Synthesis and reactivity of metal-containing monomers

74.* Azomethine copper complexes as modifying agents of epoxy matrices

B. A. Komarov,[a]* A. T. Kapasharov,[a] E. A. Dzhavadyan,[a] V. A. Lesnichaya,[a] G. I. Dzhardimalieva,[a] A. S. Burlov,[b] A. I. Uraev,[b] S. A. Mashchenko,[b] D. A. Garnovskii,[c] and A. D. Pomogailo[a]

[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: komarov@icp.ac.ru
[b]*Research Institute of Physical and Organic Chemistry, Southern Federal University,*
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation
[c]*Southern Scientific Center,*
41 ul. Chekhova, 344006 Rostov-on-Don, Russian Federation

The effect of additives of copper azomethine complexes of different structure on the character of polycondensation and physicomechanical properties of the obtained metal-containing epoxy polymers was studied. It was shown by the DSC method that the thermal stability of the starting Cu^{II} azomethine complexes depended on their structure and nature of polar functional groups. The physicomechanical properties of the unmodified and modified epoxyamine polymers at different ratios of functional groups were compared. The additives of Cu^{II} azomethine complexes of 0.42—0.43 wt.% were shown to increase the impact strength of the polymers at the ratio [NH]/EG = 1.07—1.13 (EG is epoxy group).

Key words: copper azomethine complexes, chelate complexes, epoxy resin, metal-containing epoxy polymers, polymer modification.

Preparation of composites based on complexes with coordinated polydentate ligands is being intensely developed due to their potential application as sensors[2,3] and in nonlinear optics,[4] separation and molecular recognition,[5] accumulation of gases,[6,7] catalysis,[8] information and energy storage, biomedicine, *etc.* New polymer materials based on these complexes are most frequently prepared using various procedures of modifying known polymers, such as epoxy resins, polyethers, polyurethanes, and others to impart them new unusual properties or to improve certain characteristics. It is known that the introduction of metal/metal complex into a polymer molecule improves the thermal stability of the polymer.[9,10] Catalytic additives (≥2 wt.%) of Zn^{II}, Co^{II}, and Fe^{III} acetylacetonates to sulfosemicarbazide polyurethane increases the temperature of 5% mass loss by 40—50 °C.[11] The polymer-immobilized transition metal complexes with Schiff bases are well known as efficient catalysts of reaction of oxidation of olefins and alcohols[12,13] and alkene epoxidation.[14,15]

Due to prolonged service and high exploitation characteristics, epoxy resins are leading among reactoplasts. Many areas of their application, such as electronics, aircraft building, and motor-car construction need epoxy composites with improved thermal stability and good physicomechanical characteristics. One of the ways for achieving these purposes and for imparting new functional properties can be the insertion (impregnation) of metal complexes into the structure of cross-linked epoxyamine polymers. The polycondensation of epichlorhydrin (1-chloro-2,3-epoxypropane) with ethylenediamine or *o*-phenylenediamine and introduction of the Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II} azomethine complexes, 3-formyl-4,4´-dihydroxydiphenylmethane derivatives, gave metal-chelating epoxy polymers with high antimicrobial activity[16,17] and thermal stability.[18] Thermal stability of epoxy resins with aromatic chelates is higher than that of the derivatives with aliphatic amines. Macrochelates remain stable to 325 °C, and then a continuous mass loss is observed on heating to 620 °C, indicating the decomposition of the organic moiety of the polyepoxy complex. Coatings based on metal-containing epoxy resins of the considered type exhibit efficient anticorrosion activity, in particular, this is characteristic of the Zn^{II} macrochelates on the steel surface.[19]

Special attention is recently given to the synthesis of novel bi- and tridentate azomethine ligands and their metal complexes. Their structures and properties, including molecular structures, have been described in detail.[20—23] The Cu^{II} chelates are most stable. It has previously been

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shown[24] that the metal complexes of Schiff bases are efficient precursors of self-organized nanocomposites stabilized by thermolysis products of the ligand shell of the complexes.[25,26] Since chelates of the considered type with polar and nonpolar substituents are polyfunctional. It seemed of interest to study the influence of additives of copper azomethine complexes of various structure on the polycondensation processes and physicomechanical properties of the obtained metal-containing epoxy polymers.

