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Improving the thermophysical properties of polymer composites

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To improve the thermophysical properties of polymer composites, their physicochemical modification was carried out by introducing a microdispersed filler of synthesised aluminium-copper charge into the epoxy resin. Based on the dynamics of thermophysical properties depending on the amount of filler in the synthesised aluminium-copper charge, the optimal content of the additive in the epoxy compound was determined, which is 2...2.5 mass%. The introduction of filler into the epoxy oligomer ensures the production of composites with maximum values of thermal properties. The mechanism of formation of a heterogeneous structure of composites in the presence of microdispersed filler is substantiated. There are three structural levels that are formed after the polymerisation of the material: micro-, meso- and macrostructure. It is shown that in the formation of heterogeneous composites, there is a hierarchical combination of structural levels, and the dominant influence of one of them is determined by the nature and content of the filler. It is substantiated that the structure and properties of the composites are determined by the course of structure formation processes: within a single level, between different levels in a cluster, and between clusters.

Keywords: polymer, composite, heat resistance, heat resistance, model, mechanism, transport.

Поліпшення теплофізичних властивостей полімерних композитів. *А.В. Букетов, Ю.М. Шульга, В.Ю. Стрельченко, В.В. Соценко*

Для поліпшення теплофізичних властивостей полімерних композитів проводили їх фізико-хімічну модифікацію введенням у епоксидну смолу мікродисперсного наповнювача синтезованої алюмінієво-мідної шихти. За динамікою теплофізичних властивостей від кількості наповнювача синтезованої алюмінієво-мідної шихти визначено оптимальний вміст добавки у епоксидному компаунді, який становить 2…2,5 мас.%. Введення наповнювача у епоксидний олігомер забезпечує отримання композитів з максимальними значеннями показників теплофізичних властивостей.

Обґрунтовано механізм формування гетерогенної структури композитів у присутності мікродисперсного наповнювача. Виокремлено три структурних рівні, які формуються після полімеризації матеріалу: мікро-, мезо- та макроструктура. Показано, що при формуванні гетерогенних композитів відбувається ієрархічне поєднання структурних рівнів, а домінуючий вплив одного з них визначається природою та вмістом наповнювача. Обґрунтовано, що структура і властивості композитів визначаються перебігом процесів структуроутворення: всередині окремого рівня, між різними рівнями у кластері, між кластерами.

1. Introduction

The development of the shipbuilding industry and the transport industry as a whole requires the development and implementation of new structural materials [1-6]. These include polymeric composite materials (CM) and protective adhesives based on modified synthetic binders with enhanced performance and technological characteristics. The application areas of polymeric CMs, especially in the repair and restoration of water transport vehicles, are constantly expanding. Compared to the traditional applications of such composites, namely the moulding of products or hulls of modern vessels with improved mechanical properties, the use of anti-corrosion coatings on vessel hulls, the moulding of sides and decks from plastics based on synthetic fabrics and polymer matrices, there is a constant need to create new materials with unique properties. First of all, the practical problem is solved by creating materials with the required set of adhesive and cohesive, anti-corrosion and wear resistance properties under equipment operating conditions not only under dynamic loads, but also at elevated temperatures. For this purpose, thermosetting polymers are used with high efficiency. The authors [7-26] show that thermosets are characterised by high thermal stability, resistance to aggressive environments, strength and hardness, and, most importantly, the stability of mechanical characteristics during the operation of water transport at elevated temperatures.

Elevated temperatures at which thermosets are used (especially under conditions of cyclic temperature changes) lead to softening (or melting), and, accordingly, to the loss of mechanical properties of thermoplastics. A comparative analysis of the thermophysical (heat and heat resistance) and mechanical (destructive stresses and impact strength) properties of thermoplastics and thermosets proves their effectiveness and potential, especially for ensuring the reliability of parts and products for sea and river transport.

Epoxy resins are widely used as thermosetting binders for polymer composites due to the improved physical and mechanical properties of plastics made from them. It is known [27-34] that in the overwhelming majority of cases, during polymerisation, epoxy resins acquire the required properties due to the formation of a spatial structure in the form of a mesh polymer. In this case, the properties of materials are usually determined by the structure of the amorphous mesh epoxy polymer, which has certain topological, molecular and supramolecular features. These determine the properties of epoxy composites. In turn, the structure is regulated by the chemical nature of the hardener, modifier, plasticiser, filler, as well as the technological modes of the curing reaction.

