Методом квантово-хімічного моделювання досліджені міжмолекулярні взаємодії у композитах на основі епоксиамінного сітчастого полімеру і дисперсних оксидів різної хімічної природи Al_2O_3, Fe_2O_3, TiO_2, CaO. Встановлені закономірності впливу кислотно-основних характеристик наповнювачів на міжмолекулярні взаємодії та просторову конформацію полімерів. Виявлені залежності структурних параметрів та властивостей композитів від дисперсності і щільності упаковки частинок наповнювачів у полімерній матриці

Ключові слова: міжмолекулярні взаємодії, епоксиамінний полімерний композит, дисперсний оксидний наповнювач, кислотно-основні властивості

Методом квантово-химического моделирования исследованы межмолекулярные взаимодействия в композитах на основе эпоксиаминного сетчатого полимера и дисперсных оксидов разной химической природы Al_2O_3, Fe_2O_3, TiO_2, CaO. Установлены закономерности влияния кислотно-основных характеристик наполнителей на межмолекулярные взаимодействия и пространственную конформацию полимеров. Определены зависимости структурных параметров и свойств композитов от дисперсности и плотности упаковки частиц наполнителей в полимерной матрице

Ключевые слова: межмолекулярные взаимодействия, эпоксиаминный полимерный композит, дисперсный оксидный наполнитель, кислотно-основные свойства

RESEARCH OF THE INTRAMOLECULAR INTERACTIONS AND STRUCTURE IN EPOXYAMINE COMPOSITES WITH DISPERSED OXIDES

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1. Introduction

Composites based on epoxyamine compositions, filled with dispersed fillers, are one of the most common types of polymer composite materials (PCM) in the construction industry [1–5]. This is due to the unique complex of technological and operational properties and almost unlimited possibilities for the modification of epoxyamine compositions.

Physical-chemical modification of polymers with dispersed mineral fillers of oxide nature is the most affordable way to create new epoxyamine PCM. In this case, it is possible to obtain materials with special properties – glues, mastic, coverings, restoration, sealing and injectable formulations, paint and varnish materials, binders for glass plastics and basalt plastics [6–9]. Adding dispersed oxides makes it possible to adjust technological properties of compositions [1, 5], as

well as to improve physical-mechanical and operational characteristics of PCM [2, 6, 10]. Studying the regularities of the influence of dispersed oxides on the structure and properties of epoxyamine-filled compositions solves a task on the development of new multifunctional PCM for construction sector.

2. Literature review and problem statement

When using epoxyamine compositions for building materials, it is necessary to add inorganic oxide fillers of different chemical nature. Inorganic dispersed materials based on oxides SiO_2, Al_2O_3, Fe_2O_3, TiO_2, Cr_2O_3, etc. are used for epoxy materials. In this case, cost and flammability of PCM decrease and possibility to regulate majority of technological and operational properties in a wide range appears [11–14]. Regulation of properties of PCM is believed to be associated with completeness of adhesive contact and wetting at the boundary, separating phases "epoxy polymer – filler". In this case, the nature and properties of surface oxides are virtually not considered. At the same time, the structure of epoxypolymer grid was found to change under the influence of surface functional groups (active centers) of fillers [15–21]. It is known that a certain number of surface active centers (hydroxyl-hydrate layer) with different acidity function are found on the surface of mineral oxides [22, 23].

Analysis of the literature indicates that the influence of the fillers' surface on intermolecular interactions, structure and properties of polymer composite is made over the entire technological cycle and is divided into three stages:

– at the first stage, there is an impact on spatial orientation and motion of molecules of oligomers and hardeners in viscous-fluid state of the composite (impact on rheological properties) [18–21, 24];

– at the second stage, there is catalytic or inhibiting influence of the surface-active centers on processes of reticular structure formation at transition from viscous-fluid to glassy state (impact on rheokinetic properties and molecular structure of reticular polymer) [15–17, 25 26];

– at the third stage, there is formation of intermolecular interactions between functional surface groups of fillers and the polymer grid in glassy state (impact on spatial orientation of grid's fragments and properties of composites).

An integrated gradual influence of the surface layer of a filler needs to be studied at each of the stages of formation of polymer composite material. This will help to predict operation, physical-chemical and other properties of filled composites.

At the first stage, in epoxypolymer composites there is spatial orientation of molecules of oligomers and hardeners under the influence of the filler's surface. These processes are a consequence of acidic-basic, electrostatic, dipole-dipole, donor-acceptor and other interactions between relevant functional groups on the surface of phases' separation. In papers [19–21], it was noted that the influence of dispersed fillers on the properties of epoxy composites is due to formation of boundary layers (adsorption and orientation) on the surface of separation of phases between a polymer and a filler. In a solid composite, the structure of interphase polymeric layers is fundamentally different from the matrix of reticular epoxypolymer and at certain large dimensions determines properties. According to data of [20], existence of oxides Al_2O_3 and Fe_2O_3 significantly affects the processes of structure formation in composites based on ED-20 and