Experimental

Materials and reagents. Epoxy-diane resin of Ancarez-728, Pacific Anchor Chemical (USA), and Epital (analogs of ED-20) trade marks were used as epoxy binders. An eutectic mixture of aromatic diamines, *m*-phenylenediamine (MPDA), (Aldrich) and diaminodiphenylmethane (DADPM) (Aldrich) was used as a solidifying agent, as well as the Etal-450 amine solidifier of complicated composition.

Copper acetate monohydrate $Cu(CH_3COO)_2 \cdot H_2O$ (reagent grade) (Reakhim), 3-allylsalicylaldehyde, 5-methoxysalicylaldehyde, *o*-aminothiophenol, phenylacetic acid, aniline, *p*-toluidine, *p*-bromoaniline, *p*-nitroaniline, acetophenone, *p*-bromoacetophenone, *p*-methylacetophenone, *p*-nitroacetophenone, ethanol, benzene, DMF, and $POCl_3$ (Aldrich) were used without additional purification. Toluene (pure) was dried over metallic sodium and distilled in argon.

To obtain an eutectic mixture, MPDA (40 g) and DADPM (60 g) were placed in a 250-mL round-bottom flask. The synthesis was carried out *in vacuo* on heating to 90—100 °C with periodical stirring for 1 h. Ultrasonic treatment of the working compositions was carried out with a UZDN-1M ultrasonic dispergator with a working frequency of 22 KHz in a glass ampule (inner diameter 22 mm), which had the narrowed diameter (17 mm) at a height of 30 mm and the branch at a height of 70 mm for argon blowing. This structure makes it possible to use the maximum power of ultrasonication in a minimum volume of the working medium.

The vacuum mixer was designed at the Construction Bureau of the Institute of Problems of Chemical Physics, Russian Academy of Sciences. An AOL-112 electric motor (1500 rpm) was combined with a powerful stand using a special corbel. The stand can be vertically moved with position fixation. The rotor of the electric motor was made in a closed variant and connected to a stirrer, the working part of which has a special structure that makes it possible to provide turbulent stirring of working media. The motor was connected with a flange and a core to a glass reactor (useful volume 180 mL) with a jacket for temperature-maintaining, a drain vacuum valve, and branches for controlling vacuum and inert gas filling.

The epoxy resin in the presence of azomethine additives was solidified as follows. The calculated amount of the azomethine complex (AMC) was dissolved in the eutectic (2.2—3.0 g) on heating (80 °C) and ultrasonication for 20 min in an argon flow. Then the second portion of the eutectic (4—5.5 g) was added and again ultrasonicated for 5 min. Then the mixture was transferred to the reactor of the mixer in which a weighed sample of the epoxy resin (evacuated at 70 °C for 15 min to a pressure of 0.1 Torr) was placed. The three-component system was mixed with stirring (1500 rpm) and evacuation at 70 °C for 10 min to attain a pressure of 0.1—0.2 Torr. Then the molds (for samples with a size of 80×100×3 mm between the glasses treated with an antiadhesive) were filled with a free cast. The samples were solidified in the mode: at 100 °C for 3 h, at 160 °C for 2 h, and at 180 °C for 2 h, which made it possible to achieve the maximum possible conversion for functional groups according to the calorimetric results. The quantitative data on loading all components to the reactor of the vacuum mixer are presented in Table 1. Note that the ratio of functional groups varied from 1.07 to 1.47 (on the average, 1.248) because of losses of the binder components, first of all, of the eutectic (its equivalent weight is 5 times lower than that of the epoxy resin), after sonication with AMC of different nature. The obtained mixture in an argon flow was poured to a metallic beaker and cooled in a drying box. The melting point of the eutectic mixture was ~40 °C.

