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## ДОСЛІДЖЕННЯ МЕХАНІЧНИХ ВЛАСТИВОСТЕЙ І ТЕПЛОСТІЙКОСТІ ПЛАСТИФІКОВАНИХ ЕПОКСИКОМПОЗИТІВ З МІКРОДОБАВКАМИ

У статті досліджено вплив мікронаповнювачів на механічні і теплофізичні властивості епоксидних композитів на основі пластифікованої смоли DER 331. Як мікронаповнювачі використано порошки оксиду хрому  $Cr_2O_3$  (20 мкм) та карбїду кремнію SiC (40 мкм) за вміст у від 5 до 20 мас.%. Досліджено механічні властивості: руйнівні напруження і модуль пружності при згині, ударна в'язкість. Додатково проводили випробування теплостійкості розроблених матеріалів.

Порівняльний аналіз впливу мікронаповнювачів підтверджує перевагу застосування оксиду хрому порівняно з карбїдом кремнію для покращення властивостей епоксидних композитів. При концентрації 10 мас.% оксид хрому забезпечує на 6,4 % вищу міцність матеріалів (85,2 МПа проти 80,1 МПа) та на 17,6 % вищий модуль пружності (4 ГПа проти 3,4 ГПа) порівняно з композитами, наповненими карбїдом кремнію. Ця перевага зумовлена кращою адгезією до матриці та здатністю до утворення фізичних, ковалентних та іонних зв'язків на межі поділу фаз.

Найкращі результати характерні для матеріалу з оксидом хрому, який за вмісту 15 мас.% забезпечує формування КМ зі значеннями міцності на розрив (88,3 МПа), модуля пружності (4,2 ГПа) та теплостійкості (364 К). Механізм покращення властивостей полягає у тому, що мікродисперсні частки формують структурний каркас, який створює бар'єри при поширенні тріщин (тобто, відбувається когезійне зміцнення матеріалу). Для композитів з  $Cr_2O_3$  ключовим є також утворення додаткових фізикохімічних зв'язків з матрицею, що забезпечує термостабільність нових матеріалів.

**Ключові слова:** епоксидний композит, механічні і теплофізичні властивості, наповнювачі, полімер, покриття, пластифікатор.

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## RESEARCH ON THE MECHANICAL PROPERTIES AND HEAT RESISTANCE OF PLASTICIZED EPOXY COMPOSITES WITH MICROADDITIONALS

The article investigates the influence of microfillers on the mechanical and thermophysical properties of epoxy composites based on plasticized resin DER 331. As microfillers, chromium oxide  $Cr_2O_3$  powders (20  $\mu m$ ) and silicon carbide SiC (40  $\mu m$ ) were used with a content of 5 to 20 wt%. Mechanical properties were investigated: fracture stress and modulus of elasticity during bending, impact strength. Additionally, heat resistance tests of the developed materials were conducted.

Comparative analysis of the effect of microfillers confirms the advantage of using chromium oxide compared to silicon carbide for improving the properties of epoxy composites. At a concentration of 10 wt.% chromium oxide provides 6.4% higher strength of materials (85.2 MPa vs. 80.1 MPa) and 17.6% higher modulus of elasticity (4 GPa vs. 3.4 GPa) compared to composites filled with silicon carbide. This advantage is due to better adhesion to the matrix and the ability to form physical, covalent and ionic bonds at the interface.

The best results are characteristic of the material with chromium oxide, which at a content of 15 wt.% provides the formation of CM with values of tensile strength (88.3 MPa), elastic modulus (4.2 GPa) and heat resistance (364 K). The mechanism of improving the properties is that microdispersed particles form a structural framework that creates barriers to crack propagation (i.e., cohesive strengthening of the material occurs). For composites with  $Cr_2O_3$ , the formation of additional physicochemical bonds with the matrix is also key, which ensures the thermal stability of new materials.

