- Bondar, A. G. Planirovanie eksperimenta pri optimizacii processov himicheskoj tehnologii [Text] / A. G. Bondar, G. A. Statjuha, I. A. Potjazhenko. – Kyiv: Vishha shkola, 1980. – 264 p.
- 17. Emelina, A. L. Differentsialnaya skaniruyuschaya kalorimetriya [Text] / A. L. Emelina. Moscow: Laboratoriya himicheskogo fakulteta MGU, 2009. 42 p.
- Knothe, G. A comprehensive evaluation of the melting points of fatty acids and esters determined by differential scanning calorimetry [Text] / G. Knothe, R. O. Dunn // Journal of the American Oil Chemists' Society. – 2009. – Vol. 86, Issue 9. – P. 843–856. doi: 10.1007/s11746-009-1423-2
- Sytnik, N. S. DoslIdzhennya aktivnostI glitseratu kaliyu yak katalizatoru pereeterifikatsiyi zhiriv za riznih umov provedennya protsesu [Text] / N. S. Sytnik, I. M. Demydov, K. V. Kunitsa // Visnik Natsionalnogo tehnichnogo universitetu «KhPI». – 2016. – Vol. 12, Issue 1184. – P. 188–193.

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Розроблено склади і досліджені властивості низьков'язких фурано-епоксидних олігомерів, які структуровані амінними затверджувачами для використання при ремонтно-відновлювальних будівельних роботах. Визначено діапазон оптимальних параметрів структурування полімерних систем. Досліджені структурно-топологічні параметри і реакційна здатність вихідних речовин при отриманні фураноепоксидних матеріалів. Проведено дослідження міцностних, адгезійних, сорбційних властивостей розроблених низьков'язких фурано-епоксидних полімерів

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Ключові слова: фурано-епоксидний олігомер, аміновмісткий затверджувач, адгезійні, сорбційні властивості, низьков'язка система

Разработаны составы и исследованы свойства низковязких фурано-эпоксидных олигомеров, структурируемых аминными отвердителями для использования при ремонтно-восстановительных строительных работах. Определен диапазон оптимальных параметров структурирования полимерных систем. Исследованы структурно-топологические параметры и реакционная способность исходных веществ при получении фурано-эпоксидных материалов. Проведено исследование прочностных, адгезионных, сорбционных свойств разработанных низковязких фурано-эпоксидных полимеров

Ключевые слова: фурано-эпоксидный олигомер, аминосодержащий отвердитель, адгезионные, сорбционные свойства, низковязкая система

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#### 1. Introduction

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During fulfilling repairing and recovery work of the locally destroyed concrete or reinforced concrete elements of buildings and structures in the industrial and civil construction [1], the need arises of developing low-viscosity materials based on reactive monomer-oligomeric ingredients with high wetting and adhesive capacity to the dry and moist concrete and increased combination of the deformation-strength properties [2].

When creating polymeric composites, contemporary construction materials science is oriented towards priority application of the basic principles of "Green Chemistry"[3]. These principles allow designing materials and making a selection of the optimal parameters of the technological

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# DESIGNING LOW VISCOSITY FURAN-EPOXY POLYMERS OF THE MATERIALS FOR CONSTRUCTION INDUSTRY

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process of creating multicomponent polymeric composites of low viscosity at a fundamentally new technical level. In this case the targeted formation of a rational topological structure of the system is carried out at the micro-, meso- and macro structural levels of its organization.

The determining role in this process belongs to the concept, which combines technological efficiency of the process of obtaining a polymeric material, ecological safety in the operation of construction elements with a polymeric component and economic expediency of applying designed materials.

Therefore, the development and research into polymeric systems of low viscosity for the construction industry is an actual task and is a promising trend in the materials science of construction composite materials.

#### 2. Analysis of scientific literature and the problem statement

During formation of an optimal structure of a polymeric material, of crucial importance are those parameters, which characterize reactivity of monomer-oligomeric reactive systems in the process of their chemical structuring.

The application of "Green Chemistry" principles at creating polymeric composites of low viscosity for construction purposes is a topical trend in the development of contemporary materials science [4], which is implemented in the special areas of production [5].

The use of furan ingredients acquires special meaning, obtained via hydrolysis out of the renewed plant products containing pentosan, which are applied as the binders for thermo resistant nanocomposites [6] in different spheres of technological production, including polymer materials science for the construction purposes [7]. The use of these materials in the construction industry is due to their positive economic and ecological roles [8]. Special role is played by furan compounds with multiple bonds [9], capable of self-repair of structural defects [10]. Important function at formation of the rational structure of a polymeric material is played by the amine-containing structuring agents [11], influencing the nature of macromolecules of the cured reactive oligomer [12].

