Structure of the Epoxy–Chelate Metal-Containing Matrices: Theoretical Aspects

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SYNOPSIS

A theoretical analysis has been carried out of the structure of metalliferous epoxy–chelate polymers (MECP) based on diglycidyl ether of bisphenol-A (DGEBA) hardened with metal complexes of the formula $[M(L)_n(X)_p]$, where M is the cation of the transition metal; R, a nitrogen-containing ligand; X, the anion of an organic acid; n, the number of the ligands in the complex molecule (n = 1 or 2), and p, the metal valency (p = 2 or 3). On the basis of the correlations between the tensile strength (σ_t) and tensile modulus (E_t), and flexural strength (σ_f) and flexural modulus (E_f), of MECP, $\sigma_t = f(E_t)$ and $\sigma_f = f(E_f)$, and supposing that when the condition $\sigma_{t_A} = \sigma_{t_B}$, $\sigma_{f_A} = \sigma_{f_B}$, $E_{t_A} = E_{t_B}$, $E_{f_A} = E_{f_B}$ is fulfilled, where A and B are complex hardeners of different structures but of the same class, the epoxy–chelate matrices have similar structures. The influence of the structural fragments of the hardener molecule (the metal, ligand, and anion) on the polymer properties was evaluated and it was found out that the biggest contribution to these properties belongs to the metal, the alteration of which changes the thermal stability (ΔM is the polymer mass loss after thermal treatment in air), deformability (ϵ), σ_f, E_f, and deflection temperature (DT) significantly. By this, the effect of the hardener structure change on the alteration of the MECP properties is maximal for ΔM, is minimal for the compressive strength (σ_c), and decreases in the series: $\Delta M > \epsilon > DT > \sigma_f > E_f > \sigma_c$. The type of the anion affects σ_c significantly, but the ligand type contributes the least to the polymer properties. The obtained dependencies of the MECP properties on the structural fragments of the complex hardeners allow preliminary evaluation of the structure of the chelates and epoxy–chelate compositions necessary to produce epoxy polymers with required properties. The new method of the theoretical investigation of the effect of the structural fragments (method of TIESF) of the polymer matrix on the polymer properties can be used to analyze the structures of the polymers of other classes and to predict the optimal structures, promising the production of the materials with the optimal properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The further development of the chemistry of the metalliferous epoxy–chelate polymers (MECP) synthesized by hardening of diglycidyl ether of bisphenol-A (DGEBA) with the metal complexes of the formula $[M(L)_n(X)_p]$, where M is the metal cation: Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, or MnO^{2+}; R is the ligand: ethylene diamine (en), diethylene triamine (dien), triethylene tetramine (trien), or bis-N,N'-(β-cyanoethyl)-diethylene triamine (cydien); X is 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 is the number of the ligands in the complex molecule, n = 1 or 2; and p is the metal valency, p = 2 or 3, and having high thermal stability and mechanical strength, undoubtedly is to be based on the theoretical generalization of the experimental results obtained.[1–7]

It was established that the change of the complex hardener content in the epoxy composition causes significant change in the polymerization mechanism, structure, and properties of MECP.[5] There are at least two investigation methods of the effect of com-

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plex hardener structural fragments (the metal, ligand, and anion) on polymer properties:

- the comparison of the index values of MECP based on the epoxy compositions containing equal concentrations of the chelate structural fragments,[5] and
- the comparison of the properties of the polymers having the similar matrices.

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

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol-A (DGEBA), ED-22 grade, with an epoxy equivalent weight of 170–180, made in Russia, was used as an epoxy oligomer. The salts of metals and organic acids were used as well as aliphatic amines: en, dien, trien, and cydien.

Synthesis

Complex hardeners were synthesized by directly combining the salts with the amines used in equimolar proportions, with stirring for 2–4 h at the melting points of the chelates. MECP was made by casting the epoxy compositions into metal molds and hardening for 11 h at 120°C.

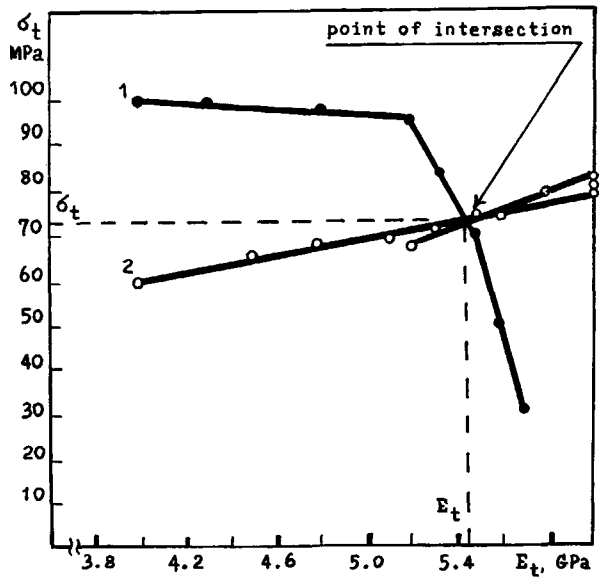


Figure 1 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [Cd(cydien)($H_2NC_6H_4COO)_2$] and (2) [Cd(trien)($H_2NC_6H_4COO)_2$] as a function of tensile modulus (E_t).

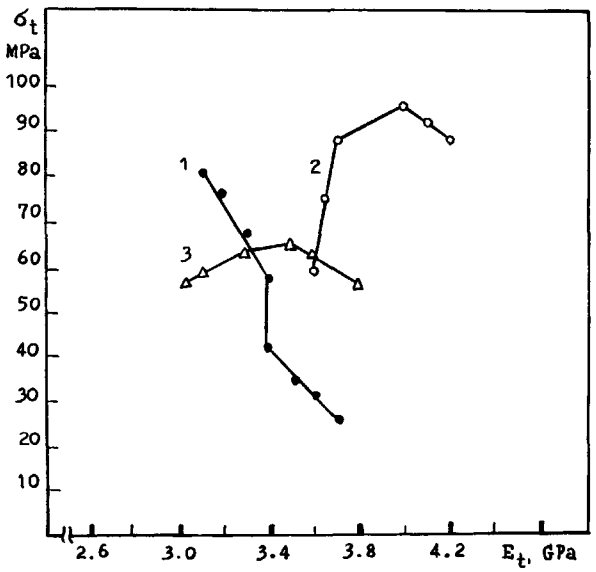


Figure 2 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [Cd(dien)$_2$($H_2NC_6H_4COO)_2$], (2) [Cd(dien)($H_2NC_6H_4COO)_2$], and (3) [Co(dien)-($CH{=}N(CH_2)C_6H_4O)_2$] as a function of tensile modulus (E_t).

Methods

The strength indices of the polymers were determined according to the standards in Ref. 8. The deflection temperature was determined according to the DIN 53458 procedure by bending the polymer specimens (120 × 15 × 10 mm^3) with continuous loading (σ = 5 MPa; the rate of the temperature rise ΔT = 50°C/h; the fixed deformation is 6 mm). To characterize the heat resistance of MECP, thermogravimetric analysis was used in the isothermal regime in air.

RESULTS AND DISCUSSION

The investigation of the structure of MECP was carried out by analyzing the contributions of the chelate hardener structural fragments to the values of the polymer indices and supposing that irrespective of the fragment structures of the epoxy–chelate metal-containing matrices the effect of such factors as sample conditioning, testing rate, and temperature is the same for all the specimens of MECP (the preparation of MECP was carried out in the iden-

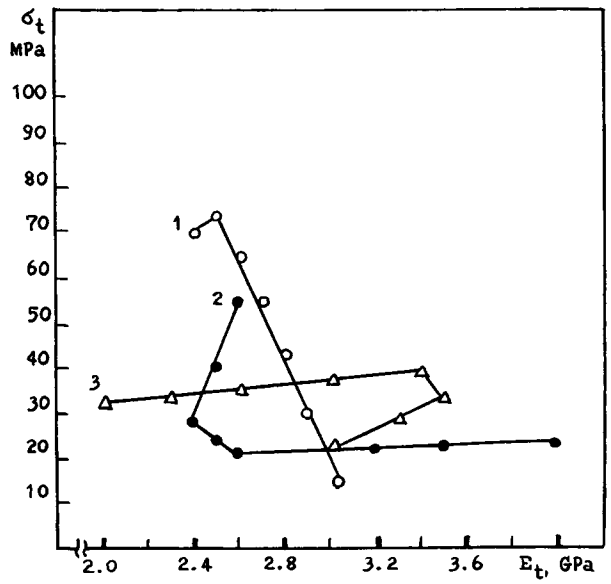


Figure 3 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [Fe(cydien)($HOC_6H_4COO)_3$], (2) [Zn(cydien)($CH_2{=}C(CH_3)COO)_2$], and (3) [Cu(trien)-($CH{=}NHC_6H_4O)_2$] as a function of tensile modulus (E_t).

tical conditions and the testing methods were equal). On the basis of the dependencies between MECP properties and hardener content in epoxy–chelate compositions,[1-7] the functions $\sigma_t = f(E_t)$ (Figs. 1–7) and $\sigma_f = f(E_f)$ (Figs. 8–12) were determined and examined.

Figures 1–12 show that the plots $\sigma = f(E)$ corresponding to the various hardeners intersect. In the points of the intersections (Fig. 1) of the func-

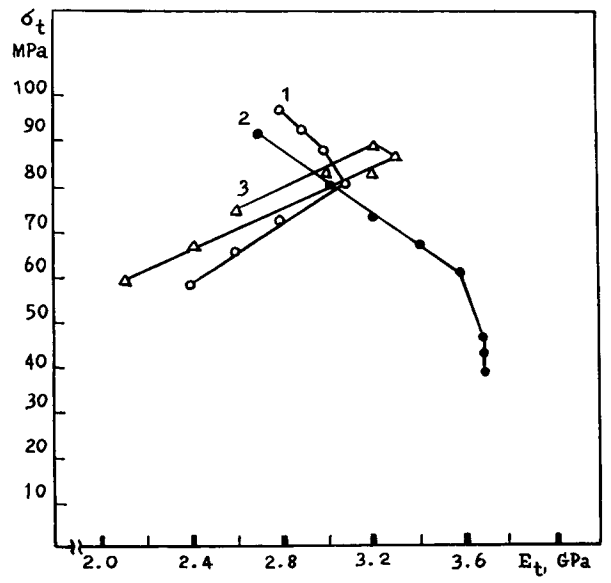


Figure 4 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [$Cu(en)_2(HOC_6H_4COO)_2$], (2) [Zn(trien)($HOC_6H_4COO)_2$], and (3) [Cu(dien)-($HOC_6H_4COO)_2$] as a function of tensile modulus (E_t).

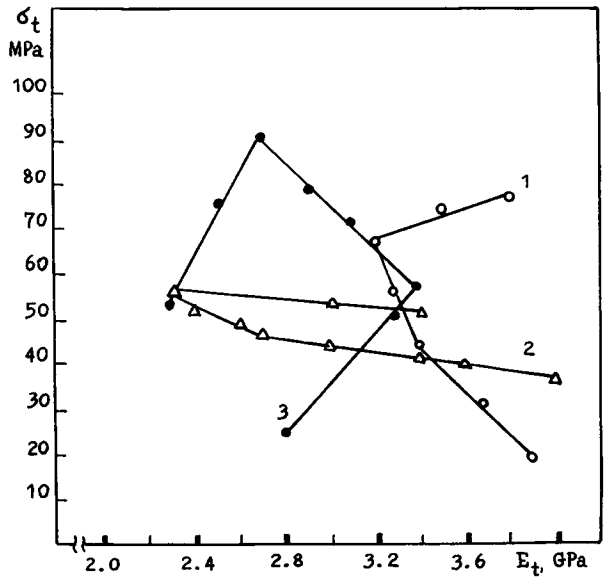


Figure 5 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [Zn(cydien)($CH_3COO)_2$], (2) [Ni(trien)($HOC_6H_4COO)_2$], and (3) [Zn(cydien)-($HOC_6H_4COO)_2$] as a function of tensile modulus (E_t).

