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STUDY OF THERMAL STABILITY AND ENERGY OF ACTIVATION
OF EPOXY COMPOSITES WITH PARTICLES OF SYNTHESISED
POWDER MIXTURE FOR INCREASING RELIABILITY OF
VEHICLES

Summary. The prospective of the application of new materials on a polymer base
is shown in this work. Given that developed composites can be efficiently used for
protection of equipment that is operated at elevated temperatures, the impact of
the nature and content of powder mixture, synthesised by high voltage electric
discharge, on the thermophysical properties of epoxy composites were studied.
Epoxy diane oligomer was chosen as the main component of the binder during
the formation of the composites. Polyethylene polyamine hardener was used for
cross-linking of epoxy composites, which allows hardening of materials at room
temperatures. The selection of powder mixture, synthesised by high voltage electric
discharge, for increase of thermophysical properties of developed materials was
justified. More so, thermal stability and activation energy of epoxy composites were
studied. Permissible limits of the temperature, at which developed materials can be
used, were established based on the conducted tests of thermophysical properties
of materials, filled by powder mixture, synthesised by high voltage electric
discharge.

Keywords: epoxy composite, thermal stability, activation energy, filler

1. INTRODUCTION

The problem of ensuring the reliability of parts of technological equipment during their use
in conditions under the impact of aggressive environments and sign-alternating or increased
temperatures is an urgent scientific and technological problem. The use of polymer composite
and protective coatings, based on them, is a prospective way of solving this problem. Such
materials are notable due to increased values of physical, mechanical and thermophysical
properties, which is a determining factor in the fight against corrosion of parts of technological
equipment of modern industry in conditions of aggressive environments impact.

It is known [2, 5, 11-18, 23] that the increase of cohesion and especially of thermophysical
properties of polymer composites is possible by their modification, plasticisation or
introduction of nano- and micro- additives with homeopathic content. The use of dispersion
fillers is urgent from both economic and ecological points of view. Authors of [4] have shown
that the introduction of disperse nanoparticles to the polymer matrix with insignificant content
(from 0.05 up to 0.15%) ensures 2.2 – 2.8 times increase of cohesion properties of protective
coatings.

Thus, it can be concluded that the development of new technologies of obtainment of
polymer composites and protective coatings, based on them, aimed at the increase of the service
life of technological equipment, is an urgent industrial task. When solving this task, it is
important to form environment-friendly and cost-effective materials for parts repair. In this
context, the use of microadditives with insignificant quantity in polymer composites is urgent from both scientific and practical points of view.

In previous works [4], the impact of the quantity of filler on the thermophysical properties of epoxy composites (thermal stability, coefficient of thermal expansion, the glass transition temperature) was experimentally studied. However, change of the structure of the composite, including the destruction of physical and chemical bonds, under the impact of thermal field is a multifaceted process [1, 3, 6-10, 14, 24].

Therefore, the studies of thermal stability of developed materials using differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) methods in the temperature range of \( \Delta T = 293 - 873 \) K is necessary to further establish the dependencies of properties of developed materials on the temperature. During the studies of materials thermal destruction processes, temperature rate was \( \nu = 10 \) K/min.

The aim of this work is the determination of dependence of thermal stability of epoxy composite materials on heating temperature as well as the determination of the energy of activation of the process of their destruction.

2. MATERIALS AND METHODS

Epoxy diane oligomer ED-20 (GOST 10587-84), which is characterised by high adhesion and cohesion strength, low shrinkage and processability when applied to complex surface profile, was selected as the main binder component for the formation of epoxy composite materials (CM).

Polyethylene polyamine (PEPA) (TS 6-05-241-202-78) hardener was used for cross-linking of epoxy composites, which allows hardening of materials at room temperatures. PEPA is a low-molecule compound, which consists of interconnected \([-\text{CH}_2-\text{CH}_2-\text{NH}]-_n\) components. CM were polymerised by the introduction of hardener in their composition at a stoichiometric ratio of components by content (mass parts) – ED-20: PEPA – 100: 10.