In spite of a rather large quantity of the publications that describe the application of furan-epoxy polymers in the construction industry, in practice there is lack of system, reliable experimental data about the set of deformation-strength, adhesive, sorption properties of polymeric systems of low viscosity, applied during the repairing and recovery work in different segments of industrial and civil construction.

It is established that the low-viscosity materials on the basis of furan-epoxy monomer-oligomeric systems, promising from the ecological, operational point of view, are not studied fully at present. In particular this is true of such aspects as the functional, structural-topological analysis (within the framework of the theory of graphs) of the main ingredients of reactive oligomer of low viscosity. There are no data about the application of "Green Chemistry" principles in the technology of formation of the composites for construction purposes on the basis of furan-epoxy polymeric materials. Existing experimental data about strength, adhesive, sorption and other properties of furan-epoxy polymeric materials with other molecular-kinetic parameters have non-systemic, at times contradictory and incomplete nature. Low-viscosity furan-epoxy polymers did not undergo any sufficient research. Additional experimental studies of the data of polymeric systems might contribute to the creation of efficient composite materials to solve vital problems when performing the repairing and recovery work in the construction industry.

3. The purpose and objectives of the study

There was certain interest in designing a material and to research into the properties of furan-epoxy reactive oligomers of low viscosity, structured by amine complex hardeners for the application as injection systems when performing the repairing and recovery construction work.

To achieve the set goal, the following tasks were tackled: - to carry out a selection of furan-epoxy polymeric systems ingredients, optimal from ecological, operational points of view, and of parameters of the technological process of creating multicomponent polymeric materials of low viscosity;

 to analyze reactivity of initial substances (monomers) taking into account the factor of its influence on the structure of a polymeric material;

 to study a combination of physical-mechanical, adhesive and sorption properties.

### 4. Materials and methods of the studies of furan-epoxy monomer-oligomeric systems

As the objects of the study we selected furan: 3-butene-2-oh-4 (2-furyl) – mono furfurylidene acetone MFA with the gross formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>, 1,5-bis(2-furyl) penta-1,4dien-3-oh - di-furfurylidene acetone DIFA with the gross formula  $C_{13}H_{10}O_3$  and the epoxy ingredients: diglycidyl ether of bisphenol A – diphenylolpropane (DHEBA) with the gross formula  $C_{21}H_{24}O_4$  (it is produced by the industry under the mark ED-24, DER-330, Epikote 827, Rutapox 0162, Epon-826, Epirez-510 and others), and also a wide range of amine containing structuring agents: ethylenediamine (EDA) with the gross formula  $C_2H_8N_2$ , diethylenetriamine (DETA) with the gross formula  $C_4H_{13}N_3$ , triethylenetetramine (TETA) with the gross formula  $C_6H_{18}N_4$ , 1-[[(2 aminoethyl) amino]metil] phenol – (ethylene diamine methylphenol) of the mark Agidol AF-2 by the gross formula  $C_9H_{14}N_2O$ , mono cyanoethyl diethylenetriamine of the mark UP-0633M - the condensation product of nitrile of acrylic acid with DETA (type A) and TETA (type B) with the corresponding gross formulas  $C_7H_{16}N_4$ and  $C_9H_{24}N_5$ , dicyano ethyl diethylenetriamine of the mark UP-0633 with the gross formula  $C_8H_{14}N_4$ , 1,3-phenylene diamine (m - phenylenediamine) - m-PDA with the gross formula C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>.

A mixture of MFA (≈30 mass %), DIFA (≈60 mass %) and other furan ingredients is produced by chemical industry under the brand "furfural acetone monomer FAM".

The studied furan-epoxy reactive oligomer (RO) is the product of a thermo mechanical combination of furfural acetone monomer FAM and bisphenol epoxy oligomer ED-24 in mass ratio 1:1. The temperature of mixing the ingredients is -60 °C, the time is -1,5 hours. RO designation: FAED-50(24).

The study of the combination of physical-mechanical, adhesive-strength and sorption properties [13], as well as other parameters of the designed furan-epoxy materials [14] was carried out by the known laboratory standardized procedures.

## **5**. Results of the study of reactivity of monomers and combination of the properties of furan-epoxy polymers

The analysis of molecular, topological structure and reactivity of parent substances (monomers) makes it possible to purposefully form the rational structure of hardened furan-epoxy reactive oligomer.

A molecular structure of the parent substances (monomers), which participate in the synthesis of furan-epoxy polymers can be described with the help of the connected graph, whose apexes are the atoms of a monomer, and the edges of the graph – bonds between these atoms. In the case of simple acyclic graph without the multiple edges-bonds, the quantity of edges T (chemical bonds) is determined by the number of its apexes A, i. e., by the number of atoms of all forms in the gross formula of the monomer in accordance with the method [15]:

$$T = A - 1. \tag{1}$$

Since

$$A = \sum_{i=1}^{i=n} a_i,$$
(2)

where  $a_i$  is the number of atoms of i - form and n - is the total number of atoms in the molecule of a monomer, then

$$\Gamma = \sum_{i=1}^{i=n} a_i - 1,$$
(3)

which is characteristic for the maximally saturated molecular structure.

