

Reaction Mechanisms of the Metal Chelates with Epoxy Oligomers and the Structures of the Epoxy-Chelate Metal-Containing Matrixes

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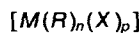
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SYNOPSIS

A theoretical generalization of the experimental results of the investigation of the properties of the metalliferous epoxy chelate polymers (MECP) based on diglycidyl ether of bisphenol-A (DGEBA) has been carried out. Shown is the possibility of adjusting the structure and properties of MECP by changing the temperature of hardening and the content of a chelate hardener in an epoxy compound and by varying the composition of a chelate molecule, i.e., its structural fragments—a metal, ligand, and anion, which leads to changing the predominant mechanism of the reaction of the epoxy oligomer with the hardener, which can be catalytic or can proceed with the amino groups of a complex cation or unconnected ligand and with an anion. As a result, the epoxy chelate matrixes of different structures are formed. A correlation between the tensile strength (σ_t) and tensile modulus (E_t), flexural strength (σ_f), and flexural modulus (E_f) of MECP— $\sigma_t = f(E_t)$ and $\sigma_f = f(E_f)$ —has been established. The form of this correlation corroborates the presumption that the polymerization mechanism of the epoxy oligomer is changed and the various structures of the polymer matrixes are formed. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

It was determined that hardening of epoxy oligomers (diglycidyl ether of bisphenol-A [DGEBA], ED-22 grade, with epoxy equivalent weight of 170–180, made in Russia) with the chelates of the formula



Scheme 1

where M is the metal cation: Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , or MnO^{2+} ; R , the ligand: ethylene diamine (en), diethylene triamine (dien), triethylene tetramine (trien), or bis- N,N' -(β -cyanoethyl)-diethylene triamine (cydien); X , the anion of an organic acid: CH_3COO^- , $CH_2=C(CH_3)COO^-$, $C_6H_5COO^-$, $HOC_6H_4COO^-$, $H_2NC_6H_4COO^-$, $CH=NHC_6H_4O^-$, or $CH=N(CH_2)C_6H_4O^-$; n , the number of the ligands in a complex, $n = 1$ or 2 ; and p , the metal valency, $p = 2$ or 3 results in ob-

taining the epoxy matrixes containing coordinately bonded metal cations and allows the properties of the synthesized metalliferous epoxy chelate polymers (MECP) to be adjusted in a wide range both by varying the structure of the chelate molecule (Scheme 1) and by changing the content thereof in an epoxy composition.¹⁻⁴

The properties of MECP were examined according to the standards in Ref. 5. Compared to the well-known epoxy polymers, MECP offers such advantages as

1. Long pot life of the epoxy-chelate compositions;
2. Short cure time at not too high temperatures;
3. High physical strength characteristics;
4. Superior thermal stability;
5. Excellent chemical resistance; and
6. Good electrical resistance.¹⁻⁴

The dependence of the strength properties of MECP on the content of some chelates is shown in Figures 1–10. The polymer properties are examined

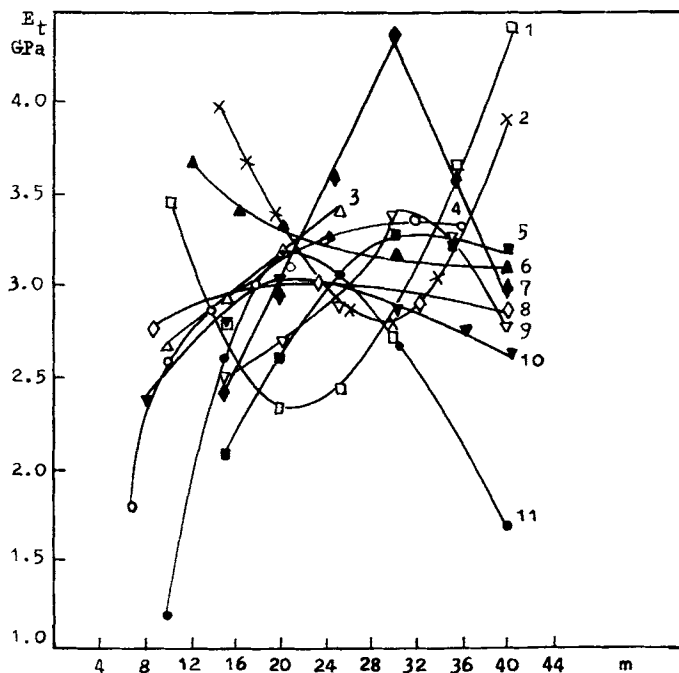


Figure 1 Dependence of E_t of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Ni(trien)(HOC₆H₄COO)₂; (2) Zn(cydien)(C₆H₅COO)₂; (3) Co(trien)(HOC₆H₄COO)₂; (4) Cu(trien)₂(HOC₆H₄COO)₂; (5) Cu(dien)(HOC₆H₄COO)₂; (6) Cd(dien)₂(H₂NC₆H₄COO)₂; (7) Ni(cydien)(HOC₆H₄COO)₂; (8) Cu(trien)(H₂NC₆H₄COO)₂; (9) Zn(cydien)(HOC₆H₄COO)₂; (10) Cu(en)₂(HOC₆H₄COO)₂; (11) Co(dien)(HOC₆H₄COO)₂.

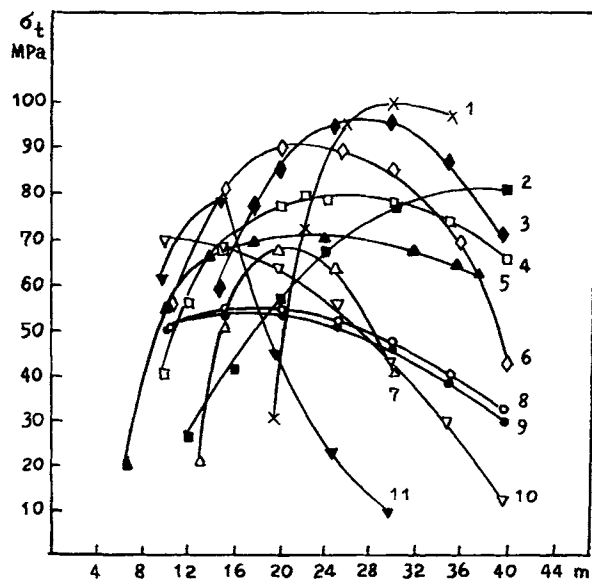


Figure 2 Dependence of σ_t of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Cd(cydien)(H₂NC₆H₄COO)₂; (2) Cd(dien)₂(H₂NC₆H₄COO)₂; (3) Cd(dien)(H₂NC₆H₄COO)₂; (4) Cd(trien)(H₂NC₆H₄COO)₂; (5) Cu(trien)₂(HOC₆H₄COO)₂; (6) Co(dien)(HOC₆H₄COO)₂; (7) Cd(en)₂(H₂NC₆H₄COO)₂; (8) Ni(trien)(HOC₆H₄COO)₂; (9) Co(cydien)(HOC₆H₄COO)₂; (10) Ni(cydien)(HOC₆H₄COO)₂; (11) Co(trien)(HOC₆H₄COO)₂.

in comparison with those of DGEBA hardened with a nonmetal-containing compound (proton instead of a metal cation) but including in its structure an aliphatic amine and salicylate-anion: [(trien)-(HOC₆H₄COOH)₂]. This compound is the product of the reaction of trien with salicylic acid at lowered temperature (40–50°C).

The mass change of [(trien)(HOC₆H₄COO)₂] in the epoxy compositions causes significant variation of the polymer properties (a ratio between the maximum and minimum values): ϵ , 3.5 times; σ_f , 2.5 times; and σ_c , σ_t , E_t , and E_f , by 20–40%; the minimum effect of the hardener content is exerted on DT, which turns by 18% (Fig. 11).

In the presence of the metal cations, the type of MECP property transformation depending on the hardeners content is different: ϵ changes 2.5–4.2 times (Fig. 3, the hardeners [Co(dien)(HOC₆H₄COO)₂] and [Cd(cydien)(H₂NC₆H₄COO)₂]), although in some cases it varies insignificantly (by 23% for [Cd(trien)(H₂NC₆H₄COO)₂], Fig. 3); σ_t and σ_c change 2.0–3.3 times (Fig. 2, [Cd(cydien)(H₂NC₆H₄COO)₂]; Fig. 9, [Cu(trien)₂(HOC₆H₄COO)₂]); the minimum shift of σ_t makes up 18% (Fig. 2, [Cd(trien)(H₂NC₆H₄COO)₂]) and that of σ_c is 16–18% (Fig. 9, [Cd(dien)(H₂NC₆H₄COO)₂]); σ_f changes 2.8 times (Fig. 10, [Cd(cydien)-(H₂NC₆-

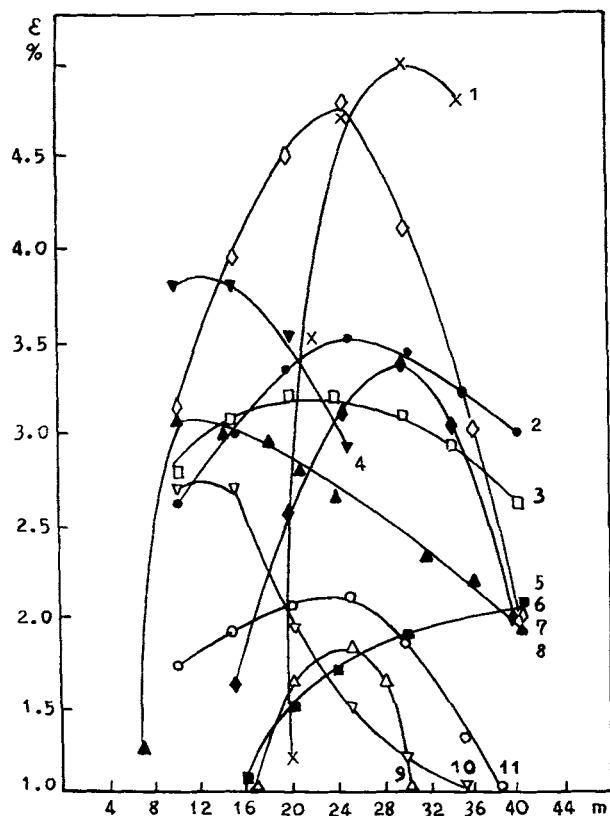


Figure 3 Dependence of ϵ of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Cd(cydien)(H₂NC₆H₄COO)₂; (2) Co(cydien)(HOC₆H₄COO)₂; (3) Cd(trien)(H₂NC₆H₄COO)₂; (4) Co(trien)(HOC₆H₄COO)₂; (5) Cd(dien)₂(H₂NC₆H₄COO)₂; (6) Co(dien)(HOC₆H₄COO)₂; (7) Cd(dien)(H₂NC₆H₄COO)₂; (8) Cu(trien)₂(HOC₆H₄COO)₂; (9) Cd(en)₂(H₂NC₆H₄COO)₂; (10) Ni(cydien)(HOC₆H₄COO)₂; (11) Ni(trien)(HOC₆H₄COO)₂.

H₄COO)₂]; and the minimum alteration of σ_f amounts to 20–28% (Fig. 4, [Co(dien)(HOC₆H₄COO)₂]; Fig. 10, [Cd(trien)(H₂NC₆H₄COO)₂]).

The chelate concentration introduced into DGEBA significantly affects the moduli of elasticity: E_t changes 2–3 times (Fig. 1, [Co(dien)(HOC₆H₄COO)₂]; Fig. 6, [Cd(en)₂(H₂NC₆H₄COO)₂]; Fig. 7, [Cd(trien)(H₂NC₆H₄COO)₂]); E_f varies 1.6–2 times (Fig. 5, [Ni(cydien)(HOC₆H₄COO)₂]; Fig. 7, [Cd(en)₂(H₂NC₆H₄COO)₂]); and in some cases, this change is insignificant—7–11% (Fig. 1, [Cu(trien)(H₂NC₆H₄COO)₂]; Fig. 7, [Cd(trien)(H₂NC₆H₄COO)₂]).