Synthesised powder mixture (SPM) was used as microdisperse filler for experimental studies, obtained with high voltage electric discharge (HVED). Powder mixture of Fe (75%) + Ti (25%) initial mass composition was used as the initial material for filler synthesis. During HVED-synthesis, stored energy of single discharge \( (W_1) \) was 1 kJ, while specific integral treatment energy \( (W_{sp}) \) was 25 MJ/kg [19-22]. The mean diameter of the initial powder mixture before HVED treatment was 45 \( \mu \)m while 90% of particles had a size higher than 10 \( \mu \)m.

Results of the studies showed that HVED treatment leads to dispersion of all treated particles and change of their phase composition with the synthesis of high-modulus compounds of TiC and Fe\(_3\)C (Table 1).

| Initial composition | Composition after treatment | Electrode system | Diameter after treatment, \( d, \mu m \) |
|---------------------|---------------------------|-----------------|----------------------------------|
| Fe (75%) + Ti (25%) | Fe (70%) + Ti (10%) + TiC (15%) + Fe\(_3\)C (5%) | 1 (point – plane) | \( d_{min} \) \( d_{max} \) \( d_{mean} \) |
|                     |                           |                 | \(~1\) \( 112 \) \( 11.5 \) |
Epoxy composites were formed by the following technology [4]: resin was heated up to the temperature of $T = 353 \pm 2$ K, at which it was held during a time of $\tau = 20 \pm 0.1$ min; oligomer and filler particles were hydrodynamically merged during the time of $\tau = 1.5 \pm 0.1$ min; the composition underwent ultrasonic treatment (UST) during the time of $\tau = 10 \pm 0.1$ min; the hardener was introduced and the composition was mixed during the time of $\tau = 5 \pm 0.1$ min. Hardening of CM was performed according to the following regime: formation of specimens and their holding during the time of $12.0 \pm 0.1$ h at the temperature of $T = 293 \pm 2$ K, heating with the rate of $\nu = 3$ K/min up to the temperature of $T = 393 \pm 2$ K, holding during the time of $\tau = 2.0 \pm 0.05$ h, slow cooling to the temperature of $T = 293 \pm 2$ K. To achieve stabilisation of structure processes in the composites, specimens were held during the time of $\tau = 24$ h on air at the temperature of $T = 293 \pm 2$ K, and only after holding, experimental studies on these specimens were conducted.

TGA and DTA analysis were carried out following these standards:
1. ISO 8301:1991. International Organization for Standardization. Thermal insulation – Determination of steady-state thermal resistance and related properties – Heat flow meter apparatus;
2. ISO 22007-2:2015, Plastics – Determination of thermal conductivity and thermal diffusivity – Part 2: Transient plane heat source (hot disc) method, International Organization for Standardization.

TGA and DTA were performed after studies of the specimens on «Thermoscan-2» derivatograph. CM were studied in the temperature range of $\Delta T = 298 - 773$ K, using quartz crucibles for specimens with the volume of $V = 0.5$ cm$^3$, and was heated at a rate $\nu = 10$ K/min. The Al$_2$O$_3$ powder ($m = 0.5$ g) was used as a standard. Mass of specimens was $m = 0.3$ g. Error of temperature determination was $\Delta T = \pm 1$ K. Precision of thermal effects determination was 3 J/g. Precision of determination of specimen’s mass was $\Delta m = 0.02$ g.

3. RESULTS AND DISCUSSION

At the first stage of the studies, thermal stability of epoxy matrix was studied. Results of this experiment and their justification are described in detail in this work [3]. In particular, results of TGA showed absence of the materials mass loss in the temperature range of $\Delta T = 293 - 570$ K (Fig. 1, curve 1 and Table 2). Further increase of the temperature leads to decrease of the specimen’s mass. This occurs due to the excretion of volatile products resulting from the destruction of chemical bonds between segments and lateral groups of macromolecules of epoxy oligomer and active centres on the surface of filler disperse particles. In addition, the beginning and ending temperatures of the mass loss process, as well as the temperatures at which the specimens’ mass was decreased by $5 - 20\%$ were experimentally found. It was established, that the temperature of the mass loss beginning for epoxy matrix was $T_0 = 588$ K, and the temperature at which the mass loss process ends was $T_k = 710$ K. At this point, relative mass loss of matrix was $\varepsilon_m = 80.7\%$ (Table 2).