The quantity of valences in the molecule the monomer N is possible to determine from the ratio:

$$N = \sum_{i=1}^{j=n} a_i \cdot N_i$$
(4)

where  $N_{\rm i}$  – is the number of valences of the atoms of the monomer  $\rm i$  – form.

The total number of valences  $N_o$ , participating in the formation of one bond (edge) of the acyclic structure of the monomer comprises:

$$N_{o} = 2T = 2\sum_{i=1}^{i=n} a_{i} - 2.$$
 (6)

The quantity of "excess" valences  $N_c$ , not participating in the formation of the maximally saturated molecular structure of the monomer, equals:

$$N_{c} = \sum_{i=1}^{i=n} a_{i} N_{i} - \left(2\sum_{i=1}^{i=n} a_{i} - 2\right) = \sum_{i=1}^{i=n} a_{i} (N_{i} - 2) + 2.$$
(7)

This "excess" of valences characterizes formal unlimitedness (formal unsaturation) of the monomer  $f_u$ , which, taking into account the fact that it takes two valences to form one bond, is evaluated according to the formula:

$$fu = \frac{\sum_{i=1}^{i=n} a_i (N_i - 2) + 2}{2},$$
(8)

where f<sub>u</sub>=0,1,2,3...

The "excess" of valences in the molecule of a monomer is used to form multiple (double, triple) bonds, unstable cycles, which subsequently participate in the formation of an inter-chain polymeric bond during the synthesis of furan-epoxy high-molecular compound.

Molecular (structural)  $f_{\rm m}$  and actual (realized)  $f_{\rm s}$  functionality of the studied monomers was also analyzed.

Reactivity of the monomers of the studied furan-epoxy systems is correlated well enough with the index of distribution of electron density on the atoms of the molecule  $J_{nlm}$ , possessing the property of additivity and so for calculating the index of the distribution of electron density of a molecule, it is sufficient to sum up the indices of the atoms, which form the molecule of the monomer [16].

$$J_{nlm} = (z + a + b) \log_2 (z + a + b) - (z - b); \ J_{nlm} = \sum_{i=1}^{n} (J_{nlm})_i,$$
(9)

where z is the atomic number of the element, which concludes the previous period of periodic system; a is the number of unpaired electrons in the atom of an element; b is the number of coupled electrons in the sublayers, populated in the given period of the analyzed element; k is the number of atoms.

Table 1 represents certain parameters, which characterize structure and reactivity of the studied monomers.

Table 1

Structural-topological and the functionality of materials

Monomer	A	Т	N	No	N <sub>c</sub>	J <sub>nlm</sub>	fu	$f_{\rm m}$	fs
MFA*	18	17	46	34	12	128	6	8	1; 3; 7; 8
DIFA*	26	25	68	50	18	203,5	9	15	1; 5; 13; 15
DHEBA	49	48	116	96	20	313,5	10	2	2
EDA	12	11	22	22	0	54,2	0	2	2
DETA	20	19	38	38	0	92,8	0	3	2; 3
TETA	28	27	54	54	0	131,4	0	4	2; 4
Agidol AF-2**	26	25	58	50	8	152,7	4	4	1; 2; 3; 4
UP-0633M-A***	27	26	56	52	4	142,9	2	4	1; 3; 4
UP-0633M-B***	35	34	72	68	4	181,5	2	5	1; 4; 5
UP-0633***	26	25	58	50	8	154,4	4	5	3; 5
m-PDA**	16	15	38	30	8	100,2	4	4	2; 4

Note: UP-0633M- A, UP-0633M- B mono cyanoethyl diethylenetriamine of the marks A and B respectively; \* – taking into account double bonds and mobile atom of hydrogen in the  $\alpha$  – position of furan cycle; \*\* – mobile atoms of hydrogen in o-and n-positions of aromatic ring were considered; \*\*\* – taking into account the bond C = N

The molecular graph of monomers is possible to represent both in the form of matrix (for example, the matrix of distances or contiguity) or by topological index (in the work we analyzed traditional Wiener index w).

For example, canonical numeration of atoms in the molecular graph of mono furfuriden acetone (MFA) takes the form (Fig. 1):

Fig. 1. Canonical numeration of atoms in the molecular graph of mono furfuriden acetone (MFA): 1; 2; 3; 4; 9; 11; 13; 15 - carbon atoms, 6; 7; 8; 10; 12; 16; 17; 18 - hydrogen atoms, 5; 14 - oxide atoms in the apexes of the graph

The traditional Wiener index W of the main components of the furfural acetone monomer FAM – furfurylidene acetones was determined by the formula [17] with regard to the matrix of topological distances of the molecular graphs of the furan monomers [18]:

$$W = \frac{1}{2} \sum_{i=1}^{i=N} \sum_{j=1}^{i=N} D_{ij},$$
 (10)

where Dij is the i-th j-th element of the matrix of distances of the graph of molecule MFA (Table 2) or DIFA, which shows the shortest distance between the apexes i and j in the molecular graph of the monomer G.