triethylegridetramine (TETA). A decrease in temperature of glass transition of filled polymers was found to be the result of intense interphase interaction due to hydrogen and donor-acceptor bonds. It was established that because of more intensive interactions with Al_2O_3 in composites, the influence of the surface is the greatest. Similar results were obtained in paper [24]. With the use of the method of quantum-chemical simulation, in article [18], values of energy of interactions between epoxy resin based on diglycidyl ether bisphenoid A and oxides Al_2O_3, SiO_2 and SiC were obtained. It was found that surface of Al_2O_3 forms the structures with the strongest bonds with epoxy resin. This is experimentally proved by research into wear resistance of materials. But the authors did not take into account the fact that on the surface of oxides, there exist a certain number of OH-groups, the nature of which may significantly affect the mechanism of interphase interactions. Thus, it was established that at the first stage of the influence of the oxide filler's surface on the properties of epoxy composites, the main factor is chemical nature of oxides.

Catalytic or inhibiting effect of the surface-active centers of the filler is associated with the nature and acidic power. The authors of [25], explored the influence of polymineral oxide fillers on activation energy and the rate of reaction of cross-link of epoxy oligomer by polyethylene polyamine (PEPA). It was established that existence of OH-groups of hydroxyl-hydrate surface layer of fillers causes an increase in the rate of cross-link reaction at a decrease in energy of the process activation. Intensity of influence of fillers' surface was found to depend on the nature of oxide fillers and acidic-basic properties of surface OH-groups. The authors of paper [15] examined compositions based on epoxy resin ED-20 and PEPA. As fillers, they used graphite, mica, and TiO_2, which differed by nature and dimensions of the particles. It was established that addition of TiO_2 has the greatest impact on kinetics of hardening of the composition. It was indicated that the catalytic effect of TiO_2 is associated with a relatively higher concentration of surface OH-groups. Catalytic activity of surface OH-groups of aluminum oxide γ-Al_2O_3 on the process of revealing of the constructive cycle was experimentally established by the authors in [16, 17]. It was found that between the surface of OH-groups γ-Al_2O_3 with acidity indicators $pK_a \approx 4$ and epoxy group, there may be a chemical bond, which causes sealing of the structure and an increase in the strength of epoxypolymer composites. It was shown that chemical interaction does not occur between the surfaces of α-Al_2O_3, Fe_2O_3, SiO_2 and epoxypolymer, and modification effect is associated with formation of hydrogen bonds. In paper [26], the authors established that the centers (OH-groups with different acidity function) of the surface of polymineral oxide fillers influence the process of formation of reticular structure of epoxyamine grid, and the number of cross-links is directly proportional to total concentration of surface active centers of the filler. It was shown that in the filled composites, the number of effective cross-link nodes and formation of the structure of a polymer layer is determined by total concentration of surface active centers of the filler and acidic power. Thus, it is possible to conclude that at the second phase of impact of the fillers' surface on the structure of epoxy composites, the main factor is the number and acidic-basic characteristics of the surface-active centers of oxide fillers.

Thus, in the course of analysis, it was found that the majority of scientific research explore the influence of the nature

of oxide fillers at the first and the second stages of composite formation. The processes that occur at the third stage are practically unexplored. Obviously, this is due to the fact that intermolecular interactions happen in glassy condition and proceed very slowly. Actually, an interaction between the surfaces of the two solid phases occurs due to formation of non-covalent bonds between the surface functional groups. As a result, low energy weak bonds are formed. That is why experimental research into the nature and characteristics of these processes is complicated and there arises the need to use the methods of quantum-chemical simulation. In addition, in well-known works, the authors do not take into account that active centers of the surface of oxides that form hydroxyl-hydrate layer are mostly represented by Brensted OH-groups with a different acidity function. In this case, possible acidic-basic character of interphase interactions is not taken into consideration.

Thus, the unresolved problem is the problem of the influence of the nature and characteristics of oxide fillers on the structure and properties of epoxyamine polymer at the stage of formation of intermolecular bonds in glassy state. In addition, given the existence of surface functional groups, the role of the acidic-basic factor in intermolecular interactions on the surface of phases' separation was not established. To address above mentioned issues, the approach, which includes theoretical methods of quantum-chemical simulation of molecular systems and indirect experimental tests, is considered appropriate.

dening continued at temperature 373 K for 4 hours. Filled compositions were prepared in the following technological sequence. Resin ED-20 was mixed with hardener DETA at stoichiometric ratio to get homogeneous mixture. In this case, viscosity of resin decreased. After that, the filler at amount of 10 vol. % was added to epoxyamine system and stirred till homogeneous mixture. Oxide fillers were air-dry dispersed materials based on oxides of different chemical nature Al_2O_3, Fe_2O_3, TiO_2, CaO. Specific surface of fillers was determined by the BET method (Brunauer, Emmett, Teller). For selected fillers, the study of morphology, surface and dimensions of particles was conducted with the use of electronic-microscopic images, made by scanning electronic microscope of JSM-6390LV make. X-ray phase analysis was performed on the X-ray diffractometer DRON-2. Acidity function of the active centers, prevailing on the surface of the fillers, was determined by potentiometric measurement of pH_{susp} in water with the method that is described in [27]. The studied properties of the oxide fillers are shown in Table 1.

