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STRENGTH OF METALLIFEROUS EPOXY-CHELATE POLYMERS

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ABSTRACT

An original technique for the production of an epoxy matrix with chemically bonded metal atoms has been shown to be the hardening of diglycidyl ether of Bisphenol-A (DGEBA) with the chelates of metals salts and organic acids and aliphatic amines. The dependence of mechanical properties of the epoxy-chelate metalliferous polymers on complex hardener structure has been established. For this purpose, the newly introduced idea of "unitized strength" has been used. The structure of the ligands exerts an insignificant effect on the strength and deflection temperature of the polymers. The anions structure alters the deflection temperature over a wide range (90–163°C) but only slightly influences the strength. The deflection temperature (a) and the strength and elongation at break (b) vary depending on the nature of the metal:

$$Zn^{2+} > Cu^{2+} > Mn^{4+} > Fe^{3+} > Co^{2+} > Ni^{2+} \qquad (a)$$

$$Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Fe^{3+} > Mn^{4+} \qquad (b)$$

The optimum set of the strength indices (breaking stresses, elasticity modules, elongation at break, deflection temperature) has been discovered by hardening the epoxy oligomer with 0.49 mol of a chelate per 1000 g of DGEBA (0.17 mol of a hardener per 1 mol of the oligomer). The strength indices decrease as compared to their maximal attainable value of 12%, which makes it possible for a given amount to be used for the evaluation of properties of unknown metal-containing epoxy-chelate compositions.

I. INTRODUCTION

The ultimate mechanical stress increase endured by a polymer can be achieved by the introduction of polar groups which have the property of strong intermolecular interaction into a polymer structure [1–4]. This principle also extends to epoxy resins. Alteration of the latters' strength properties is realized by modification with metals having high electronegativity which are introduced into the epoxy matrix as admixtures or hardeners [5–12]. The introduction of metal cations increases the tensile strength of the polymers by 85–97 MPa [13, 14], 48 MPa at 225°C, and the flexural strength by 148 MPa, and the compressive strength by 252 MPa [15–17].

The influence of metal on the mechanical properties of epoxy polymers has not been investigated systematically previously. The reason lies in the difficulty of manufacturing polymers having metal atoms linked with a polymer chain by chemical bonds by known methods.

Technologically, a simple and original production technique for polymers containing chemically bonded metal atoms is the hardening of epoxy oligomers with the chelates of the organic acids' metal salts and aliphatic amines [12, 18, 19].

II. EXPERIMENTAL

A. Materials

Diglycidyl ether of Bisphenol-A (DGEBA), ED-22 grade, with an epoxy equivalent weight of 170–180 (made in the USSR) was used as an epoxy oligomer. The salts of metals and organic acids were used as well as the aliphatic amines: ethylene diamine (en), diethylene triamine (dien), triethylene tetramine (trien), and bis-*N,N'*-(β-cyanoethyl)-diethylene triamine (cydien).

B. Methods

The gel time was determined by means of a Reotest-2 instrument. The time for gel formation was assumed to be the time corresponding to the composition viscosity η, for which $\log_{10} \eta = 6$ (mPa·s).

The properties of complex hardeners and polymers were investigated with the thermal analyzer TA 3000 (Mettler) containing a differential scanning calorimeter and thermogravimetric and thermomechanical cells.

The mechanical properties of the polymers were determined by standard methods [20, 21].

C. Synthesis

Complex hardeners were synthesized by directly combining the salts with the amines used in equimolar proportions, with stirring for 2–4 h at the melting points of the chelates. The compounds produced were identified by elemental analysis, and infrared spectroscopy confirmed the coordination of the ligands with the metals through the amino nitrogen atoms. The properties of the hardeners are given in Table 1.

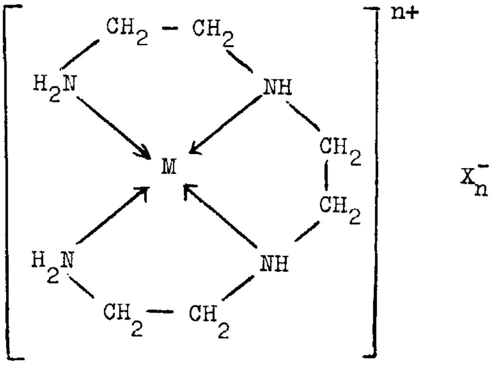
TABLE 1. Properties of Chelate Hardeners