As shown in [35-42], the widespread use of epoxy resins is due to the following factors:

- a wide raw material base and the availability of resources for their production;
- flexibility of the main chain of macromolecules;
- activity to interfacial interaction of segments and side groups of the macromolecular chain.

All of the above provides a wide range of characteristics of epoxy resin composites, such as adhesive, physical, mechanical and dielectric properties in a wide temperature range, corrosion and wear resistance. In addition, the low shrinkage rate of epoxies after polymerisation (less than 2%) is important, which allows maintaining high adhesion strength of the polymer to the metal substrate. At the same time, no significant residual stresses occur, which is an indicator of the durability of products under critical operating conditions of modern marine transport vessels.

At the same time, epoxies also have disadvantages. These include high cost, brittleness, shrinkage deformations, and in many cases, insufficient chemical resistance. This limits the use of epoxy composites in the transport industry [43]. To improve the above-mentioned properties of epoxy composites, micro- and nanoscale dispersed fillers are introduced into the binder at the moulding stage. This approach not only improves the properties of materials, but also allows for an additional reduction in the cost of the final product and solving problems associated with waste disposal and environmental protection.

Metal powders based on aluminium, iron, zinc, copper, etc. are widely used as dispersed fillers. In addition, metal oxides and carbides, such as Al_2O_3, Cr_2O_3, TiO_2, Fe_2O_3, SiO_2, SiC, TiC, B_4C, etc., have shown high efficiency in improving the properties of CMs [38-42]. Filling epoxy composites with such powders at an optimum content made it possible to increase their heat and thermal resistance, chemical resistance, mechanical and adhesive strength, and at the same time reduce residual stresses,

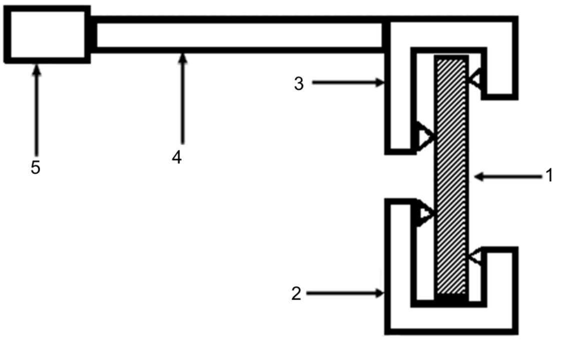

Fig. 1. Scheme of the device for determining the heat resistance of composites: 1 – sample; 2 – lower grip; 3 – upper grip; 4 - lever; 5 – load

friction coefficient, and thermal coefficient of linear expansion. It should be noted that the introduction of fillers accelerates the curing process of epoxy composites due to the activation of interfacial interaction during the structure formation of the materials.

2. Experimental

Epoxy diane oligomer grade ED-20 (GOST 10587-84) was chosen as the main component for the binder in the formation of epoxy CMs. For crosslinking the epoxy compositions, the hardener polyethylenepolyamine PEPA (TU 6-05-241-202-78) was used, which allows curing materials at normal and elevated temperatures [21-25, 38-42].

To improve the mechanical properties of polymer composite materials, it was considered appropriate to carry out their physicochemical modification. The filler used was a synthesized aluminum-copper charge (SACC), created by the authors [44, 45]. This synthesized powder with a particle size of 12...14 μm has the following chemical composition: $Al + Cu + CuAl_2 + Al_4C_3$. This filler is suitable for use to improve the thermal properties of vehicle coatings, since it contains not only metallic elements (Al and Cu), but also chemically active compounds of $CuAl_2$ and aluminum carbide. In our opinion, such elements will provide a change in the structural network of the polymer at different levels and stages of its formation, which will improve the properties of materials that are operated under the influence of a thermal field.

The coefficient of linear thermal expansion (CLTE) and heat resistance are important indicators of the thermal properties of protective functional coatings that operate under a significant temperature gradient and alternating loads. When calculating the CLTE, at the initial stage, a curve was constructed to determine the elongation of samples under temperature loading and with a decrease in the effect of the thermal field. Based on these dependences, the shrinkage of the CMs and their relative deformation were calculated. The CLTE was calculated in different temperature ranges, which allows us to study the behaviour of materials under critical temperature conditions. It should be noted that the deformation properties of CMs were analyzed by changing the parameters of samples under the influence of a thermal field (ISO 11359-2). The heat resistance of the composites was studied according to ISO 75-2. The temperature index was determined at a sample bending value of $h = 6$ mm (Fig. 1).