Traditional topological Wiener indices for MFA and DIFA comprise 18 and 27, respectively.

#### Table 2

#### Matrix of topological distances of the graph D(G) of the molecule MFA

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	0	1	2	2	1	1	2	3	3	4	4	5	5	6	6	7	7	7
2	1	0	1	2	3	2	1	2	3	4	4	5	5	6	6	7	7	7
3	2	1	0	1	2	3	2	1	2	3	3	4	4	5	5	6	6	6
4	2	2	1	0	1	3	3	2	1	2	2	3	3	4	4	5	5	5
5	1	2	2	1	0	2	3	3	2	3	3	4	4	5	5	6	6	6
6	1	2	3	3	2	0	3	5	4	5	5	6	6	7	7	8	8	8
7	2	1	2	3	5	3	0	3	4	5	5	6	6	7	7	8	8	8
8	3	2	1	2	3	4	3	0	3	4	4	5	5	6	6	7	7	7
9	3	3	2	1	2	4	4	3	0	1	1	2	2	3	3	4	4	4
10	4	4	3	2	3	5	5	4	1	0	2	3	3	4	4	5	5	5
11	4	4	3	2	3	5	5	4	1	2	0	1	1	2	2	3	2	2
12	5	5	4	3	4	6	6	5	2	3	1	0	2	3	3	4	4	4
13	5	5	4	3	4	6	6	5	2	3	1	2	0	1	1	2	2	2
14	6	6	5	4	5	7	7	6	3	4	2	3	1	0	2	3	3	3
15	6	6	5	4	5	7	7	6	3	4	2	3	1	2	0	1	1	1
16	7	7	6	5	6	8	8	7	4	5	3	4	2	3	1	0	2	2
17	7	7	6	5	6	8	8	7	4	5	3	4	2	3	1	2	0	2
18	7	7	6	5	6	8	8	7	4	5	3	4	2	3	1	2	2	0

Note: the numeration of columns and lines corresponds to the numbers of the apexes of the graph

The analysis of structure and functionality of the ingredients of furan-epoxy materials made it possible to design the variants of the compositions of the low-viscosity systems of construction purposes (Table 3).

 $(a, kJ/m^2)$ , the strength of adhesive interaction with a uniform separation of adhesive systems "steel-steel" ( $\sigma_{ad(s)}$ , MPa), "aluminum-aluminum" ( $\sigma_{ad(a)}$ , MPa) and the uniform shear of adhesive bonding "steel-steel" ( $\tau_{ad(sh)}$ , MPa), relative compressive strain with destruction ( $\epsilon$ , %), the degree of uniformity of structure (K<sub>o</sub>), determined by the results of the complete statistical analysis of the results of the strength tests of models at bending (Table 4).

Deformation-strength and adhesive properties of the materials

Table 4

Number of compo- sition	σ <sub>и</sub> , MPa	σ <sub>c</sub> , MPa	a, kJ/m²	σ <sub>ad(s)</sub> , MPa	σ <sub>ad(a)</sub> , MPa	τ <sub>ad(sh)</sub> , MPa	ε, %	Ko
1	75,6	124,2	2,6	25,6	24,5	12,3	0,8	0,78
2	77,3	129,7	3,8	28,9	29,2	12,8	1,1	0,80
3	78,2	133,1	4,7	30,1	32,4	13,3	1,2	0,83
4	80,5	130,5	4,5	29,5	30,2	13,1	1,0	0,82
5	82,3	139,8	5,6	34,8	35,5	14,5	1,4	0,86
6	85,9	140,2	5,5	35,0	35,5	14,3	1,3	0,84
7	92,1	143,6	6,2	38,2	38,7	14,9	1,1	0,89
8	87,2	135,9	6,0	33,1	34,2	14,1	1,0	0,90
9	85,8	137,5	5,8	36,8	37,6	14,4	1,2	0,92
10	87,3	134,3	6,0	35,9	36,5	14,7	1,4	0,95
11	90,1	131,9	6,2	34,9	35,1	15,6	1,0	0,93
12	84,8	133,4	5,8	33,6	34,2	14,9	0,9	0,89

Kinetic curves of water absorption with a sufficient degree С T

Reflected universion water absorption with a sufficient degree
of accuracy is described by the Fick's law [19]. The experi-
mental curves of absorption, represented in the coordinates
M/M /t and abarratorized