No.	Hardener	Molecular weight	Melting point, °C	Gel time of DGEBA at 95°C, min	Curing time of DGEBA at 120°C, min
1	$Cu(en)_2(HOC_6H_4COO)_2$	457.9	142	645	280
2	$Cu(dien)(HOC_6H_4COO)_2$	440.9	192	555	241
3	$Cu(trien)(HOC_6H_4COO)_2$	484.0	139	230	100
4	$Cu(trien)_2(HOC_6H_4COO)_2$	628.3	97	45	60
5	$Cu(cydien)(HOC_6H_4COO)_2$	546.9	125	492	214
6	$Zn(trien)(HOC_6H_4COO)_2$	521.9	117	221	96
7	$Zn(cydien)(HOC_6H_4COO)_2$	584.8	35	451	196
8	$Co(trien)(HOC_6H_4COO)_2$	497.4	112	451	196
9	$Ni(trien)(HOC_6H_4COO)_2$	551.3	113	180	80
10	$Fe(trien)(HOC_6H_4COO)_3$	613.5	65	205	90
11	$MnO(trien)(HOC_6H_4COO)_2$	491.4	117	148	65
12	$Co(cydien)(HOC_6H_4COO)_2$	560.3	90	942	410
13	$Ni(cydien)(HOC_6H_4COO)_2$	614.1	68	376	160
14	$Fe(cydien)(HOC_6H_4COO)_3$	676.3	47	428	186
15	$Cu(trien)(CH{=}NHC_6H_4O)_2$	450.1	80	70	31
16	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	428.4	228	35	15
17	$Co(dien)(HOC_6H_4COO)_2$	454.4	153	726	316
18	$Cd(en)_2(H_2NC_6H_4COO)_2$	504.9	135	1500	650
19	$Cd(dien)(H_2NC_6H_4COO)_2$	487.8	113	1200	520
20	$Cd(dien)_2(H_2NC_6H_4COO)_2$	591.0	92	200	385
21	$Cd(trien)(H_2NC_6H_4COO)_2$	530.9	125	450	196
22	$Cd(cydien)(H_2NC_6H_4COO)_2$	593.8	92	525	228
23	$Cu(trien)(H_2NC_6H_4COO)_2$	482.1	123	213	93
24	$Zn(cydien)(C_6H_5COO)_2$	516.7	94	433	188
25	$Cu(trien)(CH_3COO)_2$	345.9	55	215	93
26	$Zn(cydien)(CH_3COO)_2$	428.6	<20	410	178
27	$Zn(cydien)\ (CH_2{=}C(CH_3)COO)_2$	444.7	<20	415	180

Metalliferous epoxy-chelate polymers were made by casting the compositions into metal molds where they were hardened for 11 h at 120°C.

III. RESULTS AND DISCUSSION

There are three components in a chelate hardener molecule: a metal, an anion, and a ligand. The structure of the chelate can be represented as follows:



where M is a metal, X is an anion, trien is the ligand, and $n = 2$ or 3. If organic salts and aliphatic amines are used, substitution and elimination of the anions from the salt coordination sphere into the external sphere of the complexes take place [22]. This causes the active nitrogen atoms to be blocked by the metal atom while the hydrogen atoms of NH_2 groups are neutralized by the anions, which results in a complex hardener reactivity decrease (Fig. 1).

The epoxy-chelate compositions possess protracted pot lives at 20–60°C and a sufficiently high cure rate when heated up to 100–120°C (Table 1). The structural fragments of the coordination hardeners call forth the values of curing indices.

The reaction between a chelate and epoxy oligomer takes place due to the complex dissociation which occurs when it is heated:

$$[M(trien)X_n] \rightleftarrows [M(trien)]^{n+} + nX^-$$

The resolution rate depends on the structure of the complex compound fragments and results in stability, decomposition point, and concentration of the hardener in the epoxy composition. As a rule, the chelates dissociate at 70–90°C. The temperature elevation results in complex cation decomposition:

$$[M(trien)]^{n+} \rightleftarrows M^{n+} + trien$$

The hardener eventually undergoes decay to an anion, complex cation, ligand, and metal cation. The rate of decay depends on the stability of the chelate rings in the complex cation $[M(trien)]^{n+}$ which can increase the augmentation of dentato groups in the ligands.

Analyses of the structures of the complexes and their changes at elevated temperatures show that the chelates possess a larger number of reactive groups in the reactions with epoxides than in those with pure amines. Therefore, these reactions