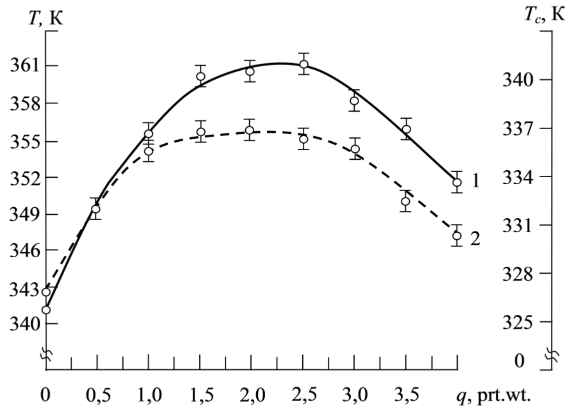

Fig. 2. Thermophysical properties of epoxy composites depending on the content of the SACC filler

In order to confirm the results of the studies, the dynamics of endo- and exothermic effects was analyzed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The Thermoscan-2 device was used for this purpose. Thermal effects were analyzed in the temperature range ΔT = 298...773 K. The weight of the composites under study was 0.3 g. Aluminium oxide particles were used as a standard.

3. Results and Discussion

The dynamics of the thermophysical properties of epoxy composites depending on the content of the SACC filler was studied. An increase in the thermal stability of the CM from 341 K (for the epoxy matrix) to 349 K was observed even with a small degree of filling of the epoxy binder with dispersed particles (0.5 prt.wt), which proves the effectiveness of the additive (Fig. 2).

With an increase in the number of dispersed particles, a monotonic increase in the heat resistance of epoxy composites was observed, and the maximum on the curve of the dependence "heat resistance - SACC content" was noted for composites with a filler content of 2...2.5 prt.wt. These materials have a heat resistance value of up to 361 K. An increase in the amount of filler to 3...4 prt.wt. leads to a decrease in the indicators of the thermal physical characteristic, since the heat resistance in this case decreases to 352...358 K.

A similar dependence was observed when analysing the glass transition temperature of CM with different SACC contents. It was proved (Fig. 2), that at a particle content of 0.5 prt.wt., the glass transition temperature of the CM significantly increases compared to the matrix (from 327 K to 332 K). An increase in the content of particles from 1 to 3 prt.wt. ensures the formation of materials with an absolute glass transition temperature of 337 K. Further increase in the amount of filler worsens the performance of this property of the developed CMs. Thus, according to the criteria of thermophysical characteristics (heat resistance and glass transition temperature), the optimal content of SACC filler in epoxy composites has been determined to be 2...2.5 prt.wt. based on 100 prt.wt. of epoxy resin. The introduction of the specified filler content into the epoxy binder provides an increase in heat resistance compared to the matrix from 341 K to 361 K, and the glass transition temperature from 327 K to 337 K. The results obtained can be explained as follows.

When analysing the behaviour of the initial epoxy matrix with increasing temperature, it should be taken into account that the epoxy polymer cured with polyethylenepolyamine has a dense, uniform structure containing globular inclusions of ≈100 nm in size [38, 41]. The size of such supramolecular formations depends on factors such as the nature of the hardener and the polymerisation process. However, with an increase in temperature, the size of the globules increases, which correspondingly leads to a decrease in the matrix density.

On the other hand, the structural network of the polymer is in the amorphous phase, which is characterised by a lower density compared to the density of globular structures (Fig. 3). In this case, it is necessary to take into account the intermolecular distribution in a unit volume of the polymer, which is characterised by the average number of cross-links between the chains of macromolecules. At the micro level, the cross-linking centers are located at a significant distance from each other in the structural network of the polymer. At the same time, the segments of the main chain of macromolecules between the cross-linking centres of the structural network have a certain mobility, which increases with increasing temperature. This can explain the transition of polymers to a viscous-fluid state at elevated temperatures, which implies a partial loss of their mechanical properties. One of the criteria for assessing the loss of mechanical properties with increasing temperature is heat resistance.

It is well known [46, 47] that the introduction of a filler forms a heterogeneous system, which is described in terms of structural levels. In this case, it is the activity of interfacial interaction and the amount of filler in the polymer system that determines the dominant influence of one of the following structural levels. Three structural levels should be distinguished: micro-, meso- and macrostructure of the material (Fig. 3). Microstructure is characterized by the bonds at the molecular and intermolecular level in the polymer volume, as described above. It should also include the presence of supramolecular formations in the form of globules, which are also included in the structural network of the polymer.