Table 1

Properties of dispersed oxide fillers

Filler	Specific surface, S_{sp}, m^2/g	pK_a of active centers	Mineral composition
Rutile GOST (State Standard 22938-78) (RT)	1.30	8.16–8.49	Rutile (TiO_2) Anatise (TiO_2)
Alumina non-metallurgic GOST (State Standard 30559-98 (AL)	20.00	9.05–9.50	Corrundum (α-Al_2O_3) Alumina (γ-Al_2O_3)
Calcite GOST (State Standard 4530-76 (CL)	7.95	9.42–10.46	Calcite ($CaCO_3$)
Hematite* TU U 8785-028-200 (HM)	11.35	9.70–11.40	Hematite (α-Fe_2O_3) Goethite (FeOOH)

Note: * – limonite, four calcium alumoferrite and ettringite were found as related minerals

3. The aim and objectives of the study

The aim of present research is to explore the influence of oxide fillers of different chemical nature Al_2O_3, Fe_2O_3, TiO_2, CaO on the structure and properties of epoxyamine polymer compositions. This will make it possible to predict and adjust operation characteristics of filled composites.

To accomplish the set goal, the following tasks were formulated:

– to explore intermolecular interactions between epoxyamine grid and oxide fillers of different chemical nature by the method of quantum-chemical modeling;

– to establish relationship between the nature and the strength of intermolecular bonds, the structure and properties of composites.

4. Materials and methods of research

We selected as materials for research the filled polymer compositions based on epoxy resin of ED-20 brand (DSTU 2093-92) and stoichiometric amount of aliphatic amine hardener diethylegridriamine of DETA brand (TU 6-02-91486). The composition hardened in the air (293–298 K) for not less than 72 hours. After that, har-

With development of software for molecular modeling, the possibility to explore spatial understanding of mutual orientation of molecules in self-organized systems and on the surface of separation of phases appeared. Within these programs, it is possible by calculation to establish energy, kinetic and thermodynamic parameters of interactions that give an idea of chemical nature of various model systems [28].

In the work, the studies of interactions on the surface of phases' separation were carried out using the HyperChem software package for molecular modeling for chemical systems. This software package uses widely known empirical methods of molecular mechanics, as well as non-empirical and semi-empirical methods in molecular chemistry.

The method of semi-empirical calculation PM3, which allows obtaining the best results for large hydrocarbon systems, was selected as the basic method. In paper [29], it was found that results of calculation under this method are adequate.

Chemical resistance of composites to water and aqueous solutions was studied by the method of immersion of samples in aggressive water medium. The tests were carried out at temperature of 298 K±5, followed by calculation of relative increase in the mass of the sample over a period of time (GOST 4650-80 and GOST 12020-72).