Table 3

Composition of	the designed	furan-epoxy	polymeric	materials
			p 0. j 0 0	

Material	Stoichiometric coefficient $\mathrm{K}_{\mathrm{c}}$
1. FAED-50(24)+EDA	_
2. FAED-50(24)+DETA	DETA: $K_c = 0,48$
3. FAED-50(24)+TETA	TETA: $K_c = 0.57$
4. FAED-50(24)+ AF-2	AF-2: K <sub>c</sub> = 1,28
5. FAED-50(24)+DETA+ UP-0633M-A	DETA: $K_c = 0,48$ ; UP-0633M-A: $K_c = 0,92$
6. FAED-50(24)+DETA+ UP-0633M-B	DETA: $K_c = 0,48$ ; UP-0633M-B: $K_c = 0,92$
7. FAED-50(24)+DETA+ UP-0633	DETA: $K_c = 0,48$ ; UP-0633: $K_c = 1,62$
8. FAED-50(24)+DETA+ m-PDA	DETA $K_c = 0,48$ ; m-PDA: $K_c = 0,62$
9. FAED-50(24)+ AF-2 +UP-0633M-A	AF-2: $K_c = 1,28$ ; UP-0633M-A: $K_c = 0,92$
10.FAED-50(24)+ AF-2 +UP-0633M-B	AF-2: $K_c = 1,28; UP-0633M-B: K_c = 0,92$
11. FAED-50(24)+ AF-2 +UP-0633	AF-2: $K_c = 1,28$ ; UP-0633: $K_c = 1,62$
12. FAED-50(24)+ AF-2+ m-PDA	AF-2: $K_c = 1,28$ ; m-PDA: $K_c = 0,62$

 $M_t/M_{\infty} - \sqrt{t}$  are characterized by the presence of "plateau" reaching sorption equilibrium, which indicates the absence of structural changes (reconstruction of super molecular structure, a change in the conformational state of macromolecules and others) in a furan-epoxy polymer in the process of diffusing water. Determining diffusion coefficients D in different sections of kinetic sorption curve (on the initial stage – at the value of Fourier criterion  $Fo \leq 0,1$  and on the final stage of absorption at  $Fo \ge 0,1$ ) made it possible to establish their equality within the limits of a statistical error of experiment. Therefore the coefficient of dif-

Note: the designation of hardener "Agidol AF-2" – AF-2

An important factor of the structured injection building material is also the complex of deformation-strength, adhesive characteristics.

They were experimentally determined for the designed furan-epoxy polymeric materials: failure stress when bending ( $\sigma_{\mu}$ , MPa), compressing ( $\sigma_{c}$ , MPa), impact resilience fusion  $D(m^2/s)$  was determined by gravimetric method on the initial section of the curve of mass absorption on the workpieces, which have the form of parallelepiped with the size of edges  $2R_1 = 15 \cdot 10^{-2}$  m;  $2R_2 = 1 \cdot 10^{-2}$  m;  $2R_3 = 3 \cdot 10^{-2}$  m.

The calculation of the coefficient of water diffusion into the furan-epoxy material was conducted by the formula [20]: od of passing of the front of moisture at the fixed thickness of the sample – 0,01 m ( $\tau_w$ , year). As the simulation operational medium we selected distilled water, the temperature of the experiments  $20\pm1$  °C.

Estimated transit time of the front of moisture in the furan-epoxy sample  $\,\tau_{_{\rm W}}\,$  at its fixed thickness l=0,01 m was evaluated according to the known formula:  $\tau_{w} \cong \frac{l^{2}}{D}$ , allowing for the fact that the motion of the front of moisture in the workpiece is one-directional (Table 4). The thickness of the sample made of furan-epoxy polymer in the simulation experiment was selected based on practical considerations. With the repairing and recovery works for strengthening concrete and ferroconcrete elements of buildings and structures with damage in the form of passive cracks, maximum width and thickness of a crack opening is on average 3 mm while the width and depth of a repairing groove with regard to the most unfavorable operating conditions are located within the interval of 2-18 mm. That is why an average thickness of a monolithic polymer in the voids, cavities, vacuoles and other structural defects of concrete or ferroconcrete materials is, as a rule, 10 mm. The estimation of the parameters was carried out with the forecasted decrease in the values of the strength properties of furan-epoxy materials on average by 10–25 % during the operation period.

Under the actual conditions of operating the construction elements, taking into account the construction-engineering factors,  $\tau_w$  increases on average by 50–70 %.

The essential characteristics of water resistance of the designed materials are represented in Table 5 (an average statistical error of the experiment did not exceed 2 %).