The mesostructure is characterised by the presence of polymer boundary layers that form around the filler particles. Such polymer regions also include globules that partially open and increase in volume. The boundary layers are characterised by a smaller intermolecular distribution, which implies an increase in the crosslinking density of the polymer per unit volume (Fig. 3).

The macrostructure is characterised by cluster formations that include several mesostructures with filler and boundary layers. Clusters also contain microstructural inclusions that are not covered by mesostructures.

As a result, the formation of heterogeneous CMs occurs in a hierarchical combination of structural levels, and the dominant influence of one of them (in our case) is determined only by the filler content. In this work, only one filler is considered, therefore the activity of particles in interfacial interaction is not taken into account a priori.

It should also be taken into account that the structure and properties of composites are determined by the course of structure formation processes:

- within a single level;
- between different levels in the cluster;
- between clusters.

Within the framework of the polystructural theory [27, 38-40], the following approaches to filler optimisation have been identified with the aim of hierarchically combining structural levels to obtain composites with maximum performance characteristics:

- use of fillers with the required dispersion and sufficient physical and chemical activity;
- low viscosity of the oligomeric binder, which ensures good wetting of the dispersed phase;
- taking into account the rule of intermittent granulometry, where two requirements are crucial: 1) the mobility of the polymer macromolecules during crosslinking must be high enough to facilitate the release of the air contained therein; 2) optimal adhesion between the oligomer and the surface of the particles must be achieved even at high filling levels, while the risk of defects must be taken into account (for example, the formation of dislocations due to agglomeration of the particles of the dispersed phase or due to their insufficient wetting).
- introduction of particles in an optimal ratio, providing the complex with maximum indicators of the required (in our case, thermophysical) properties;
- optimisation of technological modes of thermal polymerisation to ensure conditions for structure formation at the micro-, meso- and macro-levels in the CM.

The considered mechanism, taking into account the levels of CM structure formation in the presence of a filler, allows us to state the formation of a meso-level centred on a dispersed particle (Fig. 3). When particles are introduced into the binder, even at a low content, boundary layers are formed around the dispersed phase in the polymer volume. The active particles of the additive form their own strain and stress fields during structure formation. The magnitude of the impact of these fields on macromolecules and supramolecular formations in the oligomer depends on both the surface characteristics of the particles (their surface topology) and the chemical activity of the filler. When introducing the SACC filler into the CM in low concentrations, these factors determine the mesostructure of the matrix, which is of decisive importance for improving the cohesive strength and, as a consequence, the thermophysical properties of the developed composites.

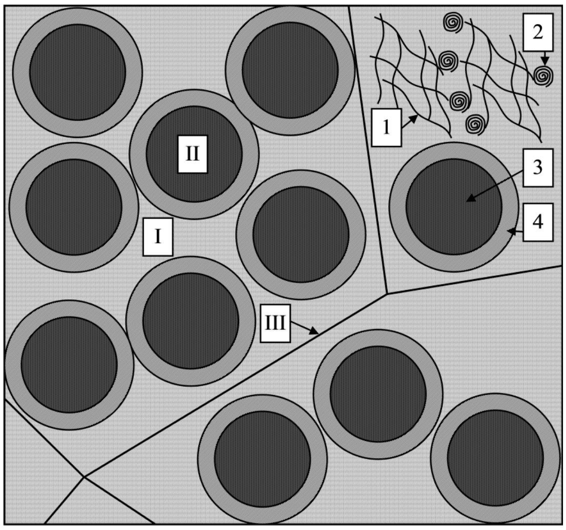

Fig. 3. Model of structural levels during crosslinking of epoxy CMs in the presence of dispersed filler: I – Microstructure (molecular and supramolecular formations): 1 – molecular formations (chains of macromolecules with crosslinks); 2 – supramolecular formations (globules). II – Mesostructure (filler and boundary layer): 3 – fraction of dispersed filler; 4 – boundary layer. III – Macrostructure in the form of cluster formations (arrow shows the cluster boundary).

Increasing the filler content, namely introducing it in an optimal ratio (in our case, 2...2.5 prt.wt.), provides an increase in the degree of crosslinking of the CM, which affects the heat resistance and glass transition temperature. This is due to an increase in the number of mesostructures in the CM. Additionally, bridges of molecular chains of the microstructure are formed between the mesostructures formed around the dispersed particles.