Bis(3-allylsalicylidene-2´-mercaptoanilinato)dicopper(II) (1). Freshly distilled *o*-aminothiophenol (1.25 g, 0.01 mol) was added to a solution of 3-allylsalicylaldehyde (1.6 g, 0.01 mol) in anhydrous toluene (50 mL), and the mixture was heated with a Dean—Stark trap for 1 h to the complete separation of water. At the end of the reaction, toluene was distilled off on a rotary evaporator, and methanol (50 mL) was poured to the residue. Copper acetate monohydrate (1 g, 0.005 mol) in methanol (50 mL) was added to the obtained solution. The mixture was refluxed for 1 h and cooled down. The obtained precipitate of the complexes was filtered off, washed with boiling methanol (2×10 mL), and dried in vacuum drying box at 100 °C. The yield was 75%, dark brown powder, m.p. 255—256 °C. Found (%): C, 58.17; H, 3.89; N, 4.32; S, 10.40. $C_{32}H_{26}Cu_2N_2O_2S_2$. Calculated (%): C, 58.08; H, 3.96; N, 4.23; S, 10.66.

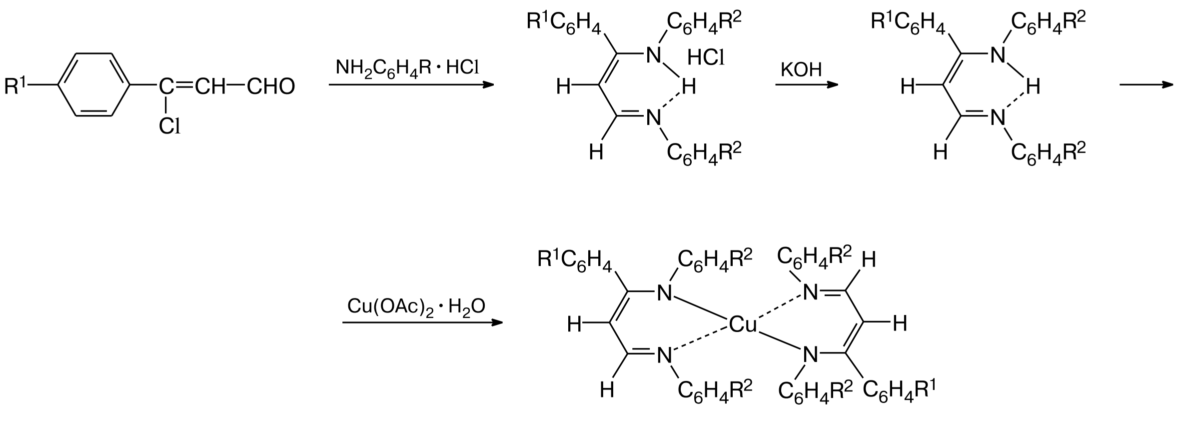
Bis(5-methoxysalicylidene-2´-mercaptoanilinato)dicopper(II) (2) was synthesized using a similar procedure from 5-methoxysalicylaldehyde (1.52 g, 0.01 mol), *o*-aminothiophenol (1.25 g,

Table 1. Quantitative data on the load of components of the epoxy binder modified by AMC additives

AMC	m_{AMC} (wt.%)	Load to reactor/g		[NH] /EG*
		ED-20	AMC+eutectic	
2	0.43	28.8	6.3	1.134
	0.40	27.9	5.5	1.02
1	0.42	28.8	5.95	1.070
	0.24	27.85	5.17	0.97
3	0.43	28.8	8.05	1.089
	0.40	27.51	5.25	0.99
4	0.38	27.97	6.47	1.203
	0.52	27.99	5.6	1.04
5	0.44	27.99	7.90	1.468
	0.41	28.03	5.44	1.00
6	0.43	28.03	7.53	1.397
	0.37	27.77	5.45	1.02
7	0.44	27.83	7.87	1.473
	0.40	28.07	5.48	1.01

* [NH]/EG is the ratio of functional NH and epoxy groups calculated taking into account losses after solidification of an eutectic mixture with AMC for the epoxy number of the Ancarez-728 resin equal to 20% (equivalent weight 215) and the calculated equivalent weight of the eutectic equal to 40.5.

Scheme 1



3—5

3: $R^1 = R^2 = Me$
4: $R^1 = Br, R^2 = OMe$
5: $R^1 = NO_2, R^2 = H$

0.01 mol), and copper acetate monohydrate (1 g, 0.005 mol). The yield was 42%, dark brown powder, m.p. >300 °C. Found (%): C, 52.47; H, 2.89; N, 4.45; S, 9.85. $C_{28}H_{19}Cu_2N_2O_4S_2$. Calculated (%): C, 52.58; H, 2.97; N, 4.38; S, 10.02.