Number of compo- sition	w, %	w <sub>max</sub> , %	$\frac{D.10^{13}}{m^2/s}$	P·10 <sup>11</sup> , kg/m·s	S, kg/m <sup>3</sup>	$ au_{p},$ year	$ au_{w},$ year			
1	0,23	2,1	4.85	1,22	25,2	1,09	6,53			
2	0,21	1,85	4,78	1,06	22,2	1,12	6,63			
3	0,18	1,6	4,15	0,80	19,2	1,33	7,64			
4	0,09	0,8	1,55	0,15	9,6	3,31	20,46			
5	0,19	1,75	4,64	0,97	21,0	1,11	6,83			
6	0,17	1,65	4,51	0,89	19,8	1,22	7,03			
7	0,20	1,8	4,75	1,03	21,6	1,12	6,76			
8	0,22	1,85	4,82	1,07	22,2	1,07	6,54			
9	0,1	0,85	1,82	0,19	10,2	2,92	17,42			
10	0,12	0,95	2,08	0,24	11,4	2,51	15,24			
11	0,14	1,05	2,19	0,27	12,6	2,38	14,48			
12	0,13	1,1	2,29	0,31	13,2	2,33	13,85			

Sorption properties of the studied furan-epoxy materials

Table 5

Note: during determining the time of reaching the sorption equilibrium  $\tau_p$  on the samples in the form of parallelepiped, the moisture movement front passed simultaneously in six directions

### 6. Discussion of the results of the studies of the properties of low-viscosity furan-epoxy polymeric systems

The analysis of obtained experimental data testifies to the high potential of the designed furan-epoxy low-viscosity injection polymeric materials, recommended for the use in the repairing-recovery and renovation works in the construction industry.

The average dynamic viscosity of the designed furan-epoxy systems on the initial stage of structuring (up to 0.5 hour) comprised 0.002-0.01 Pa·s, which characterizes high level of the technological efficiency of the materials.

Stoichiometric ratio of the ingredients of reaction system, operating requirements for its feasibility, and also desirability to exclude the gradient of temperatures by the volume of the structured furan-epoxy oligomer, led to the selection of the temperature-time mode of the hardening: the temperature is not higher than 30 °C, the time of gel formation (gelatinization) – up to 2 hours, the time of reaching 80 % of the maximum strength – not longer than 3 days.

The adhesion of the spectrum of the designed furan-epoxy materials to the dry and moist concretes is within the limits 10-12 MPa, the wear resistance is not higher than 0,01-0,03 g/g.

The analysis of the results of the study makes it possible to draw a conclusion about the high level of the values of the analyzed parameters [21] and technological acceptability of the use of the materials of this type [22]. The main criteria during the analysis were a degree of the conversion of reactive oligomers, determined by the method of sol-gel analysis (an average level of a gel fraction of the hardened products amounts to 98 %) and the operational strength of the material (the most sensitive parameter to the structural material defects in volume and on the border of the phase division "polymer-concrete" was strength at static bending). Statistical error during experimental studies did not exceed 6 %.

Water (moisture) is the main physically aggressive component of the environment, which influences buildings, structures and construction objects under operating conditions. That is why resistance to the action of moisture for the designed furan-epoxy materials for construction purposes is one of the main parameters of their workability and longevity.

The impact of water on the composites for construction purposes varies by its nature.

Molecules of water, which diffuse into the designed furan-epoxy polymer, contribute to reduction in intermolecular interaction of macromolecules or their fragments, producing a plasticizing effect. The side effect of plasticization can be dissolution and removal of some ingredients of high-molecular system (in furan-epoxides - of the residual amine-containing structuring agents EDA, DETA, TETA, AF-2 etc., catalysts of the polymerization of the furan component - of aluminum chlorides, trivalent iron and others) into the aqueous medium. In addition to this, the manifestation is possible of the complex of chemical, physical-chemical processes of interaction of polymer with water (for example, hydrolysis with the participation of the fragment of the macromolecule, which contains the bond -C=N-; interaction of the molecules of water with the secondary hydroxyl group -OH; local clustering of the molecules of water and others).

Experimentally obtained data characterize rather high level of the water resistance of the designed injection materials.

The sorption parameters can substantially change with variations in the ambient temperature, as a result of the processes of "aging" of furan-epoxy materials (for example, occurrence of structural defects – cracks, shrinkage pores etc., destructive chemical reactions with participation of water, physical processes – "washing out" of the low-molecular

fractions of system and others). The rate of the processes of "aging" of a furan-epoxy polymer at the analysis of dependence "strength at static bending – reverse temperature" in the range of temperatures 20-80 °C with a sufficient degree of accuracy and reliability are approximated in the coordinates of the Arrhenius equation by a straight line (statistical deviation of experimental points from the averaged line is 3-10 %).

This is, as a rule, the main reason for the considerable and irreversible reduction in the physical-mechanical properties of the furan-epoxy polymers of construction purposes, and, therefore, for significant decrease of the guaranteed period of service of engineering products and systems, which contain the given materials [23], accompanied by a significant decrease in the level of other operational parameters of the composite systems [24].