4. Quantum-chemical modeling of intermolecular interactions between epoxyamine grid and oxide fillers

For modeling of interactions between epoxyamine reticular polymer and the surface of oxides of different chemical nature, a fragment of the grid, which was formed as a result of reaction of cross-link of two ED-20 molecules and one DETA molecule, was used (Fig. 1). To take into consideration the influence of hydroxyl-hydrate surface layer of fillers' particles, molecules of hydroxides of metals $Al(OH)_3$, $Fe(OH)_3$, $Ti(OH)_4$, $Ca(OH)_2$ were used as models. The studied molecular complexes consisted of a fragment of the grid (EP) and a molecule of hydroxide. Fig. 2 shows 3-D models of the fragment of epoxyamine grid and molecular complexes, constructed with the use of HyperChem software package with the function of geometric optimization.
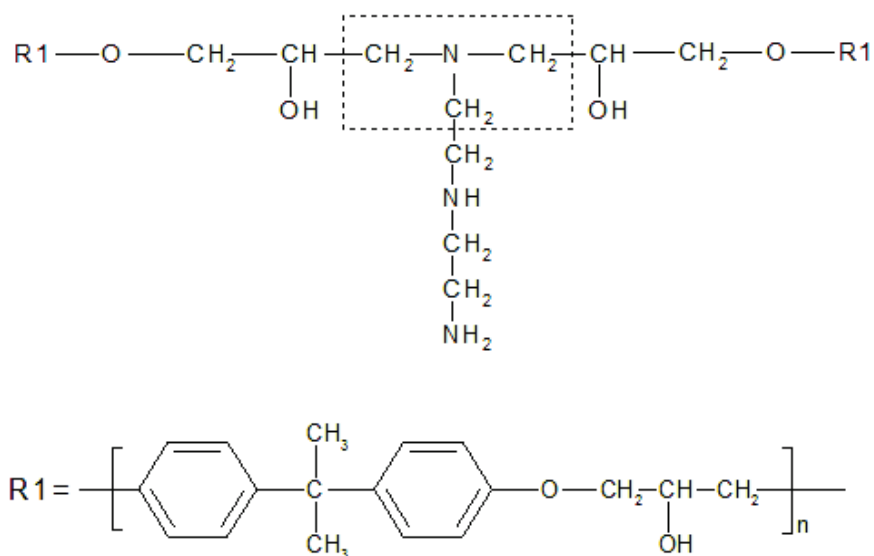
Fig. 1. Fragment of the grid of epoxyamine polymer
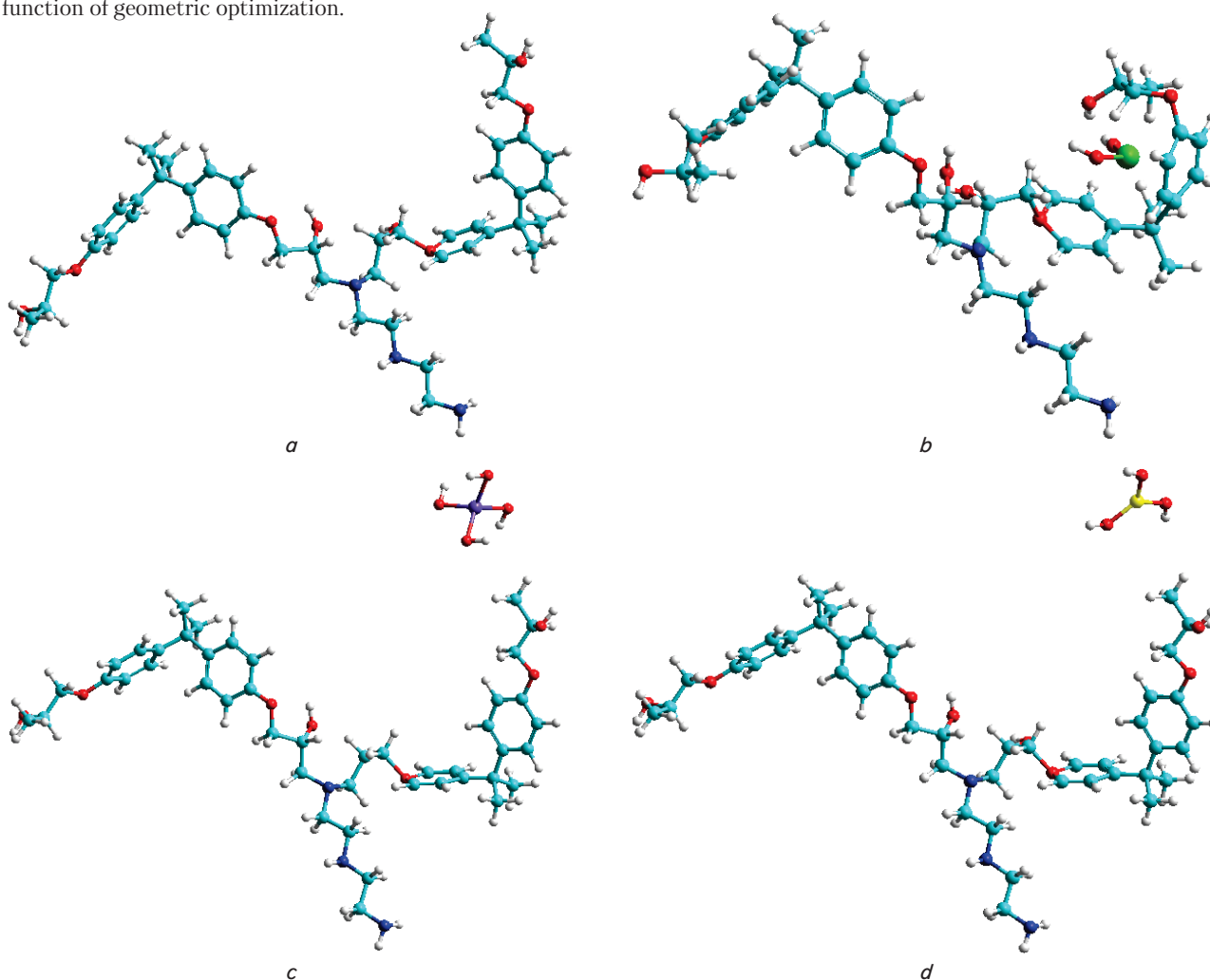
Fig. 2 3-D models of:
a — fragment of epoxyamine grid EP, b — molecular complex EP+Ca(OH)$_2$, c — EP+Ti(OH)$_4$,
d — EP+Al(OH)$_3$ with conditional designations of atoms ● — C; ● — O; ● — H; ● — N; ● — Ti; ● —Ca; ● — Al

As a result of modeling, we obtained the values of intermolecular distance and dipole moments (μ) of molecules and molecular complexes, enthalpic formation (ΔH_{form}) and energy of interaction (E_{int}) of molecules in the complexes. Energy of interaction in the complexes was determined from the following formula:

$$A+B \leftrightarrow AB;$$

$$E_{int} = \Delta H_{form}(AB) - [\Delta H_{form}(A) + \Delta H_{form}(B)].$$

Calculation results are shown in Table 2.

