Metalliferous epoxy chelate polymers: 3. Influence of structural fragments on the properties of similar matrices

Alexis V. Kurnoskin
Scientific Productive Unit 'Stekloplastik', Krjukovo, Moscow, Russia
(Received 1 October 1991; revised 12 May 1992)

The influence of the structural fragments (metal cation, ligand and anion) of metalliferous epoxy chelate polymers (MECPs) on their properties, viz strength, deformation temperature (DT) and thermal oxidative stability, has been examined. Correlations between tensile strength (σ_t) and tensile modulus (E_t) and between flexural strength (σ_f) and flexural modulus (E_f), $\sigma_t = f(E_t)$ and $\sigma_f = f(E_f)$, have been established. By supposing that, when the conditions $\sigma_{t,A} = \sigma_{t,B}$, $\sigma_{f,A} = \sigma_{f,B}$, $E_{t,A} = E_{t,B}$ and $E_{f,A} = E_{f,B}$ are fulfilled, where A and B are complex hardeners of partly different structures, the epoxy chelate matrices based on the same oligomer and these complexes have similar structures, the influence of the structural fragments on MECP properties was evaluated. It was found that the effect of chelate structure on the alteration of polymer properties is maximal for thermal oxidative stability(ΔM is the polymer mass loss after thermal treatment in air), minimal for compressive strength (σ_c) and decreases in the following order:

$$\Delta M > \varepsilon > DT > \sigma_t > E_t > \sigma_c$$

where ε is elongation at break.

(Keywords: epoxy polymers; metal-containing polymers; structural fragments; influence; properties)

INTRODUCTION

In two previous papers[1,2] a description has been given of the synthesis and properties of new chelates of transition metals with aliphatic amines (ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien) and cyanoethylated diethylenetriamine (cydien)) used as hardeners of epoxy resins. The conditions of preparation and the test methods of metalliferous epoxy chelate polymers (MECPs) based on the diglycidyl ether of bisphenol A (DGEBA) and these chelates have also been discussed. It has been found that there are two approaches to the investigation of the effects of structural fragments (metal cation, ligand and anion) of chelate hardeners on MECP properties:

(i) comparison of the indices of polymers of similar composition, and

(ii) comparison of the indices of polymers having some equal properties.

The purpose of the present paper is to realize the second method.

RESULTS AND DISCUSSION

Consider the correlation between the structure and properties of polymers. If all the properties of two polymers (strength indices, glass transition temperature, electrical and optical properties, chemical resistance, heat stability and so on) coincide, it is possible to say that these polymers have equal structures. The greater the number of coinciding properties of two polymers, the higher the probability of their structures being similar, especially in the case of set polymers obtained from the same oligomer.

The study of the structure of epoxy chelate matrices, e.g. based on DGEBA, is possible by varying the structure of the chelate hardeners by changing the hardener structural fragments and then analysing the polymer property changes. Consider the properties of MECPs having some equal indices. With this end in view, examine the dependence of polymer strength on the modulus of elasticity (*Figures 1–7*).

Figures 1 and *2* present the experimental dependences $\sigma_f = f(E_f)$ and $\sigma_t = f(E_t)$ of polymers based on DGEBA and the nickel chelates $[Ni(cydien)(HOC_6H_4COO)_2]$ and $[Ni(trien)(HOC_6H_4COO)_2]$. The strength and modulus variation is caused by the change in hardener concentration in the epoxy compounds. The above figures show the dependence $\sigma = f(E)$ as a 'curve' with a distinct 'bend'. Since the strength of network polymers is known to change linearly with the change of modulus of elasticity[3], it may be supposed that the bend points of the curves in *Figures 1–7* correspond to the abrupt change of structure of epoxy chelate matrices due to the change of complex hardener concentration. For instance, the bend points of the graphs $\sigma = f(E)$ of $[Ni(trien)(HOC_6H_4COO)_2]$ (*Figures 1* and *2*) correspond to $C_h = 0.12$, 0.18 and 0.22 mol/mol of DGEBA. As seen in *Figure 8*, the dependences of polymer properties on hardener concentration have inflections at these points as a result of the change of the epoxy matrix structure. An analogous picture is observed in examples where the curves $\sigma = f(E)$ turn back on themselves (*Figures 3* and *9*, $[Cu(trien)(CH{=}NHC_6H_4O)_2]$).

0032-3861/93/051077-12

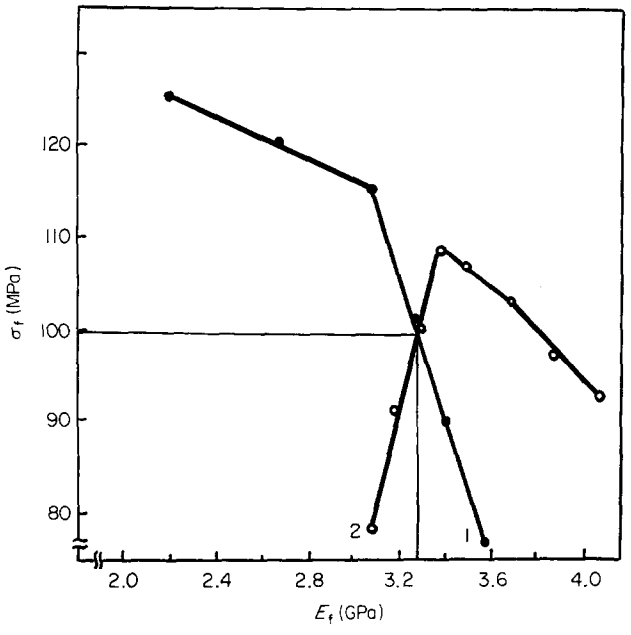

Figure 1 Flexural strength σ_f of the polymers based on DGEBA and [Ni(cydien)$(HOC_6H_4COO)_2$] (1) and [Ni(trien)$(HOC_6H_4COO)_2$] (2) as a function of flexural modulus E_f

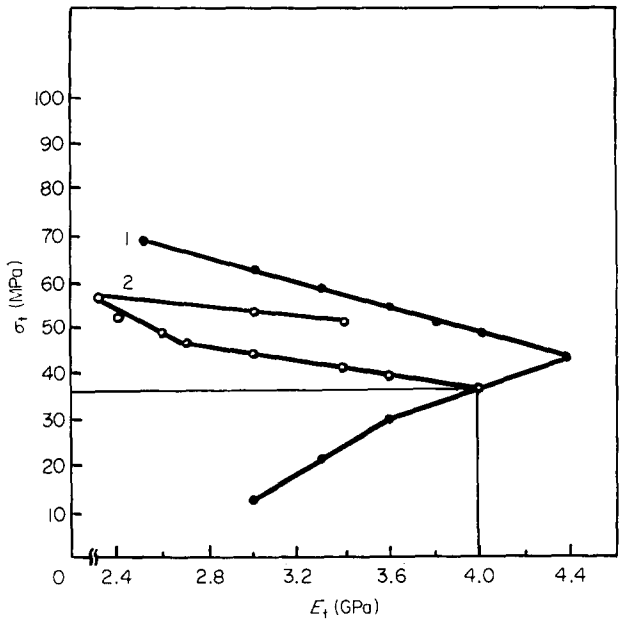

Figure 2 Tensile strength σ_t of the polymers based on DGEBA and [Ni(cydien)$(HOC_6H_4COO)_2$] (1) and [Ni(trien)$(HOC_6H_4COO)_2$] (2) as a function of tensile modulus E_t

Comparing the dependence $\sigma = f(E)$ obtained for different chelates, one can see that the plots intersect one another at one point (*Figures 1* and *2*), two points (*Figure 3*), three points (*Figure 4*) and four points (*Figure 5*), as well as have a path in common (*Figure 6*) or have no points of intersection (*Figure 7*). At the intersection points of the plots $\sigma_A = f(E_A)$ and $\sigma_B = f(E_B)$ for hardeners A and B, evidently the conditions:

$$\sigma_A = \sigma_B \qquad E_A = E_B \tag{1}$$

are satisfied, i.e. the epoxy chelate matrices based on DGEBA cured with hardeners A and B have two equal properties. These polymer matrices are formed by the same epoxy oligomer and complexes with similar structures. For example, when [Ni(cydien)$(HOC_6H_4COO)_2$] and [Ni(trien)$(HOC_6H_4COO)_2$] are used, the only difference between the hardeners is the structure of the ligands, but this difference is not very marked:

trien H_2N-$(CH_2)_2$-NH-$(CH_2)_2$-NH-$(CH_2)_2$-NH_2

cydien NC-$(CH_2)_2$-NH-$(CH_2)_2$-NH-$(CH_2)_2$-NH-$(CH_2)_2$-CN

Consequently, to compare matrices having some equal properties, it may be assumed that the matrices are similar.