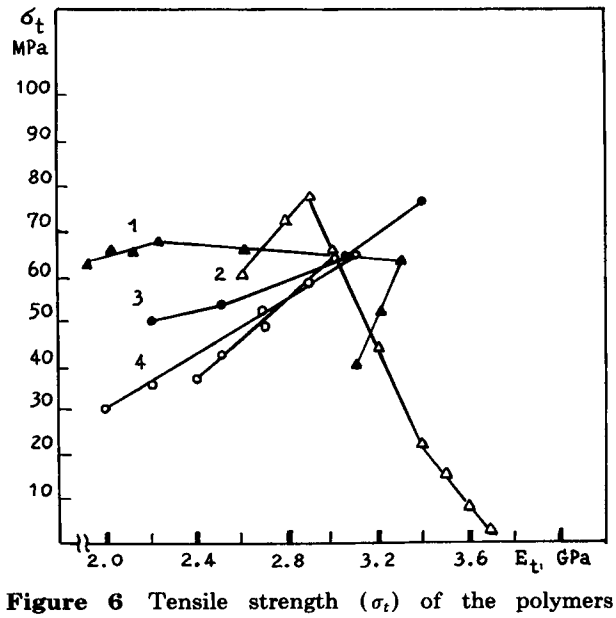


Figure 6 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [$Cd(en)_2(H_2NC_6H_4COO)_2$], (2) [Co(trien)($HOC_6H_4COO)_2$], (3) [Cu(trien)-($CH_3COO)_2$], and (4) [Cu(trien)($HOC_6H_4COO)_2$] as a function of tensile modulus (E_t).

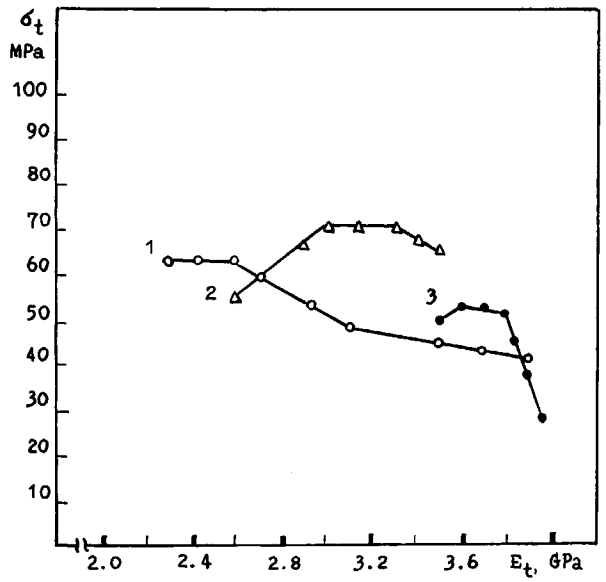


Figure 7 Tensile strength (σ_t) of the polymers based on DGEBA and (1) [Fe(trien)($HOC_6H_4COO)_3$], (2) [Cu(trien)$_2$($HOC_6H_4COO)_2$], and (3) [Co(cydien)-($HOC_6H_4COO)_2$] as a function of tensile modulus (E_t).

tions $\sigma = f(E)$, e.g., $\sigma_t = f(E_t)$, for hardeners A and B, the condition (Scheme 1) is satisfied:

$$\begin{cases} \sigma_{t_A} = \sigma_{t_B} \\ E_{t_A} = E_{t_B} \end{cases} \qquad \text{(Scheme 1)}$$

One point of the intersection of the lines $\sigma = f(E)$can correspond to several hardeners (Fig.3—[Fe(cydien)($HOC_6H_4COO)_3$], [Zn(cydien)($CH_2{=}C(CH_3)COO)_2$], [Cu(trien)($CH{=}NHC_6H_4O)_2$]: σ_t = 22 MPa, E_t = 3.0 GPa; and, e.g., Figs. 4–6 as well), i.e., the condition (Scheme 2) is satisfied for hardeners A, B, C, · · ·:

$$\begin{cases} \sigma_{t_A} = \sigma_{t_B} = \sigma_{t_C} = \cdots \\ E_{t_A} = E_{t_B} = E_{t_C} = \cdots \end{cases} \qquad \text{(Scheme 2)}$$

If the condition (Scheme 3) is fulfilled,

$$\begin{cases} \sigma_{t_A} = \sigma_{t_B} \\ E_{t_A} = E_{t_B} \\ \sigma_{f_A} = \sigma_{f_B} \\ E_{f_A} = E_{f_B} \end{cases} \qquad \text{(Scheme 3)}$$

it is possible to speak about the similarity of the structures of the metal-containing matrices obtained by hardening of DGEBA with complexes A and B. This similarity is greater the more properties of MECP that coincide (Scheme 4):

$$\begin{cases} \sigma_{t_A} = \sigma_{t_B} \\ \sigma_{f_A} = \sigma_{f_B} \\ \sigma_{c_A} = \sigma_{c_B} \\ E_{t_A} = E_{t_B} \\ E_{f_A} = E_{f_B} \\ E_{c_A} = E_{c_B} \\ \epsilon_A = \epsilon_B \\ DT_A = DT_B \\ \Delta M_A = \Delta M_B \end{cases} \qquad \text{(Scheme 4)}$$

The condition (Scheme 4) is unlikely to be fulfilled because of the difference in the chemical compositions of hardeners A and B. However, the investigation of the similarity of the structures of epoxy–chelate metal-containing polymer matrices that was carried out on the basis of the analysis of the conditions (Schemes 1–4) makes it possible to estimate the contributions of the chelate structural fragments to the values of the MECP indices.

Polymer matrices of similar structures were chosen by using Figures 1–12. Table I shows the pairs of chelate hardeners for which the plots $\sigma_t = f(E_t)$

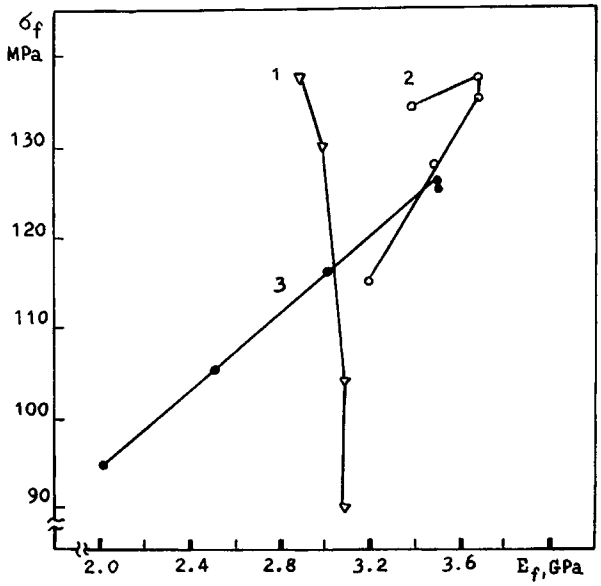


Figure 8 Flexural strength (σ_f) of the polymers based on DGEBA and chelate hardeners as a function of flexural modulus (E_f). The hardeners: (1) [Cd(cydien)-($H_2NC_6H_4COO)_2$]; (2) [Co(dien)($HOC_6H_4COO)_2$]; (3) [Cu(cydien)($HOC_6H_4COO)_2$].

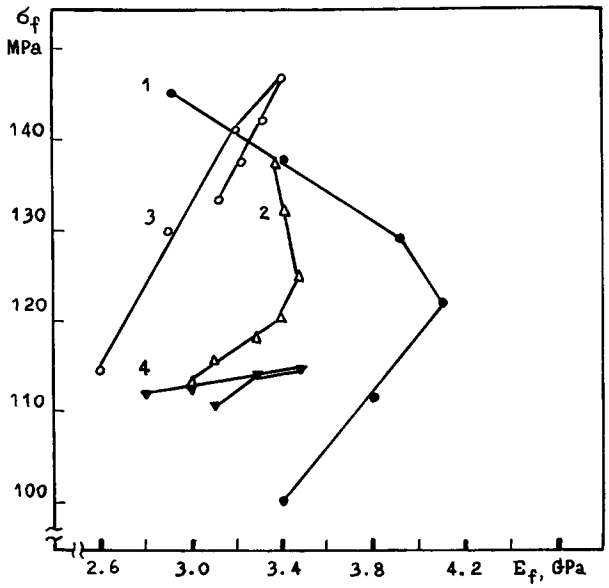


Figure 9 Flexural strength (σ_f) of the polymers based on DGEBA and chelate hardeners as a function of flexural modulus (E_f). The hardeners: (1) [Zn(cydien)-($HOC_6H_4COO)_2$]; (2) [$Cu(en)_2(HOC_6H_4COO)_2$]; (3) [Cd(dien)($H_2NC_6H_4COO)_2$]; (4) [Cu(dien)(HOC_6-$H_4COO)_2$].

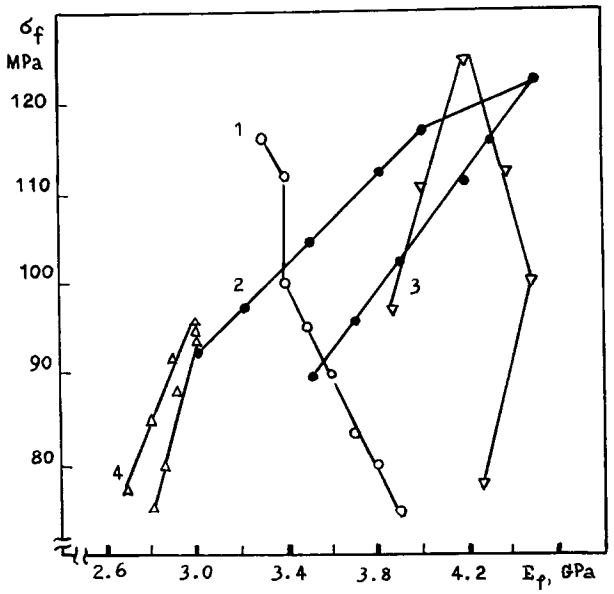


Figure 10 Flexural strength (σ_f) of the polymers based on DGEBA and chelate hardeners as a function of flexural modulus (E_f). The hardeners: (1) [$Cd(dien)_2$-($H_2NC_6H_4COO)_2$]; (2) [$Cd(en)_2(H_2NC_6H_4COO)_2$]; (3) [Zn(cydien)($C_6H_5COO)_2$]; (4) [Cd(trien)($H_2NC_6$-$H_4COO)_2$].

and $\sigma_f = f(E_f)$ intersect at least at one point, i.e., the conditions (Scheme 5.1) and (Scheme 5.2) are fulfilled:

$$\begin{cases} \sigma_{t_A} = \sigma_{t_B} \\ E_{t_A} = E_{t_B} \end{cases} \qquad \text{(Scheme 5.1)}$$

$$\begin{cases} \sigma_{f_A} = \sigma_{f_B} \\ E_{f_A} = E_{f_B} \end{cases} \qquad \text{(Scheme 5.2)}$$

It is necessary to emphasize that the realization of the conditions (Scheme 5.1) and (Scheme 5.2) is not equivalent to that of the condition (Scheme 3), because (Scheme 5.1) and (Scheme 5.2) permit the possibility of different contents of the same hardener in epoxy compositions corresponding to the fulfilment of these conditions, but the content of hardener A (or B) in the epoxy composition corresponding to the condition ($\sigma_{t_A} = \sigma_{t_B}$, $E_{t_A} = E_{t_B}$) must be the same as that corresponding to the condition ($\sigma_{f_A} = \sigma_{f_B}$, $E_{f_A} = E_{f_B}$) (Scheme 3). As seen from Table I, among 378 pairs of the chelates that were investigated, there are 83 pairs of the chelates for which the condition (Scheme 5.1) is fulfilled, 69 pairs for which the condition (Scheme 5.2) is fulfilled, 72 pairs for which both the conditions (Scheme 5.1) and (Scheme 5.2) are satisfied, and 154 pairs of the hardeners having no any points at the intersection of the lines $\sigma = f(E)$.

