  K, respectively. Comparing

the above results with those of the original matrix ( $T_{fin} = 683.7$  K), it can be concluded that  $C_{22}H_{28}N_2O_2S_5$  modifier has practically no effect on the final temperature of the exoeffect. Thus, using the complex estimation of  $T_{in}$ ,  $T_{max}$  and  $T_{fin}$  (Table 5), it can be stated that the CM, which contains this modifier with  $q = 0.50$ – $0.75$  pbw, is characterized by the best heat resistance among the entire range of materials studied.

### Conclusions

On the basis of experimental studies of thermophysical properties, there have been established permissible temperature limits, at which it is possible to use epoxy composites modified with 4,4-sulfonylbis (4,1-phenylene) bis (n,n-diethyldithiocarbamate). Namely:

1. It is advisable to introduce a modifier with  $q = 0.1$  pbw for the formation of composite materials or protective coatings on their basis with increased thermophysical properties in the epoxy binder. This composite has the maximum value of heat resistance among all materials under study  $T = 362$  K. In its turn, for the formation of a composite material characterized by both increased thermophysical, physical and mechanical properties a modifier of  $q = 1.5$  pbw should be introduced in the epoxy binder. The heat resistance by Martens of such a material is  $T = 359$  K.

2. It has been found that composites with a modifier amount of  $q = 0.1$  pbw –  $T_c = 338$  K and  $q = 0.75$  pbw –  $T_c = 343$  K are characterized by the greatest glass transition temperature. It was additionally proved that the shrinkage of the modified matrices did not exceed 1%. It should be noted that the shrinkage of materials with a modifier amount of  $q = 0.10$  pbw and  $q = 0.75$  pbw is much less than the shrinkage of the original matrix ( $\delta = 0.32$  %). This makes it possible to apply the developed materials in the form of coatings with a uniform layer on the long-dimensional surfaces of a complex profile.

3. It has been experimentally established that it is expedient to use composites with a content of the modifier 4,4-sulfonylbis (4,1-phenylene) bis (n,n-diethyldithiocarbamate) ( $C_{22}H_{28}N_2O_2S_5$ ) amount of  $q = 0.10$ – $0.25$  pbw at a maximum temperature range  $\Delta T = 303$ – $473$  K. These materials are characterized by the lowest value of the thermal coefficient of linear expansion, which is  $\alpha = (7.25$ – $7.41)10^{-5}$  K<sup>-1</sup>.

4. It is shown that the indicators of relative mass loss, as well as the final destruction temperature, are not decisive factors when choosing the optimum performance characteristics of the developed materials. On the contrary, the initial destruction temperature ( $T_0$ ) was considered the determining parameter limiting the operation of the developed materials. The material with the modifier amount of  $q = 0.75$  pbw is characterized by the greatest value of the destruction start temperature ( $T_0 = 601.8$  K) in comparison with the original matrix ( $T_0 = 600.1$  K). This indicates an insignificant effect of the modifier on the initial destruction temperature.

With the help of DTA curves, there were studied exothermic effects on modified materials under the action of a thermal field in the temperature range

$\Delta T = 591.3\text{--}683.7$  K. It was established that the maximum values of exoeffects, in comparison with the matrix ( $T_{max} = 618.3$  K), which amount  $T_{max} = 626.6\text{--}641.0$  K, are characteristic for materials with a modifier amount of  $q = 0.50\text{--}0.75$  pbw. This indicates a significant effect of the modifier on the maximum temperature of the exoeffect and on the increase in the thermal stability of materials under the influence of the thermal field. Such results are due to the stability of physical and chemical bonds in the material under the influence of increasing temperatures.

Based on the analysis of the temperatures of the exoeffect beginning and the end,  $T_{in}$  and  $T_{fin}$ , the following results are established: the best results of the modified matrices parameters of the exoeffect initial temperature ( $T_{in} = 600.1$  K) are characteristic for samples with a modifier quantity of  $q = 0.50$  pbw and  $q = 0.75$  pbw. The final temperature of the exoeffect for such materials is  $T_{fin} = 678.0$  and  $T_{fin} = 682.1$  K, respectively. Comparing the above results with the results of the study of the initial matrix ( $T_{fin} = 683.7$  K), it can be concluded that the modifier has practically no effect upon the final temperature of the exoeffect.

In addition, it is shown that relative weight losses for all modified materials, as well as the initial matrix, are  $\varepsilon_m = 73.3\text{--}78.6$  %. That is, the difference between the minimum and maximum values is only  $\Delta\varepsilon_m = 5.3$  %,

which indicates a uniform mechanism of the course of destructive processes.