Strictly speaking, complete coincidence of the structures of epoxy polymer matrices fails to be achieved

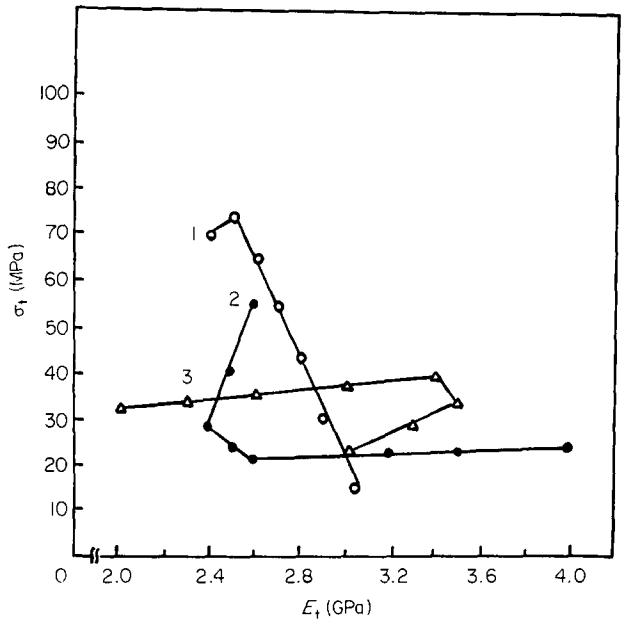

Figure 3 Tensile strength σ_t of the polymers based on DGEBA and chelate hardeners as a function of tensile modulus E_t. Hardeners: 1, [Fe(cydien)$(HOC_6H_4COO)_3$]; 2, [Zn(cydien)$(CH_2{=}C(CH_3)COO)_2$]; 3, [Cu(trien)$(CH{=}NHC_6H_4O)_2$]

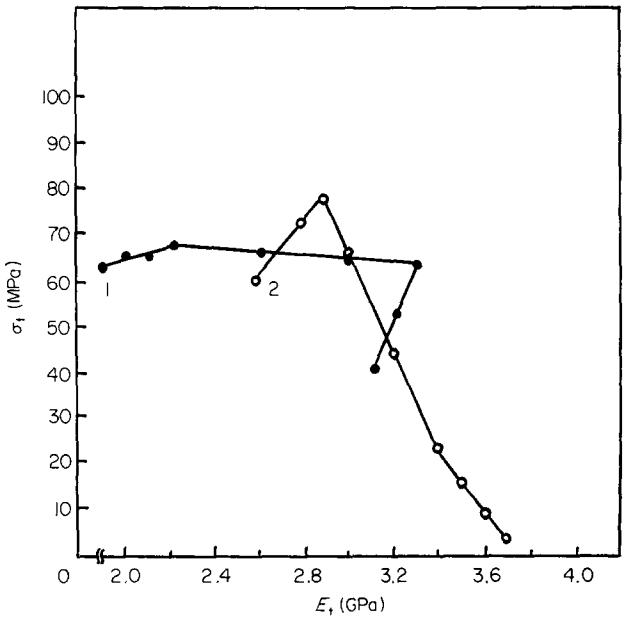

Figure 4 Tensile strength σ_t of the polymers based on DGEBA and [Cd$(en)_2(H_2NC_6H_4COO)_2$] (1) and [Co(trien)$(HOC_6H_4COO)_2$] (2) as a function of tensile modulus E_t

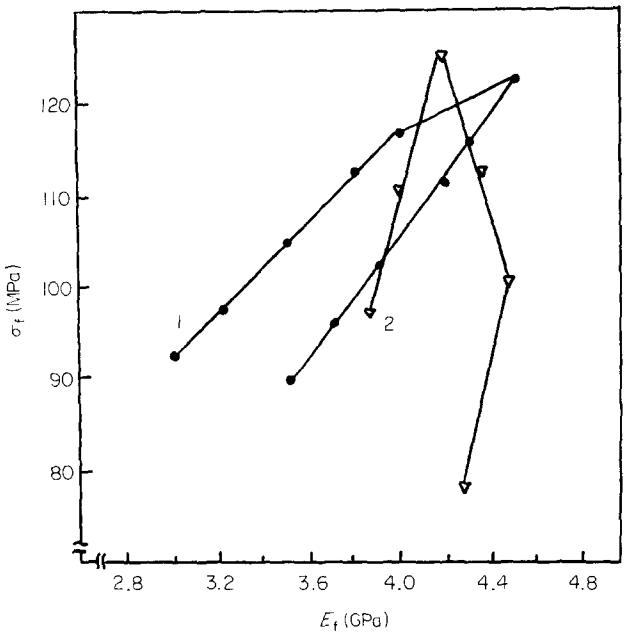

Figure 5 Flexural strength σ_f of the polymers based on DGEBA and $[Cd(en)_2(H_2NC_6H_4COO)_2]$ (1) and $[Zn(cydien)(C_6H_5COO)_2]$ (2) as a function of flexural modulus E_f

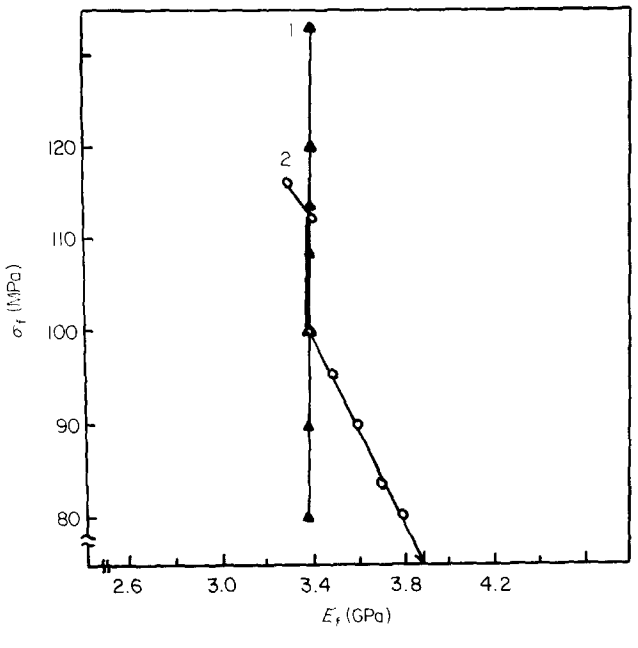

Figure 6 Flexural strength σ_f of the polymers based on DGEBA and $[Zn(trien)(HOC_6H_4COO)_2]$ (1) and $[Cd(dien)_2(H_2NC_6H_4COO)_2]$ (2) as a function of flexural modulus E_f

because of distinctions in the chemical compositions of the hardeners. One may merely speak about partial similarity of the structures. At the same time it stands to reason that the similarity is higher, the greater the number of coinciding indices of the polymers. For instance, when the conditions:

$$\sigma_{t,A}=\sigma_{t,B} \qquad \sigma_{f,A}=\sigma_{f,B} \qquad \sigma_{c,A}=\sigma_{c,B}$$

$$E_{t,A}=E_{t,B} \qquad E_{f,A}=E_{f,B} \qquad (2)$$

$$DT_A \approx DT_B \qquad \Delta M_A=\Delta M_B$$

are satisfied, the similarity of the structures of the

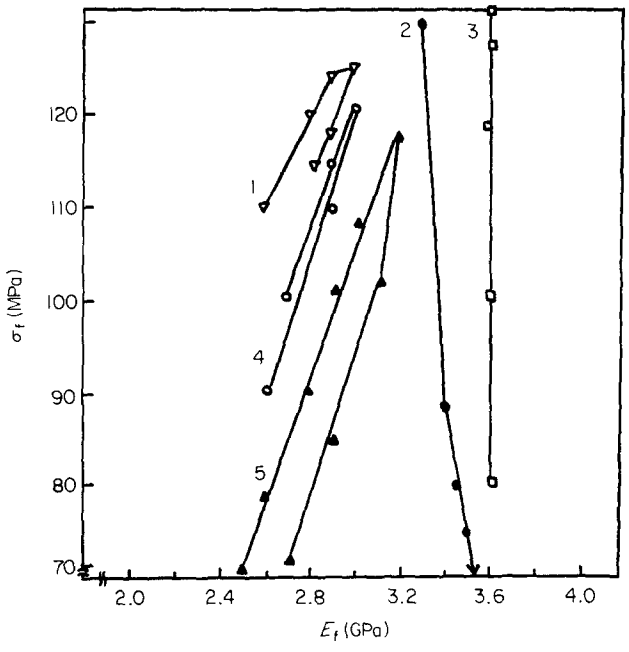

Figure 7 Flexural strength σ_f of the polymers based on DGEBA and chelate hardeners as a function of flexural modulus E_f. Hardeners: 1, $[Cu(trien)_2(HOC_6H_4COO)_2]$; 2, $[Cu(trien)(CH_3COO)_2]$; 3, $[Zn(cydien)(CH_3COO)_2]$; 4, $[Cu(trien)(H_2NC_6H_4COO)_2]$; 5, $[Cu(trien)(HOC_6H_4COO)_2]$

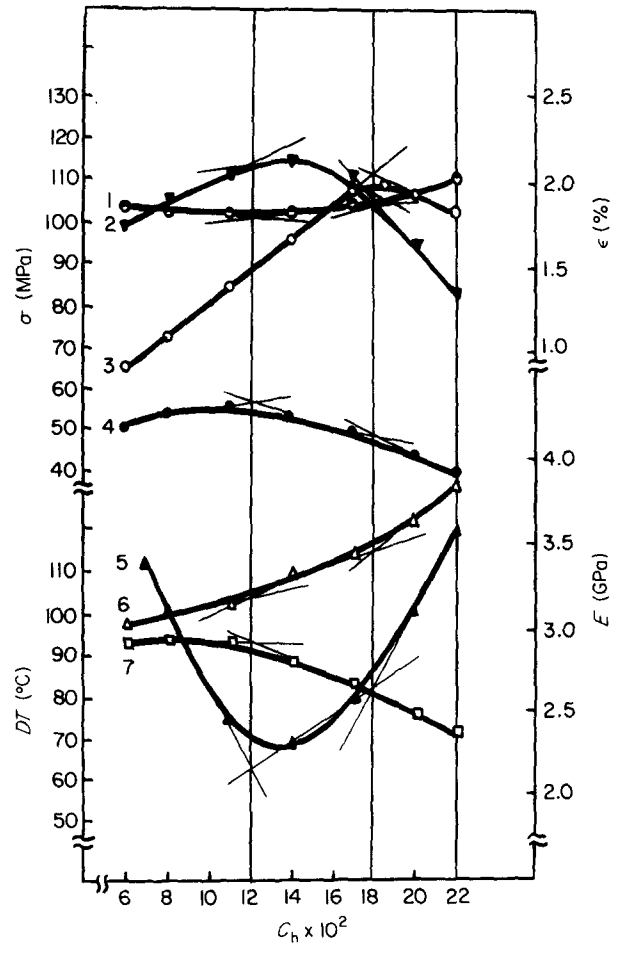

Figure 8 The change of the properties of the polymers based on DGEBA and $[Ni(trien)(HOC_6H_4COO)_2]$ at the bend points of the graphs $\sigma=f(E)$ corresponding to the hardener concentrations $C_{h,1}=0.12$, $C_{h,2}=0.18$, $C_{h,3}=0.22$ mol/mol of DGEBA. Curves: 1, σ_c; 2, ε; 3, σ_f; 4, σ_t; 5, E_t; 6, E_f; 7, DT