Table 2

Energy and dimensional parameters of molecules and molecular complexes

Complex	ΔH_{form}, kJ/mol	E_{int}, kJ/mol
Fragment of grid (EP)	−1,522.4	–
Ti(OH)$_4$	−1,170.7	–
EP+Ti(OH)$_4$	−1,931.8	181.9
Ca(OH)$_2$	−872.3	–
EP+Ca(OH)$_2$	−3,603.6	−288.7
Al(OH)$_3$	−949.1	–
EP+Al(OH)$_3$	−1,710.1	181.9
Fe(OH)$_3$	−1,515.0	–
EP+Fe(OH)$_3$	−2,276.3	181.8
Complex	Distance between molecules, Å	Dipole moment, μ, D
Fragment of grid (EP)	–	6.15
Ti(OH)$_4$	–	0.15
EP+Ti(OH)$_4$	5.9	6.20
Ca(OH)$_2$	–	0.07
EP+Ca(OH)$_2$	1.7−2.5	4.50
Al(OH)$_3$	–	2.37
EP+Al(OH)$_3$	5.6	8.14
Fe(OH)$_3$	–	3.18
EP+Fe(OH)$_3$	3.2−3.9	9.08

As a result of quantum-chemical modeling with the use of HyperChem software package, the following energy and dimensional parameters of molecules and molecular complexes were obtained. Selected systems give an idea of possible intermolecular interactions and formation of non-covalent bonds on the surface of separation of phases in epoxyamine polymer composites.

5. Experimental research into chemical resistance of samples of the filled polymer composites

For verification of the results of quantum-chemical modeling, the tests of resistance of filled composites in water and aqueous solutions were conducted. Distilled water and 0.1 nNaOH and

H_2SO_4 solutions were used as aggressive media. Dependences of an increment in mass $\Delta m = (m_0 - m) \cdot 100/m_0$ on time τ of keeping of samples in aggressive media were studied. The test results are presented in Fig. 3 and in Table 3.

To take into consideration the influence of parameters of dispersed structure of fillers, in the research, the distances between the particles in dispersed-filled polymer composites were calculated from formula:

$$a = d \cdot [(K/\omega)^{1/3} - 1],$$

where a is the distance between particles of the filler, μm; d is the size (diameter) of particles, μm; K is the coefficient that characterizes package density of the filler's particles; ω is the volumetric share of the filler in composite material (0.1). Calculation results are presented in Table 4.
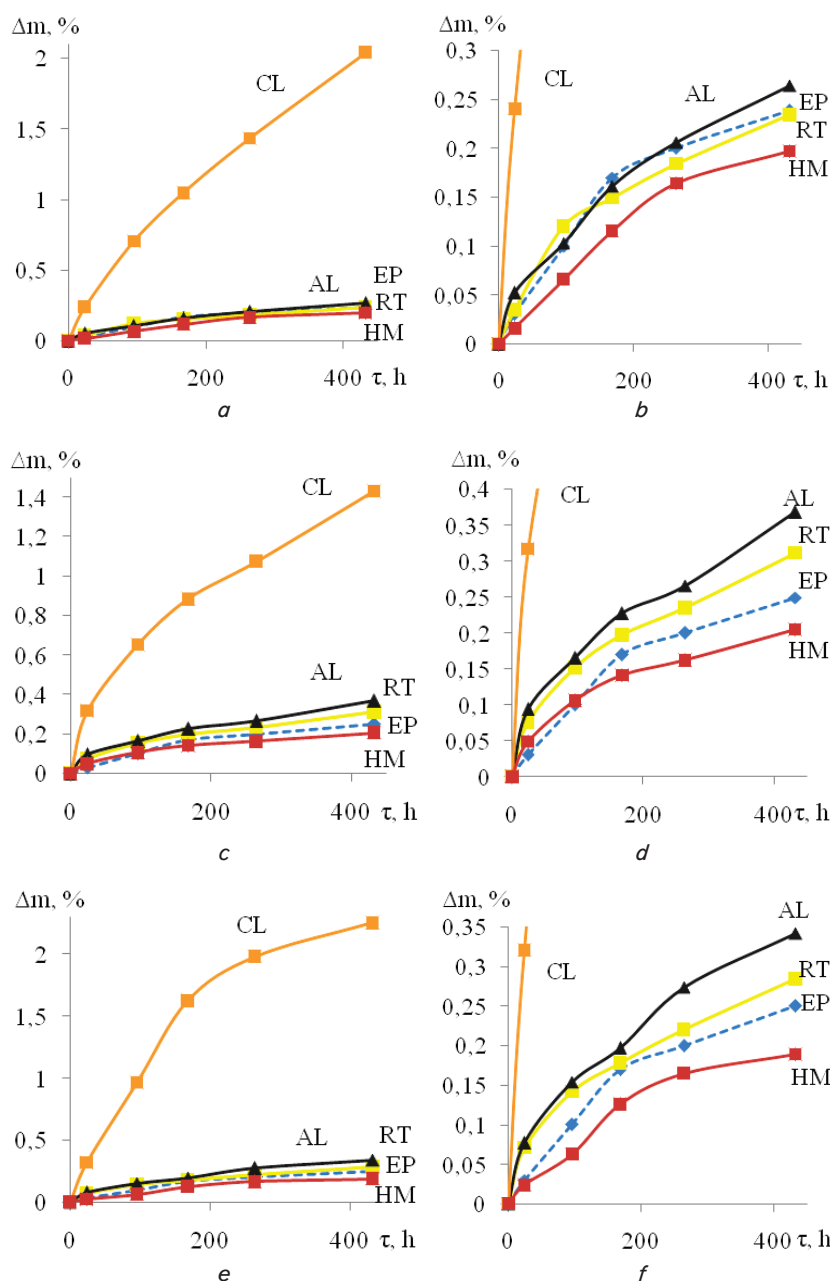