Azomethine complexes **3**—**7** were synthesized using earlier described procedures.[25—27]

Copper(II) *N*,*N*′-diaryl-β-aminovinyliminates (3—5) were synthesized according to Scheme 1.[27]

A solution of copper acetate monohydrate (0.2 g, 0.001 mol) in ethanol (20 mL) was added to a solution containing the corresponding *N*,*N*′-diaryl-β-aminovinylimine (0.68, 0.88, or 0.69 g; 0.002 mol) in anhydrous ethanol (50 mL). The mixture was refluxed for 2 h. The formed precipitates of the complexes were filtered off, washed with hot ethanol (2×5 mL), and recrystallized from an ethanol—chloroform (2 : 1) mixture.

Bis(4-methyl-*N*-[(*Z*,3*Z*)-3-(*p*-tolyl)-3-(*p*-tolylimino)prop-1-enyl]anilino)copper (3). The yield was 45%, dark green powder, m.p. 187 °C. Found (%): C, 77.84; H, 6.32; N, 7.61. $C_{48}H_{46}CuN_4$. Calculated (%): C, 77.65; H, 6.24; N, 7.54. IR (KBr), ν/cm^{-1}: 1606 ν(C=N), 1582 ν(C=C).

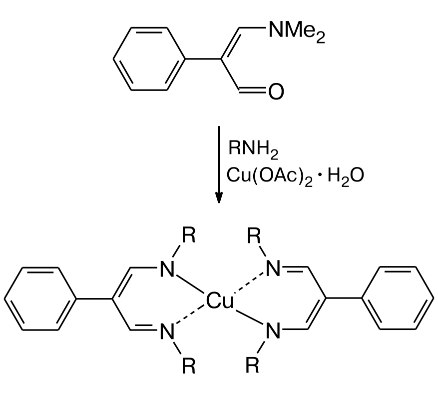
Bis(*N*-[(*Z*,3*Z*)-3-(4-bromophenyl)-3-(4-methoxyphenyl)-iminoprop-1-enyl]-4-methoxyanilino)copper (4). The yield was 53%, dark brown powder, m.p. 191—192 °C. Found (%): C, 59.27; H, 4.45; N, 6.12. $C_{46}H_{40}Br_2CuN_4O_4$. Calculated (%): C, 59.02; H, 4.31; N, 5.98. IR (KBr), ν/cm^{-1}: 1613 ν(C=N), 1587 ν(C=C).

Bis(*N*-[(*Z*,3*Z*)-3-(4-nitrophenyl)-3-phenyliminoprop-1-enyl]-anilino)copper (5). The yield was 65%, dark brown powder, m.p. 210—211 °C. Found (%): C, 61.52; H, 4.38; N, 11.48. $C_{42}H_{32}CuN_6O_4$. Calculated (%): C, 61.41; H, 4.31; N, 11.23. IR (KBr), ν/cm^{-1}: 1613 ν(C=N), 1587 ν(C=C).

Copper(II) complexes with phenylmalonodialdehyde dianils (6 and 7) were obtained by the template synthesis (Scheme 2).[28,29]

A mixture of α-phenyl-β-dimethylaminoacrylaldehyde (2.1 g, 0.012 mol), aniline (2.79 g, 0.03 mol) or *p*-anisidine (3.69 g, 0.03 mol), and copper(II) acetate monohydrate (1.2 g, 0.006 mol) in ethanol (50 mL) was refluxed for 3 h. The precipitates were filtered off, washed with hot methanol (2×5 mL), and recrystallized from a benzene—ethanol (2 : 1) mixture.

Scheme 2



6, 7

R = 4-$OMeC_6H_4$ (**6**), Ph (**7**)

Bis(4-methoxy-*N*-[(*Z*,3*E*)-3-(4-methoxyphenyl)imino-2-phenylprop-1-enyl]anilino)copper (6). The yield was 40%, dark green powder, m.p. 252—253 °C. Found (%): C, 70.70; H, 5.40; N, 7.10. $C_{46}H_{42}CuN_4O_4$. Calculated (%): C, 70.98; H, 5.44; N, 7.20. IR (KBr), ν/cm^{-1}: 1601 ν(C=N), 1569 ν(C=C).