Additionally, it is necessary to take into account the influence of the filler on the macrostructure, which manifests itself in the formation of clusters (Fig. 3). At the optimum filler content, the kinetic and thermodynamic state of a heterogeneous system tends to equilibrium due to a decrease in surface energy [48, 49]. As a result, mesostructures are uniformly combined by volume with the formation of clusters, which can have different volumes depending on the given technological modes of structure formation.

Thus, a metastable state of a heterogeneous system is formed, which ensures maximum saturation of the structure with clusters and leads to its greatest strengthening even under the influence of a thermal field. It should be noted that the formation of such a cluster metastable macrostructure is determined primarily by the following criteria:

Table 1. Coefficient of linear thermal expansion (CLTE) of composites in the testing temperature ranges

SACC content, *q*, prt.wt	Coefficient of linear thermal expansion, $a \times 10^{-5}$, K^{-1}			
	Temperature areas of research, ΔT, K			
	300…320	300…370	300…420	300…470
0	6.3	6.8	9.9	10.9
0.5	3.2	3.6	4.9	9.2
2.5	2.7	3.1	4.5	9.0
3.5	2.9	3.2	4,8	9.4

- volume (or mass) content of binder and filler;

- activation of interfacial physical and chemical interaction processes;

- the ratio of density and deformation properties of mesostructures in the polymer.

It should be noted that with a significant increase in the filler content, the systems have a binder deficiency. As a result, mesostructures with defects are formed, between which the required number of bridges at the micro level does not arise. Ultimately, cluster macrostructures are not in a metastable state, which usually leads to deterioration of the thermophysical properties of the developed composites. This is confirmed by the fracture pattern of the samples. Materials with insignificant or optimal filler content are prone to ductile fracture, while composites with excessive amount of SACC are brittle.

When analyzing the behavior of composite materials under thermal stress, another important factor is the value of their coefficient of linear thermal expansion (CLTE). This is especially important for protective coatings, since their high CLTE value leads to peeling of the adhesive from the metal base. The latter causes the destruction of coatings and premature failure of deck equipment. Therefore, the CLTE of the matrix and the developed composites was additionally studied in this work. Based on the preliminary results of the study of heat resistance and glass transition temperature of materials, CMs with the following SACC contents were selected for further testing: 0.5, 2.5, and 3.5 prt.wt.

It was established (Fig. 4, Table 1) that among all the selected samples, the epoxy matrix is characterized by the maximum values of CLTE 6.3×10^{-5} K^{-1} in the temperature range ΔT = 300...320 K. It should be noted that this indicator for carbon steels used in deck equipment is 1.1×10^{-5}, K^{-1}. So the difference is quite significant. The introduction of a filler reduces this indicator to $(2.7...3.2) \times 10^{-5}$ K^{-1}, with the lowest values of 2.7×10^{-5} K^{-1} observed for the CM with a particle content of 2.5 prt.wt.

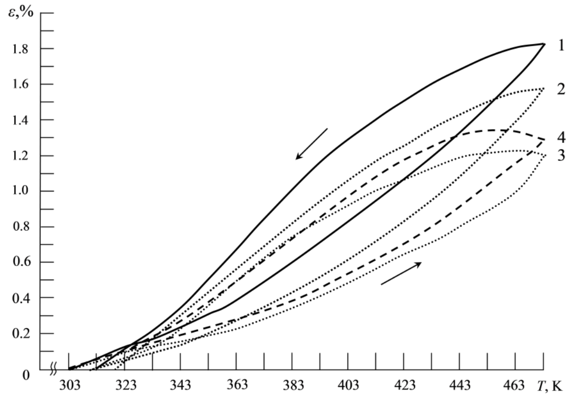

Fig. 4. Dilatometric curves of epoxy matrix (1) and composites with SACC additive: 0.5 prt.wt (2); 2.5 prt.wt (3); 3.5 prt.wt (4).

Analysis of the results over a wider temperature range allows us to state that the coefficient of thermal expansion of all materials increases with increasing temperature. In particular, in the temperature range from 300 K to 420 K (this region covers the glass transition temperature of the CM), an increase in the CLTE of the matrix by a factor of 1.6 was observed. The lowest CLTE of 4.5×10^{-5} K^{-1} was observed in this region for the cermet with 2.5 prt.wt SACC. It can be argued that this temperature range is optimal for the operation of the developed composites, since the absolute values of the CLTE for them are relatively small. When the temperature range under study was increased to 470 K, a sharp increase in the CLTE was observed for all materials. In particular, for dispersed-filled CMs, the CLTE approaches that of epoxy matrix and is in the range of $(9.0...9.4) \times 10^{-5}$ K^{-1}. This is almost 2 times higher than the value typical for the previous temperature test range (300...420 K).