**Keywords:** epoxy composite, mechanical and thermophysical properties, fillers, polymer, coating, plasticizer.

**Problem statement.** Modern technologies require the development of materials with high mechanical properties and resistance to thermal loads [1-12]. Epoxy composites remain one of the most promising polymer systems due to their improved adhesion, strength and chemical resistance. However, their brittleness and limited thermal resistance necessitate modification [1-4].

**Analysis of recent studies and publications.** For plasticization of epoxy matrices, phthalic acid ethers, dibutyl phthalate, and also diethylene glycol DEG-1 are widely used [8]. We previously established the optimal content of DEG-1 in an epoxy binder based on the oligomer DER 331 and substantiated that from the point of view of rheological, mechanical properties and heat resistance in the resin (100 wt.%) it is advisable to introduce 12 wt.% of the plasticizer. As a hardener, polyethylenepolyamine (PEPA) was used in an amount of 12 wt.%, which provides an optimal polymerization rate at room temperature [5, 7].

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To further strengthen the structure and improve the properties of CM, it is advisable to introduce fillers of various nature and sizes. These include microparticles, in particular chromium oxide ( $\text{Cr}_2\text{O}_3$ ) and silicon carbide (SiC). They are added to increase impact resistance and thermal stability.

**The purpose of the work** is to investigate the mechanical properties and heat resistance of plasticized epoxy composites with microadditives in the form of chromium oxide and silicon carbide.

**Materials and research methods.** During the formation of polymer compositions, the epoxy resin DER 331 (ISO 9001) was chosen as the basis, which is the reaction product of epichlorohydrin and bisphenol A. The epoxy oligomer was plasticized with aliphatic resin DEG-1 in an amount of 12 wt.% per 100 wt.% DER 331. Polyethylene polyamine (TU 2413-357-00203447-99) was used to cure epoxy compositions. As microdispersed additives, the work used powders of chromium oxide ( $\text{Cr}_2\text{O}_3$ ) (ISO 4621:1986) and silicon carbide (SiC) (ISO 8486-2:2007) with particle sizes of 20  $\mu\text{m}$  and 40  $\mu\text{m}$ , respectively.

The values of the ultimate stress and the modulus of elasticity in bending were determined using a four-point loading scheme according to ASTM D 790-03. The impact toughness was tested by the Charpy impact without notch (ISO 179-1). The heat resistance of the isotropic polymer composites was tested using Martens according to ISO 75-2.

**Discussion of the results.** The study of the influence of chromium oxide microadditions revealed a significant improvement in the performance characteristics of the epoxy composite in the content range of 10...15 wt.% (Fig. 1). The destructive stresses demonstrate an intensive increase to 85.2 MPa at 10 wt.% and 88.3 MPa at 15 wt.%, which is explained by the formation of a volumetric dispersed-filled structure.  $\text{Cr}_2\text{O}_3$  particles, having a high surface energy, create an effective barrier system for the propagation of microcracks.