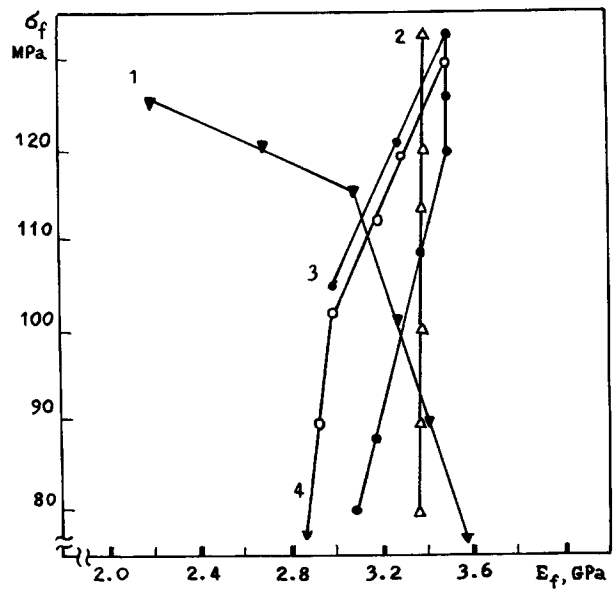


Figure 11 Flexural strength (σ_f) of the polymers based on DGEBA and chelate hardeners as a function of flexural modulus (E_f). The hardeners: (1) [Ni(cydien)-($HOC_6H_4COO)_2$]; (2) [Zn(trien)($HOC_6H_4COO)_2$]; (3) [(trien)($HOC_6H_4COOH)_2$]; (4) [Co(trien)(HOC_6-$H_4COO)_2$].

Presented in Table II are the polymers having similar structures, their compositions that satisfy the condition (Scheme 5.1), the properties of MECP corresponding to these compositions, and comparison of the noncoinciding indices, which allows the contributions of the chelate structural fragments to the properties of the polymers to be estimated. These polymers were chosen on the basis of the data of Table I. There are more than 72 pairs of hardeners in Table I because the lines $\sigma = f(E)$ for some polymers have more than one point of intersection (e.g., Figs. 3–6 and 9–11).

The pairs of hardeners for which the condition (Scheme 5.1) is achieved are classified according to structural characteristics: the chelates with the same metal and ligand in their molecules (3 pairs), the same metal and anion (6 pairs), and ligand and anion (11 pairs and 2 nonmetal containing pairs); the chelates having the same metal (2 pairs), or ligand (9 pairs), or anion (31 pairs) only. The hardeners of the completely different molecules make up a majority (41 pairs), which points to the fact that the coincidence of the properties (Scheme 5.1) results in most cases from the compensating effect of the chelate structural fragments when the polymer matrix is formed.

Considering the example of the complexes possessing the same fragments, the contributions of these structural fragments of hardener molecules to the values of the MECP indices have been determined. For this purpose on the basis of the experimental data,[1-7] the masses of hardeners corresponding to the condition (Scheme 5.1) (m_i), i.e., to the intersection point $\sigma_{t_{AB}} = f(E_{t_{AB}})$, and the properties of the polymers corresponding to the given m_i were determined; the comparison of X_A and X_B that characterizes the contributions of the chelate structural fragments to the values of the indices X_A and X_B was carried out (Table II). Thus, the generalized picture has been obtained (Table III), i.e., depending on the type of the hardener structural fragments, the contribution of these fragments into the values of the polymer indices decreases in the following series:

$$\epsilon = \text{metal} > \text{anion} \gg \text{ligand}$$
$$\sigma_f = \text{metal} \gg \text{ligand} \gg \text{anion}$$
$$\sigma_c = \text{anion} \gg \text{ligand} \gg \text{metal}$$
$$E_f = \text{metal} > \text{ligand} \gg \text{anion}$$
$$DT = \text{ligand} > \text{metal} > \text{anion}$$

and for the thermal stability:

$$\text{metal} > \text{ligand} > \text{anion}$$

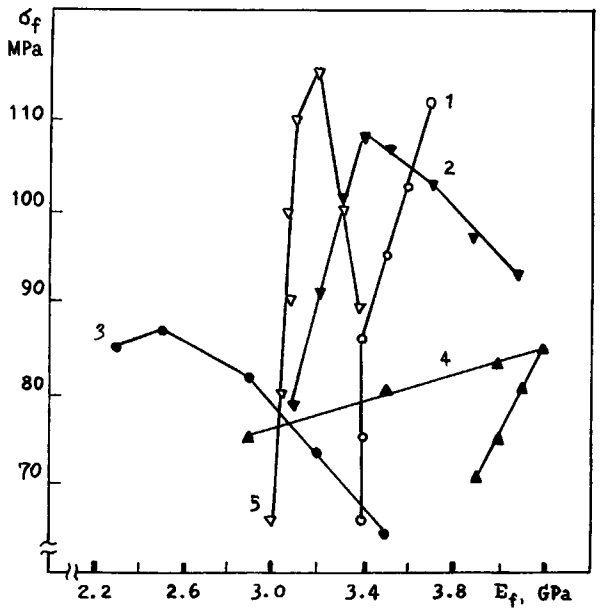


Figure 12 Flexural strength (σ_f) of the polymers based on DGEBA and chelate hardeners as a function of flexural modulus (E_f). The hardeners: (1) [Fe(cydien)-($HOC_6H_4COO)_3$]; (2) [Ni(trien)($HOC_6H_4COO)_2$]; (3) [Zn(cydien)($CH_2{=}C(CH_3)COO)_2$]; (4) [Fe(trien)-($HOC_6H_4COO)_3$]; (5) [Co(cydien)($HOC_6H_4COO)_2$].

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

The metal type contributes most of the all to the MECP properties, and when changed, significantly affects the thermal-oxidative stability and strength (ϵ, σ_f, E_f) of the epoxy matrices excluding σ_c, which is affected mainly by the anion. The metal is of prime importance to the thermal stability of MECP. This fact is confirmed by the dependence of the thermal-oxidative resistance of MECP on the metal cation radius that determines the strength of the chelate rings in the hardener molecules depending also on the ligand structure.[6]

In case of the anions having similar structures, the type thereof affects the thermal stability insignificantly (Table II, no. 1: $HOC_6H_4COO^-$ and $CH{=}NHC_6H_4O^-$), but this influence increases for anions differing in size (Table II, nos. 2 and 3: $HOC_6H_4COO^-$ and CH_3COO^-). This can be explained by the screening effect of the anions produced on the cations: The smaller the anion size, the less it screens the metal cation and the greater the contribution of the cation to the increase of the thermal stability of MECP.

The metal atom introduction into the epoxy ma-

Table I Analysis of the Graphs $\sigma = f(E)$ of Polymers Based on DGEBA and Chelate Hardeners A and B with the Composition $[M(R)_n(X)_2]$: (+) Polymers Correspond to the Condition $\sigma_{t_A} = \sigma_{t_B}$, $E_{t_A} = E_{t_B}$; (x) Polymers Correspond to the Condition $\sigma_{f_A} = \sigma_{f_B}$, $E_{f_A} = E_{f_B}$; (±) Polymers Correspond to Both Conditions x and +

		X	HOC_6H_4COO															$H_2NC_6H_4COO$						C_6H_5COO	$CH_2=C(CH_3)COO$		CH_3COO	$CH=NHC_6H_4O$			HOC_6H_4COO
		R	en	dien		trien							cydien					en	dien		cydien	trien		cydien				trien		dien	trien
		n	2	1		2	1						1					2	1	2	1			1				1			1
No.	Hardener	M	Cu	Cu	Co	Cu	Cu	Zn	Co	Ni	Fe	MnO	Cu	Zn	Co	Ni	Fe	Cd					Cu	Zn					Cu		Co	H
1	$Cu(en)_2(HOC_6H_4COO)_2$		■	±	±		x	±	±		+		x	±		±	+	+		+	x		+					x			x
2	$Cu(dien)(HOC_6H_4COO)_2$		±	■	+		x	±	±				x	+	x	±	+	+		x	x		±					x		x	x
3	$Co(dien)(HOC_6H_4COO)_2$		±	+	■		x	±	x				x	±	x			+					+			x		x			x
4	$Cu(trien)_2(HOC_6H_4COO)_2$					■		+	+	+	+		x	+		±	+	+		+	x		+	+	+	+		+		+	
5	$Cu(trien)(HOC_6H_4COO)_2$		x	x	x		■		±	+	+	+			x	±	+	±			x	x	+	+	±			+	±		±
6	$Zn(trien)(HOC_6H_4COO)_2$		±	±	±	+		■	x	±	±		x	±	±	±	x	x	+	±			+	+		+		±			x
7	$Co(trien)(HOC_6H_4COO)_2$		±	±	x	+	±	x	■	+	±		x	±	x	±	+	+			x	x	+	+	±			±	±	*	x
8	$Ni(trien)(HOC_6H_4COO)_2$					+	+	±	+	■	+	+		±	±	±	±	±		±			+	±	±	±		±	x		x
9	$Fe(trien)(HOC_6H_4COO)_3$		+			+	+	±	±	+	■			+	±	x	±	+		±			+	+	x	±		±			
10	$MnO(trien)(HOC_6H_4COO)_2$						+			+		■		+		+	+								+			+	+		
11	$Cu(cydien)(HOC_6H_4COO)_2$		x	x	x	x		x	x				■			x					x		x					x			x
12	$Zn(cydien)(HOC_6H_4COO)_2$		±	+	±	+		±	±	±	+	+		■		+	±	±	x	±			+	+		±		±	+	+	
13	$Co(cydien)(HOC_6H_4COO)_2$			x	x		x	±	x	±	±				■	±	x	x			x			+	x			x	x	x	x
14	$Ni(cydien)(HOC_6H_4COO)_2$		±	±		±	±	±	±	±	x	+	x	+	±	■	±	±	x	+	x		±	+	+	+		+	x	±	x
15	$Fe(cydien)(HOC_6H_4COO)_3$		+	+		+	+	x	+	±	±	+		±	x	±	■	±	±		x				±	x		±	+		
16	$Cd(en)_2(H_2NC_6H_4COO)_2$		+	+	+	+	±	x	+	±	+			±	x	±	±	■		±	x		+	±		±		±		+	x
17	$Cd(dien)(H_2NC_6H_4COO)_2$							+						x		x			■		±			+		+				+	
18	$Cd(dien)_2(H_2NC_6H_4COO)_2$		+	x		+		±		±	±			±		+	x	±		■				+		±		±	+	±	x
19	$Cd(cydien)(H_2NC_6H_4COO)_2$		x	x		x	x						x		x	x		x	±		■	+	x								x
20	$Cd(trien)(H_2NC_6H_4COO)_2$						x		x						x	x					+	■			x				x		
21	$Cu(trien)(H_2NC_6H_4COO)_2$		+	±	+	+	+	+	+	+	+		x	+		±		+			x		■	+				+			
22	$Zn(cydien)(C_6H_5COO)_2$					+	+	+	+	±	+			+	+	+		±	+	+			+	■		+		+			
23	$Zn(cydien)(CH_2=C(CH_3)COO)_2$					+	±		±	±	x	+			x	+	±						x		■	+		+	±		+
24	$Zn(cydien)(CH_3COO)_2$				x	+		+		±	±			±		+	x	±	+	±				+	+	■		+		±	
25	$Cu(trien)(CH_3COO)_2$		x	x	x	+	+	±	±	±	±	+	x	±	x	±	±	±		±			+	+	+	+		■		x	x
26	$Cu(trien)(CH=NHC_6H_4O)_2$						±		±	x		+		+	x		+			+		x			±				■		±
27	$Co(dien)(CH=N(CH_2)C_6H_4O)_2$			x		+		±	+					+	x	±		+	+	±						±		x		■	x
28	$(trien)(HOC_6H_4COOH)_2$		x	x	x		±	x	x	x			x		x	x		x		x	x				+			x	±	x	■