On the further stages of studies, similar parameters of thermal stability were determined for the studied CM. It was discovered (Fig. 1 and Table 2), that the beginning of thermal destruction for materials with fillers was observed in the temperature range of $T = 616 - 627$ K. Hence, it can be stated that the thermal stability of the composites was increased when compared to the thermal stability of the initial matrix, as the processes of thermal destruction of studied materials...
occur at higher temperatures. First, this is due to the increase of the quantity of chemical bonds on the unit of polymer volume due to the presence of the disperse filler. Further, polymer around the particles is in the state of outer surface layers, which increase the degree of its cross-linking. Accordingly, it increases the values of composites thermal stability.

Similar to previous results, an increase of the value of the CM mass loss process ending temperature when compared to the studied epoxy matrix, was observed, which characterises the end of materials thermal destruction process. It was shown (Table 2), that introduction of SPM filler increases the temperature of composites thermal destruction recorded at the end (in comparison with matrix) from $T_e = 710$ K to $T_e = 722 - 785$ K. As noted above, this is due to the impact of physical and chemical nature and topology of disperse particles surface on the passage of the processes of interphase interaction during CM structure formation, which, accordingly, is definitive for the formation of composites with increased thermal stability and increased values of other thermophysical properties.

Mass loss of CM was additionally analysed by TGA curves. It was shown (Table 2), that the relative mass loss of epoxy matrix was $\varepsilon_{m} = 80.7\%$. Introduction of particles led to the decrease of the value from $\varepsilon_{m} = 80.7\%$ (for epoxy matrix) to $\varepsilon_{m} = 56.7 - 69.7\%$. It was shown (Table 2), that during the thermal destruction of CM, the great impact was caused not only by the nature of the filler but also by its quantity in the system. Analysis of the results of studies has shown that the introduction of the particles leads to a significant decrease in CM mass loss only in the case of fillers optimal content. In particular, the addition of SPM in the quantity of $q = 0.50 - 2.00$ mass parts provides 1.4-times decrease of the value of relative mass loss (from $\varepsilon_{m} = 80.7\%$ (for epoxy matrix) to $\varepsilon_{m} = 56.7 - 59.7\%$). Thus, it can be stated that particles of SPM significantly slow down the processes of thermal destruction and, consequently, improve the durability of epoxy composites that are used in the conditions of thermal field impact.

| Tab. 2 | Thermal stability of CM, filled by SPM particles |
|--------|---------------------------------------------|
| Filler content, $q$, mass parts | $T_0$, K | $T_5$, K | $T_{10}$, K | $T_{20}$, K | $T_e$, K | $\varepsilon_{m}$, % |
| Matrix | 0 | 588 | 624 | 636 | 649 | 710 | 80.7 |
| Synthesised powder mixture (SPM) | 0.05 | 627 | 634 | 640 | 656 | 785 | 69.7 |
| | 0.50 | 621 | 629 | 636 | 650 | 722 | 56.7 |
| | 2.00 | 616 | 626 | 633 | 647 | 737 | 59.7 |
| Note: $T_0$ – temperature of mass loss beginning (beginning of destruction); $T_5$, $T_{10}$, $T_{20}$ – temperature of mass losses (5%, 10% and 20%, respectively); $T_e$ – ending temperature of mass loss (end of destruction); $\varepsilon_{m}$ – relative mass loss. |

To further study the processes of thermal destruction of matrix and epoxy composites, materials underwent parallel study using DTA method. Analysis of the DTA curve in the temperature range of $\Delta T = 273 - 373$ K allowed detecting the presence of exothermic effect (Fig. 1). Change of mass in this temperature range in all studied specimens was not observed. It was considered that in this case, the presence of exothermic effect is caused by the formation of additional physical bonds in polymer materials due to their additional hardening. More so, this leads to an additional increase in the degree of cross-linking of developed materials.
Fig. 1. TGA curves of studied samples
Further, the exothermic effect in specimens under the impact of the thermal field in the temperature range of $\Delta T = 460 - 660$ K was observed. During the analysis of thermal destruction processes, the beginning and ending temperatures of exoeffects are important. It was shown (Fig. 1, curve 2 and Table 3), that the lowest temperature of exothermic processes beginning ($T_n = 460$ K) was observed for epoxy matrix. This indicates that at this temperature intensive relaxation of physico-chemical bonds in polymer structure grid starts. With further increase of the temperature, these bonds can disintegrate, while the ending of the processes of structure rearrangement and matrix destruction was observed at the ending temperature of exoeffect, which was $T_k = 649$ K. It can be considered that this is the limit at which matrix destruction was finished, that is, at this temperature range, an intensive decrease of specimen’s mass was observed (Fig. 1, curve 1).