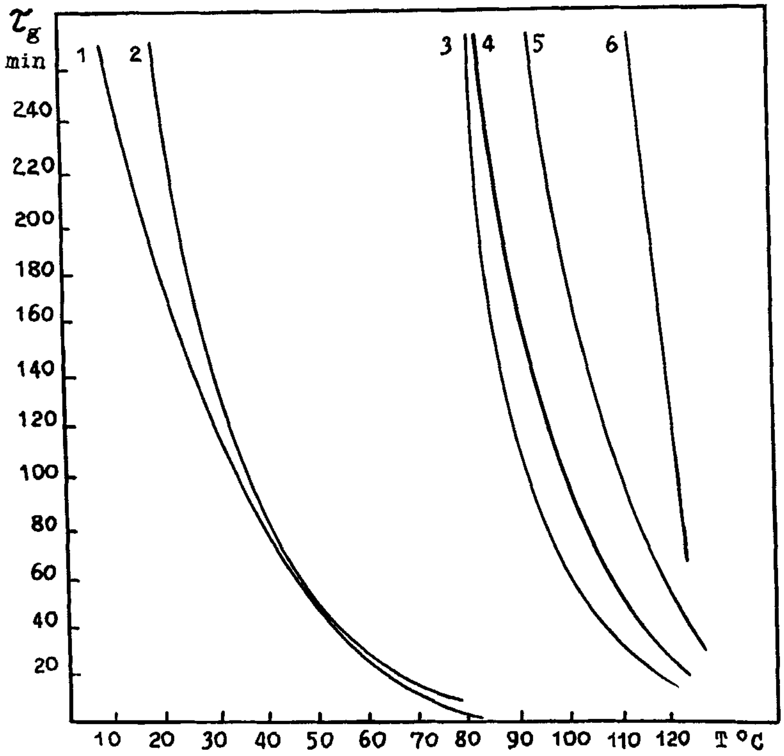


FIG. 1. Gel time of DGEBA (τ_g) as a function of temperature (T) for the hardeners: (1) trien, (2) dien, (3) $[Cd(dien)_2(H_2NC_6H_4COO)_2]$, (4) $[Cu(trien)_2(HOC_6H_4COO)_2]$, (5) $[Cu(trien)(HOC_6H_4COO)_2]$, (6) $[Cd(dien)(H_2NC_6H_4COO)_2]$.

proceed not only by the amino groups in the coreactive cure mechanism, but also by the interaction with the anion X^- and catalysis by the complex cation $[M(trien)]^{n+}$ and metal cation M^{n+}.

Gel and curing times depend on both dissociation of the chelate and complex cation, the hardener amino groups content, and the metal ion characteristics, viz., radius, charge, coordination number of the cation, and the complex compound spatial configuration.

It can be noted from Table 1 that the gel and curing times of the epoxy-chelate compositions increase depending on ligand (1), metal (2), and anion (3) in the series:

$$\text{trien} > \text{cydien} > \text{dien} > \text{en} \quad (1)$$

$$Mn^{4+} > Ni^{2+} > Fe^{3+} > Zn^{2+} > Cu^{2+} > Co^{2+} \sim Cd^{2+} \quad (2)$$

$$NH{=}CHC_6H_4O^- > H_2NC_6H_4COO^- > CH_3COO^- > CH_2{=}C(CH_3)COO^- > C_6H_5COO^- > HOC_6H_4COO^- \quad (3)$$

The use of the various hardener structural fragments has an important effect on the mechanical properties of the epoxy-chelate polymers. The ligand structure effect on polymer properties was investigated by considering the example of the hardeners with the formula

$[M(R)_n(X)_2]$

where $M = Cu^{2+}, Cd^{2+}$
$X = HOC_6H_4COO^-, H_2NC_6H_4COO^-$
R = en ($n = 2$); dien, trien, cydien ($n = 1$)

Table 2 indicates the dependence of the highest polymers mechanical properties on the ligand. The hardener quantities corresponding to the values of the indices are shown in Table 10.

Immediate comparison of the data presented in Table 2 does not show the laws related to ligand structure alteration. Thus, in the case of $[Cu(R)_n(HOC_6H_4COO)_2]$ application, the maximal deflection temperature (130°C) can be achieved for R = trien, the maximal flexural strength is 138 MPa for R = en, the tensile strength is 97 MPa for R = en, and the compressive strength (120 MPa) is independent of R. When $[(Cd(R)_n(H_2NC_6H_4COO)_2]$ is used, the maximal deflection temperature (103 °C) can be achieved for R = dien, the flexural strength is 147 MPa for R = dien, the tensile strength is 100 MPa for R = cydien, and the compressive strength is 137 MPa for R = dien.

For the reasons given above, the new idea of a "unitized index" for the metalliferous polymers has been introduced to solve the problem of the effect of hardener structural fragments on polymer properties.

The unitized index is an important guide in determining the mathematical means of the indices values characterizing one property of the polymers under investigation which have the same structural fragment. When the influence of the ligand structure is examined, the same structural fragment of the polymers is considered to be the ligand. For instance, in the case of the en application, the value of the unitized deflection temperature (UDT) is calculated by the formula:

TABLE 2. Mechanical Properties of Epoxy Chelate Polymers Based on DGEBA as a Function of Ligand Structure

	Hardener							
	$[Cu(R)_n(HOC_6H_4COO)_2]$				$[Cd(R)_n(H_2NC_6H_4COO)_2]$			
	R				R			
Properties	en, $n = 2$	dien, $n = 1$	trien, $n = 1$	cydien, $n = 1$	en, $n = 2$	dien, $n = 1$	trien, $n = 1$	cydien, $n = 1$
DT (°C)	110	100	130	115	70	103	75	100
σ_c (MPa)	120	115	120	120	125	137	98	124
σ_f (MPa)	138	115	115	126	123	147	96	138
σ_t (MPa)	97	89	65	90	68	96	80	100
E_f (GPa)	3.5	3.5	3.2	3.5	4.5	3.4	3.0	3.1
E_t (GPa)	3.1	3.3	3.1	7.6	3.4	4.2	6.0	4.4
ϵ (%)	5.0	5.0	3.5	5.0	1.8	3.4	.2	5.0

$$\mathrm{UDT} = \frac{\mathrm{DT}_1 + \mathrm{DT}_2}{2}$$

where DT_1 is the deflection temperature of DGEBA hardened with $[Cu(en)_2(HOC_6H_4COO)_2]$
DT_2 is the deflection temperature of DGEBA hardened with $[Cd(en)_2(H_2NC_6H_4COO)_2]$