The deflection temperature is very responsive to the chelate content in a polymer and therefore to the concentration of the metal cations in a matrix (Fig. 8): The minimum change of DT makes up 26–40% ([Cd(dien)(H₂NC₆H₄COO)₂], [Cd(en)₂(H₂NC₆H₄COO)₂]), i.e., 1.5–2 times higher than the

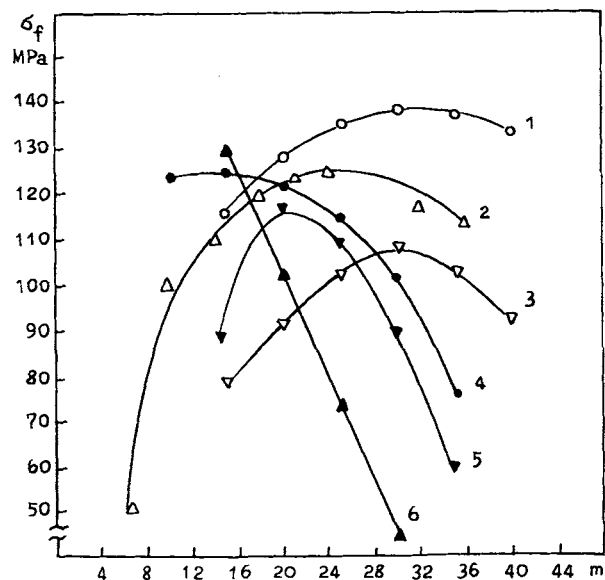


Figure 4 Dependence of σ_f of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Co(dien)(HOC₆H₄COO)₂; (2) Cu(trien)₂(HOC₆H₄COO)₂; (3) Ni(trien)(HOC₆H₄COO)₂; (4) Ni(cydien)(HOC₆H₄COO)₂; (5) Co(cydien)(HOC₆H₄COO)₂; (6) Co(trien)(HOC₆H₄COO)₂.

shift of DT for [(trien)(HOC₆H₄COO)₂], whereas the maximum alteration is 3.5 times (from 40°C to 140°C for the chelate [Cu(trien)₂(HOC₆H₄COO)₂]).

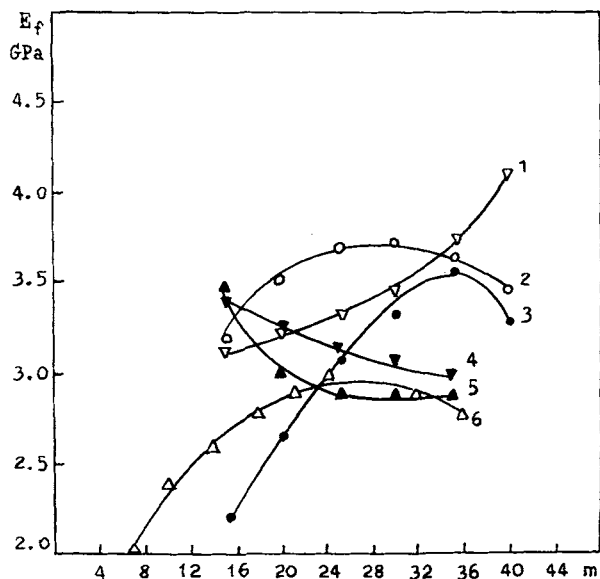


Figure 5 Dependence of E_f of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Ni(trien)(HOC₆H₄COO)₂; (2) Co(dien)(HOC₆H₄COO)₂; (3) Ni(cydien)(HOC₆H₄COO)₂; (4) Co(cydien)(HOC₆H₄COO)₂; (5) Co(trien)(HOC₆H₄COO)₂; (6) Cu(trien)₂(HOC₆H₄COO)₂.

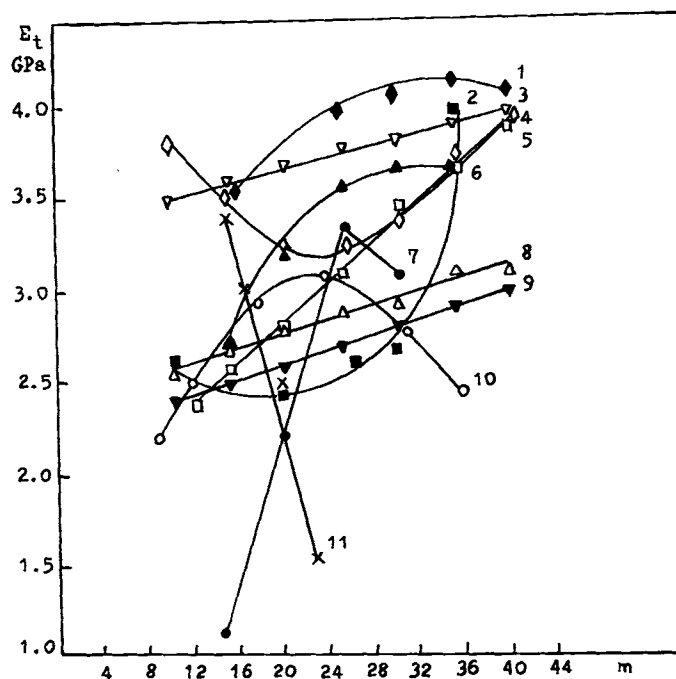


Figure 6 Dependence of E_t of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Cd(dien)(H₂NC₆H₄COO)₂; (2) Zn(cydien)-(CH₂=C(CH₃)COO)₂; (3) Co(cydien)(HOC₆H₄COO)₂; (4) Zn(cydien)(CH₃COO)₂; (5) Fe(trien)(HOC₆H₄COO)₃; (6) Zn(trien)(HOC₆H₄COO)₂; (7) Cd(en)₂(H₂NC₆H₄COO)₂; (8) MnO(trien)(HOC₆H₄COO)₂; (9) Fe(cydien)(HOC₆H₄COO)₃; (10) Cu(trien)(HOC₆H₄COO)₂; (11) Cu(trien)(CH₃COO)₂.

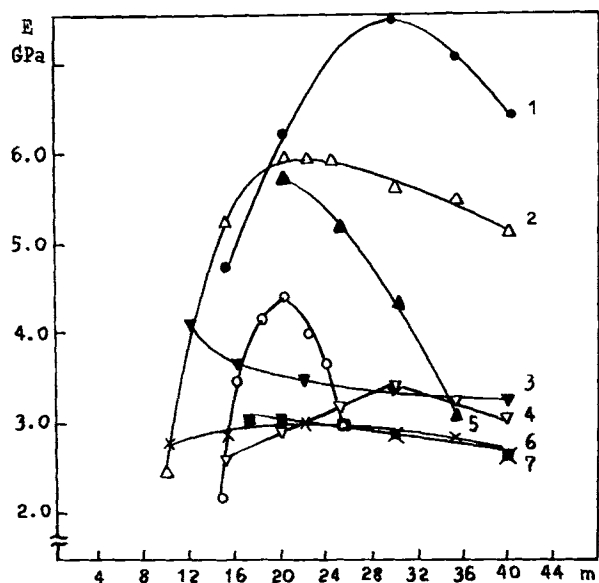


Figure 7 Dependence of E_t and E_f of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Cu(cydien)(HOC₆H₄COO)₂, E_t ; (2) Cd(trien)(H₂NC₆H₄COO)₂, E_t ; (3) Cd(dien)₂(H₂NC₆H₄COO)₂, E_f ; (4) Cd(dien)(H₂NC₆H₄COO)₂, E_f ; (5) Cd(cydien)(H₂NC₆H₄COO)₂, E_t ; (6) Cd(trien)(H₂NC₆H₄COO)₂, E_f ; (7) Cd(cydien)(H₂NC₆H₄COO)₂, E_f ; (8) Cd(en)₂(H₂NC₆H₄COO)₂, E_f .

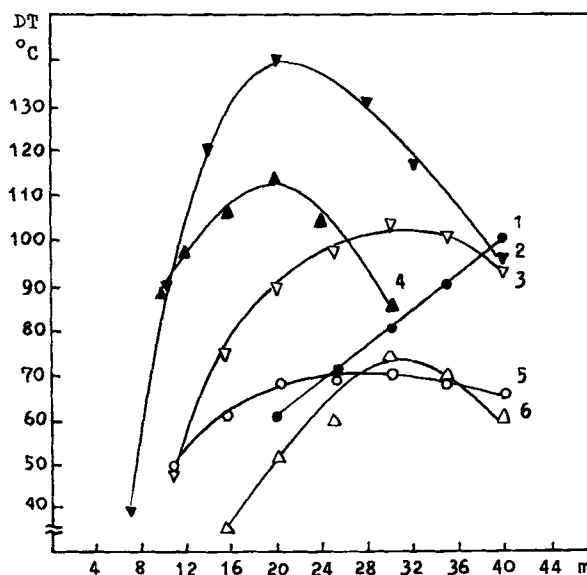


Figure 8 Dependence of DT of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) Cd(cydien)(H₂NC₆H₄COO)₂; (2) Cu(trien)₂(HOC₆H₄COO)₂; (3) Cd(dien)(H₂NC₆H₄COO)₂; (4) Cd(dien)₂(H₂NC₆H₄COO)₂; (5) Cd(en)₂(H₂NC₆H₄COO)₂; (6) Cd(trien)(H₂NC₆H₄COO)₂.

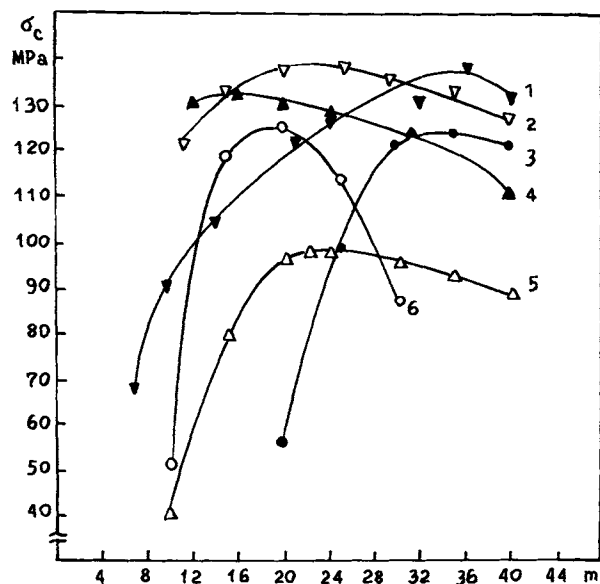


Figure 9 Dependence of σ_c of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) $\text{Cu}(\text{trien})_2(\text{HOC}_6\text{H}_4\text{COO})_2$; (2) $\text{Cd}(\text{dien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (3) $\text{Cd}(\text{cydien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (4) $\text{Cd}(\text{dien})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (5) $\text{Cd}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (6) $\text{Cd}(\text{en})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$.

The above analysis clearly illustrating the possibility of adjusting the properties of MECP by varying the hardener concentration is of practical importance since it permits manufacturing polymers with a different set of properties. Besides, the established dependencies of the polymer properties on the quantity of the chelates are of the theoretical importance for they are regarded as the initial points to examine the influence of the chelate molecule structural fragments (a cation, anion, and ligand—Scheme 1) with equal molar concentration on the polymer matrix properties and to study the mechanism of the reaction between the complexes and DGEBA and the structures of the epoxy–chelate metal-containing matrices.

INFLUENCE OF THE CHELATE STRUCTURAL FRAGMENTS ON THE PROPERTIES OF THE POLYMER MATRIX

The dependence of the maximum strength and deflection temperature of MECP on the quantity of the hardeners was investigated and it was established that the optimum set of these properties corresponding to their maximum values (with deviation of $\pm 12\%$) can be reached by using 0.17 mol of a chelate per 1 mol of DGEBA regardless of the chelate

structure.³ Therefore, to examine the effect of the chelate structural fragments on the properties of MECP, the concentration of these fragments equal 0.17 mol per 1 mol of the oligomer will be taken.

On the basis of the dependence of the MECP properties on the hardener content (Figs. 1–11), the values of the strength indices corresponding to 0.17 mol of the complexes were established (Table I). Proceeding from the data of Table I, the values of the unitized indices of the polymers properties were calculated.^{3,4}

For the ligands, the unitized indices have the following values:

	en ₂	dien	trien	cydien
UDT (°C)	89.5	92.5	99.0	87.5
US (MPa)	94.3	110.2	95.7	109.5

Scheme 2

Obviously, as in case of the maximum attainable values of these properties,³ the ligand type affects insignificantly the strength and deflection temperature if the ligands have the same molar concentration in polymer matrix.