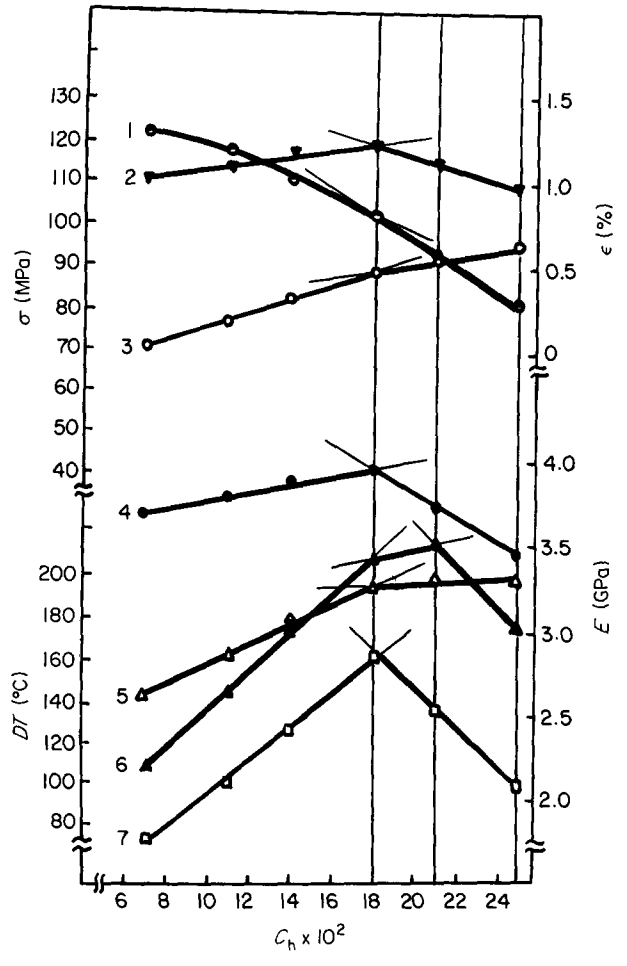

Figure 9 The change of the properties of the polymers based on DGEBA and [Cu(trien)(CH=NHC$_6$H$_4$O)$_2$] at the bend points of the graphs $\sigma = f(E)$ corresponding to the hardener concentrations $C_{h,1} = 0.18$, $C_{h,2} = 0.21$, $C_{h,3} = 0.25$ mol/mol of DGEBA. Curves: 1, σ_c; 2, ε; 3, σ_f; 4, σ_t; 5, E_f; 6, E_t; 7, DT

polymers is higher than that observed when only the conditions:

$$\sigma_{t,A} = \sigma_{t,B} \qquad \sigma_{f,A} = \sigma_{f,B}$$
$$E_{t,A} = E_{t,B} \qquad E_{f,A} = E_{f,B} \tag{3}$$

are satisfied. Absolute coincidence of the structures of the polymer matrices is unlikely to be attained, however, even if one and the same hardener is used.

Analysing the dependence $\sigma = f(E)$ for the tension and flexure or MECBs, one can see that there exist complexes the use of which results in the formation of matrices satisfying the conditions:

$$\sigma_{t,A} = \sigma_{t,B} \qquad E_{t,A} = E_{t,B}$$
$$\sigma_{f,A} = \sigma_{f,B} \qquad E_{f,A} = E_{f,B} \tag{4}$$

These conditions (4) are not equivalent to conditions (3), for which:

$$(C_{h,A})_t = (C_{h,A})_f$$
$$(C_{h,B})_t = (C_{h,B})_f$$
$$C_{h,A} \neq C_{h,B}$$

while conditions (4) imply the possibility of lack of coincidence of hardener concentrations:

$$(C_{h,A})_t \neq (C_{h,A})_f$$
$$(C_{h,B})_t \neq (C_{h,B})_f$$
$$C_{h,A} \neq C_{h,B}$$

Although the similarity of the compositions of the polymers is lacking, the fulfilment of conditions (4) makes it possible to examine the effect of the structural fragments of complex hardeners on MECP properties.

Table 1 shows pairs of chelate hardeners the application of which permits conditions (4) to be satisfied.

The influence of chelate structural fragments on the properties of MECPs is analysed as follows:

(i) Using the dependence $\sigma_f = f(E_f)$, the position of the intersection point of the curves $\sigma_{f,A} = f(E_{f,A})$ and $\sigma_{f,B} = f(E_{f,B})$ obtained for hardeners A and B is determined. The conditions

$$\sigma_{f,A} = \sigma_{f,B} \qquad E_{f,A} = E_{f,B}$$

are satisfied for this intersection point.

(ii) The concentrations of chelates $(C_{h,A})_f$ and $(C_{h,B})_f$ corresponding to the intersection point are determined according to the plots $\sigma_f = f(C_h)$ and $E_f = f(C_h)$.

(iii) Using the experimentally established dependence of the properties of the polymers on the hardener content, viz. the plots $\sigma_t = f(C_h)$, $\sigma_c = f(C_h)$, $\varepsilon = f(C_h)$, $E_t = f(C_h)$, $DT = f(C_h)$ and $\Delta M = f(C_h)$, the values of the indices corresponding to $(C_{h,A})_f$ and $(C_{h,B})_f$ are determined.

(iv) The obtained values of the polymer indices are compared. For this purpose the change of the index ΔX_{AB} corresponding to the transition from chelate A to chelate B is calculated by the formula:

$$\Delta X_{AB} = \frac{|X_A - X_B|}{X_A} \times 100\%$$

The influence of a structural fragment of the given pair of chelates on a polymer index is defined by the calculated value of ΔX_{AB}.

(v) The mean value of $\overline{\Delta X_{AB}}$ for the whole set of chelate pairs possessing one variable structural fragment (metal cation, ligand or anion), i.e. having two coinciding fragments (ligand and anion, metal and anion, or metal and ligand), are calculated. This index ($\overline{\Delta X_{AB}}$) characterizes the influence of the change of a structural fragment of an epoxy chelate polymer matrix on the properties of the polymers.

(vi) The mutual influence of the structural fragments of an epoxy chelate polymer matrix on the properties of MECPs is characterized by $\overline{\Delta X_{AB}}$ calculated for a set of chelate pairs having two variable fragments (ligand and anion, metal and anion, or metal and ligand), i.e. having one coinciding fragment (metal, ligand or anion), as well as by $\overline{\Delta X_{AB}}$ calculated for pairs of chelates of completely different structures.

As seen from *Table 1*, chelate hardeners, the application of which allows polymers satisfying conditions (4) to be obtained, may have almost equal concentrations:

$$0.95 \leqslant C_{h,A}/C_{h,B} \leqslant 1.05$$

but different properties: $\Delta\sigma_t = 51.2\%$ (No. 78), $\Delta E_t = 120\%$ (No. 8), $\Delta\varepsilon = 77.8\%$ (No. 9), $\Delta\sigma_c = 42.5\%$ (No. 39), $\Delta(DT) = 82.3\%$ (No. 8) (also Nos. 2, 23 and 62).

Table 1 Contribution of chelate hardener structure fragments to properties of polymers based on DGEBA and hardeners A and B. Polymers correspond to the conditions: $\sigma_{f,A}=\sigma_{f,B}$, $E_{f,A}=E_{f,B}$ and $\sigma_{t,A}=\sigma_{t,B}$, $E_{t,A}=E_{t,B}$