Bis(*N*-[(*Z*,3*E*)-2-phenyl-3-phenyliminoprop-1-enyl]anilino)-copper (7). The yield was 65%, dark green powder, m.p. 264—265 °C. Found (%): C, 76.43; H, 5.32; N, 8.65. $C_{42}H_{34}CuN_4$. Calculated (%): C, 76.63; H, 5.20; N, 8.51. IR (KBr), ν/cm^{-1}: 1607 ν(C=N), 1573 ν(C=C).

Physicomechanical properties. Samples for tests were prepared according to GOST 4647-80 (ASTM D 1822-68) (impact viscosity) and ASTM D 638-96, D 882-95a (rupture strength). The following physicomechanical characteristics were studied: rupture strength (σ_R), impact viscosity (α_n), relative rupture strain (ε_R), and elasticity tensile modulus (E_s). The σ—ε curves were obtained with a Zwick tensile machine with a deformation rate of 1 mm min^{-1}. The impact viscosity was determined using a Zwick impact copra. Strength parameters were measured with the accuracy ≤15% (σ_R, α_n, and ε_R), and the E_s values were measured with the accuracy ≤4%.

Thermomechanical measurements were carried out on an UIP-70 instrument (Central Design Bureau, Moscow, Russia) with a scanning rate of 2.5 °C min^{-1} and a load of 0.2 MPa. The accuracy of glass transition temperature determination (T_g) in a range of 130—170 °C was ±2 °C.

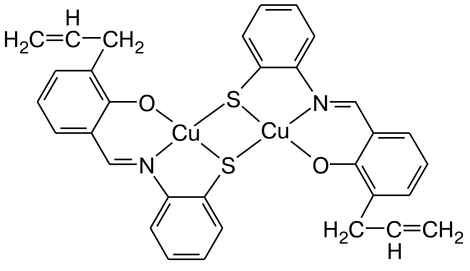
A DSC 828 Mettler Toledo differential scanning microcalorimeter was used to detect DSC data.

Calorimetric tests were carried out using a DAK-1-1 isothermic calorimeter.

Results and Discussion

Synthesis and characterization of the Cu^{II} azomethine complexes. To study the influence of additives of the copper complexes of different composition and structure (**1**—**7**) on the character of the polycondensation process and physicomechanical properties of the obtained metal-containing epoxy polymers, we chose copper azomethine chelates of two types: copper(II) compounds with N-, O-, and S-tridentate Schiff bases based on 3-allylsalicyl- (**1**) or 5-methoxysalicyl- (**2**) aldehydes and *o*-mercaptoaniline and copper mononuclear complexes based on differently substituted β-aminovinylimines with the CuN$_4$ coordination node (**3**—**7**).

The structures of the complexes were determined previously.[23,27,28] The structures of complexes **1** and **2** were determined from the data of elemental analysis, IR and EXAFS spectroscopy, and magnetochemical measurements. These complexes include dimeric structures[23] with a strong antiferromagnetic interaction between the copper atoms (**1**: $2J = -950$ cm^{-1}) with a Cu—Cu distance of 2.96±0.02 Å. According to the elemental analysis data, complexes **3**—**7** have the composition[27,28] CuL$_2$. The characteristic shifts to the long-wavelength range by 15—60 cm^{-1} of the ν(CH=N) absorption bands in the IR spectra of complexes **3**—**7** compared to the initial ligands indicate their chelate structure.



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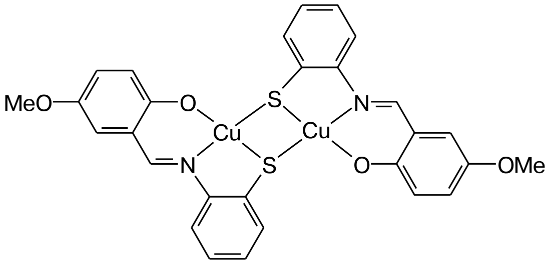

2

Compounds **2**, **3**, **5**, and **6** have enhanced thermal stability differed for the complexes depending on their structure and nature of functional groups. Some characteristics of the thermal properties of AMC obtained by the thermogravimetric and DSC studies are presented in Table 2. As can be seen from Table 2, the thermal stability of the examined AMC depends substantially on their composition and nature of functional substituents. For example, complexes **2**, **3**, and **6** have higher temperatures of decomposition onset than the complexes bearing reactive functional groups. The presence of boron atoms, nitro groups, or double bonds as substituents at the benzene ring can decrease both the temperature of mass loss onset and the chemical resistance to the components of the used epoxy condensation system. Compound **5** contains two polar methoxy groups in the *para*-position, which results in a low temperature of decomposition onset.