Table II Contribution of Chelate Hardener Structure Fragments into Properties of MECP

No.	Hardener Identification in the Pair	The Pair of Hardeners for Which $\begin{cases}\sigma_{t_A} = \sigma_{t_B} \\ E_{t_A} = E_{t_B}\end{cases}$	Intersection Points of Graphs $\sigma_t = f(E_t)$ for Hardeners A and B		Mass of Hardener Corresponding to the Intersection Point $\sigma_t = f(E_t)$, (m_i)		Polymer Indices (X) Corresponding to m_i						Comparison of Polymer Indices $\Delta X = \frac{\lvert X_A - X_B \rvert}{X_A} \cdot 100\%$					
			σ_t (MPa)	E_t (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA	ϵ (%)	σ_f (MPa)	E_f (GPa)	σ_c (MPa)	DT (°C)	ΔM after 10 h at 280°C (%)	$\Delta\epsilon$	$\Delta\sigma_f$	ΔE_f	$\Delta\sigma_c$	ΔDT	$\Delta(\Delta M)$
I. The hardeners with identical metal and ligand																		
1	A	$Cu(trien)(HOC_6H_4COO)_2$	32	2.1	8	0.06	1.4	75	2.5	78	108	4.4[a]						
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	32	2.1	10	0.07	1.0	72	2.5	121	70	3.6[a]	28.6	4.0	0	55.1	35.2	18.2
2	A	$Zn(cydien)(HOC_6H_4COO)_2$	67	3.2	27	0.16	2.5	127	4.0	118	120	32.0						
	B	$Zn(cydien)(CH_3COO)_2$	67	3.2	20	0.16	2.0	127	3.6	95	100	7.8	20.0	0	10.0	19.5	16.7	75.6
3	A	$Zn(cydien)(HOC_6H_4COO)_2$	53	3.3	31	0.18	1.9	121	4.0	122	108	46.0						
	B	$Zn(cydien)(CH_3COO)_2$	53	3.3	26	0.21	1.2	115	3.6	95	99	12.0	36.8	5.0	10.0	22.1	8.3	73.9
													$\overline{\Delta\epsilon}$ = 28.5	$\overline{\Delta\sigma_f}$ = 3.0	$\overline{\Delta E_f}$ = 6.7	$\overline{\Delta\sigma_c}$ = 32.2	$\overline{\Delta DT}$ = 20.1	$\overline{\Delta(\Delta M)}$ = 55.9
II. The hardeners with identical metal and anion																		
4	A	$Cu(en)_2(HOC_6H_4COO)_2$	83	3.1	22	0.16	4.6	118	3.4	95	108	4.0						
	B	$Cu(dien)(HOC_6H_4COO)_2$	83	3.1	25	0.19	4.6	114	3.3	105	93	5.8	0	3.4	2.9	10.5	13.9	5.0
5	A	$Zn(trien)(HOC_6H_4COO)_2$	90	2.7	15	0.10	4.6	133	3.4	119	105	7.6						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	90	2.7	19	0.11	5.0	140	3.3	109	113	10.5	8.7	5.3	2.9	8.4	7.6	38.2
6	A	$Ni(trien)(HOC_6H_4COO)_2$	35	4.0	39	0.24	1.1	95	4.0	115	69	16.0						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	35	4.0	33	0.18	1.1	87	3.5	100	77	21.8	0	8.4	12.5	13.0	11.6	36.3
7	A	$Fe(trien)(HOC_6H_4COO)_3$	63	2.6	15	0.08	1.7	68	2.3	120	75	3.3						
	B	$Fe(cydien)(HOC_6H_4COO)_3$	63	2.6	22	0.11	1.9	75	3.4	115	118	12.1	11.8	10.3	47.8	4.2	57.3	266.7
8	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	63	3.3	25	0.17	1.8	93	3.0	114	68	30.0[b]						
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	63	3.3	22	0.13	1.6	98	3.5	130	110	24.6	11.1	5.4	16.7	14.0	61.8	
9	A	$Cd(dien)(H_2NC_6H_4COO)_2$	96	4.0	25	0.17	3.1	142	3.2	138	96	28.0[c]						
	B	$Cd(cydien)(H_2NC_6H_4COO)_2$	96	4.0	26	0.15	4.7	132	3.0	102	72	23.8[b]	51.6	7.0	6.3	26.1	25.0	
													$\overline{\Delta\epsilon}$ = 13.9	$\overline{\Delta\sigma_f}$ = 6.6	$\overline{\Delta E_f}$ = 14.9	$\overline{\Delta\sigma_c}$ = 12.7	$\overline{\Delta DT}$ = 29.5	$\overline{\Delta(\Delta M)}$ = 86.6

III. The hardeners with identical ligand and anion																		
10	A	Cu(trien)($HOC_6H_4COO)_2$	63	3.0	21	0.15	3.5	117	3.2	120	130	19.0[a]						
	B	Co(trien)($HOC_6H_4COO)_2$	63	3.0	17	0.11	3.5	118	3.3	121	102	3.2	0	0.9	3.1	0.8	27.5	
11	A	Cu(trien)($HOC_6H_4COO)_2$	62	3.1	20	0.14	3.4	115	3.1	119	130	18.4[a]						
	B	Co(trien)($HOC_6H_4COO)_2$	62	3.1	18	0.12	3.5	112	3.2	123	102	3.4	2.9	2.6	3.2	3.4	21.5	
12	A	Zn(trien)($HOC_6H_4COO)_2$	38	3.7	35	0.23	1.2	74	3.4	126	130	23.7						
	B	Ni(trien)($HOC_6H_4COO)_2$	38	3.7	36	0.22	1.3	103	3.7	110	73	13.6	8.3	39.2	8.8	12.7	43.8	42.6
13	A	Zn(trien)($HOC_6H_4COO)_2$	44	3.7	33	0.21	1.3	83	3.4	127	129	22.0						
	B	Fe(trien)($HOC_6H_4COO)_3$	44	3.7	35	0.19	1.0	84	4.2	130	70	12.9	23.1	1.2	23.5	2.4	45.7	41.4
14	A	Co(trien)($HOC_6H_4COO)_2$	60	2.6	10	0.07	3.8	130	3.5	117	68	2.5						
	B	Fe(trien)($HOC_6H_4COO)_3$	60	2.6	16	0.09	1.6	70	2.5	121	82	3.4	57.9	46.2	28.6	3.4	20.6	36.0
15	A	Co(trien)($HOC_6H_4COO)_2$	47	3.2	19	0.13	3.6	108	3.2	121	105	3.7						
	B	Fe(trien)($HOC_6H_4COO)_3$	47	3.2	28	0.16	1.1	82	3.8	128	84	7.6	71.4	24.1	18.8	5.8	20.0	105.4
16	A	Zn(cydien)($HOC_6H_4COO)_2$	74	2.5	14	0.08	3.3	145	2.8	102	95	7.8						
	B	Fe(cydien)($HOC_6H_4COO)_3$	74	2.5	15	0.07	2.2	112	3.7	93	100	4.7	33.3	22.8	32.1	8.8	5.3	39.7
17	A	Zn(cydien)($HOC_6H_4COO)_2$	30	2.9	39	0.23	1.3	103	3.5	129	98	54.0						
	B	Fe(cydien)($HOC_6H_4COO)_3$	30	2.9	35	0.18	0.9	42	3.5	126	95	18.6	30.8	59.2	0	2.3	3.1	65.6
18	A	Co(cydien)($HOC_6H_4COO)_2$	53	3.7	20	0.12	3.0	89	3.4	119	55	3.2						
	B	Ni(cydien)($HOC_6H_4COO)_2$	53	3.7	26	0.14	1.4	112	3.1	111	87	13.7	53.3	25.8	8.8	6.7	58.2	328.1
19	A	Co(cydien)($HOC_6H_4COO)_2$	51	3.8	25	0.15	3.5	110	3.1	116	100	5.1						
	B	Ni(cydien)($HOC_6H_4COO)_2$	51	3.8	27	0.15	1.3	110	3.2	110	85	14.8	62.9	0	3.2	5.2	15.0	190.2
20	A	Ni(cydien)($HOC_6H_4COO)_2$	68	2.6	16	0.09	2.8	124	2.2	120	91	4.8						
	B	Fe(cydien)($HOC_6H_4COO)_3$	68	2.6	18	0.09	2.1	95	3.5	104	115	8.1	25.0	23.4	59.1	13.3	26.4	68.8
													$\overline{\Delta\epsilon}$ = 33.5	$\overline{\Delta\sigma_f}$ = 22.3	$\overline{\Delta E_f}$ = 17.2	$\overline{\Delta\sigma_c}$ = 5.9	$\overline{\Delta DT}$ = 26.1	$\overline{\Delta(\Delta M)}$ = 102.0
21	A	Cu(trien)($HOC_6H_4COO)_2$	40	2.4	11	0.08	1.8	86	2.7	95	117	10.0						
	B	(trien)($HOC_6H_4COOH)_2$	40	2.4	25	0.20	1.6	90	3.3	98	100	27.0	11.1	4.7	22.2	3.2	14.5	
22	A	Cu(trien)($HOC_6H_4COO)_2$	38	2.5	35	0.24	1.6	73	2.7	104	102	21.0[a]						
	B	(trien)($HOC_6H_4COOH)_2$	38	2.5	27	0.22	1.6	77	2.9	97	100	28.0	0	5.5	7.4	6.7	2.0	
													$\overline{\Delta\epsilon}$ = 5.6	$\overline{\Delta\sigma_f}$ = 5.1	$\overline{\Delta E_f}$ = 14.8	$\overline{\Delta\sigma_c}$ = 5.0	$\overline{\Delta DT}$ = 8.3	
IV. The hardeners with identical metal																		
23	A	Cu(dien)($HOC_6H_4COO)_2$	77	2.8	22	0.17	4.0	113	3.0	100	88	4.6						
	B	Cu(trien)($H_2NC_6H_4COO)_2$	77	2.8	16	0.11	2.2	112	2.9	123	128	6.6	45.0	0.9	3.3	23.0	45.5	43.5
24	A	Cu(dien)($HOC_6H_4COO)_2$	80	2.9	24	0.18	4.4	114	3.3	103	92	5.1						
	B	Cu(trien)($H_2NC_6H_4COO)_2$	80	2.9	17	0.12	2.3	115	3.0	124	129	7.2	47.7	0.9	9.1	20.4	40.2	41.2
													$\overline{\Delta\epsilon}$ = 46.4	$\overline{\Delta\sigma_f}$ = 0.9	$\overline{\Delta E_f}$ = 6.2	$\overline{\Delta\sigma_c}$ = 21.7	$\overline{\Delta DT}$ = 42.9	$\overline{\Delta(\Delta M)}$ = 42.4