No.	Hardener identification in the pair	The pair of hardeners A and B for which $\sigma_{f,A}=\sigma_{f,B}$ and $E_{f,A}=E_{f,B}$	Intersection point of graphs $\sigma_f=f(E_f)$ for the hardeners A and B		Mass of hardener corresponding to the intersection point, C_h (mol/mol of DGEBA)	Polymer indices (X) corresponding to C_h					ΔM (%) after: 10 h at 280°C; *50 h at 280°C; **40 h at 260°C; ***25 h at 260°C	$\frac{C_{h,A}}{C_{h,B}}$	Comparison of polymer indices $\Delta X=\frac{\lvert X_A-X_B\rvert}{X_A}\times 100\%$					
			σ_f (MPa)	E_f (GPa)		σ_t (MPa)	E_t (GPa)	ε (%)	σ_c (MPa)	DT (°C)			$\Delta\sigma_t$	ΔE_t	$\Delta\varepsilon$	$\Delta\sigma_c$	$\Delta(DT)$	$\Delta(\Delta M)$
I. Hardeners with identical metal and ligand																		
1	A	$Cu(trien)(HOC_6H_4COO)_2$	78	2.80	0.239	41	2.5	1.8	107	105	21.5*							
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	78	2.80	0.113	35	2.6	1.2	118	94	4.6*	2.11	14.6	4.0	33.3	10.3	10.5	78.6
2	A	$Zn(cydien)(HOC_6H_4COO)_2$	106	3.60	0.215	35	3.1	1.4	128	100	57.0							
	B	$Zn(cydien)(CH_3COO)_2$	106	3.60	0.226	49	3.3	1.0	96	95	14.2	0.95	40.0	6.5	28.6	25.0	5.0	75.1
													$\overline{\Delta\sigma_t}=$ 27.3	$\overline{\Delta E_t}=$ 5.3	$\overline{\Delta\varepsilon}=$ 31.0	$\overline{\Delta\sigma_c}=$ 17.7	$\overline{\Delta(DT)}=$ 7.8	$\overline{\Delta(\Delta M)}=$ 76.9
II. Hardeners with identical metal and anion																		
3	A	$Cu(en)_2(HOC_6H_4COO)_2$	112	3.00	0.111	73	2.8	3.7	70	100	4.3							
	B	$Cu(dien)(HOC_6H_4COO)_2$	112	3.00	0.308	83	3.2	3.1	115	96	21.0	0.36	13.7	14.3	16.2	64.3	4.0	388.4
4	A	$Zn(trien)(HOC_6H_4COO)_2$	100	3.40	0.189	52	3.6	1.6	128	125	18.2							
	B	$Zn(cydien)(HOC_6H_4COO)_2$	100	3.40	0.233	25	2.8	1.3	130	98	63.8	0.81	51.9	22.2	18.8	1.6	21.6	250.5
5	A	$Ni(trien)(HOC_6H_4COO)_2$	100	3.25	0.148	53	2.4	2.1	103	88	5.5							
	B	$Ni(cydien)(HOC_6H_4COO)_2$	100	3.25	0.166	43	4.4	1.2	106	80	18.0	0.89	18.9	83.3	42.9	2.9	9.1	227.3
6	A	$Fe(trien)(HOC_6H_4COO)_3$	79	3.40	0.139	48	3.1	1.2	126	85	6.0							
	B	$Fe(cydien)(HOC_6H_4COO)_3$	79	3.40	0.111	62	2.7	1.9	114	118	12.0	1.25	29.2	12.9	58.3	9.5	38.8	100.0
7	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	101	3.40	0.114	63	1.7	1.2	123	64	25.0***							
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	101	3.40	0.138	68	3.3	1.7	130	107	26.0***	0.83	7.9	94.1	41.7	5.7	67.2	4.0
8	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	91	3.56	0.108	59	1.5	1.0	122	62	24.8***							
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	91	3.56	0.112	56	3.3	1.5	130	113	22.5***	0.96	5.1	120.0	50.0	6.6	82.3	9.3
9	A	$Cd(dien)(H_2NC_6H_4COO)_2$	131	3.00	0.146	90	3.8	2.7	137	92	26.4***							
	B	$Cd(cydien)(H_2NC_6H_4COO)_2$	131	3.00	0.149	94	5.0	4.8	102	73	23.4***	0.98	4.4	31.6	77.8	25.5	20.7	11.4
													$\overline{\Delta\sigma_t}=$ 18.7	$\overline{\Delta E_t}=$ 54.1	$\overline{\Delta\varepsilon}=$ 43.7	$\overline{\Delta\sigma_c}=$ 16.6	$\overline{\Delta(DT)}=$ 34.8	$\overline{\Delta(\Delta M)}=$ 141.6
III. Hardeners with identical ligand and anion																		
10	A	$Cu(trien)(HOC_6H_4COO)_2$	90	2.90	0.218	48	2.8	2.0	110	115	21.0*							
	B	$Co(trien)(HOC_6H_4COO)_2$	90	2.90	0.150	34	3.2	3.4	122	107	4.7	1.45	29.2	14.3	70.0	10.9	7.0	
11	A	$Cu(trien)(HOC_6H_4COO)_2$	110	3.15	0.190	57	2.9	2.7	114	123	20.2*							
	B	$Co(trien)(HOC_6H_4COO)_2$	110	3.15	0.133	48	3.1	3.5	121	106	3.7	1.43	15.8	6.9	29.6	6.1	13.8	
12	A	$Zn(trien)(HOC_6H_4COO)_2$	109	3.40	0.171	57	3.6	1.8	127	123	16.0							
	B	$Ni(trien)(HOC_6H_4COO)_2$	109	3.40	0.185	47	2.7	1.8	105	80	9.2	0.92	17.5	25.0	0	17.3	35.0	42.5
13	A	$Zn(trien)(HOC_6H_4COO)_2$	79	3.40	0.222	41	3.7	1.2	126	130	22.8							
	B	$Fe(trien)(HOC_6H_4COO)_3$	79	3.40	0.139	48	3.1	1.2	126	85	6.0	1.60	17.1	16.2	0	0	34.6	73.7

Table 1 Continued

No.	Hardener identification in the pair	The pair of hardeners A and B for which $\sigma_{f,A}=\sigma_{f,B}$ and $E_{f,A}=E_{f,B}$	Intersection point of graphs $\sigma_f=f(E_f)$ for the hardeners A and B: σ_f (MPa)	E_f (GPa)	Mass of hardener corresponding to the intersection point, C_h (mol/mol of DGEBA)	Polymer indices (X) corresponding to C_h: σ_t (MPa)	E_t (GPa)	ε (%)	σ_c (MPa)	DT (°C)	ΔM (%) after: 10 h at 280°C; *50 h at 280°C; **40 h at 260°C; ***25 h at 260°C	$\frac{C_{h,A}}{C_{h,B}}$	Comparison of polymer indices $\Delta X=\frac{\lvert X_A-X_B\rvert}{X_A}\times 100\%$: $\Delta\sigma_t$	ΔE_t	$\Delta\varepsilon$	$\Delta\sigma_c$	$\Delta(DT)$	$\Delta(\Delta M)$
14	A	$Co(trien)(HOC_6H_4COO)_2$	75	2.85	0.171	23	3.4	2.9	122	108	6.1							
	B	$Fe(trien)(HOC_6H_4COO)_3$	75	2.85	0.111	55	2.8	1.3	124	92	4.3	1.54	139.1	17.6	55.2	1.6	14.8	29.5
15	A	$Zn(cydien)(HOC_6H_4COO)_2$	107	3.64	0.212	36	3.2	1.4	127	99	60.4							
	B	$Fe(cydien)(HOC_6H_4COO)_3$	107	3.64	0.078	73	2.5	2.2	94	101	5.0	2.72	102.8	21.9	57.1	26.0	2.0	91.7
16	A	$Co(cydien)(HOC_6H_4COO)_2$	112	3.10	0.115	54	3.7	3.3	124	73	3.1							
	B	$Ni(cydien)(HOC_6H_4COO)_2$	112	3.10	0.144	53	3.7	1.4	111	87	13.8	0.80	1.9	0	57.6	10.5	19.2	345.2
17	A	$Co(cydien)(HOC_6H_4COO)_2$	96	3.32	0.091	53	3.7	3.0	119	55	3.0							
	B	$Ni(cydien)(HOC_6H_4COO)_2$	96	3.32	0.172	40	4.2	1.1	104	80	19.1	0.53	24.5	13.5	63.3	12.6	45.5	536.7
18	A	$Ni(cydien)(HOC_6H_4COO)_2$	90	3.43	0.183	35	3.9	1.1	100	77	21.8							
	B	$Fe(cydien)(HOC_6H_4COO)_3$	90	3.43	0.096	68	2.6	2.1	107	117	9.2	1.91	94.3	33.3	90.9	7.0	51.9	57.8
													$\overline{\Delta\sigma_t}=$ 49.1	$\overline{\Delta E_t}=$ 16.5	$\overline{\Delta\varepsilon}=$ 47.1	$\overline{\Delta\sigma_c}=$ 10.2	$\overline{\Delta(DT)}=$ 24.9	$\overline{\Delta(\Delta M)}=$ 168.2
19	A	$Cu(trien)(HOC_6H_4COO)_2$	105	3.00	0.197	54	2.9	2.6	115	123	20.3*							
	B	$(trien)(HOC_6H_4COOH)_2$	105	3.00	0.082	43	2.1	1.8	80	85	10.0	2.40	20.4	27.6	30.8	30.4	30.9	
20	A	$Cu(trien)(HOC_6H_4COO)_2$	114	3.14	0.141	61	3.0	3.4	120	130	18.5*							
	B	$(trien)(HOC_6H_4COOH)_2$	114	3.14	0.088	45	2.1	1.8	88	88	12.0	1.60	26.2	30.0	47.1	26.7	32.3	
													$\overline{\Delta\sigma_t}=$ 23.3	$\overline{\Delta E_t}=$ 28.8	$\overline{\Delta\varepsilon}=$ 39.0	$\overline{\Delta\sigma_c}=$ 28.6	$\overline{\Delta(DT)}=$ 31.6	
IV. Hardeners with identical metal																		
21	A	$Cu(dien)(HOC_6H_4COO)_2$	112	2.84	0.154	76	2.6	3.5	97	85	13.1*							
	B	$Cu(trien)(H_2NC_6H_4COO)_2$	112	2.84	0.240	81	2.9	2.2	142	123	21.5*	0.64	6.6	11.5	37.1	46.4	44.7	64.1
22	A	$Cu(dien)(HOC_6H_4COO)_2$	112	2.90	0.162	77	2.7	3.7	99	87	4.5							
	B	$Cu(trien)(H_2NC_6H_4COO)_2$	112	2.90	0.113	77	2.9	2.2	122	128	6.6	1.43	0	7.4	40.5	23.2	47.1	46.7
													$\overline{\Delta\sigma_t}=$ 3.3	$\overline{\Delta E_t}=$ 9.5	$\overline{\Delta\varepsilon}=$ 38.8	$\overline{\Delta\sigma_c}=$ 34.8	$\overline{\Delta(DT)}=$ 45.9	$\overline{\Delta(\Delta M)}=$ 55.4
V. Hardeners with identical ligand																		
23	A	$Zn(trien)(HOC_6H_4COO)_2$	93	3.40	0.195	47	3.7	1.5	128	127	19.0							
	B	$Cu(trien)(CH_3COO)_2$	93	3.40	0.197	50	2.2	2.0	112	95	13.0	0.99	6.4	40.5	33.3	12.5	25.2	31.6
24	A	$Co(trien)(HOC_6H_4COO)_2$	119	3.34	0.116	60	3.0	3.7	121	102	3.2							
	B	$Cu(trien)(CH_3COO)_2$	119	3.34	0.157	68	3.1	3.5	97	98	10.5	0.74	13.3	3.3	5.4	19.8	3.9	228.1
25	A	$Co(trien)(HOC_6H_4COO)_2$	79	2.90	0.164	25	3.3	3.1	121	108	5.5							
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	79	2.90	0.121	35	2.7	1.2	117	100	4.8	1.36	40.0	18.1	61.3	3.3	7.4	12.7