The value of the unitized strength (US) is calculated by

$$\mathrm{US} = \frac{(\sigma_c + \sigma_f + \sigma_t)_1 + (\sigma_c + \sigma_f + \sigma_t)_2}{6}$$

where $(\sigma_c + \sigma_f + \sigma_t)_1$ is the sum of the breaking stresses of DGEBA hardened with $[Cu(en)_2(HOC_6H_4COO)_2]$
$(\sigma_c + \sigma_f + \sigma_t)_2$ is the sum of the breaking stresses of DGEBA hardened with $[Cd(en)_2(H_2NC_6H_4COO)_2]$

and so on.

Based on the present procedure, the dependence of the unitized indices of the epoxy-chelate polymers on ligand type is obtained:

	en	dien	trien	cydien
UDT, °C	90.0	101.5	102.5	107.5
US, MPa	112.0	116.5	95.7	116.3
UM, GPa	3.6	3.6	3.8	4.7
UE, %	3.4	4.2	3.4	5.0

Comparison of these unitized indices leads to the conclusion that the ligand structure has an insignificant influence on deflection temperature (the decrease only for en) and strength (the decrease for trien).

The effect of anion type on the metalliferous polymers properties was examined by studying the hardeners with the formula

$[M(R)(X)_2]$

where $M = Cu^{2+}, Zn^{2+}$
R = trien, cydien
$X = CH_3COO^-, C_6H_5COO^-, H_2NC_6H_4COO^-, HOC_6H_4COO^-, CH{=}NHC_6H_4O^-, CH_2{=}C(CH_3)COO^-$

Tables 3 and 4 list the highest polymer mechanical properties used as a basis for the calculation of unitized indices values:

	CH_3COO^-	$C_6H_5COO^-$	$HOC_6H_4COO^-$
UDT, °C	101.0	95.5	130.0
US, MPa	107.5	112.3	111.0
UM, GPa	3.6	4.3	3.5
UE, %	3.4	2.7	4.3

TABLE 3. Mechanical Properties of Epoxy Chelate Polymers Based on DGEBA as a Function of Anion Structure (trien is the ligand; Cu^{2+} is the cation)

	Anion			
Properties	CH_3COO^-	$H_2NC_6H_4COO^-$	$HOC_6H_4COO^-$	$CH{=}NHC_6H_4O^-$
DT (°C)	102	134	130	163
σ_c (MPa)	133	145	120	122
σ_f (MPa)	130	120	115	95
σ_t (MPa)	77	88	65	39
E_f (GPa)	3.3	3.0	3.2	3.3
E_t (GPa)	3.4	3.0	3.1	3.5
ϵ (%)	4.0	2.5	3.5	1.3

It is obvious that the anions affect the polymer's strength slightly, while the deflection temperature depends largely on their structure.

Hardeners containing CH_3COO^-, $C_6H_5COO^-$ and $CH_2{=}C(CH_3)COO^-$ yield deflection temperatures of 90–102°C. Complexes with $HOC_6H_4COO^-$, $H_2NC_6H_4COO^-$, and $CH{=}NHC_6H_4O^-$ provide a deflection temperature not lower than 130°C, which is caused by the structures of these chelates. Since the anions are in the external sphere of the complexes, the number of crosslinkages in the polymer matrix is conditioned by their structures. Anions of the CH_3COO^-, $C_6H_5COO^-$, and $CH_2{=}C(CH_3)COO^-$ types, being monofunctional, break the epoxy ring and, having added to the carbon atom, do not form additional crosslinkages:

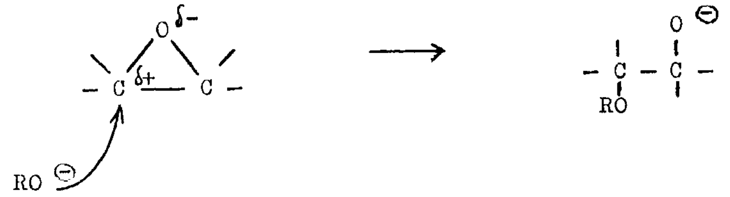


TABLE 4. Mechanical Properties of Epoxy Chelate Polymers Based on DGEBA as a Function of Anion Structure (cydien is the ligand; Zn^{2+} is the cation)