Table II *(Continued)*

No.	Hardener Identification in the Pair	The Pair of Hardeners for Which $\begin{cases}\sigma_{t_A} = \sigma_{t_B} \\ E_{t_A} = E_{t_B}\end{cases}$	Intersection Points of Graphs $\sigma_t = f(E_t)$ for Hardeners A and B		Mass of Hardener Corresponding to the Intersection Point $\sigma_t = f(E_t)$, (m_i)		Polymer Indices (X) Corresponding to m_i						Comparison of Polymer Indices $\Delta X = \frac{\lvert X_A - X_B \rvert}{X_A} \cdot 100\%$					
			σ_t (MPa)	E_t (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA	ϵ (%)	σ_f (MPa)	E_f (GPa)	σ_c (MPa)	DT (°C)	ΔM after 10 h at 280°C (%)	$\Delta\epsilon$	$\Delta\sigma_f$	ΔE_f	$\Delta\sigma_c$	ΔDT	$\Delta(\Delta M)$
V. The hardeners with identical ligand																		
25	A	$Zn(trien)(HOC_6H_4COO)_2$	70	3.2	20	0.13	3.0	128	3.4	123	110	11.0						
	B	$Cu(trien)(CH_3COO)_2$	70	3.2	16	0.16	3.5	123	3.3	97	98	9.5[a]	16.7	3.9	2.9	21.1	10.9	
26	A	$Co(trien)(HOC_6H_4COO)_2$	65	3.1	16	0.11	3.8	124	3.4	121	100	3.1						
	B	$Cu(trien)(CH_3COO)_2$	65	3.1	17	0.17	3.0	120	3.3	100	97	10.5[a]	21.1	3.2	2.9	17.4	3.0	
27	A	$Co(trien)(HOC_6H_4COO)_2$	38	3.3	21	0.14	3.4	95	3.1	121	107	4.3						
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	38	3.3	24	0.18	1.3	87	3.2	105	156	8.8[a]	61.8	8.4	3.2	13.2	45.8	
28	A	$Co(trien)(HOC_6H_4COO)_2$	29	3.3	23	0.16	3.2	85	3.0	121	108	5.0						
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	29	3.3	32	0.24	1.2	92	3.3	89	123	17.6[a]	62.5	8.2	10.5	26.4	13.9	
29	A	$Ni(trien)(HOC_6H_4COO)_2$	54	2.7	15	0.09	1.9	78	3.1	101	95	1.7						
	B	$Cu(trien)(CH_3COO)_2$	54	2.7	19	0.19	2.3	97	3.4	108	94	12.0[a]	21.1	24.4	9.7	6.9	1.1	
30	A	$Ni(trien)(HOC_6H_4COO)_2$	51	2.4	25	0.15	2.1	102	3.3	103	85	6.3						
	B	$Cu(trien)(CH_3COO)_2$	51	2.4	20	0.20	2.0	91	3.4	112	92	13.5[a]	4.8	10.8	3.0	8.7	8.2	
31	A	$Fe(trien)(HOC_6H_4COO)_3$	58	2.8	18	0.10	1.4	72	2.8	123	87	3.8						
	B	$Cu(trien)(CH_3COO)_2$	58	2.8	18	0.18	2.8	104	3.3	105	96	11.0[a]	100.0	44.4	17.9	14.6	10.3	
32	A	$Fe(cydien)(HOC_6H_4COO)_3$	22	3.0	38	0.19	0.7	38	3.6	123	88	19.0						
	B	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	22	3.0	33	0.25	0.6	60	3.7	116	93	12.5	14.3	57.9	2.8	5.7	5.7	34.2
													$\overline{\Delta\epsilon}$ = 37.8	$\overline{\Delta\sigma_f}$ = 20.2	$\overline{\Delta E_f}$ = 6.6	$\overline{\Delta\sigma_c}$ = 14.3	$\overline{\Delta DT}$ = 12.4	
33	A	$Cu(trien)(CH{=}NHC_6H_4O)_2$	35	2.6	15	0.11	1.2	78	2.8	118	87	4.6[a]						
	B	$(trien)(HOC_6H_4COOH)_2$	35	2.6	36	0.29	1.1	12	1.7	92	98	37.0	8.3	84.6	39.3	22.0	12.6	
VI. The hardeners with identical anion																		
34	A	$Cu(en)_2(HOC_6H_4COO)_2$	90	2.9	27	0.20	4.9	122	3.5	107	92	6.6						
	B	$Co(dien)(HOC_6H_4COO)_2$	90	2.9	27	0.20	4.4	136	3.7	107	113	9.0	10.2	11.5	5.7	0	22.8	36.4
35	A	$Cu(en)_2(HOC_6H_4COO)_2$	88	3.0	25	0.19	4.8	120	3.4	103	97	5.0						
	B	$Co(dien)(HOC_6H_4COO)_2$	88	3.0	17	0.13	4.2	121	3.4	95	75	6.1	12.5	0.8	0	7.8	22.3	22.0
36	A	$Cu(en)_2(HOC_6H_4COO)_2$	80	3.1	20	0.15	4.4	116	3.3	88	110	3.8						
	B	$Zn(trien)(HOC_6H_4COO)_2$	80	3.1	17	0.11	3.9	132	3.4	121	108	9.1	11.4	13.8	3.0	37.5	1.8	139.5
37	A	$Cu(en)_2(HOC_6H_4COO)_2$	73	2.8	15	0.11	3.7	113	3.0	70	100	4.4						
	B	$Co(trien)(HOC_6H_4COO)_2$	73	2.8	12	0.08	3.8	120	3.6	118	85	2.7	2.7	6.2	20.0	68.6	15.0	38.6
38	A	$Cu(en)_2(HOC_6H_4COO)_2$	78	2.9	18	0.13	4.2	115	3.2	80	108	3.8						
	B	$Co(trien)(HOC_6H_4COO)_2$	78	2.9	15	0.10	3.8	130	3.5	120	98	3.0	9.5	13.0	9.4	50.0	9.3	21.1
39	A	$Cu(en)_2(HOC_6H_4COO)_2$	78	2.9	18	0.13	4.2	115	3.2	80	108	3.8						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	78	2.9	24	0.14	3.3	133	3.9	115	125	18.0	21.4	15.7	21.9	43.8	15.7	373.7

40	A	$Cu(en)_2(HOC_6H_4COO)_2$	67	2.8	13	0.10	3.5	113	2.9	59	87	5.0						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	67	2.8	17	0.10	2.4	124	2.4	119	91	5.6	31.4	9.7	17.2	101.7	4.6	12.0
41	A	$Cu(dien)(HOC_6H_4COO)_2$	80	3.1	24	0.18	4.4	114	3.3	103	92	5.1						
	B	$Zn(trien)(HOC_6H_4COO)_2$	80	3.1	17	0.11	3.9	132	3.4	121	108	9.1	11.4	15.8	3.0	17.5	17.4	78.4
42	A	$Cu(dien)(HOC_6H_4COO)_2$	78	2.9	23	0.18	4.2	113	3.1	102	90	4.8						
	B	$Co(trien)(HOC_6H_4COO)_2$	78	2.9	15	0.10	3.8	130	3.5	120	98	3.0	9.5	15.0	12.9	17.6	8.9	4.2
43	A	$Cu(dien)(HOC_6H_4COO)_2$	68	2.5	18	0.14	2.8	110	2.6	93	75	5.0						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	68	2.5	15	0.08	2.7	125	2.1	120	90	4.4	3.6	13.6	19.2	29.0	20.0	12.0
44	A	$Co(dien)(HOC_6H_4COO)_2$	88	2.8	29	0.22	4.3	138	3.7	109	110	10.0						
	B	$Zn(trien)(HOC_6H_4COO)_2$	88	2.8	15.5	0.10	4.6	132	3.4	120	105	8.0	7.0	4.3	8.1	10.1	4.5	20.0
45	A	$Co(dien)(HOC_6H_4COO)_2$	85	2.9	16	0.12	4.0	119	3.3	93	65	6.0						
	B	$Zn(trien)(HOC_6H_4COO)_2$	85	2.9	16	0.11	4.2	132	3.4	121	106	8.3	5.0	10.9	3.0	30.1	63.1	38.3
46	A	$Co(dien)(HOC_6H_4COO)_2$	80	2.6	14	0.11	3.8	112	3.0	90	53	5.8						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	80	2.6	15	0.09	3.9	145	2.9	104	97	8.4	2.6	29.5	3.3	15.6	83.0	44.8
47	A	$Co(dien)(HOC_6H_4COO)_2$	86	2.7	30	0.22	4.2	139	3.7	110	110	11.0						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	86	2.7	21	0.12	4.8	137	3.6	112	119	12.4	14.3	1.4	2.7	1.8	8.2	5.5
48	A	$Co(dien)(HOC_6H_4COO)_2$	88	2.8	29	0.22	4.3	138	3.7	109	110	10.0						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	88	2.7	20	0.12	5.0	138	3.4	110	116	11.0	16.3	0	8.1	0.9	5.5	10.0
49	A	$Co(dien)(HOC_6H_4COO)_2$	84	2.8	15	0.11	3.9	115	3.2	92	55	5.9						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	84	2.8	22	0.13	4.3	135	3.7	113	121	14.0	10.3	17.4	15.6	22.8	120.0	137.3
50	A	$Cu(trien)_2(HOC_6H_4COO)_2$	65	2.8	14	0.07	3.0	110	2.6	103	120	2.4						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	65	2.8	18.5	0.10	2.2	123	2.5	118	91	6.6	26.7	11.8	3.8	14.6	24.2	175.0
51	A	$Cu(trien)(HOC_6H_4COO)_2$	63	3.0	21	0.15	3.5	117	3.2	120	130	19.0[a]						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	63	3.0	20	0.11	1.9	121	2.7	118	90	7.7	45.7	3.4	15.6	1.7	30.8	
52	A	$Cu(trien)(HOC_6H_4COO)_2$	62	3.1	20	0.14	3.4	115	3.1	119	130	18.4[a]						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	62	3.1	21.5	0.12	1.8	119	2.8	116	90	9.2	47.1	3.5	9.7	2.5	30.8	
53	A	$Zn(trien)(HOC_6H_4COO)_2$	53	3.7	28	0.18	1.7	104	3.4	128	125	17.4						
	B	$Co(cydien)(HOC_6H_4COO)_2$	53	3.7	20	0.12	3.0	89	3.4	119	55	3.2	76.5	14.4	0	7.0	56.0	81.6
54	A	$Zn(trien)(HOC_6H_4COO)_2$	54	3.7	27	0.18	1.8	107	3.4	127	123	16.6						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	54	3.7	25	0.14	1.5	115	3.1	113	90	12.6	16.7	7.5	8.8	11.0	26.8	24.1
55	A	$Co(trien)(HOC_6H_4COO)_2$	65	2.7	11	0.07	3.8	130	3.5	118	78	2.6						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	65	2.7	18	0.10	2.3	124	2.5	119	90	6.3	39.5	4.6	28.6	0.8	15.4	142.3
56	A	$Co(trien)(HOC_6H_4COO)_2$	63	3.0	17	0.11	3.5	118	3.3	121	102	3.2						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	63	3.0	21	0.12	1.8	120	2.8	117	90	8.9	48.6	1.7	15.2	3.3	11.8	178.1
57	A	$Co(trien)(HOC_6H_4COO)_2$	23	3.4	25	0.17	2.9	74	2.9	121	108	6.0						
	B	$Ni(cydien)(HOC_6H_4COO)_2$	23	3.4	37	0.20	1.0	70	3.5	93	71	2.7	65.5	5.4	20.7	23.1	34.3	55.0
58	A	$Ni(trien)(HOC_6H_4COO)_2$	55	2.3	20	0.12	2.0	91	3.2	102	90	3.6						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	55	2.3	10	0.06	2.1	143	2.5	96	80	6.7	5.0	57.1	21.9	5.9	11.1	86.1
59	A	$Ni(trien)(HOC_6H_4COO)_2$	51	3.3	11	0.07	1.8	68	3.0	102	93	1.9						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	51	3.3	32	0.19	1.8	120	4.0	123	106	4.8	0	76.5	33.3	20.6	14.0	152.6
60	A	$Ni(trien)(HOC_6H_4COO)_2$	43	3.1	33	0.20	1.6	106	3.6	107	77	11.4						
	B	$Zn(cydien)(HOC_6H_4COO)_2$	43	3.1	35	0.20	1.6	111	3.8	126	100	50.0	0	4.7	5.6	17.8	30.0	338.6
61	A	$Ni(trien)(HOC_6H_4COO)_2$	38	3.8	37	0.23	1.2	98	3.8	112	72	14.4						
	B	$Co(cydien)(HOC_6H_4COO)_2$	38	3.8	35	0.21	3.2	60	3.0	92	90	6.5	166.7	38.8	21.1	17.9	25.0	54.9
62	A	$Ni(trien)(HOC_6H_4COO)_2$	54	2.7	15	0.09	1.9	78	3.1	101	95	1.7						
	B	$Fe(cydien)(HOC_6H_4COO)_3$	54	2.7	26	0.13	1.7	62	3.4	121	113	15.0	10.5	20.5	9.7	19.8	18.9	782.4
63	A	$Ni(trien)(HOC_6H_4COO)_2$	45	2.8	31	0.19	1.8	108	3.5	106	80	10.0						
	B	$Fe(cydien)(HOC_6H_4COO)_3$	45	2.8	30	0.15	1.4	50	3.4	125	105	16.9	22.2	53.7	2.9	17.9	31.3	69.0
64	A	$Fe(trien)(HOC_6H_4COO)_3$	41	3.9	40	0.22	1.0	70	3.8	130	62	18.0						
	B	$Co(cydien)(HOC_6H_4COO)_2$	41	3.9	33	0.20	3.3	69	3.0	98	91	6.0	230.0	1.4	21.1	24.6	46.8	66.7
													$\overline{\Delta\epsilon}$ = 31.6	$\overline{\Delta\sigma_f}$ = 15.6	$\overline{\Delta E_f}$ = 12.0	$\overline{\Delta\sigma_c}$ = 20.8	$\overline{\Delta DT}$ = 26.8	$\overline{\Delta(\Delta M)}$ = 110.3