#### References

- [1] Nazarov, VG 2008, *Surface modification of polymers*, MGUP, Moscow. (in Russian)
- [2] Simonov-Emelyanov, ID 2005, 'Principles of creation and processing of polymeric composite materials', *Plastics masses*, no. 1, pp. 11–15. (in Russian)
- [3] Artemenko, SE, Kadyikova, YuA & Golovnya, IS 2009, 'Investigation of the effect of basalt fillers on structure and properties of polyethylene', *News of Volgograd State Technical University*, vol. 1, no. 2, pp. 42–45. (in Russian)
- [4] Kerber, ML, Vinogradov, VM, Golovkin, GS, Berlina, AA (ed.) 2008, *Polymeric composites: structure, properties, technology*, Professiya, StPetersburg. (in Russian)
- [5] Nikolaev, AF, Kryzhanovskiy, VK, Burlov, VV, Kryzhanovskiy, VK (ed) 2008, *Technology of Polymeric Materials*, Professiya, StPetersburg. (in Russian)
- [6] Buketov, AV, Sapronov, OO, Aleksenko, VL 2015, *Epoxy nanocomposites: monograph*, KSMA, Kherson.
- [7] Buketov, AV, Sapronov, OO & Brailo, MV 2014, 'Investigation of the physico-mechanical and thermophysical properties of epoxy composites with a two-component bidisperse filler', *Strength of Materials*, vol. 46, no. 5, pp. 717–721.
- [8] Stuhlyak, PD, Buketov, AV & Dobrotvor, IG 2008, *Epoxy composite materials modified energy fields*, Zbruch, Ternopil. (in Ukrainian)

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## Вплив температури на структуру і теплофізичні властивості епоксидних композитів, модифікованих 4,4-сульфонілбіс (4,1-фенілен) біс (n,n-діетилдітіокарбаматом)

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Встановлено вплив модифікатора 4,4-сульфонілбіс (4,1-фенілен) біс (n,n-діетилдітіокарбамата) ( $C_{22}H_{28}N_2O_2S_5$ ) на теплофізичні властивості епоксидної матриці в діапазоні температур  $\Delta T = 303\text{--}873$  K. Досліджено теплостійкість за Мартенсом, термічний коефіцієнт лінійного розширення, температуру склування та усадку модифікованої матриці. В результаті аналізу одержаних даних встановлено оптимальну концентрацію  $C_{22}H_{28}N_2O_2S_5$  модифікатора, що вагомо покращує теплофізичні властивості епоксидної матриці. Показано, що для формування композитних матеріалів (КМ) або захисних покриттів із підвищеними показниками теплофізичних властивостей необхідно в епоксидне в'язуче ввести оптимальний вміст модифікатора  $q = 0.10\text{--}0.25$  масових частин на 100 масових частин смоли ЕД-20. У такому випадку формується композит зі теплостійкістю за Мартенсом  $T = 360\text{--}362$  K.

На основі експериментального вивчення теплофізичних властивостей із використанням методів диференціально-термічного (ДТА) і термогравіметричного (ТГА) аналізу визначено допустимі межі температури, для яких можна використовувати модифіковані епоксидні композити. Найбільшим значенням температури початку деструкції у порівнянні з матрицею ( $T_0 = 600.1$  K) характеризуються КМ із вмістом модифікатора  $q = 0.75$  масових частин і показником  $T_0 = 601.8$  K. Різниця між мінімальним і максимальним значенням складає всього  $\Delta T_0 = 1.7$  K, що вказує на незначущий позитивний вплив модифікатора на початкову температуру деструкції.

З допомогою кривих ДТА виявлено екзотермічні ефекти в результаті дії теплового поля на КМ у діапазоні температур  $\Delta T = 591.3\text{--}683.7$  K. Встановлено, що максимальні значення екзоефектів у порівнянні з матрицею ( $T_{max} = 618.3$  K) складають  $T_{max} = 626.6\text{--}641.0$  K і характерні для КМ із вмістом  $q = 0.50\text{--}0.75$  масових частин модифікатора СФЕК. Різниця між мінімальним (показник матриці) і максимальним значеннями складає  $\Delta T_{max} = 22.7$  K, що вказує на значний позитивний вплив модифікатора на максимальну величину екзоефекту. Це свідчить про підвищення термостабільності КМ, що зумовлено стійкістю фізико-хімічних зв'язків у матеріалі і покращенням його фізико-механічних властивостей в умовах дії високих температур.

Ключові слова: *епоксидний композит, модифікатор, температура склування, термостійкість, усадка.*