26	A	Ni(trien)$(HOC_6H_4COO)_2$	104	3.38	0.160	51	2.5	2.0	103	86	6.6							
	B	Cu(trien)$(CH_3COO)_2$	104	3.38	0.177	58	2.5	2.5	104	96	11.0	0.90	13.7	0	25.0	1.0	11.6	66.7
27	A	Fe(trien)$(HOC_6H_4COO)_3$	78	3.46	0.133	50	3.0	1.2	126	88	5.6							
	B	Cu(trien)$(CH_3COO)_2$	78	3.46	0.226	43	1.8	1.3	128	88	16.0	0.59	14.0	40.0	8.3	1.6	0	185.7
28	A	Fe(cydien)$(HOC_6H_4COO)_3$	67	3.40	0.121	58	2.7	1.8	118	116	13.7							
	B	Zn(cydien)$(CH_2{=}C(CH_3)COO)_2$	67	3.40	0.222	22	2.7	0.7	112	98	10.3	0.55	62.1	0	61.1	5.1	15.5	24.8
													$\overline{\Delta\sigma_t}=$	$\overline{\Delta E_t}=$	$\overline{\Delta\varepsilon}=$	$\overline{\Delta\sigma_c}=$	$\overline{\Delta(DT)}=$	$\overline{\Delta(\Delta M)}=$
													24.9	17.0	32.4	7.2	10.6	91.6
29	A	Cu(trien)$(CH{=}NHC_6H_4O)_2$	84	3.16	0.151	38	3.0	1.3	110	122	6.2*							
	B	(trien)$(HOC_6H_4COOH)_2$	84	3.16	0.211	40	2.5	1.6	98	100	28.0	0.72	5.3	16.7	23.1	10.9	18.0	
30	A	Cu(trien)$(CH{=}NHC_6H_4O)_2$	94	3.23	0.227	33	3.5	1.2	93	138	14.8*							
	B	(trien)$(HOC_6H_4COOH)_2$	94	3.23	0.201	40	2.4	1.6	98	100	27.0	1.13	21.2	31.4	33.3	5.4	27.5	
													$\overline{\Delta\sigma_t}=$	$\overline{\Delta E_t}=$	$\overline{\Delta\varepsilon}=$	$\overline{\Delta\sigma_c}=$	$\overline{\Delta(DT)}=$	
													13.3	24.1	28.2	8.2	22.8	
VI. Hardeners with identical anion																		
31	A	$Cu(en)_2(HOC_6H_4COO)_2$	134	3.30	0.275	96	2.7	5.0	119	77	21.0							
	B	Co(dien)$(HOC_6H_4COO)_2$	134	3.30	0.183	90	3.1	4.7	105	115	7.9	1.50	6.3	14.8	6.0	11.8	49.4	62.4
32	A	$Cu(en)_2(HOC_6H_4COO)_2$	126	3.48	0.230	94	2.9	5.0	113	86	11.0							
	B	Co(dien)$(HOC_6H_4COO)_2$	126	3.48	0.142	88	3.1	4.4	98	90	6.4	1.62	6.4	6.9	12.0	13.3	4.7	41.8
33	A	$Cu(en)_2(HOC_6H_4COO)_2$	118	3.30	0.163	84	3.1	4.5	94	108	3.9							
	B	Co(dien)$(HOC_6H_4COO)_2$	118	3.30	0.120	84	2.9	4.0	93	65	6.0	1.36	0	6.5	11.1	1.1	39.8	53.8
34	A	$Cu(en)_2(HOC_6H_4COO)_2$	133	3.40	0.267	97	2.8	5.0	118	79	19.0							
	B	Zn(trien)$(HOC_6H_4COO)_2$	133	3.40	0.098	92	2.7	4.7	120	104	7.6	2.72	5.2	3.6	6.0	1.7	31.6	60.0
35	A	$Cu(en)_2(HOC_6H_4COO)_2$	121	3.40	0.200	90	3.0	4.9	107	92	6.8							
	B	Zn(trien)$(HOC_6H_4COO)_2$	121	3.40	0.150	65	3.4	2.4	125	117	13.5	1.33	27.8	13.3	51.0	16.8	27.2	98.5
36	A	$Cu(en)_2(HOC_6H_4COO)_2$	127	3.45	0.239	95	2.9	5.0	115	84	12.5							
	B	Co(trien)$(HOC_6H_4COO)_2$	127	3.45	0.103	79	2.9	3.8	120	97	3.0	2.31	16.8	0	24.0	4.3	15.5	76.0
37	A	$Cu(en)_2(HOC_6H_4COO)_2$	119	3.30	0.171	85	3.1	4.7	97	105	4.2							
	B	Co(trien)$(HOC_6H_4COO)_2$	119	3.30	0.116	60	3.0	3.7	121	102	3.2	1.47	29.4	3.2	21.3	24.7	2.9	23.8
38	A	$Cu(en)_2(HOC_6H_7COO)_2$	138	3.40	0.297	97	2.7	4.8	120	75	26.2							
	B	Zn(cydien)$(HOC_6H_4COO)_2$	138	3.40	0.116	90	2.7	5.0	110	115	11.0	2.56	7.2	0	4.2	8.3	53.3	58.0
39	A	$Cu(en)_2(HOC_6H_4COO)_2$	115	3.10	0.134	77	3.0	4.2	80	107	3.8							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	115	3.10	0.133	57	3.5	1.6	114	88	11.8	1.01	26.0	16.7	61.9	42.5	17.8	210.5
40	A	Cu(dien)$(HOC_6H_4COO)_2$	114	3.40	0.231	87	3.3	5.0	108	100	9.0							
	B	Zn(trien)$(HOC_6H_4COO)_2$	114	3.40	0.163	61	3.6	1.9	127	120	15.0	1.42	29.9	9.1	62.0	17.6	20.0	66.7
41	A	Cu(dien)$(HOC_6H_4COO)_2$	111	3.16	0.301	86	3.2	3.4	114	98	19.4							
	B	Co(trien)$(HOC_6H_4COO)_2$	111	3.16	0.130	50	3.1	3.6	121	105	3.6	2.32	41.9	3.1	5.9	6.1	7.1	81.4
42	A	Cu(dien)$(HOC_6H_4COO)_2$	113	3.22	0.278	88	3.2	4.1	112	100	15.1							
	B	Co(trien)$(HOC_6H_4COO)_2$	113	3.22	0.126	47	3.1	3.6	121	105	3.5	2.21	46.6	3.1	12.2	8.0	5.0	76.8
43	A	Cu(dien)$(HOC_6H_4COO)_2$	113	3.12	0.170	78	2.8	4.0	100	87	4.6							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	113	3.12	0.138	55	3.6	1.5	113	90	12.6	1.23	29.5	28.6	62.5	13.0	3.4	173.9
44	A	Cu(dien)$(HOC_6H_4COO)_2$	111	3.16	0.177	80	2.9	4.1	103	90	4.8							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	111	3.16	0.147	52	3.7	1.3	110	86	14.1	1.20	35.0	27.6	68.3	6.8	4.4	193.8
45	A	Co(dien)$(HOC_6H_4COO)_2$	133	3.40	0.299	42	1.7	1.8	88	40	20.0							
	B	Zn(trien)$(HOC_6H_4COO)_2$	133	3.40	0.098	92	2.7	4.7	120	104	7.6	3.05	119.0	58.8	161.1	36.4	160.0	62.0
46	A	Co(dien)$(HOC_6H_4COO)_2$	123	3.40	0.127	87	3.0	4.1	94	72	6.1							
	B	Zn(trien)$(HOC_6H_4COO)_2$	123	3.40	0.143	68	3.4	2.5	125	115	12.8	0.89	21.8	13.3	39.0	33.0	59.7	109.8