| Filler content, $q$, mass parts | Temperature ranges of exoeffects | Maximum value of exoeffects, $T_{max}$, K |
|---------------------------------|---------------------------------|----------------------------------------|
|                                 | $T_n$, K | $T_k$, K | $\Delta T_1$, K | $\Delta T_2$, K | |
| Matrix                          | 0       | 460     | 469             | 472             | 3,1 | 518 |
| Synthesised powder mixture (SPM)| 0,05    | 479     | 655             | 177             | 2,0 | 530 |
|                                 | 0,50    | 461     | 656             | 195             | 2,4 | 528 |
|                                 | 2,00    | 462     | 651             | 189             | 2,4 | 531 |

Note: $T_n$ – beginning temperature of the exoeffect; $T_k$ – ending temperature of the exoeffect; $\Delta T_1$ – temperature range of the exoeffect; $\Delta T_2$ – difference of the temperatures between the specimen where transformation occurs, and the standard, where no transformations take place.

Introduction of the filler increases the beginning temperature of the materials thermal destruction from $T_n = 460$ K (for epoxy matrix) to $T_n = 461 - 479$ K. The temperature recorded at the end of the thermal destruction was also moved to the right by the abscissa axis and for all studied composites was in range of $T_k = 651 - 656$ K. These facts indicate that the presence of dispersed particles leads to the formation of materials with a strongly-stitched 3-dimensional polymer grid. This allows extending the life of materials that operate at elevated temperatures.

Additionally, the maximal value of the exoeffect temperature was determined, which was $T_{max} = 518$ K for matrix. It was shown (Table 3), that introduction of the filler in different content ensures increase of the maximum of exothermic processes peak to $T_{max} = 528 - 531$ K, while the highest value ($T_{max} = 531$ K) was observed in the case of addition of filler in the quantity of $q = 2.00$ mass parts for 100 mass parts of ED-20 epoxy oligomer. It can be concluded that the movement of exoeffect peak to the area of high temperatures indicates the increase of resistance of physico-chemical bonds in the materials to destruction. It can be further concluded that these conditions are the same for the formation of composite with the highest resistance to destructive processes and micro-transformations in the structure under the impact of the temperature.

Conclusively, it should be noted that analysis of DTA and TGA curves as well as previously conducted studies of CM thermophysical properties (thermal stability, coefficient of thermal expansion, the glass transition temperature), indicates the following: Developed materials,
especially the composite with filler content of $q = 2.00$ mass parts for 100 mass parts of ED-20 epoxy oligomer, are advisable to operate in the temperature range of $\Delta T = 273 - 473$ K, as the further increase of thermal field impact intensity leads to the beginning of thermal destruction processes, which cause the premature destruction of materials.

On the next stage of the studies, the energy of activation of thermal destruction of epoxy matrix and developed composite materials with particles of CPM with different content was determined. Analysis of TGA curves allowed the determination of the destruction temperature and relative mass loss of specimens during the heating of epoxy composites. Energy of CM activation was calculated using this data. In addition, analysis of thermal effects that occur in CM during the heating was performed in the context of results of DTA and TGA studies.

TGA curves allow determination of energy of activation of thermal-oxidation destruction $E_a$, calculated using Broido’s method based on double logarithmization [1]. The condition for the application of Broido’s method is the determination of the first order of decomposition, which is relevant for a wide range of polymers [4]. Polymers mass loss is a prove of 1st order ($n = 1$) provided that there is a linear dependency $\ln(100/(100 - \Delta m))$ from reversed temperature $1000/T$, K$^{-1}$. Given the mass loss ($\Delta m$) of the specimen at given temperature $T$, a line was drawn, and the activation energy was determined through the tangent of the slope of the logarithmic dependence $\Delta m$ on reversed temperature $T$. Further, the value of destruction activation energy, kJ/mol, was found according to the expression:

$$E_a = -R \cdot \tan(\phi).$$  

During the graphical determination of activation energy, a graph was built as a direct line, by tangent of the slope $\phi$ of which $E_a$ was determined (Fig. 2). Then:

$$-\tan(\phi) = \frac{y_i}{x_i},$$  

$$E = R \cdot \frac{y_i}{x_i},$$

where $x_i = x_{\text{begin}} - x_{\text{end}}$ – length of the line along the axis of the abscissa; $y_i = y_{\text{begin}} - y_{\text{end}}$ – the length of the line along the vertical axis; $[x_{\text{begin}}; y_{\text{begin}}]$ and $[x_{\text{end}}; y_{\text{end}}]$ – coordinates of beginning and end of the line, respectively.

![Fig. 2. Method of graphic determination of activation energy](image)
Given the above, Broido's method can be represented analytically in the form of an equation [1]:

\[
\ln \left( \ln \frac{100}{100 - \Delta m} \right) = -\frac{E}{R} \cdot \frac{1}{T} + const
\]

(4)

where:
\(\Delta m\) – specimens mass loss at every studied temperature in the range of materials decomposition,\%;
\(E\) – energy of activation, kJ/mol;
\(R\) – universal gas constant, \(R = 8.31\ \text{J/(mol}\cdot\text{K})\);
\(T\) – temperature, K

Mass of the specimens was determined according to the derivatograms (Fig. 1) in range of temperatures of \(\Delta T = 573 - 713\ \text{K}\) with the step of \(\Delta T = 10\ \text{K}\). Obtained values of the specimen’s mass (expressed in grams) were transformed to percents according to the expression:

\[(100 - \Delta m)\% = \left(100 - \left(\frac{m_h + \Delta m}{\Delta m} \times 100\right)\right)\% ,\]

(5)

where:
\(m_h\) – initial mass of the specimen at the initial temperature of studies \(T_1 = 573\ \text{K}\), \((m_h = const), g\);
\(\Delta m\) – specimens mass loss, g.

Mass of the specimens at the initial temperature of studies \(T_1 = 573\ \text{K}\) according to this method was considered as 100%.

Using the equation (4), values of the double logarithm of the specimen’s mass change were evaluated. Results of this evaluation are given in Table 4.

Tab. 4

Results of the evaluation of the double value of the logarithm of specimen’s mass change
Given the specimen’s mass loss (Δm) at the temperature of T, a line was drawn, and the activation energy E was determined through the tangent of slope of the logarithmic dependence Δm on reversed temperature 1/T. Processing of the experimental results, which consists in the mathematical transformation of mass loss curve, was performed in the MS-Excel software. Graphs of logarithmic dependence of specimen’s mass loss Δm on reversed temperature $10^3/T$ are shown on Fig. 3.

Analysis of destruction rates (Fig. 3) of studied composites allowed to derive of the equation of the dependence of specimen’s mass loss Δm on reversed temperature $10^3/T$ for epoxy matrix and CM with different content of SPM disperse particles. Based on obtained equations, the values of energy of activation E of thermal-oxidation destruction of developed materials were calculated (Table 5).

![Graph](image)

Fig. 3. Graphic dependency of destruction ration of CM with SPM particles:
- matrix; ■ – 0,05%; ▲ – 0,5%; × - 2,00%

### Tab. 5

| q, mass parts | $X_{\text{begin}}$ | $X_{\text{end}}$ | $X_i$ | $Y_{\text{begin}}$ | $Y_{\text{end}}$ | $Y_i$ | $tq(\phi)$ | E, kJ/mol |
|---------------|---------------------|------------------|-------|-------------------|-----------------|------|-------------|-----------|
| 0             | 1.531               | 1.403            | 0.128 | -1.053            | -3.108          | 2.055| 16.057      | 133.5     |
| 0.05          | 1.605               | 1.403            | 0.202 | 0.204             | -3.066          | 3.270| 16.190      | 134.6     |
| 0.50          | 1.605               | 1.403            | 0.202 | 0.204             | -2.815          | 3.052| 15.108      | 135.6     |
| 2.00          | 1.605               | 1.403            | 0.202 | 0.290             | -2.763          | 3.053| 15.116      | 135.7     |
It was considered, that the increase of activation energy indicates the decrease of thermal destruction processes rate. The value of activation energy for epoxy matrix was discovered as \( E = 133.5 \text{ kJ/mol} \) (Table 5). Introduction of particles of SPM filler in the quantity of \( q = 0.05 - 2.00 \) mass parts for 100 mass parts of ED-20 epoxy oligomer ensures increase, yet insignificant, of this characteristic up to \( E = 134.6 - 135.7 \text{ kJ/mol} \). This additionally confirms the results of studies shown above and indicates the durability of physico-chemical bonds in CM under the impact of the temperature.