The frost resistance of the studied furan-epoxy polymers comprises not less than 500 cycles.

A distinguishing feature of this research is the application of the "*Green Chemistry*" *principles*: using monomer-oligomer system out of the renewed sources of raw material, total exclusion of organic solvents and diluents from the formula, high degree of transformation of source material (monomers) into end products (polymers) and others.

On the basis of performed computational-theoretical and experimental studies of the combination of strength, technological, sorption and other properties of furan-epoxy polymers, and of estimated reactivity of parent substances (monomers), it is possible to develop a set of practical low-viscosity reaction systems for the repairing and recovery works in the construction industry with regard to certain special features of performing this work. All ingredients of the studied materials are industrially manufactured goods.

This study is the continuation of scientific designs with the use of furan-epoxy reactive oligomers with different molecular-topological parameters, used, for example, in the gas and oil industry.

#### 7. Conclusions

1. Technologically efficient initial ingredients (monomers) were selected: furfuliden acetones, low-molecular diglycidyl ethers, individual and binary (complex) amine-containing structuring agents – for the low-viscosity injection furan-epoxy polymeric materials with adjustable functional parameters. The range of the optimal intervals of structuring was defined: dynamic viscosity during the first stage of consolidation 0,002–0,01 Pa·s, technologically substantiated temperature-time mode of the structuring of monomer-oligomeric reaction system – temperature is up to 30 °C, the time of gel formation – up to 2 hours, the time of reaching the degree of operational strength (80 % by the maximum) – to 3 days.

2. The analysis of molecular, topological structure and reactivity of initial reactive ingredients (monomers) displayed that the applied ingredients are characterized by the high level of reactivity. The average level of implemented functionality for furfurylidene acetones at the optimal parameters of the formation of furan-epoxy polymers comprises: - 6, diglycidyl ethers - 2, amine-containing structuring agents - 3. The traditional topological Wiener index (for example, for applied furfurylidene acetones of the designed polymeric materials it comprises 18 and 27), which indicates rather high level of volatility of reactivity and topological parameters of parent substances during formation of the optimal structure of furan-epoxy low-viscosity polymeric materials. This becomes possible due to the use of the rational formulation-technological composition of the furan-epoxy polymer, recommended for using in the construction industry, with the known molecular, topological parameters and the characteristics of reactivity.

3. Deformation-strength, adhesive and sorption parameters of the designed low-viscosity injection furan-epoxy systems are characterized by the high level of their properties: strength at bending, compression, impact resilience are all within the limits, respectively, 75,6–90,1; 124,2–143,6 MPa; 2,6-6,2 kJ/m<sup>2</sup>, bonding strength of different substrata at a uniform separation on the average is 25,5–38,5 MPa; the coefficient of water diffusion  $-1,55-4,78{\cdot}10^{-13}$  of  $m^2/s.$  The proposed variants of the formulation compositions (4,9-12, Table 3) of repairing and recovery polymeric materials make it possible to reconstruct the destroyed elements of construction structures with high quality. To increase the duration of their efficient operation. In this case, the average transit time of the moisture front in the polymeric material (with fixed thickness of 0,01 m), which indirectly characterizes the operational reliability of polymeric composition system, comprises 13,85-20,46 years.

#### References

- 1. Kireeva, Yu. I. Stroitelnyie i otdelochnyie materialyi na sovremennom ryinke [Text] / Yu. I. Kireeva. Moscow: Eksmo, 2006. 304 p.
- Matthews, F. World of materials and technologies / Composites. Mechanics and technology [Text] / F. Matthews, R. Rawlings. Moscow: Technosphere, 2004. – 408 p.
- Anastas, P. T. Green Chemistry: Theory and Practice [Text] / P. T. Anastas, J. C. Warner. New York: Oxford University Press, 1998. – 140 p.
- Fache, M. Amine hardeners and epoxy cross-linker from aromatic renewable resources [Text] / M. Fache, C. Montérémal, B. Boutevin, S. Caillol // European Polymer Journal. – 2015. – Vol. 73. – P. 344–362. doi: 10.1016/j.eurpolymj.2015.10.032
- Fernández-Francos, X. R. Structural analysis of the curing of epoxy thermosets crosslinked with hyperbranched poly(ethyleneimine) s [Text] / X. R. Fernández-Francos, X. Ramis // European Polymer Journal. – 2015. – Vol. 70. – P. 286–305. doi: 10.1016/ j.eurpolymj.2015.07.031
- Monti, M. Thermal and combustion behavior of furan resin/silica nanocomposites [Text] / M. Monti, H. Hoydonckx, F. Stappers, G. Camino // European Polymer Journal. – 2015. – Vol. 67. – P. 561–569. doi: 10.1016/j.eurpolymj.2015.02.005
- Purnomo, A. P. Investigation of Solution-Based Healing of Furan-Functionalized Epoxy-Amine Thermoset [Text] / A. P. Purnomo // A Thesis Submitted to the Faculty of Drexel University by Purnomo Adi Pratama in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering, 2011. – P. 1–108.