Table 1 Continued

No.	Hardener identification in the pair	The pair of hardeners A and B for which $\sigma_{f,A}=\sigma_{f,B}$ and $E_{f,A}=E_{f,B}$	Intersection point of graphs $\sigma_f=f(E_f)$ for the hardeners A and B: σ_f (MPa)	E_f (GPa)	Mass of hardener corresponding to the intersection point, C_h (mol/mol of DGEBA)	Polymer indices (X) corresponding to C_h: σ_t (MPa)	E_t (GPa)	ε (%)	σ_c (MPa)	DT (°C)	ΔM (%) after: 10 h at 280°C; *50 h at 280°C; **40 h at 260°C; ***25 h at 260°C	$\frac{C_{h,A}}{C_{h,B}}$	Comparison of polymer indices $\Delta X=\frac{\lvert X_A-X_B\rvert}{X_A}\times 100\%$: $\Delta\sigma_t$	ΔE_t	$\Delta\varepsilon$	$\Delta\sigma_c$	$\Delta(DT)$	$\Delta(\Delta M)$
47	A	Co(dien)$(HOC_6H_4COO)_2$	136	3.54	0.210	88	2.9	4.5	108	112	9.4							
	B	Zn(cydien)$(HOC_6H_4COO)_2$	136	3.54	0.128	83	2.8	4.2	113	121	14.0	1.64	5.7	3.4	6.7	4.6	8.0	48.9
48	A	Co(dien)$(HOC_6H_4COO)_2$	134	3.66	0.180	91	3.2	4.7	104	115	7.7							
	B	Zn(cydien)$(HOC_6H_4COO)_2$	134	3.66	0.134	81	2.8	3.8	114	123	15.8	1.34	11.0	12.5	19.1	9.6	7.0	105.2
49	A	Cu(trien)$_2(HOC_6H_4COO)_2$	119	2.78	0.097	70	3.0	3.0	115	137	6.0							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	119	2.78	0.122	60	3.3	1.8	116	90	9.8	0.80	14.3	10.0	40.0	0.9	34.3	63.3
50	A	Cu(trien)$_2(HOC_6H_4COO)_2$	118	2.87	0.184	67	3.4	2.3	135	114	22.0							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	118	2.87	0.127	58	3.4	1.7	115	89	10.7	1.45	13.4	0	26.1	14.8	21.9	51.4
51	A	Cu(trien)$(HOC_6H_4COO)_2$	113	3.12	0.183	59	2.9	2.8	116	125	20.0*							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	113	3.12	0.138	55	3.6	1.5	113	90	12.6	1.33	6.8	24.1	46.4	2.6	28.0	
52	A	Cu(trien)$(HOC_6H_4COO)_2$	111	3.16	0.186	58	2.9	2.8	113	124	20.1*							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	111	3.16	0.147	52	3.7	1.3	110	86	14.1	1.27	10.3	27.6	53.6	2.7	30.6	
53	A	Zn(trien)$(HOC_6H_4COO)_2$	93	3.38	0.202	47	3.7	1.4	128	128	20.0							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	93	3.38	0.177	39	4.1	1.1	102	79	20.3	1.14	17.0	10.8	21.4	20.3	38.3	1.5
54	A	Co(trien)$(HOC_6H_4COO)_2$	111	3.16	0.130	50	3.1	3.6	121	105	3.6							
	B	Ni(cydien)$(HOC_6H_4COO)_2$	111	3.16	0.147	52	3.7	1.3	110	86	14.1	0.88	4.0	19.4	63.9	9.1	18.1	291.7
55	A	Ni(trien)$(HOC_6H_4COO)_2$	106	3.56	0.173	49	2.6	1.9	104	84	7.9							
	B	Zn(cydien)$(HOC_6H_4COO)_2$	106	3.56	0.215	35	3.1	1.4	128	100	59.6	0.80	28.6	19.2	26.3	23.1	19.0	654.4
56	A	Ni(trien)$(HOC_6H_4COO)_2$	100	3.30	0.150	52	2.4	2.0	103	87	5.6							
	B	Co(cydien)$(HOC_6H_4COO)_2$	100	3.30	0.097	53	3.7	3.1	120	60	3.0	1.55	1.9	54.2	55.0	16.5	31.0	46.4
57	A	Ni(trien)$(HOC_6H_4COO)_2$	105	3.60	0.167	50	2.5	2.0	103	85	7.2							
	B	Fe(cydien)$(HOC_6H_4COO)_3$	105	3.60	0.080	72	2.5	2.1	95	108	6.0	2.09	44.0	0	5.0	7.8	27.1	16.7
58	A	Fe(trien)$(HOC_6H_4COO)_3$	76	3.03	0.116	54	2.9	1.3	125	90	4.5							
	B	Co(cydien)$(HOC_6H_4COO)_2$	76	3.03	0.197	42	3.9	3.3	100	92	5.7	0.59	22.2	34.5	153.8	20.0	2.2	26.7
													$\overline{\Delta\sigma_t}=$ 22.4	$\overline{\Delta E_t}=$ 15.2	$\overline{\Delta\varepsilon}=$ 40.2	$\overline{\Delta\sigma_c}=$ 13.5	$\overline{\Delta(DT)}=$ 27.4	$\overline{\Delta(\Delta M)}=$ 106.0
VII. Different hardeners																		
59	A	Cu(trien)$(HOC_6H_4COO)_2$	93	3.00	0.211	50	2.8	2.3	112	118	20.8*							
	B	Cd(en)$_2(H_2NC_6H_4COO)_2$	93	3.00	0.168	64	3.3	1.8	113	68	30.0***	1.26	12.0	17.9	21.7	0.9	42.4	
60	A	Cu(trien)$(HOC_6H_4COO)_2$	84	2.70	0.077	42	2.4	1.8	95	117	9.0*							
	B	Zn(cydien)$(CH_2{=}C(CH_3)COO)_2$	84	2.70	0.130	33	2.5	1.4	107	81	5.0	0.59	21.4	4.2	22.2	12.6	30.8	
61	A	Cu(trien)$(HOC_6H_4COO)_2$	82	2.84	0.232	43	2.6	1.8	108	110	21.3*							
	B	Zn(cydien)$(CH_2{=}C(CH_3)COO)_2$	82	2.84	0.149	29	2.4	1.1	107	89	5.9	1.56	32.6	7.7	38.9	0.9	19.1	
62	A	Zn(trien)$(HOC_6H_4COO)_2$	112	3.40	0.166	59	3.6	1.8	126	121	15.4							
	B	Cd(dien)$_2(H_2NC_6H_4COO)_2$	112	3.40	0.173	78	3.2	1.9	124	85	32.0	0.96	32.2	11.1	5.6	1.6	29.8	107.8