Table II *(Continued)*

No.	Hardener Identification in the Pair	The Pair of Hardeners for Which $\begin{cases}\sigma_{t_A} = \sigma_{t_B}\\ E_{t_A} = E_{t_B}\end{cases}$	Intersection Points of Graphs $\sigma_t = f(E_t)$ for Hardeners A and B		Mass of Hardener Corresponding to the Intersection Point $\sigma_t = f(E_t)$, (m_i)		Polymer Indices (X) Corresponding to m_i						Comparison of Polymer Indices $\Delta X = \frac{\lvert X_A - X_B \rvert}{X_A} \cdot 100\%$					
			σ_t (MPa)	E_t (GPa)	g per 100 g of DGEBA	Mol per 1 Mol of DGEBA	ϵ (%)	σ_f (MPa)	E_f (GPa)	σ_c (MPa)	DT (°C)	ΔM after 10 h at 280°C (%)	$\Delta\epsilon$	$\Delta\sigma_f$	ΔE_f	$\Delta\sigma_c$	ΔDT	$\Delta(\Delta M)$
VII. The different hardeners																		
65	A	$Cu(trien)(HOC_6H_4COO)_2$	65	3.1	22	0.15	3.4	117	3.2	120	130	19.0[a]						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	65	3.1	24	0.16	1.8	105	3.8	117	68	28.8[b]	47.1	10.3	18.8	2.5	47.7	
66	A	$Cu(trien)(HOC_6H_4COO)_2$	47	2.6	13	0.09	2.2	93	2.8	104	122	14.0[a]						
	B	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	47	2.6	12	0.09	1.9	88	2.4	108	60	3.1	13.6	5.4	14.3	3.8	50.8	
67	A	$Cu(trien)(HOC_6H_4COO)_2$	40	2.5	34	0.24	1.7	78	2.8	106	105	20.4[a]						
	B	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	40	2.5	15	0.12	1.7	88	2.6	107	83	4.0	0	12.8	7.1	0.9	21.0	
68	A	$Zn(trien)(HOC_6H_4COO)_2$	75	3.2	19	0.12	3.3	130	3.4	122	110	10.6						
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	75	3.2	28	0.16	1.8	110	3.4	126	96	30.0	45.5	15.4	0	3.3	12.7	183.0
69	A	$Zn(trien)(HOC_6H_4COO)_2$	65	3.5	23	0.15	2.4	120	3.4	125	117	13.5						
	B	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	65	3.5	20	0.16	2.1	119	3.6	94	105	7.6	12.5	0.8	5.9	24.8	10.3	43.7
70	A	$Co(trien)(HOC_6H_4COO)_2$	23	3.4	25	0.17	2.9	74	2.9	121	108	6.0						
	B	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	23	3.4	35	0.27	0.5	57	3.8	118	88	13.8	82.8	23.0	31.0	2.5	18.5	130.0
71	A	$Ni(trien)(HOC_6H_4COO)_2$	52	3.2	12	0.07	1.8	70	3.1	102	94	1.8						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	52	3.2	28	0.19	1.7	64	1.8	100	70	31.7[b]	5.6	8.6	41.9	2.0	25.5	
72	A	$Ni(trien)(HOC_6H_4COO)_2$	43	3.1	33	0.20	1.6	106	3.6	107	77	11.4						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	43	3.1	30	0.20	1.1	55	1.6	87	70	32.5[b]	31.3	48.1	55.6	18.7	9.1	
73	A	$Ni(trien)(HOC_6H_4COO)_2$	50	3.4	10	0.06	1.7	65	3.0	103	92	2.3						
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	50	3.4	18	0.10	1.3	87	3.6	130	112	21.0	23.5	33.8	20.0	26.2	21.7	813.0
74	A	$Ni(trien)(HOC_6H_4COO)_2$	42	3.4	34	0.21	1.5	105	3.7	108	76	12.0						
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	42	3.4	16	0.09	1.1	82	3.7	130	110	19.0	26.7	21.9	0	20.4	44.7	58.3
75	A	$Ni(trien)(HOC_6H_4COO)_2$	52	3.2	12	0.07	1.8	70	3.1	102	94	1.8						
	B	$Zn(cydien)(C_6H_5COO)_2$	52	3.2	33	0.22	1.2	88	4.4	114	95	18.8	33.3	25.7	41.9	11.8	1.1	944.4
76	A	$Ni(trien)(HOC_6H_4COO)_2$	38	3.8	37	0.23	1.2	98	3.8	112	72	14.4						
	B	$Zn(cydien)(C_6H_5COO)_2$	38	3.8	38	0.25	0.9	65	4.3	113	92	21.1	25.0	33.7	13.2	0.9	27.8	46.5
77	A	$Ni(trien)(HOC_6H_4COO)_2$	54	2.7	15	0.09	1.9	78	3.1	101	95	1.7						
	B	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	54	2.7	10	0.07	2.1	86	2.3	110	50	2.3	10.5	10.3	25.8	8.9	47.4	35.3
78	A	$Ni(trien)(HOC_6H_4COO)_2$	49	2.6	29	0.18	1.9	108	3.4	105	82	8.5						
	B	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	49	2.6	11	0.09	2.0	87	2.4	109	57	2.7	5.3	19.4	29.4	3.8	30.5	68.2
79	A	$Ni(trien)(HOC_6H_4COO)_2$	51	3.3	11	0.07	1.8	68	3.0	102	93	1.9						
	B	$Zn(cydien)(CH_3COO)_2$	51	3.3	27	0.21	1.1	112	3.6	95	98	13.0	38.9	64.7	20.0	6.9	5.4	584.2
80	A	$Ni(trien)(HOC_6H_4COO)_2$	40	3.5	35	0.21	1.4	103	3.7	109	74	12.9						
	B	$Zn(cydien)(CH_3COO)_2$	40	3.5	32	0.26	0.6	91	3.6	96	90	17.3	57.1	11.7	2.7	11.9	21.6	34.1
81	A	$Fe(trien)(HOC_6H_4COO)_3$	45	3.4	30	0.17	1.1	84	4.0	128	78	9.0						
	B	$Cd(dien)_2(H_2NC_6H_4COO)_2$	45	3.4	17	0.10	1.2	84	3.7	130	111	20.1	9.1	0	7.5	1.6	42.3	123.3
82	A	$Fe(trien)(HOC_6H_4COO)_3$	46	3.4	29	0.16	1.1	83	3.9	128	82	8.2						
	B	$Zn(cydien)(CH_3COO)_2$	46	3.4	29	0.23	1.0	105	3.6	95	95	14.5	9.1	26.5	7.7	25.8	1.2	76.8
83	A	$Zn(cydien)(HOC_6H_4COO)_2$	67	2.4	13	0.07	3.0	145	2.7	101	91	7.5						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	67	2.4	19	0.13	1.5	120	4.3	124	66	25.7[b]	50.0	17.2	59.3	22.8	27.5	
84	A	$Zn(cydien)(HOC_6H_4COO)_2$	64	3.2	28	0.16	2.3	125	4.1	120	116	35.0						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	64	3.2	24.5	0.17	1.8	103	3.7	115	68	29.1[b]	21.7	17.6	9.8	4.2	41.4	