The values of the unitized indices for the anions are the following:

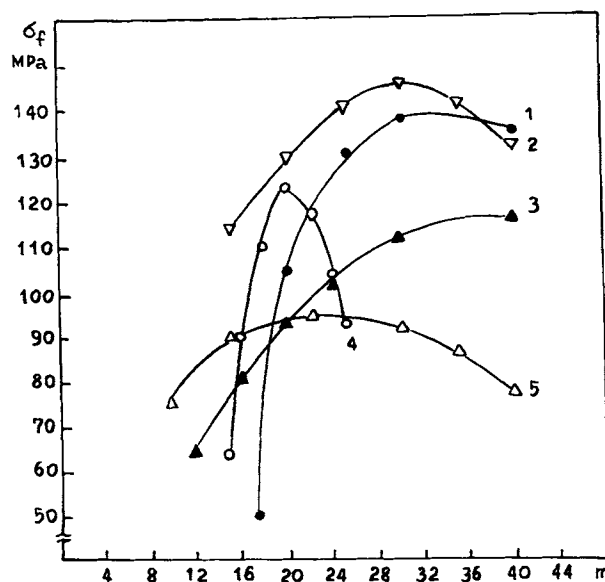


Figure 10 Dependence of σ_f of the polymers based on DGEBA on m (mass p per 100 mass p of DGEBA). The hardeners: (1) $\text{Cd}(\text{cydien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (2) $\text{Cd}(\text{dien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (3) $\text{Cd}(\text{dien})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (4) $\text{Cd}(\text{en})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (5) $\text{Cd}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$.

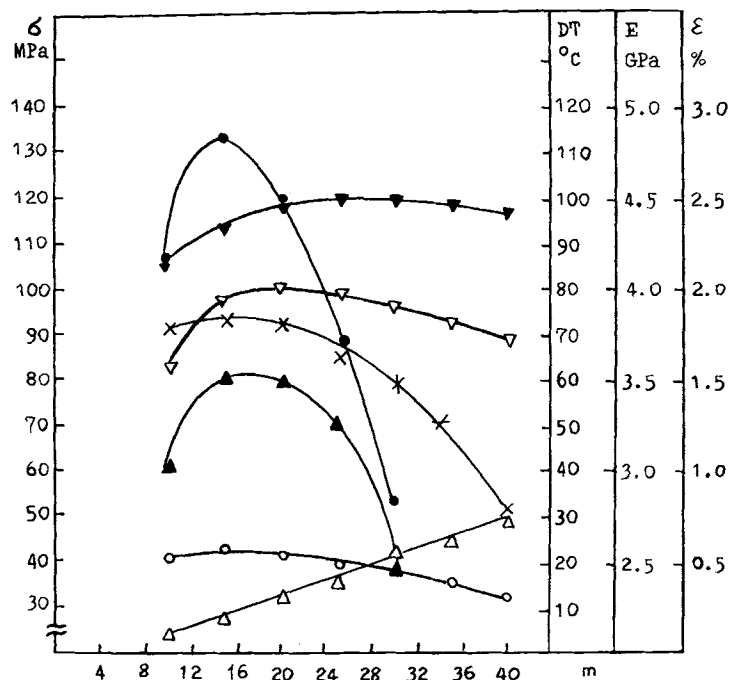


Figure 11 Dependence of the properties of the polymers based on DGEBA and [(trien)(HOC₆H₄COOH)₂] on *m* (mass *p* per 100 mass *p* of DGEBA): (▲) *E_f*; (●) *σ_f*; (△) *E_i*; (○) *σ_i*; (X) *ε*; (∇) *σ_c*; (▼) *DT*.

	CH ₃ COO ⁻	C ₆ H ₅ COO ⁻	HOC ₆ H ₄ COO ⁻	H ₂ NC ₆ H ₄ COO ⁻
UDT (°C)	99.0	87.0	121.5	134.0
US (MPa)	93.0	102.0	101.0	116.7

Scheme 3

The force of the anions, if they are in equal concentration in the epoxy system, remains the same as for the maximum attainable values of the properties: The anions slightly affect the strength, but the deflection temperature increases as the anion functionality grows.

The values of the unitized indices for the metal cations,

	Cu ²⁺	Zn ²⁺	Co ²⁺	Ni ²⁺	Fe ³⁺	MnO ²⁺
EDT (°C)	114.0	117.0	103.0	82.5	90.5	103.0
US (MPa)	101.7	99.8	81.8	86.5	79.2	66.7

Scheme 4

make it possible to arrange the cations in the series of the index values' decrease depending on the metal type (given in parentheses are the series for the maximum attainable values of the properties³):

- UDT: Zn²⁺ > Cu²⁺ > MnO²⁺ ~ Co²⁺ > Fe³⁺ > Ni²⁺
 (Zn²⁺ > Cu²⁺ > MnO²⁺ > Fe³⁺ > Co²⁺ > Ni²⁺)
 US: Cu²⁺ > Zn²⁺ > Ni²⁺ > Co²⁺ > Fe³⁺ > MnO²⁺
 (Zn²⁺ > Cu²⁺ > Co²⁺ > Ni²⁺ > Fe³⁺ > MnO²⁺)

Scheme 5

The significant effect of the cations on the properties of MECP is emphasized by the rearrangements in the series of UDT and US (for UDT: Co²⁺ and Fe³⁺;

Table I Properties of MECP Based on 1 Mol of DGEBA Hardened with 0.17 Mol of the Chelates

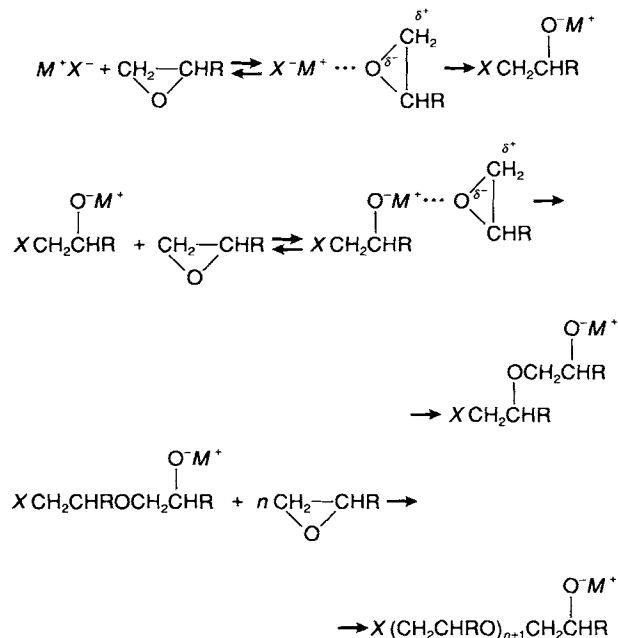
No.	Hardener	m (g per 100 g of DGEBA)	DT (°C)	σ_c (MPa)	σ_f (MPa)	σ_t (MPa)	E_f (GPa)	E_t (GPa)	ϵ (%)
I. Ligand-type influence									
1	Cu(en) ₂ (HOC ₆ H ₄ COO) ₂	22.4	109	95	118	83	3.4	3.0	4.6
2	Cu(dien)(HOC ₆ H ₄ COO) ₂	21.6	88	100	113	78	3.0	2.8	4.0
3	Cu(trien)(HOC ₆ H ₄ COO) ₂	23.7	130	120	118	63	3.2	3.0	3.1
4	Cu(cydien)(HOC ₆ H ₄ COO) ₂	26.8	98	106	119	84	3.1	7.4	5.0
5	Cd(en) ₂ (H ₂ NC ₆ H ₄ COO) ₂	24.7	70	114	93	63	3.0	3.3	1.8
6	Cd(dien)(H ₂ NC ₆ H ₄ COO) ₂	23.9	97	138	138	94	3.1	4.0	3.0
7	Cd(trien)(H ₂ NC ₆ H ₄ COO) ₂	26.0	68	98	95	80	3.0	5.9	3.1
8	Cd(cydien)(H ₂ NC ₆ N ₄ COO) ₂	29.1	77	116	132	100	2.9	4.4	5.0
II. Anion-type influence									
9	Cu(trien)(CH ₃ COO) ₂	16.9	98	100	110	63	3.3	3.0	3.0
10	Cu(trien)(H ₂ NC ₆ H ₄ COO) ₂	23.6	134	140	122	88	3.0	3.0	2.5
11	Cu(trien)(HOC ₆ H ₄ COO) ₂	23.7	130	120	118	63	3.2	3.0	3.1
12	Cu(trien)(CH=NHC ₆ H ₄ O) ₂	22.1	140	107	85	38	3.2	3.1	1.3
13	Zn(cydien)(CH ₃ COO) ₂	21.0	100	95	125	65	3.5	3.2	1.8
14	Zn(cydien)(C ₆ H ₅ COO) ₂	25.3	87	120	117	69	4.4	2.8	1.8
15	Zn(cydien)(HOC ₆ H ₄ COO) ₂	28.7	113	120	123	62	4.1	3.2	2.1
16	Zn(cydien)(CH ₂ =C(CH ₃)COO) ₂	21.8	95	107	79	26	3.0	2.5	1.0
17	Co(dien)(HOC ₆ H ₄ COO) ₂	22.3	113	101	130	91	3.6	3.2	4.7
18	Co(dien)(CH=N(CH ₂)C ₆ H ₄ O) ₂	21.0	104	93	118	65	3.6	3.5	2.1
III. Metal-type influence									
19	Cu(trien)(HOC ₆ H ₄ COO) ₂	23.7	130	120	118	63	3.2	3.0	3.1
20	Zn(trien)(HOC ₆ H ₄ COO) ₂	25.6	121	126	110	58	3.4	3.6	1.9
21	Co(trien)(HOC ₆ H ₄ COO) ₂	24.4	108	121	80	25	3.0	3.4	3.1
22	Ni(trien)(HOC ₆ H ₄ COO) ₂	27.0	85	114	105	50	3.4	2.5	2.0
23	Fe(trien)(HOC ₆ H ₄ COO) ₃	30.1	80	128	83	45	4.0	3.5	1.1
24	MnO(trien)(HOC ₆ H ₄ COO) ₂	24.1	103	128	49	23	2.8	3.5	0.7
25	Cu(cydien)(HOC ₆ H ₄ COO) ₂	26.8	98	106	119	84	3.1	7.4	5.0
26	Zn(cydien)(HOC ₆ H ₄ COO) ₂	28.7	113	120	123	62	4.1	3.2	2.1
27	Co(cydien)(HOC ₆ H ₄ COO) ₂	27.5	98	113	104	48	3.1	3.8	3.5
28	Ni(cydien)(HOC ₆ H ₄ COO) ₂	30.0	80	106	101	43	3.3	4.4	1.2
29	Fe(cydien)(HOC ₆ H ₄ COO) ₃	33.1	101	125	50	44	3.4	2.8	1.4
IV. Without metal									
30	(trien)(HOC ₆ H ₄ COOH) ₂	20.4	98	100	120	44	3.5	2.3	1.8

for US: Cu²⁺ and Zn²⁺, Co²⁺ and Ni²⁺) and indicates that the concentration of the cations is very important for the formation of the metal-containing matrix. Thus, when DGEBA is hardened with the metal chelates of the same molar concentration, the type of cation is considered to be of prime importance for the formation of the matrix structure.