63	A	Zn(trien)($HOC_6H_4COO)_2$	100	3.40	0.189	52	3.6	1.6	128	125	18.2							
	B	Cd(dien)$_2$($H_2NC_6H_4COO)_2$	100	3.40	0.132	65	3.3	1.6	120	110	25.5	1.43	25.0	8.3	0	6.3	12.0	40.1
64	A	Zn(trien)($HOC_6H_4COO)_2$	106	3.40	0.176	56	3.6	1.7	127	123	16.7							
	B	Cd(dien)$_2$($H_2NC_6H_4COO)_2$	106	3.40	0.150	72	3.2	1.8	128	102	28.0	1.17	28.6	11.1	5.9	0.8	17.1	67.7
65	A	Zn(trien)($HOC_6H_4COO)_2$	110	3.40	0.169	58	3.5	1.9	126	121	15.8							
	B	Co(dien)($CH{=}N(CH_2)C_6H_4O)_2$	110	3.40	0.255	62	3.2	2.1	87	75	14.0	0.66	6.9	8.6	10.5	31.0	38.0	11.4
66	A	Co(trien)($HOC_6H_4COO)_2$	82	2.90	0.163	26	3.3	3.1	121	108	5.4							
	B	Zn(cydien)($CH_2{=}C(CH_3)COO)_2$	82	2.90	0.153	28	2.4	1.1	107	90	6.0	1.07	7.7	27.3	64.5	11.6	16.7	11.1
67	A	Ni(trien)($HOC_6H_4COO)_2$	99	3.30	0.148	53	2.4	2.1	103	88	5.5							
	B	Cd(en)$_2$($H_2NC_6H_4COO)_2$	99	3.30	0.162	65	3.1	1.8	116	70	28.9***	0.91	22.6	29.2	14.3	12.6	20.5	
68	A	Ni(trien)($HOC_6H_4COO)_2$	106	3.56	0.173	49	2.6	1.9	104	84	7.9							
	B	Cd(en)$_2$($H_2NC_6H_4COO)_2$	106	3.56	0.118	64	1.7	1.3	124	64	25.2***	1.47	30.6	34.6	31.6	19.2	23.8	
69	A	Ni(trien)($HOC_6H_4COO)_2$	109	3.40	0.185	47	2.7	1.8	105	80	9.2							
	B	Cd(dien)$_2$($H_2NC_6H_4COO)_2$	109	3.40	0.161	75	3.2	1.8	125	95	30.0	1.15	59.6	18.5	0	19.0	18.8	226.1
70	A	Ni(trien)($HOC_6H_4COO)_2$	98	3.90	0.142	53	2.3	2.1	102	89	4.8							
	B	Zn(cydien)($C_6H_5COO)_2$	98	3.90	0.095	86	3.9	2.8	132	58	7.3	1.49	62.3	69.6	33.3	29.4	34.8	52.1
71	A	Ni(trien)($HOC_6H_4COO)_2$	77	3.10	0.093	55	2.8	1.9	101	95	1.8							
	B	Zn(cydien)($CH_2{=}C(CH_3)COO)_2$	77	3.10	0.176	25	2.5	1.0	107	97	7.5	0.53	54.5	10.7	47.4	5.9	2.1	316.7
72	A	Ni(trien)($HOC_6H_4COO)_2$	105	3.60	0.167	50	2.5	2.0	103	85	7.2							
	B	Zn(cydien)($CH_3COO)_2$	105	3.60	0.230	48	3.3	0.9	96	94	15.0	0.73	4.0	32.0	55.0	6.8	10.6	108.3
73	A	Fe(trien)($HOC_6H_4COO)_3$	82	3.75	0.155	47	3.3	1.1	128	83	7.7							
	B	Cd(dien)$_2$($H_2NC_6H_4COO)_2$	82	3.75	0.092	42	3.4	1.1	130	105	19.0	1.68	10.6	3.0	0	1.6	26.5	146.8
74	A	Fe(trien)($HOC_6H_4COO)_3$	72	3.94	0.100	58	2.7	1.4	124	87	5.9							
	B	Cd(dien)$_2$($H_2NC_6H_4COO)_2$	72	3.94	0.081	35	3.6	0.6	130	105	17.8	1.23	39.7	33.3	57.1	4.8	20.7	201.7
75	A	Fe(trien)($HOC_6H_4COO)_3$	80	3.60	0.144	48	3.1	1.1	127	86	6.5							
	B	Zn(cydien)($CH_3COO)_2$	80	3.60	0.270	35	3.6	0.7	96	86	19.0	0.53	27.1	16.1	36.4	24.4	0	192.3
76	A	Zn(cydien)($HOC_6H_4COO)_2$	110	3.75	0.209	39	3.2	1.5	127	100	59.7							
	B	Cd(en)$_2$($H_2NC_6H_4COO)_2$	110	3.75	0.121	65	1.8	1.4	125	65	25.5***	1.73	66.7	43.8	6.7	1.6	35.0	
77	A	Zn(cydien)($HOC_6H_4COO)_2$	100	3.40	0.233	25	2.8	1.3	130	98	63.8							
	B	Cu(trien)($CH_3COO)_2$	100	3.40	0.187	54	2.4	2.3	109	95	12.5	1.25	116.0	14.3	76.9	16.2	3.1	80.4
78	A	Ni(cydien)($HOC_6H_4COO)_2$	99	3.30	0.166	43	4.4	1.2	106	80	18.0							
	B	Cd(en)$_2$($H_2NC_6H_4COO)_2$	99	3.30	0.162	65	3.1	1.8	116	70	28.9***	1.02	51.2	29.5	50.5	9.4	12.5	
79	A	Ni(cydien)($HOC_6H_4COO)_2$	114	3.10	0.136	56	3.5	1.6	112	87	12.0							
	B	Cu(trien)($H_2NC_6H_4COO)_2$	114	3.10	0.169	88	3.0	2.5	140	135	12.0*	0.80	57.1	14.3	56.3	25.0	55.2	
80	A	Ni(cydien)($HOC_6H_4COO)_2$	107	3.20	0.155	49	4.0	1.3	109	84	15.9							
	B	Co(dien)($CH{=}N(CH_2)C_6H_4O)_2$	107	3.20	0.317	56	3.1	1.7	82	39	20.0	0.49	14.3	22.5	30.8	24.8	53.6	25.8
81	A	Fe(cydien)($HOC_6H_4COO)_3$	108	3.64	0.075	74	2.5	2.2	93	100	4.8							
	B	Cd(en)$_2$($H_2NC_6H_4COO)_2$	108	3.64	0.120	64	1.8	1.4	124	64	25.0***	0.63	13.5	28.0	36.4	33.3	36.0	
82	A	Fe(cydien)($HOC_6H_4COO)_3$	87	3.40	0.101	65	2.7	2.0	109	120	10.5							
	B	Cu(trien)($CH_3COO)_2$	87	3.40	0.206	47	2.0	1.8	111	100	14.0	0.49	27.7	25.9	10.0	1.8	16.7	33.3
83	A	Cd(en)$_2$($H_2NC_6H_4COO)_2$	118	4.10	0.130	66	2.2	1.6	125	66	25.8***							
	B	Zn(cydien)($C_6H_5COO)_2$	118	4.10	0.118	83	3.5	2.5	129	69	10.4	1.10	25.8	59.1	56.3	3.2	4.5	
84	A	Cd(en)$_2$($H_2NC_6H_4COO)_2$	120	4.26	0.131	67	2.2	1.6	125	67	26.0***							
	B	Zn(cydien)($C_6H_5COO)_2$	120	4.26	0.158	72	3.0	1.9	122	85	14.1	0.83	7.5	36.4	18.8	2.4	26.9	
85	A	Cd(en)$_2$($H_2NC_6H_4COO)_2$	116	4.30	0.128	66	2.0	1.6	125	66	25.6***							
	B	Zn(cydien)($C_6H_5COO)_2$	116	4.30	0.171	67	2.9	1.8	120	90	15.1	0.75	1.5	45.0	12.5	4.0	36.4	
86	A	Cd(en)$_2$($H_2NC_6H_4COO)_2$	104	3.94	0.116	63	1.7	1.2	124	64	25.0***							
	B	Zn(cydien)($C_6H_5COO)_2$	104	3.94	0.099	86	3.9	2.8	134	60	8.0	1.17	36.5	129.4	133.3	8.1	6.3	

Table 1 Continued

No.	Hardener identification in the pair	The pair of hardeners A and B for which $\sigma_{f,A}=\sigma_{f,B}$ and $E_{f,A}=E_{f,B}$	Intersection point of graphs $\sigma_f=f(E_f)$ for the hardeners A and B: σ_f (MPa)	E_f (GPa)	Mass of hardener corresponding to the intersection point, C_h (mol/mol of DGEBA)	Polymer indices (X) corresponding to C_h: σ_t (MPa)	E_t (GPa)	ε (%)	σ_c (MPa)	DT (°C)	ΔM (%) after: 10 h at 280°C; *50 h at 280°C; **40 h at 260°C; ***25 h at 260°C	$\frac{C_{h,A}}{C_{h,B}}$	Comparison of polymer indices $\Delta X=\frac{\lvert X_A-X_B\rvert}{X_A}\times 100\%$: $\Delta\sigma_t$	ΔE_t	$\Delta\varepsilon$	$\Delta\sigma_c$	$\Delta(DT)$	$\Delta(\Delta M)$
87	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	107	3.60	0.119	64	1.8	1.3	124	65	25.2***							
	B	$Zn(cydien)(CH_3COO)_2$	107	3.60	0.222	50	3.3	1.1	96	96	14.0	0.54	21.9	83.3	15.4	22.6	47.7	
88	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	92	3.60	0.114	63	1.7	1.2	123	64	25.0***							
	B	$Zn(cydien)(CH_3COO)_2$	92	3.60	0.246	43	3.4	0.8	96	92	16.5	0.46	31.7	100.0	33.3	22.0	43.8	
89	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	101	3.36	0.111	62	1.7	1.1	120	62	24.8***							
	B	$Cu(trien)(CH_3COO)_2$	101	3.36	0.182	56	2.5	2.4	106	96	11.8	0.61	9.7	47.1	118.2	11.7	54.8	
90	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	90	3.60	0.109	53	3.3	1.4	130	113	22.0							
	B	$Zn(cydien)(CH_3COO)_2$	90	3.60	0.254	40	3.5	0.8	97	90	17.2	0.43	24.5	6.1	42.9	25.4	20.4	21.8
91	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	100	3.40	0.132	65	3.3	1.6	120	110	25.5							
	B	$Cu(trien)(CH_3COO)_2$	100	3.40	0.187	54	2.4	2.3	109	95	12.5	0.71	16.9	27.3	43.8	9.2	13.6	51.0
92	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	110	3.40	0.167	77	3.2	1.9	125	93	31.2							
	B	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	110	3.40	0.254	62	3.2	2.1	87	75	14.0	0.66	19.5	0	10.5	30.4	19.4	55.1
93	A	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	80	2.93	0.161	27	2.4	1.1	106	93	6.3							
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	80	2.93	0.128	36	2.8	1.3	115	110	5.0*	1.26	33.3	16.7	18.2	8.5	18.3	
94	A	$Zn(cydien)(CH_3COO)_2$	118	3.60	0.190	59	3.2	1.5	96	100	10.4							
	B	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	118	3.60	0.159	65	3.5	2.1	95	105	7.6	1.19	10.2	9.4	40.0	1.0	5.0	26.9
													$\overline{\Delta\sigma_t}=$ 29.5	$\overline{\Delta E_t}=$ 30.0	$\overline{\Delta\varepsilon}=$ 34.9	$\overline{\Delta\sigma_c}=$ 12.5	$\overline{\Delta(DT)}=$ 24.2	$\overline{\Delta(\Delta M)}=$ 93.5
											$\overline{\Delta X}$:		$\overline{\Delta\sigma_t}=$ 23.5	$\overline{\Delta E_t}=$ 22.3	$\overline{\Delta\varepsilon}=$ 37.3	$\overline{\Delta\sigma_c}=$ 16.6	$\overline{\Delta(DT)}=$ 25.6	$\overline{\Delta(\Delta M)}=$ 104.7

Table 2 Influence of chelate structural fragments on polymer properties (%)

Affecting fragment	Identical fragments	Division in *Table 1*	$\overline{\Delta\sigma_t}$	$\overline{\Delta E_t}$	$\overline{\Delta\varepsilon}$	$\overline{\Delta\sigma_c}$	$\overline{\Delta(DT)}$	$\overline{\Delta(\Delta M)}$
Anion	Metal and ligand	I, Nos. 1, 2	27.3	5.3	31.0	17.7	7.8	76.9
Ligand	Metal and anion	II, Nos. 3–9	18.7	54.1	43.7	16.6	34.8	141.6
Metal	Ligand and anion	III, Nos. 10–18	49.1	16.5	47.1	10.2	24.9	168.2

Table 3 Mutual influence of chelate structural fragments on polymer properties (%)

Affecting fragments	Identical fragment	Division in *Table 1*	$\overline{\Delta\sigma_t}$	$\overline{\Delta E_t}$	$\overline{\Delta\varepsilon}$	$\overline{\Delta\sigma_c}$	$\overline{\Delta(DT)}$	$\overline{\Delta(\Delta M)}$
Ligand–anion	Metal	IV, Nos. 21, 22	3.3	9.5	38.8	34.8	45.9	55.4
Metal–anion	Ligand	V, Nos. 23–28	24.9	17.0	32.4	7.2	10.6	91.6
Metal–ligand	Anion	VI, Nos. 31–58	22.4	15.2	40.2	13.5	27.4	106.0

Polymers with close values of the strength indices:

$$\Delta\sigma < 10\% \qquad \Delta E < 10\%$$

show a significant discrepancy in DT:

$$31.6\% < \Delta(DT) < 53.3\%$$

and differ in the amount of complexes:

$$1.36 < C_{h,A}/C_{h,B} < 2.72$$

(Nos. 33, 34, 38 and 57).