Therefore, the results of the studies allowed to establish the values of activation energy, which causes the onset of reactions of thermal destruction of epoxy composites. It can be stated that the material, which contains particles of synthesised powder mixture in the quantity of \( q = 2.00 \) mass parts for 100 mass parts of ED-20 epoxy oligomer was characterised by the highest complex values of thermophysical properties. Formation of such composite ensures the increase of the values of not only the beginning and ending temperatures of thermal destruction, but also the increase of activation energy from \( E = 133.5 \text{ kJ/mol} \) (for epoxy matrix) to \( E = 135.7 \text{ kJ/mol} \) for the processes of thermal destruction of materials. This indicates the increase of complex values of the thermophysical properties of CM and confirms the reliability of the results of the conducted studies as well.

### 4. ENGINEERING USE OF DEVELOPED COMPOSITES TO INCREASE THE RELIABILITY OF VEHICLES

Based on the conducted studies, the materials and regimens of forming of epoxy compositions for protective coatings were developed. Among the developed polymer-composite coatings that match the high requirements of operation belongs anti-corrosion polymer-composite coating (APCC). The main purpose of the coating is to improve the physical and mechanical, thermophysical and anticorrosive properties of marine and river transport equipment. APCC is a material based on epoxy matrix and dispersed and fibrous discrete fillers.

The material developed contains SPM filler to improve the thermophysical properties and corrosion resistance of the equipment parts. The developed material has high rates of thermophysical and anticorrosive properties, and its service life is 4 - 6 years. The low cost of the ingredients of the polymer composition, in comparison with known materials, is ensured by improving the quality and increasing the service life and inter-service periods.

The technological process of forming APCC consists of the following operations: surface preparation, preparation of compositions, coating, and polymerisation of the composite.

The quality of the preparation of the protective surface largely determines the reliability and durability of APCC. Surface preparation consists of degreasing and removing various contaminants, scale, and rust by sandblasting.

The application of developed protective coating based on APCC on ship structures is performed via pneumatic spraying of the composition with a thickness of 0.2-0.4 mm, which allows to significantly increase the thermophysical properties and corrosion durability of protective coatings.

The filler is added to the epoxy resin in appropriate proportions and hydrodynamically combined. After mixing the components, the hardener is introduced immediately before the composition is applied to the workpiece surface.

The composite material, coatings and technology of its formation and application have been implemented at the Kherson Shipyard (Kherson, Ukraine), which allows increasing the operational characteristics of the protective coatings of shafts and heat exchangers of an engine
department on ships. These parts are operated at elevated temperatures and under the influence of corrosive environments. For this purpose, it is necessary to increase both thermophysical properties and corrosion resistance.

The implementation of the developed protective coating allows:

- to increase the indices of the thermophysical properties by 1.4 - 1.6 times;
- to increase the performance of anticorrosive properties in 2.1 - 2.3 times.

5. CONCLUSIONS

According to the results of studies of the destruction processes of the epoxy composites structure, the following points can be drawn.

1. Thermal stability of composite materials, characterised by the beginning and ending temperature of the mass loss was studied using methods of thermal gravimetric analysis and differential thermal analysis. It was discovered that the introduction of powder mixture filler in the quantity of \( q = 0.05 - 2.00 \) mass parts by 100 mass parts of ED-20 epoxy oligomer ensures increase of the beginning temperature of materials thermal destruction from \( T_p = 460 \) K (for epoxy matrix) to \( T_p = 461 - 479 \) K. The temperature of the thermal destruction ending was moved to the right by the abscissa axis and all studied composites were in range of \( T_k = 651 - 656 \) K.