MECHANISM OF THE REACTION OF THE CHELATES WITH DGEBA

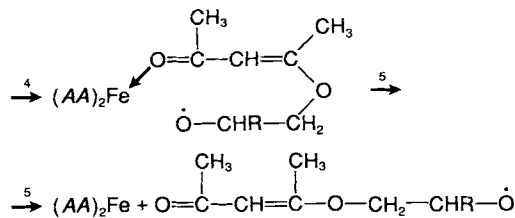
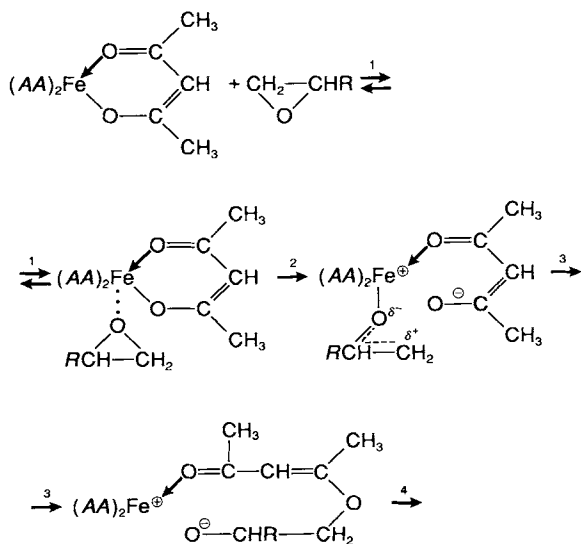
The reactions of metal-containing and complex compounds with epoxy oligomers are examined in several works.⁶⁻⁹ Being ionic compounds, metal salts react with epoxy oligomers through the coordination

of the cations with epoxy groups and the formation of a transition complex. The oxirane ring opening is accompanied by the formation of an ionic associate that acts as the initiator of ion polymerization⁶:

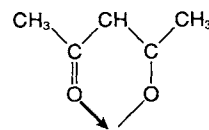


Scheme 6

where M^+ is a metal cation; X^- , an anion; R , an alkoxy group; and n , a whole number. The mechanism of the hardening of epoxy oligomers with β -diketonates of metals is such that the oxidation number of a metal is supposed to decrease^{7,8}:



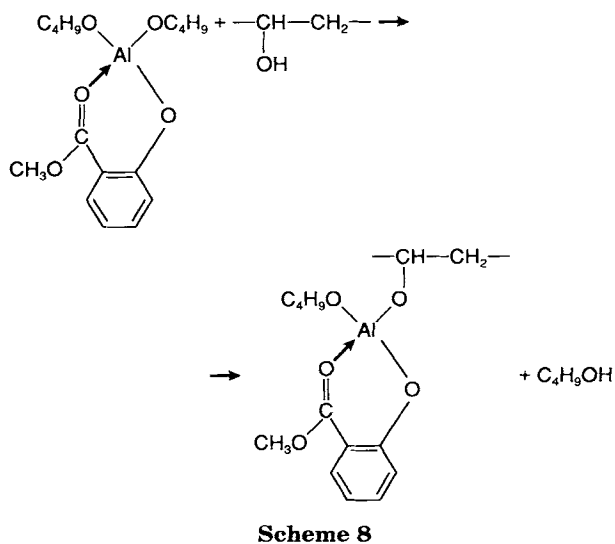
where A is



Scheme 7

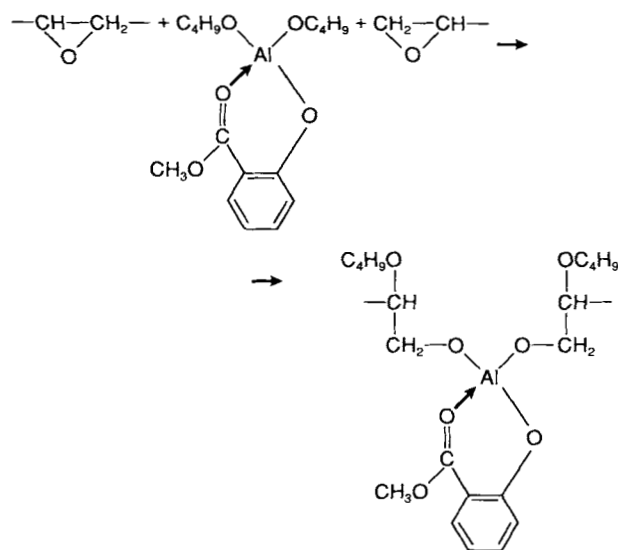
Reactions (1)–(3) are the initial stages of the anion polymerization, the further development of which is prevented by interfering into the reaction of the electron transfer process. Obviously, unlike ion polymerization with metal salts, a cation is not built into the epoxy matrix when hardened with acetylacetonates and, consequently, it does not affect significantly the finite properties of the polymers, altering merely the rate of the polymerization.

It is supposed that the hardening of epoxy oligomers with the various chelates of aluminum proceeds both at the expense of the reactions of the epoxy and hydroxyl groups with the alkoxy groups included into the compositions of the aluminum chelates and due to the reaction of the ligands with the epoxy groups. At the first stage, the hydroxyl groups of the oligomer react with the alkoxy groups to form an alcohol:



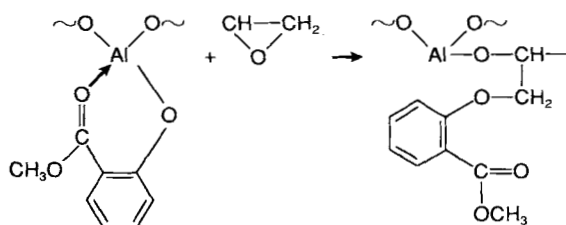
Scheme 8

The simultaneous reaction between the alkoxy groups and epoxy groups proceeds as follows:



Scheme 9

If the alkoxy groups are wanting for the epoxy ring to be opened, the latter opens the ligand:

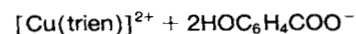


Scheme 10

The experimental studies of the MECP properties showed that the maximum values of the strength, water resistance, and thermal stability can be reached by using, respectively, 0.17, 0.11, and 0.07 mol of the chelates per 1 mol of DGEBA.^{3,4}

Proceeding from the above statement and experimental results, the interaction between the metal chelates and DGEBA was examined considering the example of the hardener $[\text{Cu}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$, which can be regarded as the ionic compound (the high polarity of the cation-anion bond is confirmed indirectly by the high solubility of this chelate both in the polar [water] and nonpolar [acetone] solvents).

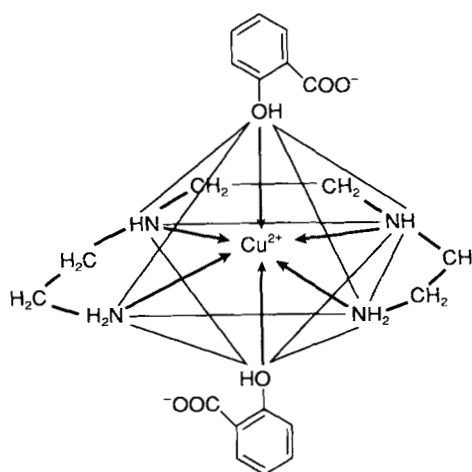
The temperature of the beginning of the active reaction between the hardener and the epoxy oligomer is defined by the temperature of the decomposition of the complex:



Scheme 11

(actually, at 20°C, the composition of DGEBA with the examined chelates have increased pot lives; when the temperature is raised to 90–110°C, gelation time shortens sharply²).

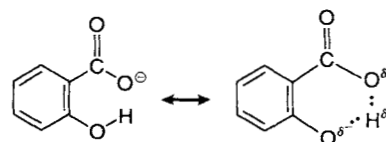
Such a scheme of the decomposition is due to the chelate structure: The cation is bonded with the ligand in the stable rings, and the anion is in the external sphere of the complex and it forms the coordinate bonds with the metal through the hydroxyl groups¹⁰:



Scheme 12

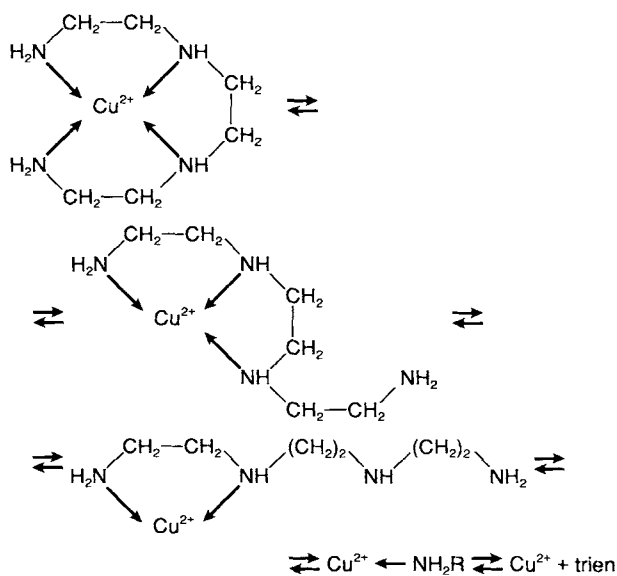
The complex cation $[\text{Cu}(\text{trien})]^{2+}$ possesses high stability due to the presence of the three closed five-membered rings in its structure (the Chugayev's Rule¹¹).

After breaking the coordinate bond with the cation (Scheme 11), the salicylate ion is stabilized at the expense of the cyclization with the hydrogen of the hydroxyl:



Scheme 13

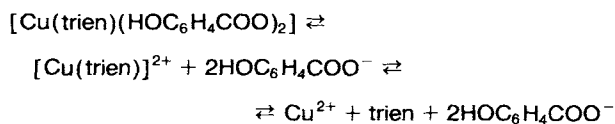
The further growth of the temperature of hardening of an epoxy chelate composition is accompanied by breaking the donor-acceptor bonds in the complex cation and its stepwise dissociation:



Scheme 14

It is necessary to take into consideration the following aspects of the problem:

1. The dissociation of the chelates



Scheme 15

is an equilibrium process and depends not only on the temperature but also on the concentration of the complex dissolved in the oligomer. The decrease in the hardener con-

centration shall reduce the content of the complex cation $[\text{Cu}(\text{trien})]^{2+}$ and anion in the system and, in turn, that of Cu^{2+} and trien. On the contrary, the introduction of the additional amount of the hardener accents the chemical equilibrium to the right.

2. For the different metals, the stability of the complex cations follows the Irving-Williams Rule—It is maximum for the copper and changes in the series of the bivalent metals^{12,13}:

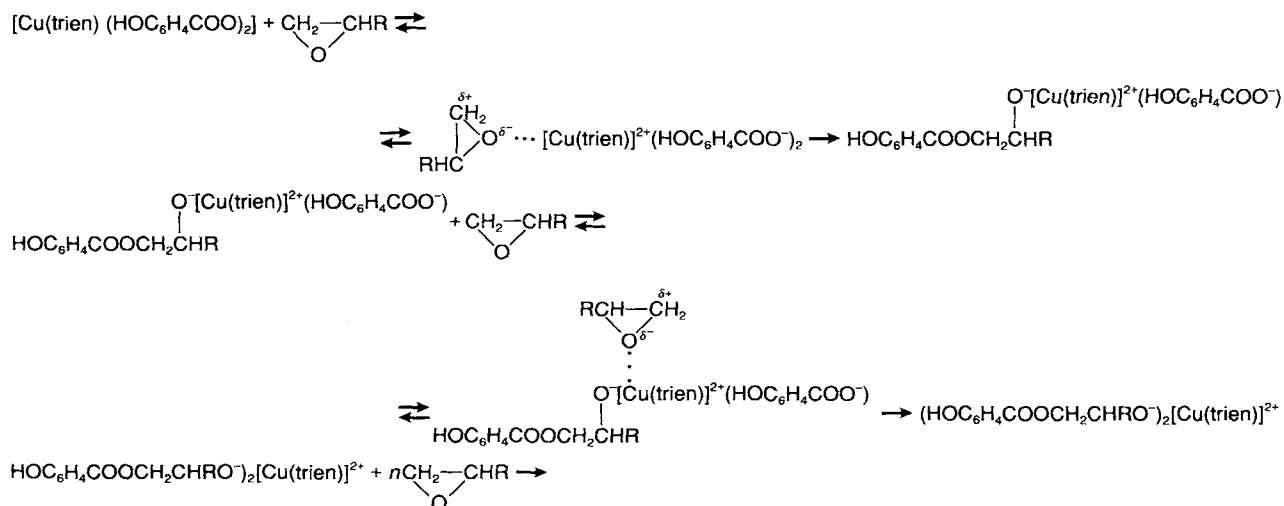


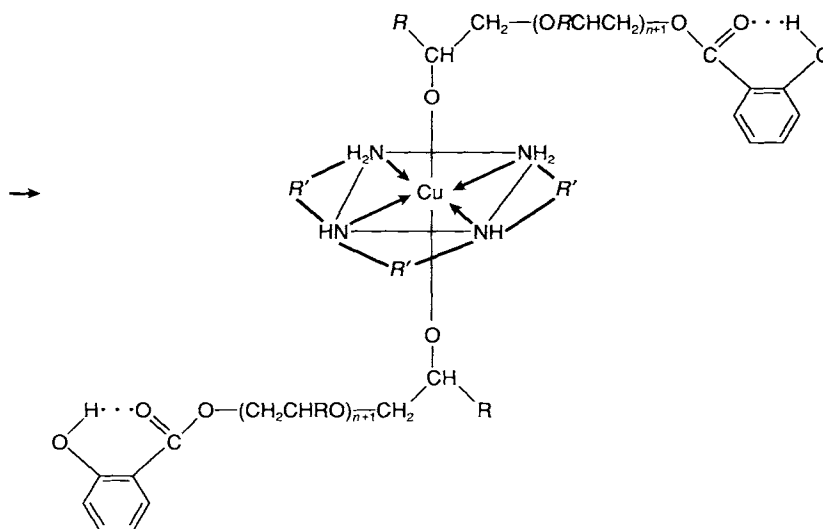
Scheme 16

Taking into consideration this factor, it is possible to adjust the temperature of the beginning of the hardening of the epoxy oligomers, which is minimal when Mn^{2+} is used, and the rate of hardening by varying the cation type.