	Anion			
Properties	CH_3COO^-	$C_6H_5COO^-$	$HOC_6H_4COO^-$	$CH_2{=}C(CH_3)COO^-$
DT (°C)	100	97	130	102
σ_c (MPa)	97	133	130	124
σ_f (MPa)	131	125	145	87
σ_t (MPa)	77	87	91	55
E_f (GPa)	3.6	4.5	4.1	4.1
E_t (GPa)	3.9	4.0	3.4	4.0
ϵ (%)	2.8	2.7	5.0	2.1

TABLE 5. Mechanical Properties of Epoxy Chelate Polymers Based on DGEBA as a Function of Anion Structure (dien is the ligand; Co^{2+} is the cation)

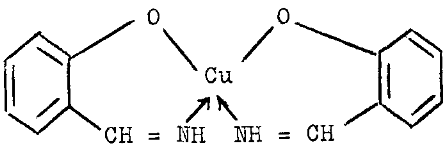
	Anion	
Properties	$HOC_6H_4COO^-$	$CH{=}N(CH_2)C_6H_4O^-$
DT (°C)	115	105
σ_c (MPa)	109	97
σ_f (MPa)	139	125
σ_t (MPa)	91	65
E_f (GPa)	3.7	3.8
E_t (GPa)	3.2	3.6
ϵ (%)	4.8	2.3

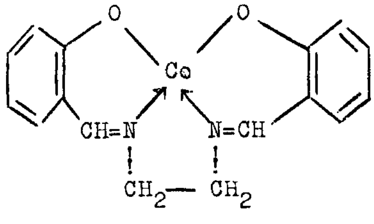
Anions of the $HOC_6H_4COO^-$, $H_2NC_6H_4COO^-$, and $CH{=}NHC_6H_4O^-$ types are bifunctional, and their functional groups ($HO-$, H_2N-, $CH{=}NH-$, COO^-) can react with the epoxy group. This leads to the formation of additional bonds, a stiffness increase of the epoxy matrix, and an extra deflection temperature. At the same time, some increase of strength can be observed, e.g., the tensile strength of DGEBA hardened with $[Zn(cydien)(HOC_6H_4COO)_2]$ is equal to 91 MPa, which is 14 MPa higher than for $[Zn(cydien)(CH_3COO)_2]$. The conservation of strength in comparison with the benzoate ion, and even its decrease, is evidence of the development of internal stresses in the polymer matrix. This is confirmed by the properties of DGEBA hardened with the copper chelate $[Cu(trien)(CH{=}NHC_6H_4O)_2]$. The complex of copper salicylaldimine, which is a highly reactive hardener due to the presence of imino and phenoxy groups, provides the maximal deflection temperature (163 °C) compared to the other anions. The polymer strength decreases markedly as a result of the internal stresses expansion due to the salicylaldimine-anion volume enlargement.

Table 5 shows the properties of the epoxy polymers based on DGEBA and the hardeners with the formula

$[Co(dien)(X)_2]$

where X = $HOC_6H_4COO^-$ or $CH{=}N(CH_2)C_6H_4O^-$. As seen from comparison of the copper and cobalt salicylaldimines structures, the cobalt chelate possesses an additional five-membered ring, bonding the nitrogen atoms through a methylene bridge:





In this instance the three fixed rings give the cobalt salicylaldimine added stability. Then the anion becomes less likely to move into the external coordination sphere of the complex during chelation with the aliphatic amines, screens the cation, and, therefore, will not react with the epoxy groups. This results in a lower cure efficiency (Table 1), a decrease in the number of crosslinkages, and leads to a marked deflection temperature reduction in the values peculiar to the acetates (105 °C). The anion in the copper complex $[Cu(trien)(CH{=}NHC_6H_4O)_2]$, which is transferred into the external coordination sphere during chelation with trien, can react with epoxy groups, and this hardener provides the highest deflection temperature. The cobalt-containing polymer strength increases due to reduction in the internal stresses as compared to the copper-containing one: the flexural strength is 125 MPa (95 MPa for the copper-containing polymer), and the tensile strength is 65 MPa (39 MPa).

Thus, the polymers strength is slightly affected by anions with the same structure and size (for example, the salicylate and anthranilate). When polyfunctional anions (salicylaldimine and salicylate) are used instead of monofunctional ones (benzoate and acetate), the strength is even less affected due to the internal stresses.