2. Analysis of the results of studies shows that introduction of particles leads to a significant decrease of CM mass loss only in the case of fillers optimal content. In particular, the addition of SPM in the quantity of \( q = 0.50 - 2.00 \) mass parts for 100 mass parts of ED-20 epoxy oligomer provides 1.4-times decrease of the value of relative mass loss (from \( \varepsilon_m = 80.7\% \) (for epoxy matrix) to \( \varepsilon_m = 56.7 - 59.7\% \)). Hence, it can be stated that particles of active filler significantly slow down the process of thermal destruction and, consequently, improve the durability of epoxy composites, which are operated under the influence of the thermal field.

3. Results of studies allowed to establish the values of activation energy, which causes the onset of reactions of thermal destruction of epoxy composites. It was shown that the material, which contains particles of synthesised powder mixture in the quantity of \( q = 2.00 \) mass parts for 100 mass parts of ED-20 epoxy oligomer was characterised by the highest complex values of thermophysical properties. Formation of such composite ensures the increase of the values of not only the beginning and ending temperatures of thermal destruction, but also the increase of activation energy from \( E = 133.5 \) kJ/mol (for epoxy matrix) to \( E = 135.7 \) kJ/mol for the processes of thermal destruction of materials. This indicates the increase of complex values of these CM thermophysical properties and similarly confirms the reliability of the results of the conducted studies.