3. The system “metal–aliphatic amine” permits oxidation-reduction reactions^{7,8} (Scheme 7), in particular, at high temperature (the dissociation of the complex cation according to Scheme 14) accompanied by the formation of suboxides (Cu_2O) or pure metals. It supposes undesirability of using the initial temperatures of stepwise hardening that exceed 110–130°C because the formation of the heterogeneous systems will decrease the strength of the polymers and composites.

Thus, at low temperatures and small concentrations of a hardener, the polymerization proceeds mainly according to the catalytic ionic mechanism:





Scheme 17

where R' is $-(CH_2)_2-$.

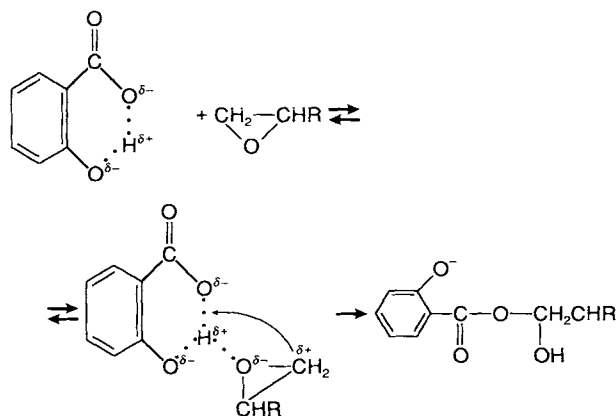
As the result of such interaction, the metal is built into the polymer matrix to form the covalent bonds with the oxygen of epoxy groups, having realized the maximum coordination number equal to six. The formation of such bonds increases the stiffness of polymer chain, decreasing ϵ , but significantly increasing the thermal stability. Actually, as is seen from Figure 3, the maximum values of ϵ correspond to the increased content of the hardeners; as mentioned above, the optimum quantity of the chelates corresponding to the maximum thermal stability is two times lower than that of the amount necessary for the maximum strength.

When the catalytic mechanism (Scheme 17) is realized, an anion reacts with epoxide only by the carbonyl group; in case of the bifunctional salicylate-anion, the hydroxyl group is deactivated because of the hydrogen bonding with the carbonyl oxygen and is closed into the stable six-membered ring. Simultaneously, with the catalytic polymerization, the interaction by the amino groups of the ligands proceeds.

With the shift of the chemical equilibrium (Scheme 11) to the right, which results from either the temperature rise or the addition of the hardener concentration, hardening of the epoxy oligomer will be realized at the expense of its interaction with the complex cation $[Cu(\text{trien})]^{2+}$ and anion $HOC_6H_4COO^-$.

The reaction of the oligomer with an anion is determined by the functionality of the latter, i.e., by the number of the active groups capable of chemical bonding in the interaction with the epoxy group. In

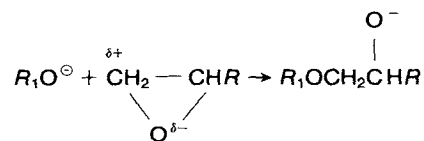
case of the salicylate ion (Scheme 13), the reaction proceeds according to the following scheme:



Scheme 18

With the anion hydroxyl being bonded with the metal by donor-acceptor bond, the interaction with the epoxy oligomer at the initial stage proceeds by the carboxyl group.

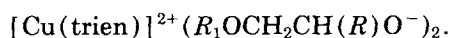
The further development of the polymerization proceeds according to the ionic mechanism:



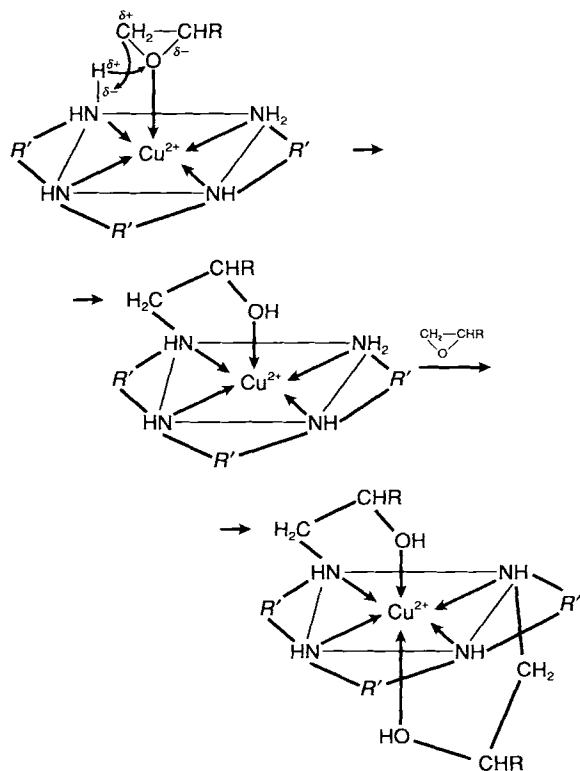
Scheme 19

where R_1 is $C_6H_4COOCH_2CH(OH)R$, and in case of the bifunctional salicylate anion, the ion com-

pletely realizes its capabilities, forming cross-linkages by both active groups. The polymerization (Schemes 18 and 19) ends with blocking of the initiating anion by the complex cation:



At temperatures lower than the temperature of the dissociation of the complex cation $[\text{Cu}(\text{trien})]^{2+}$, according to Scheme 14, the interaction is realized owing to the activation of epoxy groups by the cation and is accompanied by the simultaneous detachment of the hydrogen atom from the amino group (here should be mentioned that the formation of the donor-acceptor bond $\text{H}_2\text{N} \rightarrow \text{Cu}^{2+}$ weakens the covalent bond of the proton with the nitrogen atom of the amino group, thus increasing the proton mobility):



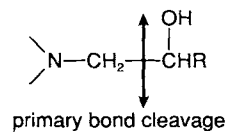
Scheme 20

The spatial configuration of the obtained compound permits the formation of the strong five-membered chelate rings at the expense of the donor-acceptor interaction of the metal with the newly formed hydroxyl groups until reaching the maximum coordination number of the copper, which is equal to six.

Hardening of the oligomer at temperatures equal to or higher than the temperature of the dissociation

of the complex cation $[\text{Cu}(\text{trien})]^{2+}$ according to Scheme 14 proceeds because of the interaction of epoxy groups with the loose amino groups of the aliphatic amine that have lost coordinate bonds with the metal. The epoxy-amine network that is formed in this case naturally preserves the capability of the donor-acceptor interaction and is chelated with the cation to form the structures analogous to Scheme 20 but less ordered.

Using the experimental data on the optimum quantity of the chelate hardeners, we estimate the specific contribution of the polymerization mechanisms in forming the epoxy chelate matrix (Table II). The structure 17, which is formed according to the catalytic ionic mechanism, as seen from Table II, is characterized by the minimum concentration of the links $\text{C}_\beta\text{—C}_\alpha\text{N}$ of the oxaliphatic bridge (only six out of 28 epoxy groups, i.e., less than 22%, react by the amino groups):



Scheme 21

which are the sites of the primary bond cleavages of the interstitial chain in thermal degradation that results from the nucleophilic character of the nitrogen atom.¹⁴

As seen from Scheme 17, the catalytic mechanism of the polymerization leads to the formation of the matrix with the minimum content of the polar hydroxyl groups, the presence of which increases water absorption. On the other hand, the presence of hydrophilic cations in the polymer structure also favors the increase in water absorption. Thus, to form a matrix having the maximum water resistance, it is necessary to suppress the metal cation hydrophilicity that can be reached when the additional hydroxyl groups bound with the cation are formed. This becomes possible with some decrease of the contribution of the catalytic polymerization mechanism and with the expansion of the contribution of the polymerization mechanism according to Scheme 20.⁴

The maximum strength of the epoxy chelate polymers corresponds to the mechanisms of predominant polymerization according to Schemes 20 and 18: six epoxy groups react with the complex cation $[\text{Cu}(\text{trien})]^{2+}$ (Scheme 20), four epoxy groups react with the anion (Scheme 18), and two epoxy groups produce cross-links according to the catalytic mechanism (Scheme 17). It is obvious that such

Table II Contribution of the Polymerization Mechanisms to the Epoxy–Chelate Matrix Structure Formation

Hardener	Maximum Values of the Properties	Quantity of the Hardener (Mol per 1 Mol of DGEBA)	Amount of Epoxy Groups per 1 Mol of the Hardener	Predominant Cure Mechanism
trien ⁵ [Cu(trien)(HOC ₆ H ₄ COO) ₂]	All the properties	0.33	6	By amino groups
	Thermal resistance	0.07	28	Catalytic
	Water resistance	0.11	18	Catalytic
	Strength	0.17	12	By amino groups of the complex cation [Cu(trien)] ²⁺ and by anion

apportionment corresponds to the formation of the optimum structure of the polymer matrix—not only to molecular but also to topological and supermolecular ones, which are no less important for the physical properties of polymers.^{15,16}

The further enlargement of the chelate concentration in an epoxy composition, which is more necessary for reaching the maximum strength, accents the chemical equilibrium (Scheme 15) up to the formation of trien and yields the same structures as those obtained in DGEBA hardening at the temperatures exceeding the temperature of the dissociation of [Cu(trien)]²⁺.

STRUCTURE OF EPOXY–CHELATE METAL-CONTAINING POLYMER MATRIX

The investigation of the structure of an epoxy–chelate metal-containing polymer matrix will be carried out proceeding from the statement that the elasticity and strength of polymers are functions of the intermolecular interaction between polymer chains; that is why the linear correlations exist among those indices. In particular, it is well known that there is a linear correlation between the strength and elasticity modulus.^{15–17}

Allowing for the effect of the hardener content in the epoxy compositions on the strength of MECP, the functions $\sigma_t = f(E_t)$ (Figs. 12–16) and $\sigma_f = f(E_f)$ (Figs. 17–20) are examined.

Figure 12 shows the function $\sigma = f(E)$ to be, as a rule, a broken line consisting of the three intersecting straight lines. The examination of Figures 12–20 allows the functions $\sigma = f(E)$ to be classified by the following features for the different hardeners:

1. The narrow range of changing σ (20–30 MPa) with the wide range of changing E . This feature is more intrinsic to the function $\sigma_t = f(E_t)$ (Fig. 12, [Cu(cydien)(HOC₆H₄COO)₂]; Fig. 13, [Cd(trien)(H₂NC₆H₄COO)₂]; Fig. 14, [Fe(trien)(HOC₆H₄COO)₃]; Fig. 15, [Cu(trien)(CH=NHC₆H₄O)₂]) and less intrinsic to the function $\sigma_f = f(E_f)$ (Fig. 19, [Cu(dien)(HOC₆H₄COO)₂]). For the non-metal containing polymer, σ_t changes by 10 MPa, whereas E_t changes by 0.6 GPa (Fig. 14, [(trien)(HOC₆H₄COOH)₂]).
2. The wide range of changing σ (50–60 MPa) with the narrow range of changing E . This

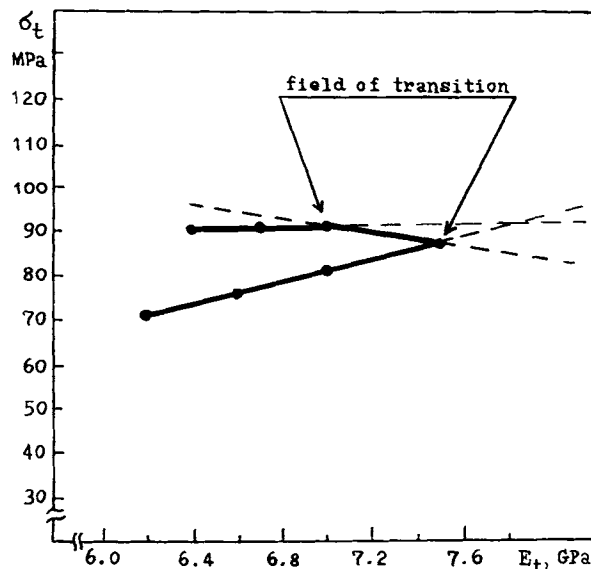


Figure 12 σ_t of the polymers based on DGEBA and [Cu(cydien)(HOC₆H₄COO)₂] as a function of E_t .