Physicomechanical properties of the native epoxy polymer and the polymer with additives of the azomethine complexes. The physicomechanical properties of the epoxyamine polymer at different ratios of functional groups was studied to establish the effect of influencing AMC additives.

The results of the tests of the initial and modified samples of the epoxy polymers prepared using the above procedure are presented in Tables 3 and 4. The data in Table 3 clearly demonstrate the substantial dependence of the physicomechanical properties of the epoxyamine polymer on the ratio of functional groups: epoxy and NH groups. Note that any deviation from the equifunctional ratio of the indicated groups results in polymer plasticization, which is confirmed by the appearance of forced elastic

Table 2. Thermal properties of the azomethine complexes

AMC	DSC data, T_{eff}/T_0 [a]		Δm_0 [b] (wt.%)	T_{decomp} [c] /°C
	endo	*exo*		
1	—	241/165	0.96	160
2	269.9/250	295	1.55	218
3	—	294/185	1.21	180
4	—	140/110	0.33	105
5	286/260	≥300	1.35	165
6	318.3/300	334.9	—	260
7	—	183.9/170	2.42	140

[a] T_{eff}/T_0 are the temperatures of the endo- and exotherm and the onset of deviation to an extreme in the Celsium temperature scale.

[b] Initial mass loss.

[c] Temperature of decomposition onset.

Table 3. Physicomechanical properties of the polymers based on the epoxy resin and solidifying agent, an eutectic mixture of MPDA and DADPM*

Entry	[NH]/EG	E_s	σ_R	ε_R (%)	α_n /kJ m^{-2}	ν (%)	T_g/°C
		MPa					
1	0.93	2370	89	5.7	10.3	7.2	122
2	0.97	2240	78	5.4	13.4	3.0	131
3	0.99	2230	86	6.7	12.6	20.2	129
*4***	1.00	2210	75	4.8	11.9	17.6	129
5	1.00	2130	59	3.4	11.6	17.0	140
6	1.15	1880	64	5.0	16.1	7.8	163
7	1.25	1870	76	7.0	12.2	17.1	165
8	1.31	1920	75	6.7	13.5	40.0	158
9	1.51	1980	86	10.7	28.2	20.6	144
10	2.00	2250	93	10.5	46.1	18.0	118

* Hereinafter, E_s is the elasticity tensile modulus, σ_R is the rupture strength, ε_R is the relative rupture strain, α_n is the impact strength, ν is the variation coefficient of impact strength, and T_g is the glass transition temperature of the polymers.

** The component of the binder were subjected to ultrasonication after degassing.

strain in the tensile diagram (see Table 3, entries *9* and *10*). An extreme dependence of all physicomechanical characteristics of the polymer is detected. The minimum of the strength properties is observed at [NH]/EG ≈ 1.22 rather than at the equifunctional ratio ([NH]/EG = 1). The maximum glass transition temperature, 166 °C, is attained at [NH]/EG ≈ 1.22, while this temperature is ~135 °C at the equifunctional ratio (see Table 3).

Table 4. Physicomechanical properties of the AMC-modified epoxy polymers based on the epoxy resin and solidifying agent, an eutectic mixture of *m*-phenylenediamine and diaminodiphenylmethane

[NH]/EG	AMC*	E_s	σ_R	ε_R (%)	α_n /kJ m^{-2}	ν (%)	T_g/°C
		MPa					
1.15	— (US)	1900	71	6.0	13.2	10.9	160
1.01	— (US)	2080	78	5.4	11.6	15.8	133
1.13	**2**	1920	68	5.8	37.4	25.5	166
1.02	**2**	2070	59	3.8	9.7	17.3	142
1.07	**1**	1930	73	5.8	38.9	25.0	147
0.97	**1**	2230	78	5.4	13.4	3.0	131
1.09	**3**	1930	73	6.1	44.7	10.2	156
0.99	**3**	2230	86	6.7	12.6	20.1	129
1.20	**4**	1830	86	10.2	18.8	14.7	155
1.04	**4**	2020	80	6.0	12.7	16.0	150
1.47	**5**	1830	88	10.8	25.2	16.5	147
1.00	**5**	2070	58	3.8	12.6	27.8	137
1.40	**6**	1830	88	11.0	18.8	9.6	155
1.02	**6**	2100	51	3.0	12.6	16.2	140
1.47	**7**	1810	87	10.1	21.0	27.9	147
1.01	**7**	2060	49	2.8	11.5	31.6	136

* US is the ultrasonic treatment of components of the binder after preliminary degassing under similar conditions.