The dependence of the epoxy-chelate polymers strength on the metal nature was investigated by considering an example of the hardeners with the formula

$$[M(R)(HOC_6H_4COO)_n]$$

where $M = Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, MnO^{2+}$ ($n = 2$); Fe^{3+} ($n = 3$)
R = trien, cydien

Tables 6 and 7 list the attainable strength properties of the polymers, which are largely dependent on the metal: the deflection temperature ranges from 92 to 130°C and the tensile strength varies from 53 to 91 MPa. In order to reveal the qualitative regularities, the values of the unitized indices of the polymers were calculated (Table 8). Data analysis shows the dependency on the metal nature of the polymer's deflection temperature (4) and strength and elongation (5) decrease:

$$Zn^{2+} > Cu^{2+} > Mn^{4+} > Fe^{3+} > Co^{2+} > Ni^{2+} \quad (4)$$

$$Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Fe^{3+} > Mn^{4+} \quad (5)$$

TABLE 6. Mechanical Properties of Epoxy Chelate Polymers Based on DGEBA as a Function of Cation Type (trien is the ligand; $HOC_6H_4COO^-$ is the anion)

	Cation					
Properties	Cu^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Fe^{3+}	Mn^{4+}
DT (°C)	130	130	108	95	92	110
σ_c (MPa)	120	128	122	117	131	128
σ_f (MPa)	115	133	130	109	84	52
σ_t (MPa)	65	92	79	55	63	53
E_f (GPa)	3.2	3.4	3.5	4.1	4.2	4.1
E_t (GPa)	3.1	3.7	3.4	4.4	3.9	3.1
ϵ (%)	3.5	4.6	3.8	2.1	1.8	1.3

TABLE 7. Mechanical Properties of Epoxy Chelate Polymers Based on DGEBA as a Function of Cation Type (cydien is the ligand; $HOC_6H_4COO^-$ is the anion)

	Cation				
Properties	Cu^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Fe^{3+}
DT (°C)	115	130	100	92	120
σ_c (MPa)	120	130	126	124	125
σ_f (MPa)	126	145	117	125	112
σ_t (MPa)	90	91	53	68	74
E_f (GPa)	3.5	4.1	3.4	3.6	3.7
E_t (GPa)	7.6	3.4	4.0	4.4	3.0
ϵ (%)	5.0	5.0	3.5	2.7	2.2

The difference between series (4) and (5) occurs because the metal ions, having high positive charges, display both a short-range interaction to form the stable covalent and coordinate bonds and a remote action with physical bond formation (van der Waals interaction) in the epoxy matrix, thus increasing the deflection temperature. Since the attraction energy of molecules is directly proportional to the dipole moment of interacting particles, and inversely proportional to the distance between them, the deflection temperature of the metalliferous polymer is determined by two metal cation characteristics: its charge and radius.

To confirm the conclusions obtained, the properties of the nonmetal-containing epoxy composition have been investigated. This composition possesses the remaining chelate structural fragments: an aliphatic amine and salicylic acid in a 1 : 2 molar ratio, respectively. In order to avoid carbonic acid amide formation, the hardener was produced when cooled without permitting the temperature to be more than 50°C:

$$2R_1COOH + NH_2R_2NH_2 \rightarrow R_1COONH_3R_2NH_3OOCR_1$$

TABLE 8. Unitized Indices of Epoxy Chelate Metalliferous Polymers (trien and cydien are the ligands; $HOC_6H_4COO^-$ is the anion)

	Cation					
Unitized indices	Cu^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Fe^{3+}	Mn^{4+}
UDT (°C)	122.5	130.0	104.0	93.5	106.0	109.8
US (MPa)	106.0	119.8	104.5	99.7	98.2	76.2
UM (GPa)	4.35	3.65	3.58	4.13	3.70	3.60
UE (%)	4.3	4.8	3.7	2.4	2.0	1.3

where R_1 is the salicylate ion radical
R_2 is an aliphatic amine radical ($NH_2R_2NH_2$ = trien)

The epoxy polymer properties attained by use of [(trien)($HOC_6H_4COOH)_2$] are listed in Table 9.

Comparison of the properties of the metalliferous and nonmetal-containing polymers (Tables 6, 8, 9) indicates that the metal cations affect the intermolecular interaction more strongly than the ligands and anions. Thus, by varying the complex hardener structural fragments, very strong epoxy polymers may be produced.

The class of metal coordination compounds which can be applied as epoxy oligomers hardeners is rather wide. This is an important reason why the properties of the new hardeners can be estimated. The optimization of the epoxy-chelate compositions has been carried out; i.e., the experimental data of the optimal quantities of the hardeners corresponding to the maximal strength of the polymers were processed (Table 10). The mean values of the optimal quantities of the hardeners necessary for a set of the indices maximal values $\overline{X}_1$ were calculated. The mean values of the optimal quantities of the hardeners necessary for the maximal value of a separate index $\overline{X}_2$, irrespective of the structure of the chelates, were also calculated. The results obtained made it possible to estimate the quantity of chelate necessary for the synthesis of a metalliferous polymer with a set of optimal properties equal to 0.49 mol of a hardener per 1000 g of DGEBA (0.17 mol of a complex per 1 mol of the oligomer).

The decrease of the strength indices of DGEBA hardened with 0.49 mol of a chelate in comparison with the maximal polymer strength is estimated in Table 11. It will be noted that in the case of separate chelates this decrease varies from 2.2 to 28.7%, but for each index it lies between the limits of 6.3 and 21.9%. On average, the strength decrease is 12%, which allows the given quantity to be used for the estimation of the properties of the epoxy polymers based on DGEBA and the unknown complexes.