In spite of the variety of epoxy chelate systems, polymers satisfying conditions (2) fail to be obtained. When the strength indices coincide, the epoxy chelate matrices exhibit considerable discrepancy in thermal oxidative stability; on the contrary, with equal heat resistance, they show different strengths and DT. For instance, the cobalt and zinc complexes $[Co(dien)(HOC_6H_4COO)_2]$ and $[Zn(cydien)(HOC_6H_4COO)_2]$ (No. 47) result in an MECP the properties of which are most suited for conditions (2) to be satisfied. However, the quantitative composition ($C_{h,A}/C_{h,B} = 1.64$) and the heat resistance ($\Delta(\Delta M) = 48.9\%$) of these polymers are different. MECPs obtained by using $[Zn(trien)(HOC_6H_4COO)_2]$ and $[Ni(cydien)(HOC_6H_4COO)_2]$ (No. 53) show similar heat resistances but have different strengths: $\Delta(\Delta M) = 1.5\%$, $10.8\% < \Delta X < 38.3\%$.

Analysis of the data of *Table 1* gives the general picture of the influence of chelate structural fragments on polymer properties, presented in *Table 2*. The data of *Table 2* allow one to come to the following conclusions:

(i) The influence of the structural fragments on MECP properties decreases in the order of the indices:

depending on ligand

$$\Delta M \gg E_t > \varepsilon > DT > \sigma_t > \sigma_c$$

depending on anion

$$\Delta M \gg \varepsilon > \sigma_t > \sigma_c \gg DT > E_t$$

depending on metal

$$\Delta M \gg \sigma_t > \varepsilon \gg DT > E_t > \sigma_c$$

(ii) With respect to the extent of influence on polymer properties, the chelate structural fragments can be arranged in the following order:

influence on σ_t	metal > anion > ligand
E_t	ligand ≫ metal ≫ anion
ε	metal > ligand > anion
σ_c	anion > ligand > metal
DT	ligand > metal ≫ anion
ΔM	metal > ligand ≫ anion

(The sign > corresponds to the increase of the contribution of the preceding fragment (index) with respect to the next one by 1.1–1.5 times; the sign ≫ by more than 1.5 times.)

Comparison of the results obtained with the trends established for the condition $C_{h,A} = C_{h,B} = 0.170$ mol/mol of DGEBA[2] testifies to the fact that the metal cation and the ligand, which determine the heat resistance, DT and strength (σ_t, E_t, ε, σ_f and E_f), are the most important with regard to the properties of epoxy chelate polymers. At the same time, the anion has the most influence on σ_c, which is due to the significant changes in volume and functionality of the anions used, viz. the small dimensions of the monofunctional CH_3COO^- and the large dimensions of the polyfunctional $HOC_6H_4COO^-$ and $NH{=}CHC_6H_4O^-$.

Of great interest are the data showing the change of properties of the non-metal-containing polymer matrix when a metal cation is introduced into it. For this purpose, the properties of the copper-containing epoxy polymer and those of DGEBA cured with the product of the reaction of trien with salicylic acid $[(trien)(HOC_6H_4COOH)_2]$ have been compared (*Table 1*, Nos. 19 and 20). Introduction of the metal increases DT by 30–32%, which is due to enhancement of the Van der Waals interaction in the polymer matrix, and increases the strength by 20–47%.

Comparison of the change of properties of MECPs with simultaneous alteration of two structural fragments characterizes the mutual influence of the chelate fragments on polymer matrix properties (*Table 3*). In this case the heat resistance change is maximal when varying the 'metal–ligand' pair, for the heat resistance depends on the stability of the chelate rings, which, in turn, has been shown[1] to depend on the ligand structure and on the metal type.

As DT depends, first of all, on the ligand structure (see above), the change thereof is maximal for ligand-containing pairs of fragments.

The change of σ_c is also in agreement with the above dependence of $\Delta\sigma_c$ on the type of structural fragments: as $\Delta\sigma_c$ is maximal when changing the ligand and anion, the trend remains the same for simultaneous substitution of the fragments of the 'ligand–anion' pair. Such is also the case when the indices $\Delta\sigma_t$, ΔE_t and $\Delta\varepsilon$ are changed: the maximal effect occurs for pairs of structural fragments, the components of which, when taken separately, have the strongest influence on MECP properties.

Comparison of the properties of polymers obtained by DGEBA hardening with complexes having completely different structures (*Table 1*, division VII, Nos. 59–94) shows that hardener composition is the most important factor for thermal oxidative stability ($\overline{\Delta(\Delta M)}=93.5\%$) but σ_c is the least sensitive to chelate composition alteration ($\overline{\Delta\sigma_c}=12.5\%$).

A general analysis of the results obtained (*Table 1*) enables us to conclude that the effect of chelate structure on the alteration of MECP properties is maximal for heat resistance ($\overline{\Delta(\Delta M)}=104.7\%$), minimal for σ_c ($\overline{\Delta\sigma_c}=16.6\%$) and decreases in the order:

$$\Delta M > \varepsilon > DT > \sigma_t > E_t > \sigma_c$$

CONCLUSION

The established trends of the alteration of the properties of epoxy chelate polymer matrices on changing the structural fragments thereof are of great importance both from the theoretical aspect and in terms of practical applications. The introduction of bound metal possessing a large electric charge into a polymer matrix is accompanied by considerable enhancement of the interatomic interaction in this matrix and, as a consequence, by structural changes and alteration of its properties. Quantitative evaluation of the cation effect on MECP properties shows the metal to be of prime importance for the formation of an epoxy chelate polymer network as compared with the ligand and the anion. Significant structural changes of the matrices as evidenced by the dependence $\sigma=f(E)$ and the abrupt changeable character of the influence of chelate structural fragments on polymer indices on changing the chelate concentration in an epoxy compound result, first of all, from the Van der Waals interaction of the metal cation with other atoms of the three-dimensional network, with the nearest atoms being those of a ligand. This follows from analysis of the structure of the chelate molecule, distinguished by eliminating the anion into the external sphere of the complex as a result of complex formation[4]. This anion elimination causes the chemical bonds between the metal atom and the anion in the complex molecule to become too weak in comparison with the bonds between the ligand and the metal. When the hardener reacts with an epoxy oligomer on heating, complex dissociation into the complex cation and the anion proceeds more easily and rapidly than the subsequent dissociation of the complex cation into metal cation and ligand (see scheme (7) in ref. 1). The ligand atoms screen the metal cation and consequently affect the Van der Waals interaction of the cation with the matrix atoms. Thus, it is quite natural for the ligand to be the next structural fragment following the metal cation in terms of the effect on epoxy polymer properties, since it is the atoms thereof that form the nearest environment of the cation.

Although the anion has less influence on epoxy chelate matrix properties as compared to those of the metal and ligand, one should not underestimate the role of the anion. This can be explained as follows. Besides the end service properties of the polymers, great importance is attached to those properties influencing the resolution of the problem of the synthesis and processing of chelate hardeners and epoxy chelate compounds. It is this field in which the anion plays a role; if not the key role, it is, in any case, no less important than the other fragments. The alteration of the ionization constants of the organic acids corresponding to the anions significantly changes the rate of complex formation. Besides, the properties of the hardeners such as solubility, melting point, compatibility with epoxy oligomers and reactivity in the cure reactions are considered to be a direct function of anion structure[1].

The synthesis of new chelate hardeners that satisfy processing conditions and facilitate obtaining epoxy polymers whose strength and heat resistance are even higher than those of known ones would be the result of attaining an optimal combination of all the structural fragments, viz. metal, ligand and anion.

REFERENCES

1 Kurnoskin, A. V. *Polymer* 1993, **34**, 1060
2 Kurnoskin, A. V. *Polymer* 1993, **34**, 1068
3 Irzhak, V. I., Rozenberg, B. A. and Enikolopov, N. S. 'Setchatye Polimery: Sintez, Struktura, Svoistva', Nauka, Moskva, 1979
4 Shukla, P. R., Pandey, O. P. and Narain, G. *J. Indian. Chem. Soc.* 1985, **62**, 175

NOMENCLATURE

σ_c	compressive strength
σ_f	flexural strength
σ_t	tensile strength
E_f	flexural modulus
E_t	tensile modulus
ε	elongation at break
DT	deformation temperature
ΔM	mass loss of polymer after thermal treatment in air
X	index of polymer (σ, E, ε, DT, ΔM)
ΔX	a change of polymer index (increase or decrease)
$\overline{\Delta X}$	mean value of the change of polymer index for the same series of hardeners
X_A, X_B	indices of the polymers based on DGEBA cured with chelates A and B
ΔX_{AB}	change of polymer index (increase or decrease) in the case of replacement of one chelate (A) for another (B)
C_h	concentration of hardener in epoxy compound (mol/mol of DGEBA)
$C_{h,A}$, $C_{h,B}$	concentrations of hardeners A and B in epoxy compounds
$(C_{h,A})_t$, $(C_{h,A})_f$, $(C_{h,B})_t$, $(C_{h,B})_f$	concentrations of hardeners A and B in epoxy compounds corresponding to certain values of σ_t (σ_f) and E_t (E_f): $(\sigma_t, E_t)_A$, $(\sigma_f, E_f)_A$, $(\sigma_t, E_t)_B$, $(\sigma_f, E_f)_B$