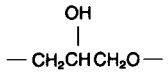
85	A	$Zn(cydien)(HOC_6H_4COO)_2$	62	3.3	29	0.17	2.1	123	4.1	121	113	39.0						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	62	3.3	26	0.17	1.8	85	2.8	110	69	30.5[b]	14.3	30.9	31.7	9.1	38.9	
86	A	$Zn(cydien)(HOC_6H_4COO)_2$	40	3.1	36	0.21	1.5	109	3.8	127	100	51.0						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	40	3.1	31	0.21	1.0	50	1.5	83	69	32.8[b]	33.3	54.1	60.5	34.6	31.0	
87	A	$Zn(cydien)(HOC_6H_4COO)_2$	70	3.2	26	0.15	2.8	129	4.0	117	125	30.0						
	B	$Cu(trien)(CH_3COO)_2$	70	3.2	16	0.16	3.5	123	3.3	97	98	9.5[a]	25.0	4.7	17.5	17.1	21.6	
88	A	$Ni(cydien)(HOC_6H_4COO)_2$	65	2.8	18.5	0.10	2.2	123	2.5	118	91	6.6						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	65	2.8	20	0.14	2.0	123	4.5	125	67	25.9[b]	9.1	0	80.0	5.9	26.4	
89	A	$Ni(cydien)(HOC_6H_4COO)_2$	59	3.3	23	0.13	1.7	117	2.9	115	90	10.7						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	59	3.3	27	0.18	1.7	72	2.3	105	69	31.3[b]	0	38.5	20.7	8.7	23.3	
90	A	$Ni(cydien)(HOC_6H_4COO)_2$	65	2.7	18	0.10	2.3	124	2.5	119	90	6.3						
	B	$Cu(trien)(H_2NC_6H_4COO)_2$	65	2.7	12	0.09	1.9	102	2.8	112	119	5.0[a]	17.4	17.7	12.0	5.9	32.2	
91	A	$Ni(cydien)(HOC_6H_4COO)_2$	60	3.2	22	0.12	1.8	118	2.9	116	90	9.8						
	B	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	60	3.2	34	0.27	2.0	110	3.4	86	67	15.4	11.1	6.8	17.2	25.9	25.6	57.1
92	A	$Fe(cydien)(HOC_6H_4COO)_3$	65	2.6	20	0.10	2.0	87	3.4	109	120	10.5						
	B	$Cd(en)_2(H_2NC_6H_4COO)_2$	65	2.6	23	0.16	1.7	115	4.0	120	68	28.0[b]	15.0	32.2	17.6	10.1	43.3	
93	A	$Fe(cydien)(HOC_6H_4COO)_3$	54	2.7	26	0.13	1.7	62	3.4	121	113	15.0						
	B	$Cu(trien)(CH_3COO)_2$	54	2.7	19	0.19	2.3	97	3.4	108	94	12.0[a]	35.3	56.5	0	10.7	16.8	
94	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	65	2.8	20	0.14	2.0	123	4.5	125	67	25.9[b]						
	B	$Zn(cydien)(C_6H_5COO)_2$	65	2.8	28	0.18	1.8	110	4.5	118	93	16.3	10.0	10.6	0	5.6	38.8	
95	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	50	3.2	29	0.19	1.5	60	1.7	94	70	32.0[b]						
	B	$Zn(cydien)(C_6H_5COO)_2$	50	3.2	34	0.22	1.2	84	4.4	114	95	19.3	20.0	40.0	158.8	21.3	35.7	
96	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	63	3.3	25	0.17	1.8	93	3.0	114	68	30.0[b]						
	B	$Zn(cydien)(CH_3COO)_2$	63	3.3	22	0.17	1.8	123	3.6	95	101	9.0	0	32.3	20.0	16.7	48.5	
97	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	59	3.3	27	0.18	1.7	72	2.3	105	69	31.3[b]						
	B	$Zn(cydien)(CH_3COO)_2$	59	3.3	24	0.19	1.5	119	3.6	95	101	10.4	11.8	65.3	56.5	9.5	46.4	
98	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	65	3.1	24	0.16	1.8	105	3.8	117	68	28.8[b]						
	B	$Cu(trien)(CH_3COO)_2$	65	3.1	17	0.17	3.0	120	3.3	100	97	10.5[a]	66.7	14.3	13.2	14.5	42.6	
99	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	69	3.3	24	0.14	1.7	102	3.4	130	107	26.0						
	B	$Zn(cydien)(CH_3COO)_2$	69	3.3	19	0.15	2.1	128	3.6	95	98	6.9	23.5	25.5	5.9	26.9	8.4	73.5
100	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	45	3.4	17	0.10	1.2	84	3.7	130	111	20.1						
	B	$Zn(cydien)(CH_3COO)_2$	45	3.4	30	0.24	0.9	100	3.6	95	92	15.5	25.0	19.0	2.7	26.9	17.1	22.9
101	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	70	3.2	25	0.14	1.8	105	3.4	128	104	27.3						
	B	$Cu(trien)(CH_3COO)_2$	70	3.2	16	0.16	3.5	123	3.3	97	98	9.5[a]	94.4	17.1	2.9	24.2	5.8	
102	A	$Cd(dien)_2(H_2NC_6H_4COO)_2$	63	3.3	22	0.13	1.6	98	3.5	130	110	24.6						
	B	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	63	3.3	32	0.26	2.1	111	3.4	88	75	14.0	31.3	13.3	2.9	32.3	31.8	43.1
103	A	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	34	2.4	17	0.13	1.4	85	2.7	106	81	5.0						
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	34	2.4	14	0.11	1.2	76	2.8	119	85	4.2[a]	14.3	10.6	3.7	12.3	4.9	
104	A	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	22	3.0	34	0.26	0.5	58	3.8	117	91	13.0						
	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	22	3.0	33	0.25	0.6	92	3.3	86	120	19.0[a]	20.0	58.6	13.2	36.0	31.9	
105	A	$Zn(cydien)(CH_3COO)_2$	61	3.2	23	0.18	1.7	121	3.6	95	101	9.7						
	B	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	61	3.2	33	0.26	2.1	110	3.3	87	72	14.8	23.5	9.1	8.3	8.4	28.7	52.6
													$\overline{\Delta\epsilon}$ = 25.6	$\overline{\Delta\sigma_f}$ = 23.5	$\overline{\Delta E_f}$ = 23.3	$\overline{\Delta\sigma_c}$ = 13.8	$\overline{\Delta DT}$ = 27.0	$\overline{\Delta(\Delta M)}$ = 188.3
															$\overline{\Delta X}$			
													28.4	19.0	16.8	15.6	25.5	123.3

[a] 280°C, 50 h.
[b] 260°C, 25 h.
[c] 260°C, 40 h.

Table III Effect of Chelate Structural Fragments on Polymer Properties

Affecting Fragments	Identical Fragments	Division in Table II	$\overline{\Delta\epsilon}$	$\overline{\Delta\sigma_f}$	$\overline{\Delta E_f}$	$\overline{\Delta\sigma_c}$ (%)	$\overline{\Delta DT}$	$\overline{\Delta(\Delta M)}$
Anion	Metal and ligand	I, NN 1–3	28.5	3.0	6.7	32.2	20.0	55.9
Ligand	Metal and anion	II, NN 4–9	13.9	6.6	14.9	12.7	29.5	86.6
Metal	Ligand and anion	III, NN 10–20	33.5	22.3	17.2	5.9	26.1	102.0

trices facilitates the increase in stiffness of the polymer chains owing to the formation of the covalent bond "cation-oxygen of the epoxy group" (Fig. 13) or because of the polymer chain cyclization due to the coordination of OH groups (Fig. 14) that results in the decrease of the segmental mobility:



in the change of the flexibility of the polymer chains and, consequently, in the change of σ_f and ϵ.[9,10] Following the metal in its significance and having much stronger effect on ϵ than that of the ligand, the anion screens the metal cation, thus preventing the cyclization of the polymer chains. In case of σ_f, the significance of the anion lessens, as this index is affected by the density of the cross-linkage that depends considerably on the number of the amino groups in the ligand.

A large positive charge of the metal cation increases in the epoxy–chelate polymer matrix van der Waals interaction that determines the values of the elasticity modulus and deflection temperature[11] that accounts for the contribution of the type of metal to E_f and DT. The increase in the density of the chemical cross-linkages and the formation of the nitrogen-bearing heterocyclic structures at the expense of the ligand that increase DT[11] provides the commensurability of the contributions of the ligand and metal cation into the deflection temperature. The low functionality of the majority of the examined anions determines their smallest effect on most of the indices except for σ_c, which is caused by a considerable change in the sizes of the used anions: The small volume of CH_3COO^- but the large volumes of $HOC_6H_4COO^-$ and $CH{=}NHC_6H_4O^-$ (Table II, nos. 1–3) affect the change of σ_c (32.2%), which for the same metal and anions makes up 12.7% (Table III) (it results from the influence of

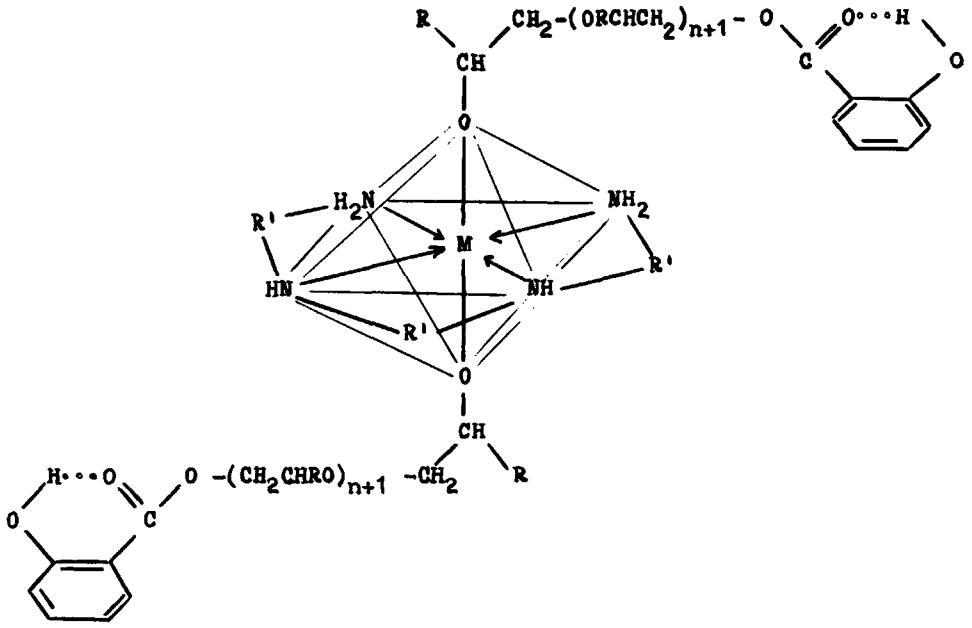


Figure 13 Structure of epoxy–chelate polymer matrix fragment created when a small concentration of complex hardener is used: M, metal atom; R', $-(CH_2)_2-$.

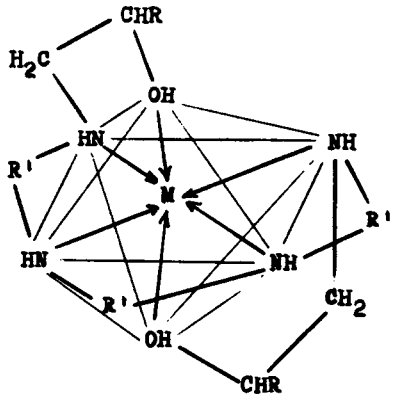


Figure 14 Structure of epoxy–chelate polymer matrix fragment created when the heightened concentrations of complex hardener are used at the cure temperatures lower than the temperature of the dissociation of the complex cation $[M(L)]^{p+}$: M, metal atom; L, ligand (e.g., L = trien); R', $-(CH_2)_2-$; p, metal valency.

the ligand volumes), and the effect is even less (5.9%) when the same ligands and anions are used (Table III) (the volume of the cations does not practically affects σ_c).