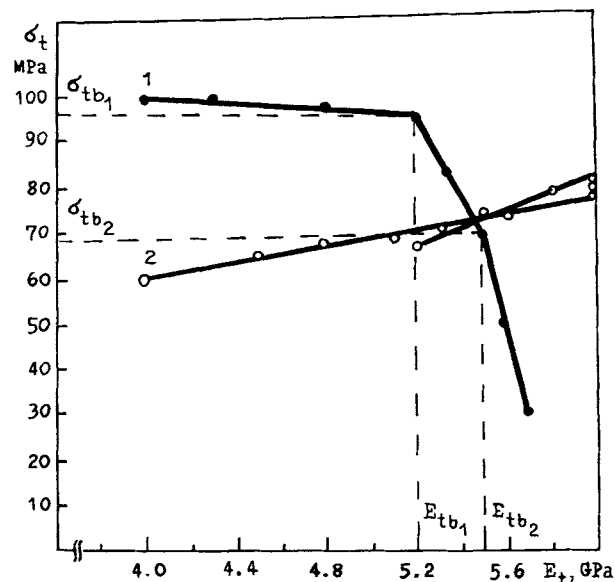


Figure 13 σ_t of the polymers based on DGEBA and (1) $[\text{Cd}(\text{cydien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$ and (2) $[\text{Cd}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$ as a function of E_t .

is more intrinsic to the function $\sigma_f = f(E_f)$ (Fig. 18, $[\text{Cu}(\text{trien})(\text{CH}_3\text{COO})_2]$ and $[\text{Cu}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; Fig. 19, $[\text{Cd}(\text{cydien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$; Fig. 20, $[\text{Cd}(\text{dien})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$,

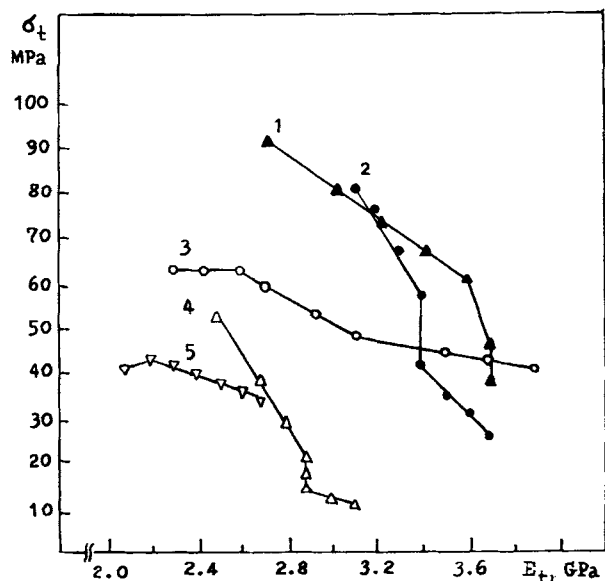


Figure 14 σ_t of the polymers based on DGEBA and the chelate hardeners as a function of E_t : (1) $[\text{Zn}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; (2) $[\text{Cd}(\text{dien})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$; (3) $[\text{Fe}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_3]$; (4) $[\text{MnO}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; (5) $(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2$.

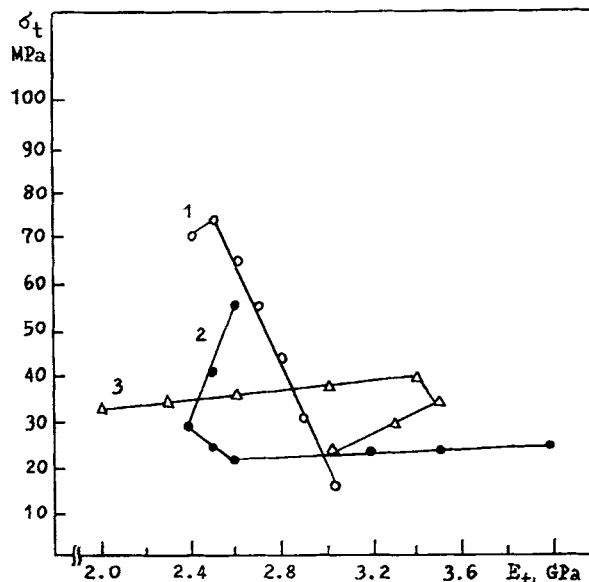


Figure 15 σ_t of the polymers based on DGEBA and (1) $[\text{Fe}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_3]$, (2) $[\text{Zn}(\text{cydien})(\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO})_2]$, and (3) $[\text{Cu}(\text{trien})(\text{CH}=\text{NHC}_6\text{H}_4\text{O})_2]$ as a function of E_t .

$[\text{Zn}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$, $[\text{Zn}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$, and $[\text{Zn}(\text{cydien})(\text{CH}_3\text{COO})_2]$) and less intrinsic to the $\sigma_t = f(E_t)$ (Fig. 14, $[\text{Cd}(\text{dien})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$ and $[\text{MnO}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; Fig. 15, $[\text{Fe}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_3]$).

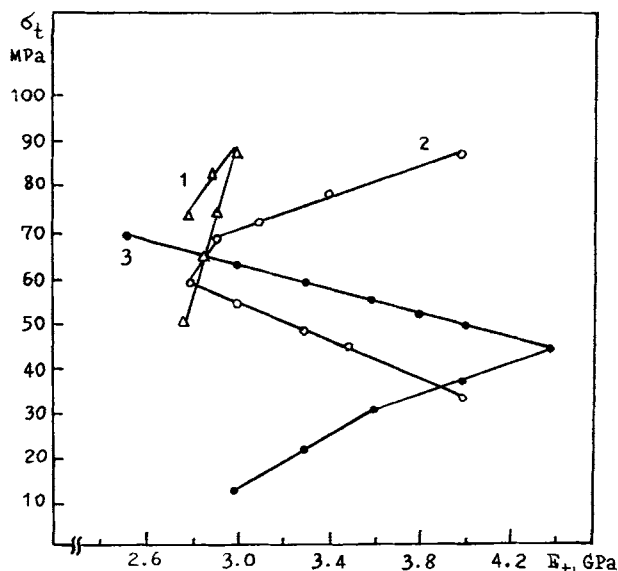


Figure 16 σ_t of the polymers based on DGEBA and (1) $[\text{Cu}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$, (2) $[\text{Zn}(\text{cydien})(\text{C}_6\text{H}_4\text{-COO})_2]$, and (3) $[\text{Ni}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2]$ as a function of E_t .

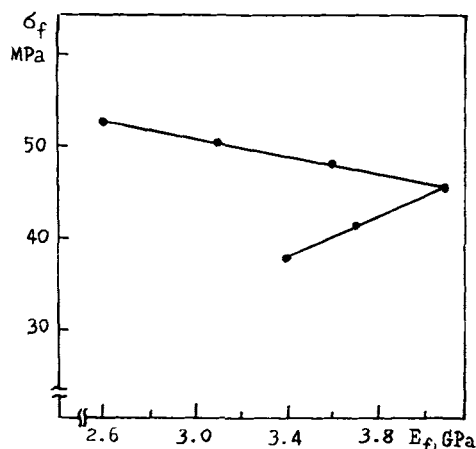


Figure 17 σ_f of the polymers based on DGEBA and $[\text{MnO}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$ as a function of E_f .

3. The simultaneous considerable alteration of σ and E : Figure 13, $[\text{Cd}(\text{cydien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$; Figure 14, $[\text{Zn}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; Figure 15, $[\text{Zn}(\text{cydien})(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_2]$; Figure 16, $[\text{Ni}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2]$, for the $\sigma_t = f(E_t)$; Figure 19, $[\text{Zn}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; and Figure 20, $[\text{Cd}(\text{en})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$ and $[\text{Ni}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2]$, for the $\sigma_f = f(E_f)$.

4. The degeneration of the transition region (a segment between the two straight lines, Fig. 12) into a point. This is a characteristic of the $\sigma_t = f(E_t)$ for the nonmetal-containing polymer (Fig. 14, $[(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$) as well as for a number of MECP: Figure 13, $[\text{Cd}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$; Figure 15, $[\text{Fe}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_3]$; and Figure 16, $[\text{Cu}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$.

The transition region degeneration is even clearer for the $\sigma_f = f(E_f)$ (Fig. 17, $[\text{MnO}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; Fig. 18, $[\text{Cu}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2]$, $[\text{Cu}(\text{trien})(\text{CH}_3\text{COO})_2]$, and $[\text{Fe}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_3]$; Fig. 19, $[\text{Cu}(\text{dien})(\text{HOC}_6\text{H}_4\text{COO})_2]$) for which the correlation between σ_f and E_f becomes linear in some cases (Fig. 19, $[\text{Cu}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2]$; Fig. 20, $[\text{Zn}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2]$ and $[\text{Zn}(\text{cydien})(\text{CH}_3\text{COO})_2]$).

The bend points of the graph $\sigma = f(E)$ correspond with the sharp change of the properties of the polymer matrixes (Fig. 21) and can be defined by the coordinates of the bend points (b) for $\sigma_t = f(E_t)$: $(\sigma_{tb_1}, E_{tb_1})$ and $(\sigma_{tb_2}, E_{tb_2})$; for $\sigma_f = f(E_f)$: $(\sigma_{fb_1}, E_{fb_1})$ and $(\sigma_{fb_2}, E_{fb_2})$ (Fig. 13).

On the basis of the graphs $\sigma = f(E)$, the structures of the epoxy-chelate polymer matrixes corre-

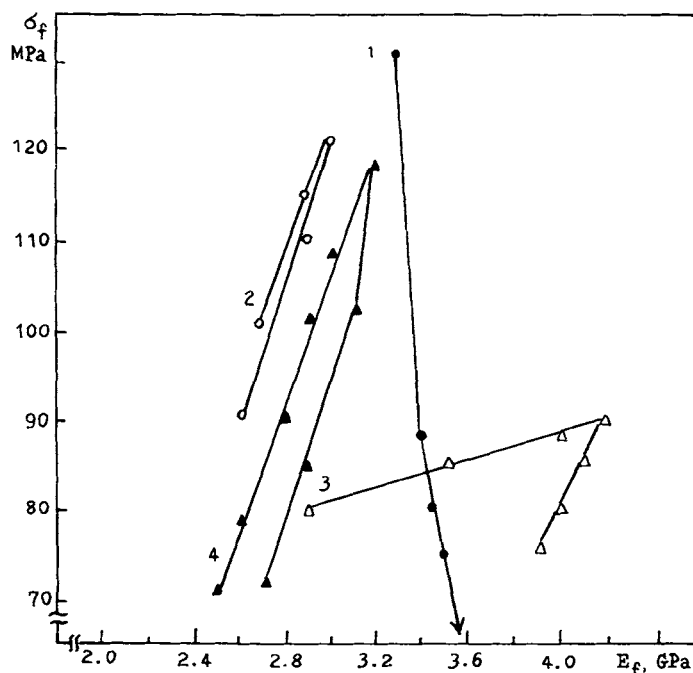


Figure 18 σ_f of the polymers based on DGEBA and the chelate hardeners as a function of E_f : (1) $\text{Cu}(\text{trien})(\text{CH}_3\text{COO})_2$; (2) $\text{Cu}(\text{trien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (3) $\text{Fe}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_3$; (4) $\text{Cu}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2$.