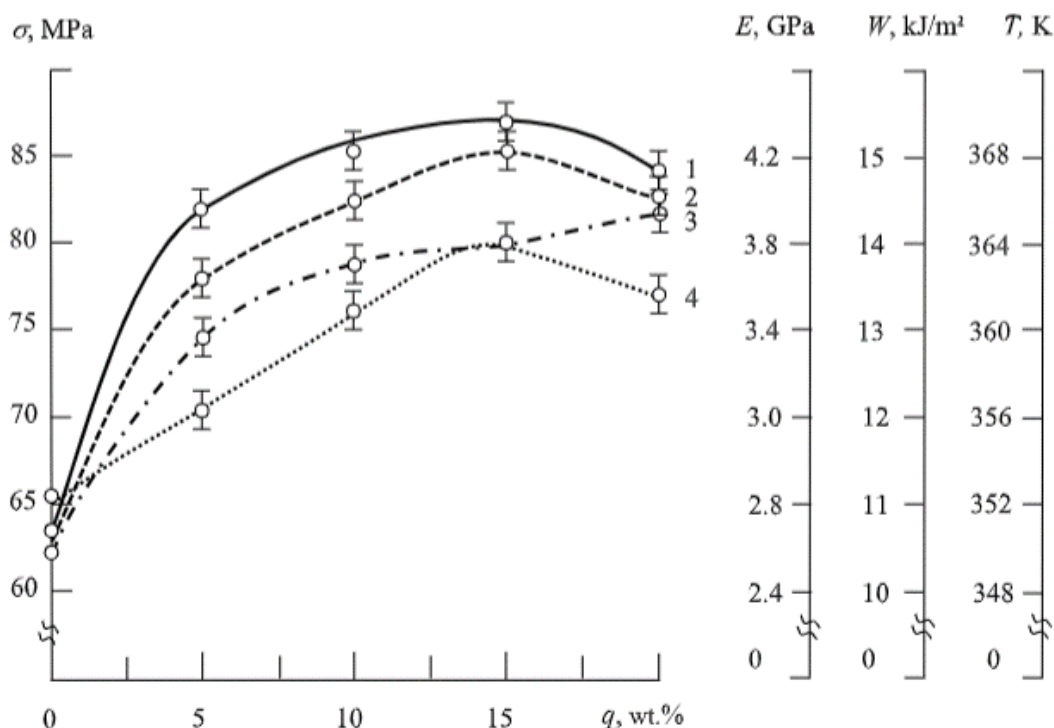


Fig. 1. Dependence of the cohesive properties of CM on the content of chromium oxide microfiller: 1 – failure stress ( $\sigma$ ); 2 – modulus of elasticity (E); 3 – impact strength (W); 4 – heat resistance (T).

The elastic modulus increases from 2.6 GPa to 4 GPa at 10 wt.% and reaches 4.2 GPa at 15 wt.%, reflecting the ability of microadditives to create a structural framework of increased rigidity.

The impact strength shows a stable increase from 10.4 kJ/m<sup>2</sup> to 13.5 kJ/m<sup>2</sup> at 10 wt.% and 13.8 kJ/m<sup>2</sup> at 15 wt.%, which indicates the activation of energy dissipation mechanisms. The filler particles are centers of multiple deflection and branching of cracks, increasing their propagation path.

The heat resistance of the composites increases from 352 K to 360 K at 10 wt.% and to 364 K at 15 wt.%, demonstrating the ability of chromium oxide to create a thermostabilizing effect. This is due to an

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increase in the thermal conductivity of the system and a decrease in the molecular mobility of polymer chains.

The strengthening mechanism is based on the principle of composite synergism, where microdispersed particles form a spatial reinforcing system. At a content of 10...15 wt.%, a critical level of filling is achieved, which provides optimal density of reinforcing elements without their agglomeration. This creates conditions for effective redistribution of stresses across the volume of the material.

A feature of  $\text{Cr}_2\text{O}_3$  is the ability to form chemical bonds with the epoxy matrix through surface hydroxyl groups. This provides strong adhesion at the phase interface and prevents defects under load. Functional groups on the surface of chromium oxide contribute to the formation of coordination bonds with functional groups of the polymer.

The optimal content range of 10...15 wt.% corresponds to the maximum efficiency of the additive. At these values, an optimal ratio between volumetric filling and effective transfer of the polymer to the state of the outer surface layers was observed [5]. Further increase in filler content leads to further improvement of CM properties.

Thermal stabilization occurs by creating thermal barriers and increasing the heat resistance of composites.  $\text{Cr}_2\text{O}_3$  particles, having high thermal conductivity, form heat-conducting paths that contribute to uniform temperature distribution.

The increase in impact strength is due to the activation of multiple energy dissipation mechanisms: crack deflection, their branching, and plastic deformation of the matrix around the particles. This leads to the conversion of kinetic energy into surface energy of newly formed surfaces.