Of great interest are the data determining the change of the properties of the polymer matrices having similar structures and satisfying the condition (Scheme 5.1) after the metal cation introduction (Table II, nos. 21 and 22). The presence of copper increases thermal stability (the inhibiting effect of copper[6]) and DT (the increase of van der Waals interaction in the matrix), though it reduces the modulus of elasticity. The decrease of E_f results, first of all, from the fact that the metal-free compositions (Table II, nos. 21 and 22) contain salicylic acid (rather than the salicylate anion in the chelate), which is known to increase the flexural modulus,[12] and, second, from the influence of cross-linking on the local segmental mobility: The metal cation introduction increases the cross-linking of the network and β-segmental mobility, whereas the modulus of elasticity augments for the lesser cross-linked networks.[13]

Considering the example of complex hardeners having one similar fragment only (Table II, Divisions IV–VI), the comparison of X_A and X_B was carried out; this comparison characterizes the mutual effect of the structural fragments on the values of the MECP indices. The generalized picture has been obtained (Table IV). The alteration of the thermal stability of MECP is mostly responsive to the change of the pair "metal–ligand," which is quite natural since this property has been shown to be determined by the stability of the chelate rings, which depends exactly on the structure of the ligands and their affinity for the metal cations. The effect of the pair "ligand–anion" on thermal stability is also determined by the strength of the chelate rings (varying of ligand) and, on the other hand, by the extent of the cation screening with the anion (the size of the anion).[1-3,6,7]

As stated above, DT is determined by two factors: van der Waals interaction in the polymer matrix (the type of the metal) and the number of cross-links (the type of the anion), which accounts for the maximal change of DT for the pairs "ligand–anion" (the change of the number of the cross-links at the expense of the ligand and anion) and "metal–ligand" (the change of the number of the cross-links at the expense of the ligand; van der Waals interaction at the expense of the metal cation) with the small weight of the pair "metal–anion."

The modulus of elasticity is determined by van der Waals interaction, and its change is minimal for the pair of structural fragments "ligand–anion" and maximal for the pair "metal–ligand," changing simultaneously the number of the cross-links and the energy of the intermolecular interaction.

The above maximal dependence of σ_c on the anion and ligand remains the same for the mutual effect of the two structural fragments that is maximal for the pair "ligand–anion" (the two fragments of the chelate molecule having the largest sizes). Proceeding from the data of Table III, at first sight, one should expect the increased effect on the MECP properties of the pair "metal–anion" in comparison

Table IV Mutual Effect of Chelate Structural Fragments on Polymer Properties

Affecting Fragments	Identical Fragments	Division in Table II	$\overline{\Delta\epsilon}$	$\overline{\Delta\sigma_f}$	$\overline{\Delta E_f}$	$\overline{\Delta\sigma_c}$ (%)	$\overline{\Delta DT}$	$\overline{\Delta(\Delta M)}$
Ligand–Anion	Metal	IV, NN 23, 24	46.4	0.9	6.2	21.7	42.9	42.4
Metal–Anion	Ligand	V, NN 25–32	37.8	20.2	6.6	14.3	12.4	34.2
Metal–Ligand	Anion	VI, NN 34–64	31.6	15.6	12.0	20.8	26.8	110.3

with the "metal–ligand." Meanwhile, there is no contradiction between the obtained dependencies (Tables III and IV): When the interaction proceeds by the scheme "metal–ligand," the cyclic structure formation accompanied by the volume enlargement is observed; at the same time, the interaction by the scheme "metal–anion," on the contrary, is characterized by the cleavage of the coordinate bonds and the shrinkage of the volume that affects the contribution of the chelate structural fragments to σ_c of MECP (Table IV).

The fact that the metal type is of prime importance to σ_f as compared with the ligand and anion (Table III) is confirmed by the practical lack of the effect of the pair "ligand–anion" on σ_f when the type of metal remains the same (Table IV), the effect of the other pairs of the structural fragments being commensurable.

The most involved is the description of the effect of the chelate structural fragments on ϵ that has been shown to depend on the alteration of the stiffness of the polymer chains because of the introduction of the metal cation and cyclization with OH groups of the epoxy oligomer (Fig. 14). When considering the mutual effect of the structural fragments on the other properties of MECP, it has already been mentioned that the influence of the separate fragments (Table III) and their aggregate in the pair (Table IV) is not additive, which results from the lack of the additivity of the properties of the complexes possessing the heterogeneous coordination sphere (the coordination sphere of the chelates concerned includes both the ligands and anions) and of the properties of the corresponding uniform ligand complexes.[14] Since the cyclization of the polymer chains at the expense of the OH groups coordinating (Fig. 14) with the simultaneous alteration of the several chelate structural fragments involves the formation of the different heterogeneous coordination spheres in the polymer matrix, the mutual influence of the pairs of the structural fragments on ϵ requires much more statistical data than those available in the present work.

Comparison of the properties of DGEBA hardened with the complexes of the completely different structures (Table II, Division VII) shows the chemical compositions to be of prime importance to the thermal-oxidative stability of MECP, i.e., for their chemical properties. The change of the strength and DT is, on average, on the same level (with σ_c excluded) and makes up 23–27%, which points to the compensating effect. The latter is due to the mutual influence of the structural fragments of the triple system "metal–ligand–anion" and the lack of the additivity of their contributions to the formation of the polymer matrix structure.

The general analysis of Table II allows one to draw the conclusion that the effect of the change in the chelate hardener structure on the alteration of the MECP properties is maximal for thermal-oxidative stability (ΔM), is minimal for compressive strength, and decreases in the following series of indices: $\Delta M > \epsilon > DT > \sigma_f > E_f > \sigma_c$.

Comparison of the data obtained by examining the contributions of the chelate structural fragments to the values of the MECP indices with the dependence of the maximal strength of these polymers on the structure of the complex hardeners[4,6] confirms that the metal type has the cardinal effect on the strength, deflection temperature, and thermal stability of MECP.

CONCLUSION

In fact, the above analysis of the MECP structure is the new method of theoretical investigation of the effect of the structural fragments of the polymer matrix on the polymer properties (method of TIESF), the basic theses of which are the following:

1. This method is used for the polymers having the signs of similar structures. For example, in this work, these signs are the same epoxy oligomer (DGEBA), the same type of hardeners (the chelates of metal organic salts with aliphatic polyamines), and equal conditions of the MECP synthesis. This thesis is illustrated by the relative scheme (Fig. 15). Suppose that the polymer matrix has the structure shown in Figure 15(a). The structures in Figure 15(b) and (c) are similar to this structure and differ from it by the type of the structural fragments (A, B, or C). The transition from A to B or to C follows the change in some properties of the polymer matrices but the reservation of one property at least.
2. The possibility of varying polymer properties in a sufficiently broad interval by changing the quantitative compound of the polymer when reserving its qualitative compound. This has been achieved in this work by the change of the masses of the chelate hardeners in the epoxy compositions followed by the alteration of the MECP properties. As seen from Figure 15(d), the substitution of structural fragment A by D deforms the polymer matrix and obviously changes its properties,

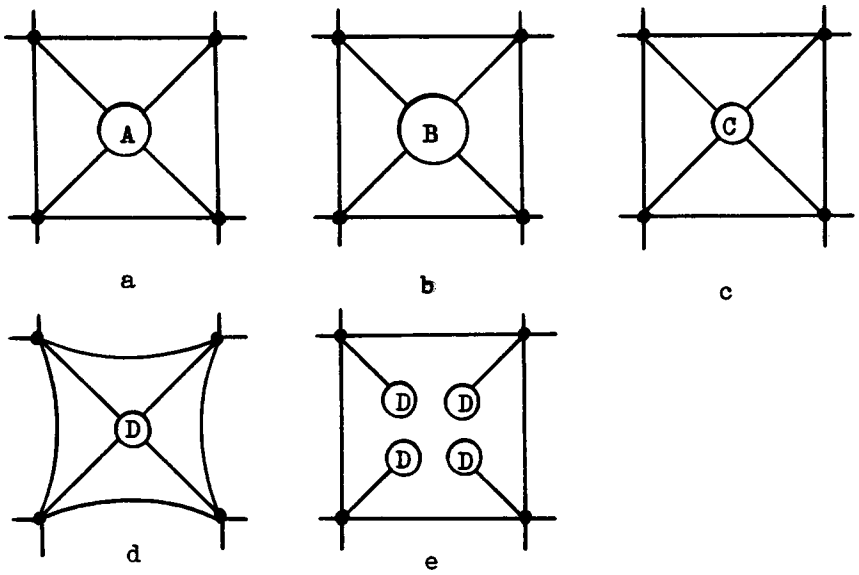


Figure 15 Scheme illustrating the principle of the similarity of polymer matrixes. a, b, c, and e are similar matrices; A, B, C, and D are different structural fragments of the matrices.

but the increase of fragment D amount restores the similarity between the matrices [Fig. 15(e)].

3. The existence of correlations between different polymer properties (the dependence $\sigma = f(E)$ has been investigated in this paper).
4. The coincidence of some correlating properties (e.g., $\sigma_{t_A} = \sigma_{t_B}$ and $E_{t_A} = E_{t_B}$) that is the consequence of the polymer matrix similarity. As a result of this coincidence, the quantitative differences of other noncoinciding polymer indices can be determined. These differences characterize the contributions of the structural fragments under investigation into the polymer indices.

The application of the method of TIESF has both theoretical and practical value. The data of Tables III and IV give the clear well-defined characteristic of the effect of the chelate structural fragments on the MECP properties. Obviously, to obtain the true conclusion about such influence, it is necessary to carry out the analogous analysis based on the fulfillment not only of the condition (Scheme 5.1) and the condition (Scheme 5.2), but of other conditions, e.g.,

$$\begin{cases} \sigma_{c_A} = \sigma_{c_B} \\ E_{c_A} = E_{c_B} \end{cases} \quad \begin{cases} DT_A = DT_B \\ T_{g_A} = T_{g_B} \end{cases} \quad \text{etc.}$$

As seen from this work, such analysis is too cumbersome to be stated here. The obtained data allow the purposeful synthesis of the polymer matrices containing such structural fragments that improve the operating polymer properties. The main conclusion following from the present analysis is that special attention must be devoted to the metal cation choice, especially for the reason that the previous investigations showed that the maximal thermal resistance of MECP will be achieved when the metal cations of the radii $R = 0.70$–0.78 Å will be used.[6]

The method of TIESF can be used not only to analyze MECP but also polymers of other types, especially in cases when the polymers contain related structural fragments, e.g., side groups of the same nature (F, Cl, Br, I, or CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $CH_3(CH_2)_3$, etc.).

SYMBOLS

σ_c	compressive strength
σ_f	flexural strength
σ_t	tensile strength
E_f	flexural modulus
E_t	tensile modulus
E_c	compressive modulus
ϵ	elongation at break
DT	deflection temperature
T_g	glass transition temperature

ΔM polymer mass loss after thermal treatment in air

X index of polymer (σ, E, σ, DT, ΔM)

ΔX a decrease of the polymer index [$\Delta\sigma$, ΔE, $\Delta\epsilon$, DT, $\Delta(\Delta M)$]

$\overline{\Delta X}$ mean value of the decrease of the polymer index for the same series of the hardeners

m_i hardener mass in the epoxy composition corresponding to the intersection point of the graphs $\sigma_t = f(E_t)$ and $\sigma_f = f(E_f)$

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