References

1. Brinkmann O., Schmachtenberg O. 2006. International Plastics Handbook: The Resource for Plastics Engineers. Cincinnati: Hanser. ISBN: 978-1569903995.
2. Broido A. 1969. “Simple sensitive graphical method of treating thermo gravimetric analyze data”. J. Polym. Sci. Part A 7(2): 1761-1773.
3. Brooker R., A. Kinloch, A. Taylor. 2010. “The Morphology and Fracture Properties of Thermoplastic- Toughened Epoxy Polymers”. The Journal of Adhesion 86(7): 726-741. DOI: https://doi.org/10.1080/00218464.2010.482415.
4. Brooker R., A. Kinloch, A. Taylor. 2010. “The morphology and fracture properties of thermoplastic-toughened epoxy polymers” Journal of Adhesion 86: 726-741.
5. Duleba B., F. Greškovič, L. Dulebová, T. Jachowicz. 2015. “Possibility of Increasing the Mechanical Strength of Carbon/Epoxy Composites by Addition of Carbon Nanotubes”. Materials Science Forum 818: 299-302. DOI: https://doi.org/10.4028/www.scientific.net/MSF.818.299.
6. Gawdzińska K., P. Szymański, K. Bryll, P. Pawłowska, M. Pijanowski. 2017. “Flexural strength of hybrid epoxy composites with carbon fiber”. Composites Theory and Practice 17(1): 47-50.
7. Marasanov V., A. Sharko, O. Sharko. 2019. “Energy Spectrum of acoustic Emission Signal in Coupled Continuous Media”. Journal of Nano- and Electronic Physics 11(3): 030281-1-030281-7.
8. Marasanov V., A. Sharko. 2018. “Information-structural modeling of the the Forerunners of Origin of Acoustic Emission Signals in Nanoscale Objects”. IEEE 38th International Conference on Electronics and Nanotechnology (ELNANO). Kyiv. Igor Sikorsky Kyiv. Polytechnic Institute. 24-26.04.2018.
9. Marasanov V., A. Sharko, O. Sharko, D. Stepanchikov. 2019. “Modeling of energy spectrum of acoustic-emission signals in dynamic deformation process of medium with microstructure”. IEEE 39th International Conference on Electronics and nanotechnology (ELNANO). Kyiv. April 16-18. P. 718-723.
10. Marasanov V., A. Sharko. 2017. “Discrete models characteristics of the forerunners of origin of the acoustic emission signals”. IEEE First Ukraine Conference on Electrical and Computer Engineering (UKRCON). Track 4: Nanoelectronics and Photonics, Electron Devices & Embedded Systems.
11. Marasanov V., A. Sharko, D. Stepanchikov. 2019. “Model of the Operator Dynamic Process of Acoustic Emission Occurrence While of Materials Deforming”. Lecture Notes in Computational Intelligence and Decision Making Advances in Intelligent Systems of Computing 1020: 48-64.
12. Matykiewicz D., M. Barczewski, D. Knapski, K. Skórczewska. 2017. “Hybrid effects of basalt fibers and basalt powder on thermomechanical properties of epoxy composites”. Composites Part B: Engineering 125: 157-164.
13. Mossety-Leszcak B., M. Kisiel, P. Szałański, M. Włodarska, U. Szeliuga, S. Pusz. 2018. “The influence of a magnetic field on the morphology and thermomechanical properties of a liquid crystalline epoxy carbon composite”. Polymer Composites 39(S4): E2573-E2583.
14. Palraj S., M. Selvaraj, K. Maruthan, G. Rajagopal. 2015. “Corrosion and wear resistance behavior of nano-silica epoxy composite coatings”. Progress in Organic Coatings 81: 132-139.
15. Prabhu T., T. Demappa, V. Harish. 2012. “Thermal degradation of HDPE short fibers reinforced epoxy composites”. OSR Journal of Applied Chemistry (IOSRJAC) 1(1): 39-44.
16. Rybak A., K. Gaska, C. Kapusta, F. Toche, V. Salles. 2017. “Epoxy composites with ceramic core – shell fillers for thermal management in electrical devices”. Polymers for Advanced Technologies 28(12): 1676-1682.
17. Salasinska K., M. Barczewski, M. Borucka, R. Górný, P. Kozikowski, M. Celiński, A. Gajek. 2019. “Thermal stability, fire and smoke behaviour of epoxy composites modified with plant waste fillers”. Polymers 11(8): 1234.
18. Salom C., M. Prolongo, A. Toribio, A. Martínez-Martínez, I. Cárcer, S. Prolongo. 2018. “Mechanical properties and adhesive behavior of epoxy-graphene nanocomposites”. International Journal of Adhesion and Adhesives 84: 119-125. DOI: https://doi.org/10.1016/j.ijadhadh.2017.12.004.
19. Shanmugam D., T. Nguyen, J. Wang. 2008. “A study of delamination on graphite/epoxy composites in abrasive waterjet machining”. Composites Part A 39(6): 923-929.
20. Sizonenko O., G. Baglyuk, A. Raichenko, E. Tafitai, E. Lipyan, A. Zaichenko, A. Torpakov, E. Gusev. 2012. “Variation in the particle size of Fe-Ti-B4C powders induced by high-voltage electrical discharge”. Powder Metallurgy and Metal Ceramics 51(3/4): 129-136. DOI: 10.1007/s11106-012-9407-4.
21. Sizonenko O., E. Grigoryev, A. Zaichenko, N. Pristash, A. Torpakov, Ye. Lypian, V. Tregub, A. Zholnin, A. Yudin, A. Kovalenko. 2017. “Plasma methods of obtainment of multifunctional composite materials, dispersion-hardened by nanoparticles”. High Temperature Materials and Processes 36(9): 891-896. DOI: 10.1515/htmp-2016-0049.
22. Sizonenko O., N. Oleinik, G. Petasyuk, G. Il’nitskaya, G. Bazalii, V. Shamraeva, É. Taftai, Torpakov A., A. Zaichenko, E. Lipyan. 2013. “Effect of high-voltage electrical discharge treatment of diamond powders on their mechanical characteristics”. Powder Metallurgy and Metal Ceramics 52(7/8): 365-369. DOI: 10.1007/s11106-013-9535-5.
23. Szeluga U., S. Pusz, B. Kumanek, K. Olszowska, A. Kobyliukh, B. Trzebicka. 2019. “Effect of graphene filler structure on electrical, thermal, mechanical, and fire retardant properties of epoxy-graphene nanocomposites-a review”. Critical Reviews in Solid State and Materials Sciences: 1-36.
24. Yu Yi-Hsiuan, M. Chen-Chi, Teng Chih-Chun, Huang Yuan-Li, Tien Hsi-Wen, Lee Shie-Heng, Wang Ikai. 2013. “Enhanced Thermal and Mechanical Properties of Epoxy Composites Filled with Silver Nanowires and Nanoparticles”. Journal of the Taiwan Institute of Chemical Engineers 44(4): 654-659. DOI: https://doi.org/10.1016/j.jtice.2013.01.001.

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