It is known[30] that the formed hydroxy groups in the epoxyamine polymers predominantly participate in the formation of intermolecular physical bonds, whose concentration and nature mainly determine the physicomechanical properties of the epoxy polymer. The concentration of physical bonds evidently increases with an increase in the relative concentration of NH groups, thus improving all strength tensile parameters.

As can be seen from Table 4, additives of the Cu^{II} AMC in a concentration of 0.42—0.43 wt.% result in a substantial increase in the impact strength of the polymers (~3 times) only at the ratio [NH]/EG = 1.07—1.13 (see Table 4). The strength rupture parameters remain almost unchanged. In essence, small additives of compounds **1**, **2**, and **3** lead to the same change in the properties as that observed at the ratio [NH]/EG = 1.5—2.0 for the initial polymer (see Table 3, entries *9* and *10*). This can be due to an increase in the concentration of physical bonds per unit volume of the modified epoxy polymer. This increase is possible due to the formation of new physical bonds of the AMC molecules with electron-donor centers of the binder components, first of all, aromatic diamines in which the AMC are dissolved under the action of ultrasonication, or products of the interaction of the AMC with the components of the epoxy binder, for example, aromatic amino groups of the solidifying agent molecules at 80 °C and/or during solidification in a temperature range of 100—180 °C.

In addition, the observed phenomenon can be caused by structural modification at the nanolevel. The dissolution of the AMC in an eutectic mixture of aromatic diamines can result in the formation of complicated associates with the AMC molecules at the center. Mixing with an epoxy oligomer in a vacuum mixer does not result in their decomposition but can create the gradient composition of amino groups between the AMC molecules and, hence, the gradient distribution of both the chemical cross-linking density in the cross-linked structure and the cohesion energy density of the polymer, which results in the efficient dissipation of dynamic energy. This is especially characteristic of the AMC, whose structure contain no functional groups capable of chemical interacting and which can be dissolved in a medium of diamines. It is substantial that modification by this AMC (structure **3**) leads to the highest effect of increasing the impact strength (see Table 4, Fig. 1). This concept is consistent with the earlier discovered effect of influencing the concentration and dispersion of the polymer itself on the temperature of the polymer based on ED-20—MPDA. It turned out that the maximum influence on the properties of the polymer is made by finely dispersed heterogeneous additives, indicating that the properties of the polymer change in both

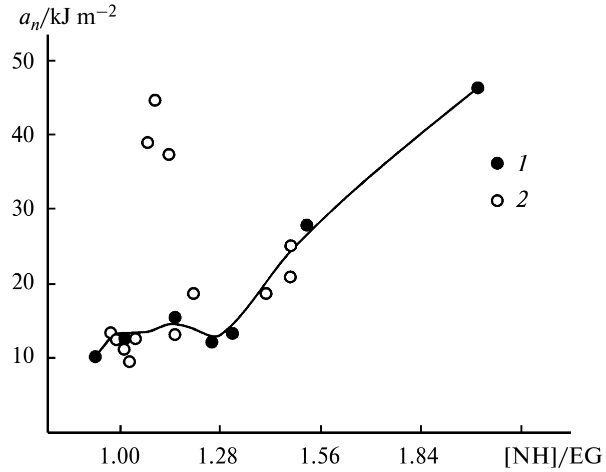

Fig. 1. Impact strength (a_n) of the epoxy polymer Ancarez-728 (eutectic mixture of aromatic diamines) *vs* ratio of functional groups [NH]/EG for the initial system (*1*) and the system modified by AMC additives (*2*).