- Hu, F. Preparation and Characterization of Fully Furan–Based Renewable Thermosetting Epoxy–Amine Systems [Text] / F. Hu, S. Kumar Yadav, J. J. La Scala, J. M. Sadler, G. R. Palmese // Macromolecular Chemistry and Physics. – 2015. – Vol. 216, Issue 13. – P. 1441 –1446. doi: 10.1002/macp.201500142
- Karahanov, R. A. Sintez i svoystva nepredelnyih soedineniy furanovogo ryada [Text] / R. A. Karahanov, V. I. Kelarev, Yu. N. Polivin // Uspehi himii. – 1993. – Vol. 62, Issue 3. – P. 184–207.
- 10. Pratama, P. A. The role of maleimide structure in the healing of furan-functionalized epoxy-amine thermosets [Text] / P. A. Pratama, A. M. Peterson, G. R. Palmese // Polymer Chemistry. 2013. Vol. 4, Issue 18. P. 5000–5006. doi: 10.1039/c3py00084b
- 11. Babaevskiy, P. G. Praktikum po polimernomu materialovedeniyu [Text] / P. G. Babaevskiy. Moscow: Himiya, 1980. 256 p.
- 12. Kryizhanovskiy, V. K. Tehnicheskie svoystva polimernyih materialov [Text] / V. K. Kryizhanovskiy, V. V. Burlov, A. D. Panimatchenko, Yu. V. Kryizhanovskaya. SPb.: Professiya, 2003. 240 p.
- Morozik, Yu. I. Obschaya formula dlya rascheta formalnoy nepredelnosti himicheskih soedineniy [Text] / Yu. I. Morozik, P. V. Fomenko, A. V. Shantroha // Zhurnal strukturnoy himii. – 2008. – Vol. 49, Issue 5. – P. 974–976.
- Bonchev, D. G. Harakterizatsiya himicheskih struktur s pomoschyu teoriiinformatsii i teorii grafov [Text] / D. G. Bonchev. Moscow: Moskovskiy universitet, 1984. – 48 p.
- Hansen, P. J. Chemical applications of graph theory [Text] / P. J. Hansen, P. C. Jurs // Journal of Chemical Education. 1988. Vol. 65, Issue 8. – P. 574–580. doi: 10.1021/ed065p661
- Gutman, I. Topological indices based on the line graph of the molecular graph [Text] / I. Gutman, E. Estrada // Journal of Chemical Information and Computer Sciences. – 1996. – Vol. 36, Issue 3. – P. 541–543. doi: 10.1021/ci950143i
- 17. Chalyih, A. E. Diffuziya v polimernyih sistemah [Text] / A. E. Chalyih. Moscow: Himiya, 1987. 312 p.
- Kuznetsova, Z. N. Uskorennyiy metod opredeleniya koeffitsienta diffuzii zhidkosti v polimernyie materialyi [Text] / Z. N. Kuznetsova, V. I. Solomatov, V. Yu. Emelyanov // Plasticheskie massyi. – 1983. – Vol. 6. – P. 42–43.
- Kandyirin, L. B. Issledovanie mehanicheskih svoystv napolnennyih kompozitsiy i polimerbetonov na osnove smesey furanovyih i epoksidnyih smol [Text] / L. B. Kandyirin, B. E. Usoltsev, V. S. Kozhevnikov // Plasticheskie massyi. – 2000. – Vol. 7. – P. 34–37.
- Anisimov, Yu. N. Formirovanie, prostranstvennaya struktura i prochnostnyie svoystva vzaimopronikayuschih polimernyih setok na osnove oligomer–oligomernyih sistem nizkotemperaturnogo otverzhdeniya [Text] / Yu. N. Anisimov, S. N. Savin // Zhurnal prikladnoy himii. – 2001. – Vol. 74, Issue 4. – P. 633–636.
- Aniskevich, K. Sorbtsionnyie harakteristiki polimerbetona pri dlitelnoy vyiderzhke v vode [Text] / K. Aniskevich, Yu. Hristova, Yu. Yansons // Mehanika kompozitnyih materialov. – 2003. – Vol. 39, Issue 4. – P. 463–476.
- Simonov-Emelyanov, I. D. Vliyanie ishodnyih komponentov i granitsyi razdela faz napolnitel–polimer na sorbtsiyu i stabilnost elektrofizicheskih i prochnostnyih harakteristik stekloplastika [Text] / I. D. Simonov-Emelyanov, V. I. Sokolov, S. I. Shalgunov, L. G. Miheeva // Plasticheskie massyi. – 2005. – Vol. 2. – P. 15–20.