Microstructural studies show that  $\text{Cr}_2\text{O}_3$  particles are distributed mainly in the intercluster spaces of the polymer, creating additional reinforcement in areas of stress concentration. Such morphology contributes to increased resistance to various types of loads.

Therefore, the introduction of micro-additions of chromium oxide in the amount of 10...15 wt.% allows achieving a comprehensive improvement in properties: increasing strength by 33...38%, modulus of elasticity by 54...62%, impact strength by 30...33%, and heat resistance by 8...12 K. The results obtained demonstrate the high efficiency of  $\text{Cr}_2\text{O}_3$  for creating adhesives and composites with increased performance characteristics.

The results of tests of the influence of silicon carbide microadditives on the properties of CM revealed their monotonic improvement compared to the original matrix (Fig. 2). An increase from 64.2 MPa to 80.1 MPa of destructive stresses was established at the optimal concentration of the additive (10 wt.%), which is associated with the ability of SiC particles to partially screen the trajectories of crack propagation. The elastic modulus increases to 3.4 GPa (at 10 wt.%), reflecting the formation of a rigid structural framework of the introduced particles. The impact strength reaches a maximum of 14 kJ/m<sup>2</sup> at 10 wt.%, which is explained by the ability of dispersion-filled CM to resist impact loads and branch cracks. At the same time, this CM is characterized by heat resistance, which is 360 K. This is evidence of the formation of a composite that is characterized by a thermostabilizing effect.

A comparative analysis of the effectiveness of the influence of  $\text{Cr}_2\text{O}_3$  and SiC particles on the properties of CM (Fig. 1 and Fig. 2) demonstrates a significant advantage of chromium oxide as a microfiller. At the optimal content of  $\text{Cr}_2\text{O}_3$  (10 wt.%), CM is formed with higher values of destructive stresses (85.2 MPa versus 80.1 MPa in CM with SiC) and elastic modulus (4 GPa versus 3.4 GPa in CM with SiC). This difference is 6.4% for strength and 17.6% for elastic modulus in favor of CM filled with  $\text{Cr}_2\text{O}_3$  particles.

The advantage of CM with  $\text{Cr}_2\text{O}_3$  is especially noticeable when comparing heat resistance indicators: at 10 wt.% it provides an increase in heat resistance to 360 K, but at 15 wt.% the value of 364 K was obtained, while CM with SiC demonstrates maximum heat resistance only up to 362 K at 15 wt.%. The difference in mechanisms is due to the better adhesion of  $\text{Cr}_2\text{O}_3$  to the epoxy matrix due to its surface chemical properties.

$\text{Cr}_2\text{O}_3$  particles form a greater number of physicochemical bonds with the functional groups of the polymer, which provides a more effective counteraction to the influence of external stresses. In addition,  $\text{Cr}_2\text{O}_3$  demonstrates better thermostabilizing properties due to higher heat resistance and the ability to create more effective thermal barriers.

Economic analysis also indicates in favor of  $\text{Cr}_2\text{O}_3$ , since its effectiveness at lower concentrations allows to reduce the costs of composite production. Thus, despite similar strengthening mechanisms, chromium oxide demonstrates higher efficiency as a microfiller for epoxy composites compared to silicon

carbide. This advantage is manifested in a more significant increase in mechanical characteristics and heat resistance, which makes  $\text{Cr}_2\text{O}_3$  a more promising material for creating high-performance structural composites.