Fig. 3. Dependences of an increment in mass Δm on duration τ of keeping samples in: a, b — distilled water, c, d — 0,1 nH$_2$SO$_4$ solution; e, f — 0,1 nNaOH solution

Table 3

Increment in mass after 600 hours of keeping in aggressive medium

Samples of composites	Increment in mass of sample Δm, %		
	H_2O	H_2SO_4	NaOH
EP	0.29	0.26	0.28
EP+CL	2.22	1.64	2.34
EP+AL	0.32	0.43	0.41
EP+RT	0.27	0.33	0.29
EP+HM	0.21	0.24	0.24

Table 4

Parameters of disperse structure fillers in the filled composites

Filler	Mean diameter of particles d, μm	Package co-efficient, K	Distance between particles, a, μm
CL	30	0.82	60.80
AL	55	0.83	111.27
RT	10	0.63	18.51
HM	3	0.58	5.40

The distance between the particles of the filler a is the parameter that describes dimensions of the element of dispersed structure that is repeated in the composite material with cubic package of particles [21].

6. Discussion of results of studying the influence of oxide fillers of different chemical nature on the structure and properties of epoxyamine polymer compositions

As Fig. 2a of the model shows, a fragment of the epoxyamine grid is rather non-symmetrical and has a spatial configuration of a high dipole moment μ=6.15 D. The rest of the molecule of diethylegridriamine is located between residues of ED-20 molecules that repel. Obviously, the residues of ED-20 molecules, which contain benzene rings with delocalized π-bond, repel from nitrogen atoms of DETA residue.

By comparing resulting energy and dimensional parameters of the molecular complexes between EP and hydroxides of metals of different chemical nature, it is necessary to note significant influence of the nature of metal (Table 2). Molecular complexes with dipole moment, which is more than μ of individual molecules, are formed at interaction in most cases. Thus, dipole moment of complex EP+Fe(OH)$_3$ (μ=9.08 D) is 1.5 times as high as dipole moment of EP (μ=6.15 D) and 3 times as high as dipole moment of Fe(OH)$_2$ (μ=3.18 D). Dipole moments of complexes EP+Ti(OH)$_4$ and EP+ Al(OH)$_3$ exceed μ of source molecules as well. In the case of EP+Ca(OH)$_2$, on the contrary, dipole moment of the complex (μ=4.50 D) is by 1.4 times less than dipole moment of EP, but by 2 orders of magnitude larger than μ of Ca(OH)$_2$. Obviously, it is connected with the fact that compared with metals of amphoteric nature (Ti, Fe, Al), Ca is strong alkaline-earth. It is characteristic that in this complex the distance between molecules is the least (1.7–2.5 Å), and interactions are the strongest (E_{int}=−288.7 kJ/mol). This is due to the fact that a molecule of Ca(OH)$_2$ interacts with EP by a fundamentally diffe-

rent mechanism from hydroxides Ti(OH)$_4$, Al(OH)$_3$ and Fe(OH)$_3$. Thus, Fig. 2, b shows that existence of a Ca(OH)$_2$ molecule causes a change in special conformation of the grid's fragment. Calcium atom is oriented to π-electron cloud of benzene ring with formation of donor-acceptor bond. At the same time, OH-groups of calcium hydroxide form hydrogen bonds with OH-groups of the residue of a ED-20 molecule. This conclusion follows from the values of the measured distance between a Ca(OH)$_2$ molecule and EP, which are compared to the length of hydrogen bond, equal to about 3 Å. In general, it should be noted that calcium hydroxide has the greatest influence on spatial conformation of epoxyamine fragment and causes substantial changes in all energy and dimensional parameters of the grid.