TABLE 9. Properties of Epoxy Polymers Based on DGEBA and [(trien)($HOC_6H_4COOH)_2$]

Properties	Values
DT (°C)	100
σ_c (MPa)	102
σ_f (MPa)	133
σ_t (MPa)	43
US (MPa)	92.7
E_f (GPa)	3.5
E_t (GPa)	2.7
UM (GPa)	3.1
ϵ (%)	1.8

TABLE 10. Optimization of Epoxy Chelate Compositions

		Optimal quantity of hardener, mol/1000 g DGEBA							
No.	Hardener	DT	σ_c	σ_f	σ_t	E_f	E_t	ϵ	$\overline{X}_1$
1	$Cu(en)_2(HOC_6H_4COO)_2$	0.44	0.87	0.87	0.79	0.66	0.44	0.87	0.70
2	$Cu(dien)(HOC_6H_4COO)_2$	0.68	0.91	0.68	0.79	0.68	0.68	0.68	0.73
3	$Cu(trien)(HOC_6H_4COO)_2$	0.50	0.43	0.50	0.43	0.50	0.43	0.43	0.46
4	$Cu(trien)_2(HOC_6H_4COO)_2$	0.32	0.57	0.38	0.51	0.38	0.57	0.16	0.41
5	$Cu(cydien)(HOC_6H_4COO)_2$	0.18	0.18	0.64	0.64	0.64	0.55	0.55	0.48
6	$Zn(trien)(HOC_6H_4COO)_2$	0.67	0.57	0.29	0.29	0.67	0.67	0.29	0.49
7	$Zn(cydien)(HOC_6H_4COO)_2$	0.43	0.68	0.26	0.34	0.51	0.51	0.34	0.44
8	$Co(trien)(HOC_6H_4COO)_2$	0.50	0.50	0.30	0.30	0.30	0.50	0.30	0.39
9	$Ni(trien)(HOC_6H_4COO)_2$	0.27	0.73	0.54	0.27	0.73	0.73	0.45	0.53
10	$Fe(trien)(HOC_6H_4COO)_3$	0.33	0.65	0.57	0.16	0.57	0.65	0.16	0.44
11	$MnO(trien)(HOC_6H_4COO)_2$	0.71	0.51	0.31	0.20	0.61	0.81	0.20	0.48
12	$Co(cydien)(HOC_6H_4COO)_2$	0.45	0.36	0.36	0.27	0.27	0.71	0.45	0.41
13	$Co(dien)(HOC_6H_4COO)_2$	0.55	0.66	0.66	0.44	0.66	0.44	0.55	0.57
14	$Ni(cydien)(HOC_6H_4COO)_2$	0.24	0.16	0.24	0.16	0.57	0.49	0.24	0.30
15	$Fe(cydien)(HOC_6H_4COO)_3$	0.30	0.52	0.22	0.22	0.22	0.59	0.22	0.33
16	$Cu(trien)(CH{=}NHC_6H_4O)_2$	0.56	0.22	0.78	0.56	0.67	0.67	0.56	0.57
17	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	0.47	0.35	0.35	0.58	0.35	0.35	0.58	0.43
18	$Cd(en)_2(H_2NC_6H_4COO)_2$	0.59	0.40	0.40	0.40	0.40	0.50	0.50	0.46
19	$Cd(dien)_2(H_2NC_6H_4COO)_2$	0.34	0.34	0.68	0.68	0.20	0.20	0.68	0.45
20	$Cd(dien)(H_2NC_6H_4COO)_2$	0.61	0.51	0.61	0.61	0.61	0.72	0.61	0.61
21	$Cd(trien)(H_2NC_6H_4COO)_2$	0.57	0.41	0.41	0.41	0.41	0.38	0.41	0.43
22	$Cd(cydien)(H_2NC_6H_4COO)_2$	0.67	0.59	0.51	0.51	0.34	0.34	0.51	0.50
23	$Cu(trien)(H_2NC_6H_4COO)_2$	0.48	0.66	0.48	0.48	0.48	0.48	0.48	0.51
24	$Zn(cydien)(C_6H_5COO)_2$	0.58	0.28	0.39	0.23	0.58	0.29	0.29	0.38
25	$Cu(trien)(CH_3COO)_2$	0.29	0.72	0.43	0.43	1.16	0.43	0.43	0.56
26	$Zn(cydien)(CH_3COO)_2$	0.51	0.93	0.28	0.23	0.35	0.93	0.35	0.51
27	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	0.56	0.90	0.27	0.22	0.90	0.79	0.22	0.55
$\overline{X}_2$		0.47	0.54	0.46	0.41	0.53	0.55	0.44	0.49

TABLE 11. Mechanical Properties Decrease of Polymers Based on 1000 g DGEBA Hardened with 0.49 mol Chelate in Comparison with the Strength Indices Maximal Values