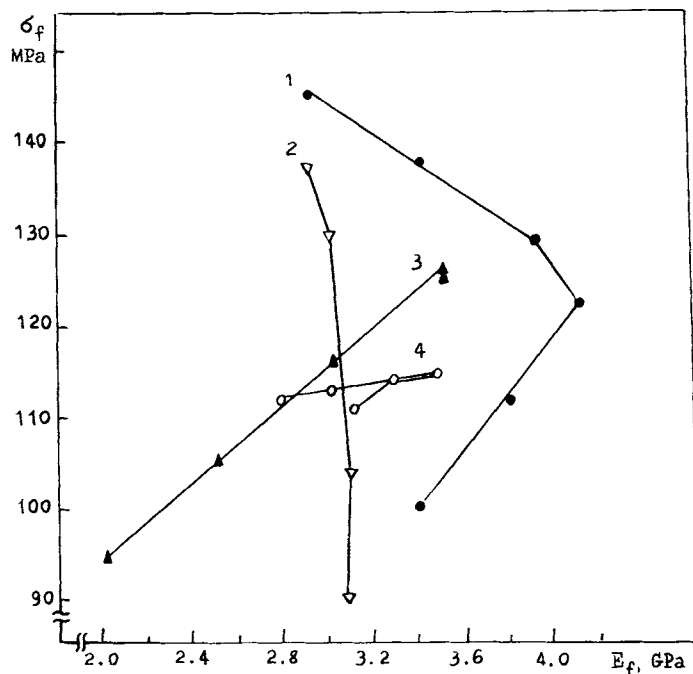


Figure 19 σ_f of the polymers based on DGEBA and the chelate hardeners as a function of E_f : (1) $\text{Zn}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2$; (2) $\text{Cd}(\text{cydien})(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (3) $\text{Cu}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2$; (4) $\text{Cu}(\text{dien})(\text{HOC}_6\text{H}_4\text{COO})_2$.

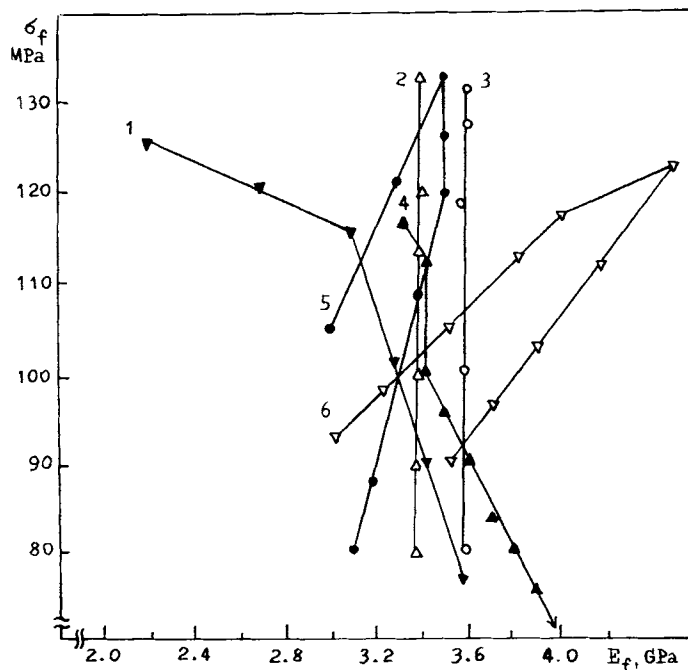


Figure 20 σ_f of the polymers based on DGEBA and the chelate hardeners as a function of E_f : (1) $\text{Ni}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2$; (2) $\text{Zn}(\text{trien})(\text{HOC}_6\text{H}_4\text{COO})_2$; (3) $\text{Zn}(\text{cydien})(\text{CH}_3\text{COO})_2$; (4) $\text{Cd}(\text{dien})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$; (5) $(\text{trien})(\text{HOC}_6\text{H}_4\text{COOH})_2$; (6) $\text{Cd}(\text{en})_2(\text{H}_2\text{NC}_6\text{H}_4\text{COO})_2$.

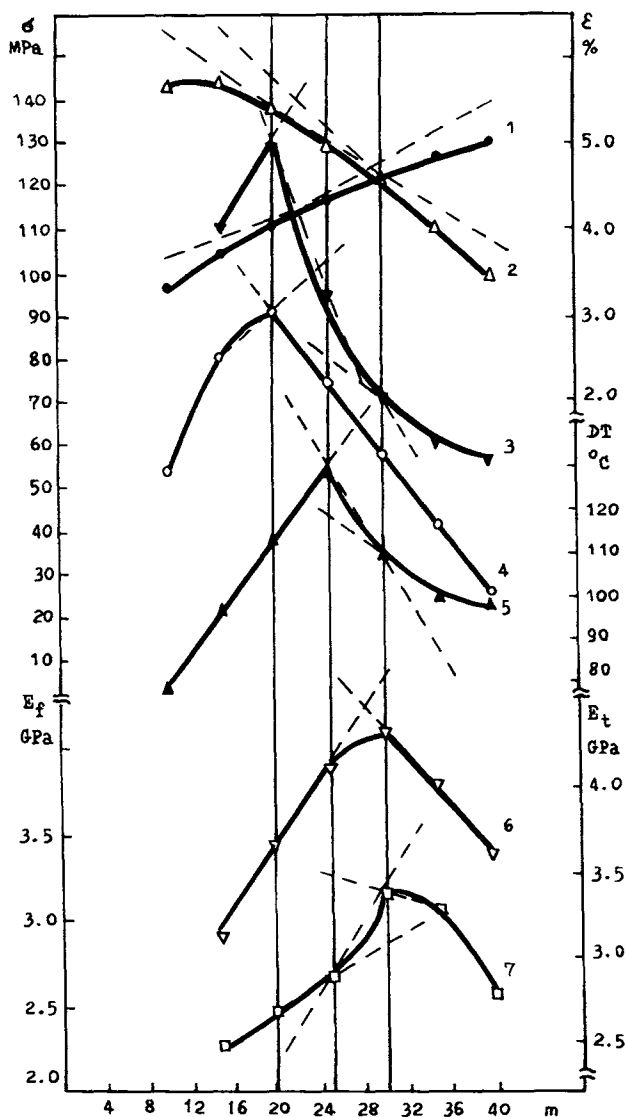


Figure 21 The property changes of the polymers based on DGEBA and $[\text{Zn}(\text{cydien})(\text{HOC}_6\text{H}_4\text{COO})_2]$ in the bend points of the graphs $\sigma = f(E)$ (m_b mass p of the hardener per 100 mass p of DGEBA): $m_{b_1} = 20$ g; $m_{b_2} = 25$ g; $m_{b_3} = 30$ g (Table III, No. 12); (1) σ_c ; (2) σ_f ; (3) ϵ ; (4) σ_t ; (5) DT ; (6) E_f ; (7) E_t .

sponding to the bend points can be examined. Table III shows the mean values of the hardeners mass (m_b) corresponding to the bend points of the graphs $\sigma = f(E)$. Regardless of the chelate composition, the hardener mass corresponding to the bend points is an average of 0.16–0.17 mol per 1 mol of DGEBA that coincides with the optimum quantity of the complexes necessary for reaching the maximum strength of MECP.³ Hence, the bend points of the graphs $\sigma = f(E)$ correspond to the optimum struc-

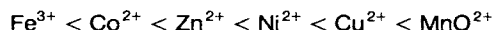
ture of the epoxy–chelate matrices. The distance between the two points makes up, as a rule, 0.03–0.04 mol of a chelate per 1 mol of DGEBA.

The three intersecting straight lines that make up the function $\sigma = f(E)$ accord with the three types of MECP structures (Table II):

1. The structure formed with the small concentration of a hardener by means of the predominant polymerization by the catalytic ion mechanism (Scheme 17).
2. The structure formed with the optimum quantity of a chelate by means of the predominant polymerization by the anion and complex cation (Schemes 18 and 20).
3. The structure formed with the hardener excess due to the predominant formation of the epoxy–amine network resulting from the reaction between the epoxy oligomer and unconnected amine (Scheme 15).

To examine the dependence of m_b on the chelate hardener structure, the mean values of m_b corresponding to the complex of the formula (1) are considered (Tables IV–VI).

As follows from Table IV depending on the cation type, the hardener mass necessary for reaching the bend point of $\sigma = f(E)$ increases in the series



Scheme 22

changing from the first to the last term of the series almost 1.5 times. As mentioned above, the type of metal determines the strength of the complex cation $[\text{M}(\text{R})_n]^{p+}$, for example, $[\text{Cu}(\text{trien})]^{2+}$, the stepwise dissociation of which results in the formation of the polymer matrix at the expense of the coordinately uncombined amino groups' inclusion into the reaction (Schemes 14 and 15).

The series of the dependence of m_b on the metal cation type (Scheme 22) coincides, except for the tetravalent manganese, with the Irving–Williams Rule (Scheme 16) [Fig. 22(a) and (b)] and is determined by the electron affinity of the metal atoms [Fig. 22(c)] that is due to the character of the coordinate bond resulting from the electron donor–acceptor interaction. The shift of the chemical equilibrium (Scheme 15) up to the trien generation takes place with an increase of the complex cation con-

Table III Dependence $\sigma = f(E)$: The Coordinates of the Bend Points (Figs. 12–20)

		Hardener Mass Corresponding to the Bend Points of the Graphs (m_b)							
		$\sigma_t = f(E_t)$				$\sigma_f = f(E_f)$			
		m_b				m_b			
No.	Hardener	σ_{tb} (MPa)	E_{tb} (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA	σ_{fb} (MPa)	E_{fb} (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA
1	Cu(en) ₂ (HOC ₆ H ₄ COO) ₂	80	3.1	20	0.15	120	3.4	25	0.18
		88	3.0	25	0.18	125	3.5	30	0.22
2	Cu(dien)(HOC ₆ H ₄ COO) ₂	87	3.3	30	0.23	115	3.5	30	0.23
		89	3.2	35	0.27	114	3.3	32	0.24
3	Co(dien)(HOC ₆ H ₄ COO) ₂	90	3.2	20	0.15	135	3.7	25	0.19
		86	2.7	30	0.22	138	3.7	30	0.22
4	Cu(trien) ₂ (HOC ₆ H ₄ COO) ₂	70	3.0	18	0.09	124	2.9	21	0.11
		70	3.3	24	0.12	125	3.0	24	0.12
5	Cu(trien)(HOC ₆ H ₄ COO) ₂	63	3.0	20	0.14	118	3.2	21	0.15
		65	3.1	21	0.15	104	3.1	28	0.20
6	Co(trien)(HOC ₆ H ₄ COO) ₂	78	2.9	15	0.10	102	3.0	20	0.13
		23	3.4	25	0.17	74	2.9	25	0.17
7	Zn(trien)(HOC ₆ H ₄ COO) ₂	61	3.6	25	0.16	Without bend points			
		46	3.7	30	0.19				
8	Ni(trien)(HOC ₆ H ₄ COO) ₂	54	2.3	20	0.12	108	3.4	30	0.18
		46	2.7	30	0.18	103	3.7	36	0.22
9	Fe(trien)(HOC ₆ H ₄ COO) ₃	63	2.6	15	0.08	83	4.0	30	0.16
		48	3.1	27	0.15	85	4.2	35	0.19
10	MnO(trien)(HOC ₆ H ₄ COO) ₂	22	2.9	25	0.17	45	4.1	30	0.21
		15	2.9	30	0.21				
11	Cu(cydien)(HOC ₆ H ₄ COO) ₂	85	7.5	28	0.17	126	3.5	35	0.22
		90	7.0	40	0.25				
12	Zn(cydien)(HOC ₆ H ₄ COO) ₂	90	2.7	20	0.12	129	3.9	25	0.15
		58	3.4	30	0.18	122	4.1	30	0.18
13	Co(cydien)(HOC ₆ H ₄ COO) ₂	53	3.7	15	0.09	116	3.2	20	0.12
		52	3.8	25	0.15	110	3.1	25	0.15
14	Ni(cydien)(HOC ₆ H ₄ COO) ₂	43	4.4	30	0.18	115	3.1	25	0.15
		30	3.6	35	0.21	76	3.6	35	0.21
15	Fe(cydien)(HOC ₆ H ₄ COO) ₃	74	2.5	15	0.08	86	3.4	20	0.10
		30	2.9	35	0.18	64	3.4	25	0.12
16	Cd(en) ₂ (H ₂ NC ₆ H ₄ COO) ₂	68	2.2	20	0.13	123	4.5	20	0.13
		64	3.3	25	0.17	117	4.0	22	0.15
17	Cd(dien)(H ₂ NC ₆ H ₄ COO) ₂	87	3.7	20	0.14	142	3.2	26	0.18
		95	4.0	25	0.17	147	3.4	30	0.20
18	Cd(dien) ₂ (H ₂ NC ₆ H ₄ COO) ₂	42	3.4	16	0.09	100	3.4	23	0.13
		57	3.4	20	0.11	112	3.4	30	0.17
19	Cd(cydien)(H ₂ NC ₆ H ₄ COO) ₂	95	5.2	25	0.14	104	3.1	20	0.12
		100	4.3	30	0.17	130	3.0	25	0.14

Table III (Continued from the previous page)