As a result of geometric optimization of molecular complexes, it was established that hydroxides Ti(OH)$_4$, Al(OH)$_3$ and Fe(OH)$_3$ are oriented by hydroxylic groups to OH-groups of the grid's fragment. In this case, they are located on the opposite side from the residue of a diethanolamine molecule (Fig. 2, c−e). Location like this is, obviously, the most energy- and spatially conditioned by conformation. The values of enthalpies of formation of the studied molecules and molecular complexes are negative (Table 2). Absolute values of ΔH_{form} complexes are by 1.5–4 times higher than ΔH_{form} of separate molecules. In other words, intermolecular interactions between the studied molecules are energetically predefined. At the same time, obtained results of modeling make it possible to argue that interactions between the hydroxides of amphoteric metals and epoxyamine grid are weak and low-energy. The distances between EP and metal hydroxides are small (3.2–5.9 Å) and are comparable with the distance, which are characteristic for formation of a hydrogen bond (about 3 Å). Energy of interaction of hydroxides Ti(OH)$_4$, Al(OH)$_3$ and Fe(OH)$_3$ and EP grid fragment have close values at different distances between molecules in complexes. Small values of energies of interaction at sufficiently high values of dipole moments (μ=6.20–9.08 D) indicate formation of low-energy inductive and, possibly, dipole-dipole (orientationally) intermolecular interactions. The obtained data show that existence of amphoteric hydroxides does not cause a change in spatial conformation of the EP fragment (Fig. 2, c−e). From results of quantum-chemical modeling, it follows that ability of metal hydroxides affect the conformation of a fragment of the epoxyamine grid increases in the series: Ti(OH)$_3$<Al(OH)$_3$<Fe(OH)$_3$<Ca(OH)$_2$. This series coincides with the series, in which basic properties increase (acidic properties weaken) of the active Branstad centers (OH-groups) with the central elements: Ti^{4+}<Al^{3+}<Fe^{3+}<Ca^{2+} [22]. There is also correlation with pK_a of active centers that prevail on the surface of the fillers (Table 1).

Thus, as a result of quantum-chemical modeling, it was found that the influence of the oxide filler on the structure and spatial conformation of epoxyamine grid depends on the surface acidic-basic properties and increases at an increase of basic (alkaline) properties of an oxide due to strong intermolecular interactions (formation of hydrogen and donor-acceptor bonds), the spatial conformation of epoxyamine grid changes significantly. It was shown that between OH-groups of the surface of oxides of amphoteric nature and the epoxyamine grid, weak low-energy bonds of orientation and induction character are formed. In this case, spatial conformation of the grid's fragment does not change. In general, we can conclude that the nature and energy of intermolecular bonds,

which affect the structure of epoxyamine polymer composites, are determined by surface acidic-basic properties and the chemical nature of the oxide filler.

The obtained results of experimental research into chemical resistance (Fig. 3, Table 3) show a significant effect of oxide fillers on an increment in the mass of filled epoxyamine polymers after keeping in aqueous media. Composite, filled with calcite (EP+CL) differs from the others, and compared with the non-filled, reveals the least resistance to the influence of all media. Addition of calcite reduces resistance of polymer composite to H_2O by 8.5 times, to H_2SO_4 solution – by 5.7 times, and to NaOH solution – by 9 times. Obviously, low chemical resistance of composite with calcite is due to the fact that, as it was determined, existence of calcium oxide affects spatial conformation of an epoxyamine fragment and all energy and dimensional parameters of the grid. As a result of strong intermolecular interactions between epoxyamine grid and the surface of calcium oxide, composites of heterogeneous structure and non-homogeneous distribution of compacted areas are formed. In addition, existence of strong intermolecular interactions may be the cause of formation of internal stresses in the composite. All these factors obviously cause a decrease in chemical resistance of composites.

The results of chemical resistance of composites EP+AL, EP+RT, EP+HM are close to resistance of non-filled polymer EP. Influence of fillers on chemical resistance of composites is ambiguous and cannot be attributed to the acidic-basic properties of the oxide filler. This may be due to the fact that selected oxides Al_2O_3, Fe_2O_3, TiO_2 are amphoteric and acidic-basic properties of the surface-active centers are close [23]. Thus, it is evident that views about the acidic-basic properties of fillers for explanation of the influence of amphoteric oxides on chemical resistance of filled polymer composites are not sufficient.

When acidic-basic properties of dispersed oxides are close, it is necessary to consider the effect of parameters of dispersed structure: specific surface, dispersion (dimensions of particles), package coefficient. These factors are believed to affect the structure, density and dimensions of the interphase polymeric layer, which determines most of operation and physical-chemical properties of composites [21, 30]. Calculation results (Table 4) show that parameter a of composites, which characterizes package density of a filler in the polymer matrix, increases in the series of composites EP+HM (5.40)<EP+RT (18.51)<EP+AL (111.27). This series coincides with the series, in which resistance of filled composites increases in all aggressive media. As a result, we can prove the assumption of decreasing possibility of pegridration of molecules of aggressive medium at an increase in package density of the filler in the material, which is related to extension of the diffusion path. It should be noted that the calculated parameter a in the composite with calcite EP+CL (60.80) is 2 times as low as in composite EP+AL (111.27). In addition, chemical resistance of EP+CL is three times as low. This fact once again proves the previously made conclusions. In this case, the factor of acidic-basic properties of a filler prevails.

Thus, as a result of the conducted studies, it was found that at interaction between the epoxyamine grid and the surface of oxide fillers in a glassy state, non-covalent low-energy bonds are formed. Interactions occur between the functional groups of the reticular polymer (OH-groups, benzene rings with delocalized π-bond) and OH-groups of hydroxyl-hydrate layer of the oxides' surface. The main factors that affect

characteristics of intermolecular bonds, conformation structure and chemical resistance of composites are acidic-basic properties, dispersion and package density of particles of the filler in the polymer matrix.