No.	Hardener	Hardener mass, g	The decrease of strength index, %							
			DT	σ_c	σ_f	σ_t	E_f	E_t	ϵ	$\overline{X}_1$
1	$Cu(en)_2(HOC_6H_4COO)_2$	22.4	2.7	20.8	14.5	14.4	5.7	3.2	10.0	10.2
2	$Cu(dien)(HOC_6H_4COO)_2$	21.6	13.0	13.0	1.7	12.4	14.3	15.2	20.0	12.9
3	$Cu(trien)(HOC_6H_4COO)_2$	23.7	0	0	0	3.1	0	3.2	11.4	2.5
4	$Cu(trien)_2(HOC_6H_4COO)_2$	30.8	16.6	8.7	1.6	4.2	3.3	0	22.6	8.1
5	$Cu(cydien)(HOC_6H_4COO)_2$	26.8	15.7	11.7	5.6	6.7	11.4	2.6	0	7.7
6	$Zn(trien)(HOC_6H_4COO)_2$	25.6	6.2	0.8	17.3	37.0	0	2.7	58.7	17.5
7	$Zn(cydien)(HOC_6H_4COO)_2$	28.7	13.1	7.7	15.2	31.9	0	2.9	56.0	18.1
8	$Co(trien)(HOC_6H_4COO)_2$	24.4	0	0	39.2	68.4	14.3	0	38.9	23.0
9	$Ni(trien)(HOC_6H_4COO)_2$	27.0	10.5	11.1	3.7	9.1	17.1	40.9	4.8	13.9
10	$Fe(trien)(HOC_6H_4COO)_3$	30.1	15.2	2.3	1.2	28.6	4.8	10.3	38.9	14.5
11	$MnO(trien)(HOC_6H_4COO)_2$	24.1	6.4	0	5.8	56.6	14.6	7.3	46.2	19.6
12	$Co(cydien)(HOC_6H_4COO)_2$	27.5	4.0	11.1	14.5	9.4	8.8	5.0	0	7.5
13	$Co(dien)(HOC_6H_4COO)_2$	22.3	0	6.4	5.8	0	2.7	0	4.2	2.7
14	$Ni(cydien)(HOC_6H_4COO)_2$	30.1	13.0	14.5	19.2	36.8	8.3	0	55.6	21.1
15	$Fe(cydien)(HOC_6H_4COO)_3$	33.1	16.7	0	60.7	52.7	5.4	3.3	50.0	27.0
16	$Cu(trien)(CH{=}NHC_6H_4O)_2$	22.1	14.1	12.3	10.5	2.6	3.0	8.6	0	7.3
17	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	21.0	0	4.1	5.6	0	5.3	2.8	8.7	3.8
18	$Cd(en)_2(H_2NC_6H_4COO)_2$	24.7	0	8.8	23.6	5.9	33.3	0	0	10.2
19	$Cd(dien)_2(H_2NC_6H_4COO)_2$	29.0	19.1	6.2	5.1	4.9	17.1	13.5	5.0	10.1
20	$Cd(dien)(H_2NC_6H_4COO)_2$	23.9	5.8	0	6.1	1.0	8.8	4.8	11.8	5.5
21	$Cd(trien)(H_2NC_6H_4COO)_2$	26.0	9.3	0	1.0	0	0	1.7	3.1	2.2
22	$Cd(cydien)(H_2NC_6H_4COO)_2$	29.1	12.0	6.5	0.7	0	6.5	34.1	0	8.5
23	$Cu(trien)(H_2NC_6H_4COO)_2$	23.6	0	3.4	34.4	0	0	0	0	5.4
24	$Zn(cydien)(C_6H_5COO)_2$	25.3	9.3	9.8	6.4	20.7	4.4	27.5	33.3	15.9
25	$Cu(trien)(CH_3COO)_2$	16.9	4.9	24.1	15.4	18.2	0	14.7	25.0	14.6
26	$Zn(cydien)(CH_3COO)_2$	21.0	0	1.0	4.6	16.9	0	17.9	35.7	10.9
27	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	21.8	5.9	12.9	12.6	52.7	26.8	37.5	52.4	28.7
$\overline{X}_2$			7.9	6.3	12.3	18.3	8.0	9.6	21.9	12.0

CONCLUSION

The established laws of the chelate hardeners structure effect on polymer strength indicate that the metal nature is of prime importance, since the metal cations change both the strength and deflection temperature which testifies to the strong electrostatic interaction between cations and the epoxy matrix.

SYMBOLS

DT	deflection temperature
σ_c	compressive strength
σ_f	flexural strength
σ_t	tensile strength
E_f	flexural modulus
E_t	tensile modulus
ϵ	elongation at break
UDT	unitized deflection temperature
US	unitized strength
UM	unitized modulus
UE	unitized elongation at break
$\overline{X}_1$	the mean value of the optimal quantity of a chelate necessary for the set of the indices maximal values of DGEBA hardened with this chelate
$\overline{X}_2$	the mean value of the optimal quantity of the chelates necessary for the maximal value of a separate index

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