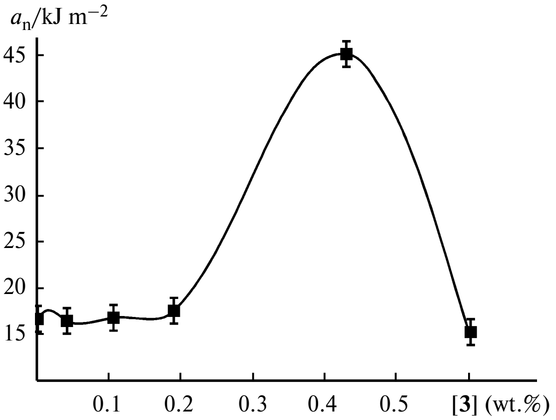

Fig. 2. Impact strength (a_n) of the epoxy polymer Ancarez-728 *vs* AMC-**3** at the ratio of functional groups [NH]/EG = 1.09—1.16.

the contact zone and the whole volume with a change in the topological level of the structural organization of the polymer. Further studies are planned for the elucidation of the assumed mechanism in more detail.

A comparison of the obtained data with the properties of the initial polymer (Table 5) at close (1.09—1.16) ratios of functional groups shows the improvement of the physicomechanical properties of the modified polymers in nearly the whole studied range of AMC-**3** concentrations. The elasticity tensile modulus increases by 3—16%, and the rupture strength and relative rupture strain increase by 14—40 and 18—22%, respectively. Note that the glass transition temperature remains almost unchanged.

The dependence of the impact strength on the concentration of AMC-**3** is extreme with a maximum at 0.43 wt.% (Fig. 2), and the increase is 2.8 times. This can be due to the fact that the properties of the cross-linked epoxyamine polymer change upon modification by additives of stable AMC due to the existence of an optimum average statistical distance between the AMC molecules uniformly distributed over the binder volume rather than due to the appearance of gradient properties in the contact zone.

The results of the modification of the epoxy polymer based on the Epital binder at a solidifying agent concentration of 16.2 and 17.8 wt.% with AMC-**3** additives are presented in Table 6. This epoxy-diane polymer based on the complicated solidifying of a complicated mixture of a diamine mixture (Etal-450) is characterized by the improvement of all strength tensile parameters: the elasticity tensile modulus increases by 4—6%, the rupture strength increases by 35—47%, and the relative rupture strain increases by 17—27%. The glass transition temperature and impact strength remain almost unchanged.

Thus, the principal possibility of using azomethine complexes of transition metals as modifiers of the epoxyamine polymers based on epoxy-diane resins was experimentally shown. A threefold increase in the impact strength was found for the ratio of functional groups in the range 1.05 < [NH]/EG < 1.16 and a additive concentration of 0.42—0.43 wt.%.

Table 5. Physicomechanical properties of the epoxyamine polymer based on the Ancarz-728 resin and an eutectic mixture of aromatic diamines MPDA and DADPM *vs* concentration of the modifying additive AMC-**3** in a range of 1.09—1.16 of the ratio of functional groups

[NH]/EG	[AMC-3] (wt.%)	E_s	σ_R	ε_R (%)	α_n /kJ m^{-2}	ν (%)	T_g/°C
		MPa					
1.15	0	1880	64	5.0	16.1	7.8	163
1.11	0.0038	2180	87	5.9	16.6	16.2	157
1.16	0.045	2080	89	7.0	16.2	22.4	166
1.11	0.192	2140	89	6.3	17.2	11.2	159
1.09	0.43	1610	73	6.1	44.7	10.2	156
1.09	0.603	2130	90	6.6	15.1	13.2	144

Table 6. Physicomechanical properties of the AMC-**3**-modified epoxy polymers based on the epoxy-diane resin Epital and solidifying agent Etal-450

[Etal-450]	AMC-3	E_s	σ_R	ε_R (%)	α_n /kJ m^{-2}	ν (%)	T_g/°C
wt.%		MPa					
16.2	0	2590	59	2.9	9.7	10	74
16.2*	0.40	2750	87	3.7	8.9	15.0	73
17.8	0	2540	66	3.4	11.7	15	88
17.8*	0.41	2650	89	4.0	10.1	18.3	84

* The data were obtained by the extrapolation of the dependence of the physicomechanical properties of the epoxyamine polymer on the concentration of the solidifying agent Etal-450.

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