The positive effect of the filler on reducing the CLTE of the CM can be explained by the following factors. We proceeded from the fact that the original epoxy polymer, like any polar liquid, is characterised by the presence of ordered regions – associates, which are formed as a result of physical and chemical interaction during crosslinking of the matrix. Typically, with increasing temperature, their mobility and shape increase due to thermal motion. Figure 3 shows that the associates exist in the form of macromolecules with cross-links (molecular structure) and globules (supramolecular structure). In this way, physical and chemical bonds are formed at the micro level. As a result, spatially cross-linked polymers are considered as densely cross-linked aggregates placed in a structural amorphous matrix grid. It should be noted that between the highly crosslinked aggregates in the polymer system, there is a molecular structure with unevenly distributed bonds. This is a prerequisite for the existence of a sol fraction alongside a gel fraction in a cured polymer system. It is the presence of the sol fraction that leads to a deterioration in the cohesive properties and, as a consequence, the thermophysical properties of the matrix when it is used at temperatures above the gelling temperature.. These properties can be improved by increasing the content of the gel fraction in the CM, namely by introducing a filler in the optimal amount. In this case, mesostructures are formed, which include polymer boundary layers with a high degree of crosslinking.

It should be noted that the contributions of the main components (binder and filler) to the structure-forming processes should not be considered as a simple sum of their partial effects, since the synergistic effect should be taken into account. The main factors that determine the specificity of interfacial phenomena are the surface energies of the matrix and the dispersed phase, and the specific surface area of the filler particles is of particular importance. Accordingly, as in our case, it can be argued that the filler has a reinforcing effect (meaning strength properties) on the polymer system. This reinforcing effect is primarily due to the formation of boundary surface layers around the filler particles. That is, mesostructures must be formed in the process of crosslinking CM. In this case, the strength enhancement can be achieved due to the high adhesion of the matrix to the surface of the filler, which should contain active functional groups or atoms on the surface.

In addition, the presence of the filler causes the emergence of energy fields, including the internal van der Waals field, in the polymer regions bordering the surface of the solid phase. This leads to an ordering of the polymer structure in these areas under the influence of the surface potential of the dispersed particles. Thus, surface boundary layers are formed, which, as noted in [46, 47], do not have clear boundaries but exist in the form of an intermediate phase. In contrast to the described mesostructures, which are formed on the basis of a filler and boundary layers, the matrix region adjacent to the interface (microstructure) has significantly different properties. Therefore, it is important to fill the CM with an optimal (critical) content of the additive, which will ensure the transition of the maximum volume of the polymer to the state of the boundary layer (mesostructure).

It is also necessary to take into account the factors described in [25-27, 38-42], which determine the properties of the mesostructure (boundary layers) under the influence of the solid microdispersed filler phase.

1. *Entropic factor* determines the geometric restrictions on the spatial arrangement of macromolecular chains and supramolecular formations in the polymer. It is assumed that the presence of a solid phase surface, regardless of its chemical activity, is a condition for limiting the segmental mobility of macrochains. On the contrary, the activity of the side groups of the main chain of macromolecules increases simultaneously. This effect does not depend on temperature, manifests itself mainly in the boundary layers and is levelled in the polymer regions remote from the particle surface (microlevel). The dominance of the entropy factor in the formation of the CM structure leads to a deterioration in both the cohesive and thermophysical properties of materials.

2. *Energy (adsorption) factor* determines the packing density and the magnitude of intermolecular forces in the boundary layers. It mainly takes into account the topology and surface activity of the filler. Both criteria regulate the segmental and group mobility of macromolecules, which is the basis for the compaction and reorientation of chains in the boundary layers. The contribution of the energy factor decreases with increasing temperature.