Obtained regularities do not take into account existence of plasticizers, solvents, accelerators and other low-molecular components, which are usually contained by epoxy composite polymeric materials. It is obvious that existence of these substances significantly affects the considered phenomena and needs additional research. On the other hand, the resulting information can be used to select these components, and, accordingly, regulation of the structure and properties of composites. It should be noted that the present research is limited to oxide fillers. But it is known that filled epoxy composite materials can include polymineral clay (aluminosilicate), carbon (soot, graphite) and dispersed materials, different by chemical nature. Similar studies in above systems are relevant and are of theoretical and practical interest.

7. Conclusions

1. Using the method of quantum-chemical modeling, research into intermolecular interactions between epoxyamine grid and oxides of different chemical nature was carried out. In order to take into account a hydroxyl-hydrate surface layer of oxides, molecular complexes of the fragment of the epoxyamine grid and metal hydroxides $Al(OH)_3$, $Fe(OH)_3$, $Ti(OH)_4$, $Ca(OH)_2$ were used as models. As a result of modeling, it was found that $Ca(OH)_2$ molecule forms strong intermolecular bonds and has the greatest influence on the spatial conformation of an epoxyamine fragment. It was shown that a calcium atom is oriented to π-electron cloud of benzene ring with formation of donor-acceptor bond. In this case, OH-groups of calcium hydroxide form hydrogen bonds with OH-groups of the residue of ED-20 molecule in the grid. The studied intermolecular interactions of epoxyamine grid and hydroxides of amphoteric metals $Al(OH)_3$, $Fe(OH)_3$, $Ti(OH)_4$ indicate formation of low-energy inductive and, possibly, dipole-dipole (orientation) connections. It was established that existence of amphoteric hydroxides does not cause a change in the spatial conformation of the fragment of the grid. The ability of metal hydroxides to affect the structure of a fragment of epoxyamine grid was found to increase in the series: $Ti(OH)_3<Al(OH)_3<Fe(OH)_3<Ca(OH)_2$. The resulting series completely coincides with the series, in which basic properties of active Branstad centers (OH-groups) with the central elements $Ti^{4+}<Al^{3+}<Fe^{3+}<Ca^{2+}$ increase (acidic properties decrease). It was shown that the influence of the oxide filler on the structure and spatial configuration of the epoxyamine grid depends on the surface acidic-basic properties and increases at an increase in basicity (alkalinity) of an oxide.

2. As a result of experimental research into epoxy composites, filled with dispersed oxide fillers, it was found that resistance of composites to aqueous aggressive media depends on acidic-basic properties, dispersion and package density of particles of oxide fillers. It was found that at addition of strongly basic oxides (calcite), chemical resistance of composites changes by 5–9 times. In this case, obviously, composites of heterogeneous structure and non-homogeneous distribution of compacted areas are formed. Existence of strong intermolecular interactions may cause formation of internal stresses in the composite. It was found that when

adding amphoteric oxides of rutile (RT), alumina (AL) of hematite (HM), the main factors that affect chemical resistance of filled composites are dispersion and package density of particles of the filler in the polymer matrix. Calculation parameter *a* of composites, which characterized package density of the filler in the polymer matrix, increases in the series of fillers HM<RT<AL. This series coincides with the series, in which resistance of filled composites in all aggressive media decreases. It is obvious that with an increase in package density of the filler, possibility of pegridration of molecules of aggressive environment into the material decreases, which is associated with extension of the diffusion path.

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Виконано порівняльні дослідження триботехнічних характеристик полімерного композитного матеріалу «Moglice» і розробленого матеріалу ДК-6. Випробування виконувалися на парах тертя «чавун – моглайс» і «чавун – ДК-6». Дослідження необхідні для практичного застосування матеріалів ДК-6 або «Moglice» при відновленні зношених поверхонь тертя. Отримано позитивні результати порівняльних випробувань полімерного композитного матеріалу ДК-6 в порівнянні з «Moglice»

Ключові слова: напрямні ковзання верстатів, триботехнічні характеристики, полімерні композитні матеріали, коефіцієнт тертя

Выполнены сравнительные исследования триботехнических характеристик полимерного композитного материала «Moglice» и разработанного материала ДК-6. Испытания выполнялись на парах трения «чугун – моглайс» и «чугун – ДК-6». Исследования необходимы для практического применения материалов ДК-6 или «Moglice» при восстановлении изношенных поверхностей трения. Получены положительные результаты сравнительных испытаний полимерного композитного материала ДК-6 по сравнению с «Moglice»

Ключевые слова: направляющие скольжения станков, триботехнические характеристики, полимерные композитные материалы, коэффициент трения

TRIBOTECHNICAL RESEARCH INTO FRICTION SURFACES BASED ON POLYMERIC COMPOSITE MATERIALS

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1. Introduction

A decrease in the operation resource of machinery caused by wear is a serious problem. In technically advanced countries the cost of repair and maintenance of machinery makes up 10...15 % (up to 25 %) on average of the cost of equipment per year. For machines operating under particularly difficult conditions, the cost of major repairs reaches 50 % of their price.

A larger part of machine parts (80...85 %) fail due to intensive wear. At the same time, correct application of