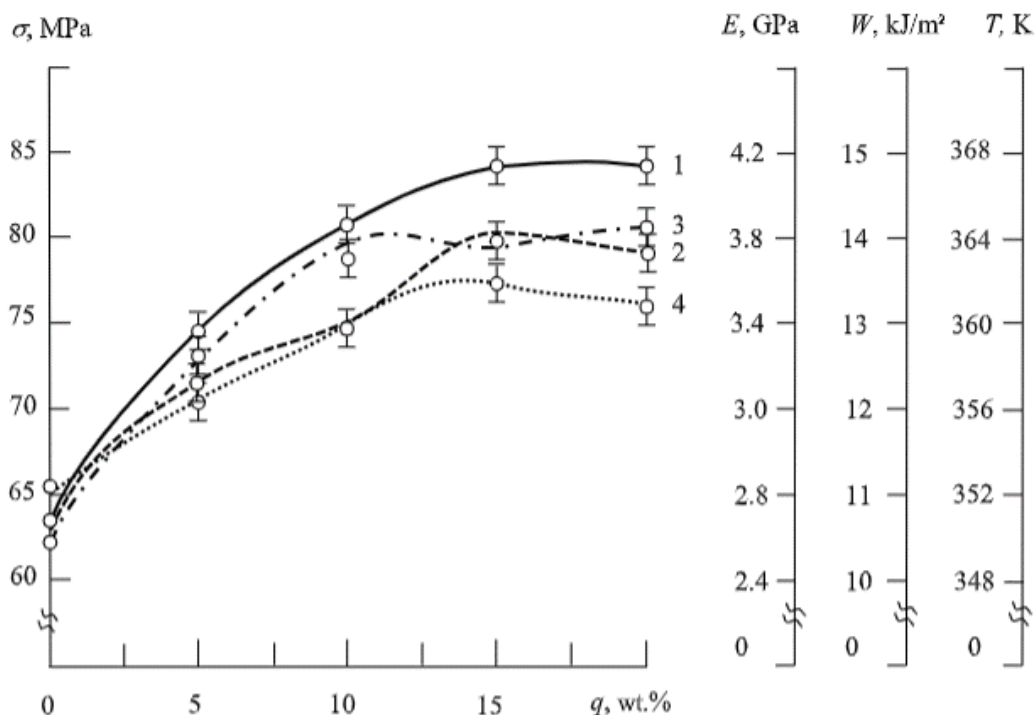


Fig. 2. Dependence of the cohesive properties of CM on the content of silicon carbide microfiller: 1 – fracture stress ( $\sigma$ ); 2 – modulus of elasticity ( $E$ ); 3 – impact strength ( $W$ ); 4 – heat resistance ( $T$ ).

### Conclusions.

1. Microfillers ( $\text{Cr}_2\text{O}_3$  and SiC) demonstrate high efficiency at a significantly higher (compared to nanoadditives) content in composites (10...15 wt.%). The best results are characteristic of the material with chromium oxide, which at a content of 15 wt.% ensures the formation of CM with values of tensile strength (88.3 MPa), elastic modulus (4.2 GPa) and heat resistance (364 K). The mechanism of improving properties is that microdispersed particles form a structural framework that creates barriers to crack propagation (i.e., cohesive strengthening of the material occurs). For composites with  $\text{Cr}_2\text{O}_3$ , the formation of additional physicochemical bonds with the matrix is also key, which ensures the thermal stability of new materials.

2. Comparative analysis of microfillers confirms the advantage of using chromium oxide compared to silicon carbide to improve the properties of epoxy composites. At a concentration of 10 wt.% chromium oxide provides 6.4% higher strength of materials (85.2 MPa vs. 80.1 MPa) and 17.6% higher modulus of elasticity (4 GPa vs. 3.4 GPa) compared to composites filled with silicon carbide. This advantage is due to better adhesion to the matrix and the ability to form physical, covalent and ionic bonds at the interface.

3. The synergistic effect of combining the plasticizer DEG-1 (12 wt.%) with fillers of different size classes allows for a controlled modification of the composite structure: microparticles ( $\text{Cr}_2\text{O}_3$ ) form a volumetric reinforcing framework, which increases the stiffness and heat resistance of the composites. This opens up prospects for the creation of new hybrid composites with predicted properties.

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