3. *Chemical factor* is determined by the number of chemically active centres on the additive surface capable of interacting with binder mac-

Table 2. Thermal resistance of composites

SACC content, *q*, prt.wt.	T_0, К	T_5, К	T_{10}, К	T_{20}, К	$T_{к}$, К	ε_m, %
0	600	619	626	645	734	73
0.5	618	632	641	656	748	68
2.5	626	645	654	669	768	62
3.5	621	635	645	660	754	66

Notes: T_0 is the temperature of the mass loss onset (beginning of destruction); T_5, T_{10}, T_{20} are the mass loss temperatures (5 %, 10 %, 20 %); T_k is the final mass loss temperature (end of destruction); ε_m is the relative mass loss.

romolecules. The contribution of the chemical component is decisive when filling the CM with particles in a critical proportion. It takes into account the kinetics of interaction reactions due to selective adsorption, as well as the inhibition of reactions by functional groups of the additive.

It should be noted that during the structure formation of composites in the presence of a filler, it is necessary to take into account the above factors in combination. Only they determine the course of physical and chemical processes with the formation of boundary layers. The latter are a component of the mesostructure as a unit of the cluster (macrostructure), which is the basis for improving the thermal and physical properties of new materials.

We analyzed the behaviour of boundary layers and materials in general at elevated temperatures using the DTA and DTG methods. We have experimentally determined (Fig. 5, Table 2) the percentage of mass loss of the matrix and epoxy composites with different SACC contents at elevated temperatures. At the same time, we considered temperature as a significant indicator characterizing the onset of mass loss of samples, since it is a sign of the destruction of chemical bonds.

It is shown (Table 2) that the temperature of the onset of epoxy matrix mass loss is 600 K, while for CM with filler it is in the range of 618...626 K. That is, it can be stated that the onset of CM destruction occurs in the higher temperature region due to the presence of mesostructures that cause an increase in the gel fraction in the CM. It can be assumed that the destruction in the epoxy matrix occurs only at the micro level due to the rupture of chemical bonds between macrochains and the emergence of globular formations. Similarly, the same thermal degradation occurs in the CM, but to a lesser extent, due to the existence of mesostructures.

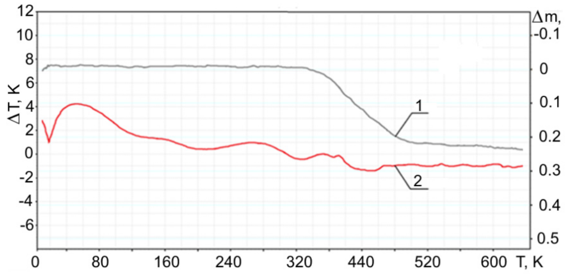

Fig.5. Experimental curves according to thermogravimetric (1) and differential thermal (2) analysis for epoxy matrix [39]

In addition, it should be noted that among the studied CMs, the sample with the amount of additive of 2.5 prt.wt. has the highest temperature (626 K) of the onset of mass loss. As mentioned above, this was believed to be due to the formation of clusters in addition to the mesostructure. The clusters most effectively affect the thermal stability of the material when it is filled with an additive in a critical ratio. In this case, the mesostructures are maximally compacted in the clusters, which affects the cohesive characteristics of the composite.

The trend described above is observed when analyzing the mass loss of the samples over the entire temperature range studied (Table 2). No less important are the indicators of the final mass loss. It has been established (Table 2) that the epoxy matrix has the highest mass loss (ε_m = 73 %) among all the materials studied. On the contrary, the material with a SACC content of 2.5 prt.wt has the lowest relative mass loss (62 %). The obtained results are in good agreement with the results of tests of other thermophysical properties of the CM described above.

In addition to the mass loss, we analysed the DTA curves of the developed materials (Fig. 5, Table 3) and determined the magnitude of the exothermic effects. We determined the onset of the exo-effect, its maximum and temperature range.

Table 3. Temperature regions of exothermic effects of composites according to DTA

SACC content, q, prt.wt.	Exothermic effect intervals			The value of the maximum exogenous effect, T_{max}, K
	T_n, K	$T_к$, K	ΔT, K	
0	460	659	199	518
0.5	464	675	212	527
2.5	471	699	228	529
3.5	467	683	216	528

Note: T_n is the initial temperature; $T_к$ is the final temperature; ΔT is the temperature interval of the exo-effect.

It has been established (Table 3) that for the epoxy matrix the initial temperature of the exoeffect is minimal (460 K). For all CMs, it is in the range of 464...471 K. The temperature of the maximum exo-effect for the CMs increases from 518 K (for the matrix) to 527...529 K.