		Hardener Mass Corresponding to the Bend Points of the Graphs (m_b)							
		$\sigma_t = f(E_t)$				$\sigma_f = f(E_f)$			
				m_b				m_b	
No.	Hardener	σ_{tb} (MPa)	E_{tb} (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA	σ_{fb} (MPa)	E_{fb} (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA
20	Cd(trien)(H ₂ NC ₆ H ₄ COO) ₂	78	6.0	20	0.13	96	3.0	22	0.14
		82	6.0	22	0.14	94	3.0	28	0.18
21	Cu(trien)(H ₂ NC ₆ H ₄ COO) ₂	88	3.0	23	0.16	121	3.0	22	0.15
22	Zn(cydien)(C ₆ H ₅ COO) ₂	68	2.9	25	0.16	125	4.2	20	0.13
		58	2.8	30	0.20	100	4.5	30	0.20
23	Zn(cydien)(CH ₂ =C(CH ₃)COO) ₂	28	2.4	20	0.16	87	2.5	15	0.12
		21	2.6	30	0.24	82	2.9	20	0.16
24	Cu(trien)(CH ₃ COO) ₂	63	3.0	17	0.17	88	3.4	20	0.20
		53	2.5	19	0.19				
25	Zn(cydien)(CH ₃ COO) ₂	68	3.2	20	0.16	Without bend points			
		45	3.4	30	0.23				
26	Cu(trien)(CH=NHC ₆ H ₄ O) ₂	39	3.4	25	0.18	87	3.3	25	0.18
		34	3.5	30	0.21	95	3.3	35	0.25
27	Co(dien)(CH=N(CH ₂)C ₆ H ₄ O) ₂	65	3.5	15	0.12	110	3.4	30	0.24
		63	3.3	30	0.24	110	3.3	35	0.28
28	(trien)(HOC ₆ H ₄ COOH) ₂	42	2.2	18	0.14	133	3.5	15	0.12
						120	3.5	20	0.16
Mean values of m_b					0.16				0.17

Table IV Dependence of the Mass of the Hardener [$M(R)(\text{HOC}_6\text{H}_4\text{COO})_p$] Corresponding to the Bend Points of the Graph $\sigma = f(E)$ on the Metal Cation Type

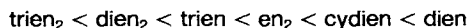
		Hardener Mass (Mol per 1 Mol of DGEBA) (m_b)								
		$\sigma_t = f(E_t)$				$\sigma_f = f(E_f)$				
		1st Bend Point		2nd Bend Point		1st Bend Point		2nd Bend Point		
		R								Mean Value for the Cation
M		Trien	Cydien	Trien	Cydien	Trien	Cydien	Trien	Cydien	
$p = 2$										
Co ²⁺		0.10	0.09	0.17	0.15	0.13	0.12	0.17	0.15	0.135
Ni ²⁺		0.12	0.18	0.18	0.21	0.18	0.15	0.22	0.21	0.181
Cu ²⁺		0.14	0.17	0.15	0.25	0.15	0.22	0.20		0.183
Zn ²⁺		0.16	0.12	0.19	0.18		0.15		0.18	0.163
MnO ²⁺		0.17		0.21		0.21				0.197
2H ⁺		0.14				0.12		0.16		0.140
$p = 3$										
Fe ³⁺		0.08	0.08	0.15	0.18	0.16	0.10	0.19	0.12	0.133

Table V Dependence of the Mass of the Hardener $[M(R)(X)_2]$ Corresponding to the Bend Points of the Graph $\sigma = f(E)$ on the Ligand Type

Hardener Mass (Mol per 1 Mol of DGEBA) (m_b)										
		$\sigma_t = f(E_t)$				$\sigma_f = f(E_f)$				
		1st Bend Point		2nd Bend Point		1st Bend Point		2nd Bend Point		
M										
		Cu ²⁺	Cd ²⁺	Cu ²⁺	Cd ²⁺	Cu ²⁺	Cd ²⁺	Cu ²⁺	Cd ²⁺	
X										
R	HOC ₆ ~ ~H ₄ COO ⁻	H ₂ NC ₆ H ₄ ~ ~COO ⁻	HOC ₆ H ₄ ~ ~COO ⁻	H ₂ NC ₆ ~ ~H ₄ COO ⁻	HOC ₆ H ₄ ~ ~COO ⁻	H ₂ NC ₆ ~ ~H ₄ COO ⁻	HOC ₆ ~ ~H ₄ COO ⁻	H ₂ NC ₆ ~ ~H ₄ COO ⁻	Mean Value for the Ligand	
en ₂	0.15	0.13	0.18	0.17	0.18	0.13	0.22	0.15	0.164	
dien	0.23	0.14	0.27	0.17	0.23	0.18	0.24	0.20	0.208	
dien ₂		0.09		0.11		0.13		0.17	0.125	
trien	0.14	0.13	0.15	0.14	0.15	0.14	0.20	0.18	0.154	
trien ₂	0.09		0.12		0.11		0.12		0.110	
cydien	0.17	0.14	0.25	0.17	0.22	0.12		0.14	0.173	

centration; this increase, in its turn, takes place when the hardener content enlarges in an epoxy composition. That is why m_b depends on the metal type in a chelate: The easier the complex cation dissociates, the less is the adequate amount of the hardener for reaching the bend point and forming the epoxy-amine network.

The analysis of the dependence of m_b on the hardener ligand type presented in Table V indicates that m_b increases in the series:



Scheme 23

Table VI Dependence of the Mass of the Hardener $[M(R)(X)_2]$ Corresponding to the Bend Points of the Graph $\sigma = f(E)$ on the Anion Type

Hardener Mass (Mol per 1 Mol of DGEBA) (m_b)										
		$\sigma_t = f(E_t)$				$\sigma_f = f(E_f)$				
		1st Bend Point		2nd Bend Point		1st Bend Point		2nd Bend Point		
M										
		Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺	
R										
X	Trien	Cydien	Trien	Cydien	Trien	Cydien	Trien	Cydien	Mean Value for the Anion	
CH ₃ COO ⁻	0.17	0.16	0.19	0.23	0.20				0.190	
C ₆ H ₅ COO ⁻		0.16		0.20		0.13		0.20	0.173	
HOC ₆ H ₄ COO ⁻	0.14	0.16	0.15	0.19	0.15		0.20		0.165	
H ₂ NC ₆ H ₄ COO ⁻	0.16				0.15				0.155	
CH ₂ =C(CH ₃)COO ⁻		0.16		0.24		0.12		0.16	0.170	
CH=NHC ₆ H ₄ O ⁻	0.18		0.21		0.18		0.25		0.205	

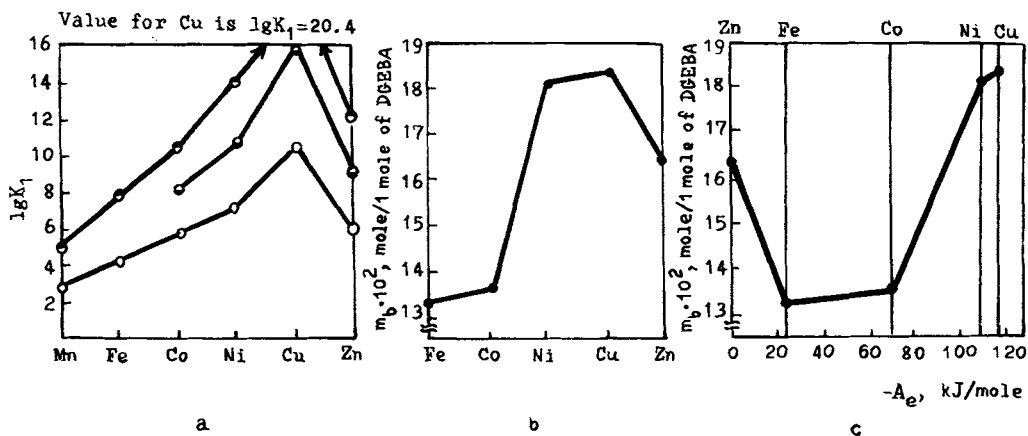
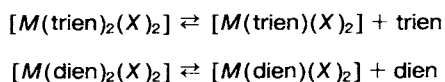


Figure 22 (a) The stability of some complexes of the transition metals with nitrogen-type ligands as a function of atomic number.¹² K_1 is an equilibrium constant of a complex: (○) en; (◻) dien; (◻) trien. (b) The hardener mass in the bend point of the dependence $\sigma = f(E)$ (m_b) as a function of the transition metals atomic number. The mean values of m_b for the cations and trien/cydien are presented. (c) The hardener mass in the bend point of the dependence $\sigma = f(E)$ (m_b) as a function of electron affinity energy (A_e).¹⁸⁻²⁰

changing from the first to the last term of the series almost two times. In the bend point of the $\sigma = f(E)$, the predominant formation of the epoxy-amine network is initiated by the reaction of the oligomer with the loose amine formed due to the dissociation of the complex cation (Scheme 14). In the hardeners $[M(\text{trien})_2(X)_2]$ and $[M(\text{dien})_2(X)_2]$, the second molecule of the ligands is weakly bonded to the metal by reason of the coordination saturation of the metal and the chelates dissociate easily:



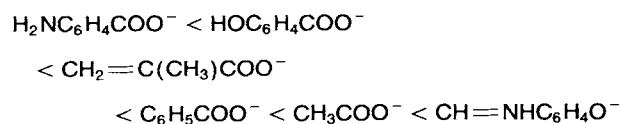
Scheme 24

It is obvious that the metal bonding with one molecule of tetradentate trien results in the greater coordination saturation of M than does the metal bonding with the one molecule of tridentate dien; that is why the stability of the complex $[M(\text{trien})_2(X)_2]$ is less and the shift of the chemical equilibrium (Scheme 24) requires less quantity of the hardener to the formation of the free amine than that of the $[M(\text{dien})_2(X)_2]$.

In going from trien to dien (Scheme 23), the number of the dentate groups in the ligands decreases: There are two NH_2 and two NH groups in trien and four NH_2 groups in en₂—thus, there are close values of m_b for these ligands (0.154 and 0.164, respectively, Table V), and there are three NH and

two CN groups in cydien, two NH_2 and one NH group in dien, which results in the m_b rise.

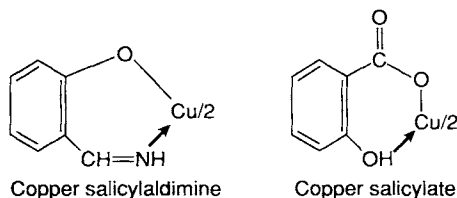
Depending on the anion type, m_b increases in the following series (Table VI):



Scheme 25

In comparison with the other structural fragments of the chelate hardener (a ligand and metal cation), the anion type is less important for m_b : When it alters, m_b decreases 1.3 times. Taking into consideration the fact that the structure of the anions affects the formation of the polymer matrix structure and changes the rate of the chelate dissociation slightly according to Scheme 11 (since an anion is in the external sphere of a complex), it is natural to expect that the addition of the anion functionality at the expense of the reactive groups' number growth in its structure is to be accompanied with the reduction of the quantity of the hardener necessary for the reaction with epoxy groups. It is the relationship we observe in the obtained series (Scheme 25): The primary NH_2 group in the anthranilate ion is reactive when the polymer network is formed; the salicylate anion that possesses the hydroxyl has less functionality; and following them are the methacrylate ion (the double bond) and monofunctional

benzoate and acetate anions. The copper salicylal-dimine requiring the greatest amount of the hardener to reach the bend point is a special case. This is because of the structure of this complex: Unlike the other neutral chelates (salicylate and anthranilate), the salicylal-dimine rings do not contain the carboxyl group that enhances the stability of the chelates and so requires the greater hardener quantities for the polymerization with epoxy oligomers:



CONCLUSION

The analysis of the structure and attributes of MECP shows the promising character of using the chelate hardeners for the creation of the polymers possessing a different set of properties. It can be reached by changing the structure of the chelates and the hardener content in the epoxy compositions and by varying the conditions of hardening, which results in the formation of the polymer matrixes of distinct structures as a result of the conversion of the epoxy oligomer polymerization mechanism.

SYMBOLS

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	deflection temperature
UDT	unitized deflection temperature
US	unitized strength
m	hardener mass in the composition based on DGEBA
m_b	hardener mass corresponding to the bend point of the dependence $\sigma = f(E)$

(σ_{tb}, E_{tb}) bend point coordinates,
and (σ_{fb}, E_{fb})
 A_e electron affinity energy

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Received December 4, 1991

Accepted January 21, 1992