However, in our opinion, the most important thing is the analysis of the exoeffect interval with increasing sample temperature. It has been established that it expands from 199 K (for the matrix) to 212...228 K (for the developed CMs). It is the range of the exo-effect that indirectly indicates the rate of destructive processes in the material with increasing temperature. It has been proven that the largest exo-effect interval is for the composite with the SAMS content of 2.5 wt.%. The limits for it are defined as ΔT = 228 K, which is 29 K higher than the similar range typical for the epoxy matrix. This confirms that chemical bonds are broken more slowly under the influence of temperature due to better packing in meso- and macrostructures..

Thus, a comprehensive assessment of the thermophysical properties of the developed epoxy composites showed that the CM containing SACC filler in the amount of 2.5 prt. wt. is characterised by the best thermophysical properties among the entire range of materials studied.

4. Conclusions

The results of the study allow us to make the following statements.

1. Based on the dynamics of heat resistance and glass transition temperature depending on the amount of filler in the synthesised aluminium-copper charge, the optimal content of the additive in the epoxy compound was determined, which is 2...2.5 prt.wt. The introduction of filler into the epoxy oligomer provides composites with the highest values of thermal properties among all the materials studied. At the same time, the heat resistance increases from 341 K (for the epoxy matrix) to 361 K, and the glass transition temperature from 327 K to 337 K.

2. The minimum values of the CLTE were observed for a composite with an aluminium-copper charge content of 2.5 prt.wt. In the temperature range ΔT = 300...320 K, the CLTE was 2.7×10^{-5} K^{-1}, and in the temperature range 300...420 K it was 4.5×10^{-5} K^{-1}, which is 2.3 times lower than that of the epoxy matrix.

3. The thermal stability of the developed composites was investigated by thermogravimetric and differential thermal analysis. It has been shown that the material with an additive amount of 2.5 parts by weight has the highest initial mass loss temperature (626 K) and the lowest relative mass loss (62%). The exo-effect interval of this material is ΔT = 228 K, which is 29 K higher than the similar interval for the epoxy matrix. This confirms that chemical bonds are broken more slowly under the influence of temperature due to better packing of meso- and macrostructures. It is also believed that this was due to the formation of clusters in such a material, in addition to the mesostructure. Such cluster formations most intensively affect the heat resistance of the material at a critical additive content. It is in this case that the mesostructures are maximally compacted in clusters, which affects the cohesive characteristics of the composite.

4. The mechanism of formation of a heterogeneous structure of the composites in the presence of microdispersed filler is substantiated. Three structural levels formed after polymerisation of the material are distinguished: micro-, meso- and macrostructure. Microstructure refers to the bonds at the molecular and intermolecular levels in the polymer volume. The structural network of the polymer also includes supramolecular formations in the form of globules.

The mesostructure is characterised by the presence of polymer boundary layers formed around the filler particles. These polymer regions also include globules that partially open and increase in volume. The boundary layers are characterised by a smaller intermolecular distribution, which means an increase in the crosslinking density of the polymer per unit volume. The macrostructure is characterised by cluster formations including several mesostructures with filler and boundary layers. Clusters also have microstructural inclusions that are not covered by mesostructures.

Heterogeneous composites are formed in a hierarchical combination of structural levels, with the dominant influence of one of them determined by the nature and content of the filler. It has been substantiated that the structure and properties of composites are determined by the sequence of structure formation processes: within a single level, between different levels in a cluster, and between clusters.

The considered mechanism, taking into account the levels of structure formation of composites in the presence of a filler, allows us to state the formation of a meso-level with a centre in the form of a dispersed particle. When particles are introduced into the binder, even at a low content, boundary layers are formed around the dispersed phase in the polymer volume. In addition, the effect of the filler on the macrostructure, which is manifested in cluster formation, should be taken into account. At the optimum filler content, the kinetic and thermodynamic state of the heterogeneous system tends to equilibrium due to the reduction of surface energy. As a result, mesostructures are uniformly combined by volume with the formation of clusters, which can have different volumes depending on the given technological modes of structure formation. Thus, a metastable state of the heterogeneous system is formed, which ensures maximum saturation of the structure with clusters and leads to its greatest strengthening even under the influence of a thermal field.

5. A model of structural levels is proposed for crosslinking epoxy composites in the presence of a dispersed filler. Three structural levels are distinguished in the model: micro, meso, and macrostructure of the material:

I – Microstructure: molecular formations (chains of macromolecules with cross-links) and supramolecular formations (globules);

II – Mesostructure: a particle of dispersed filler and polymer boundary layer around it;

III – Macrostructure in the form of cluster formations.

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