Metalliferous epoxy chelate polymers: 2. Influence of structural fragments on properties

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The influence of the structural fragments (metal cation, ligand and anion) of metal-containing chelate hardeners on the properties of cured diglycidyl ether of bisphenol A (DGEBA), viz. strength, deformation temperature and thermal oxidative stability, has been examined. It has been established that the metal cation has the most effect on the properties of metalliferous epoxy chelate polymers (MECPs), that of the anion being the least. A structural change in a hardener molecule has been found to influence greatly the polymer heat resistance and, to a lesser extent, the compressive strength.

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

INTRODUCTION

It has been found that the application of chelates of transition metals (Cu, Co, Cd, Zn, Ni, Fe, Mn) with aliphatic amines (ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien) and cyanoethylated diethylenetriamine (cydien)) as hardeners of the diglycidyl ether of bisphenol A (DGEBA) made it possible to produce metalliferous epoxy chelate polymers (MECPs) possessing increased strength, deformation temperature (*DT*) and heat resistance [1–4]. The structure of the chelate hardeners is regarded as the combination of three fragments, namely, metal cation, nitrogen ligand and organic acid anion. The number of combinations of these structural fragments is rather large, so a purposeful study of the metal complexes is needed in order to achieve further improvement in the service properties of epoxy polymers.

There are at least two approaches to the investigation of the influence of chelate structural fragments on the properties of MECP:

(i) comparison of the indices of polymers possessing similar compositions, and

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

The purpose of the present paper is to realize the first method, and that of the following paper to realize the second method.

RESULTS AND DISCUSSION

The general formula of chelate hardeners can be represented as:

$$[M(R)_n(X)_p] \quad (1)$$

where M is a metal cation, R is a ligand, X is an anion, n is the ligand number and p is the metal valency.

The synthesis and properties of these chelates, the cure cycle used to prepare MECPs, and the methods of the polymer tests are described in ref 4. As a result of epoxy oligomer hardening the chelate structural fragments become structural fragments of the epoxy chelate polymer matrix obtained. Formula (1) shows that investigation of the influence of chelate structural fragments on the properties of polymer matrices can be carried out by a comparative analysis of the indices of the polymers obtained by epoxy oligomer hardening with complexes having one changeable structural fragment, e.g. changeable metal in $[M(trien)(HOC_6H_4COO)_2]$, changeable ligand in $[Cu(R)_n(HOC_6H_4COO)_2]$ and changeable anion in $[Zn(cydien)(X)_2]$.

Presented in *Figures 1–8* are the indices of DGEBA hardened with nickel chelates $[Ni(cydien)(HOC_6H_4COO)_2]$ (hardener A) and $[Ni(trien)(HOC_6H_4COO)_2]$ (hardener B) as a function of the hardener concentration C_h in the epoxy compounds, the influence of alteration of the type of ligand (trien or cydien) being studied. For this purpose, by using the formula:

$$\Delta X_{AB} = \frac{|X_A - X_B|}{X_A} \times 100\% \quad (2)$$

where X is the value of a polymer index, the change (increase or decrease) of the index ΔX_{AB} was calculated. The above change occurs on substitution of the ligand in the molecule of hardener A by that of hardener B, the concentrations of the ligands being equal. The function:

$$\Delta X_{AB} = f(C_h)$$

defines the influence of the change in structural fragment (in this case, the transition from the ligand cydien to the ligand trien) on the polymer index alteration (decrease or increase) depending on the hardener concentration.

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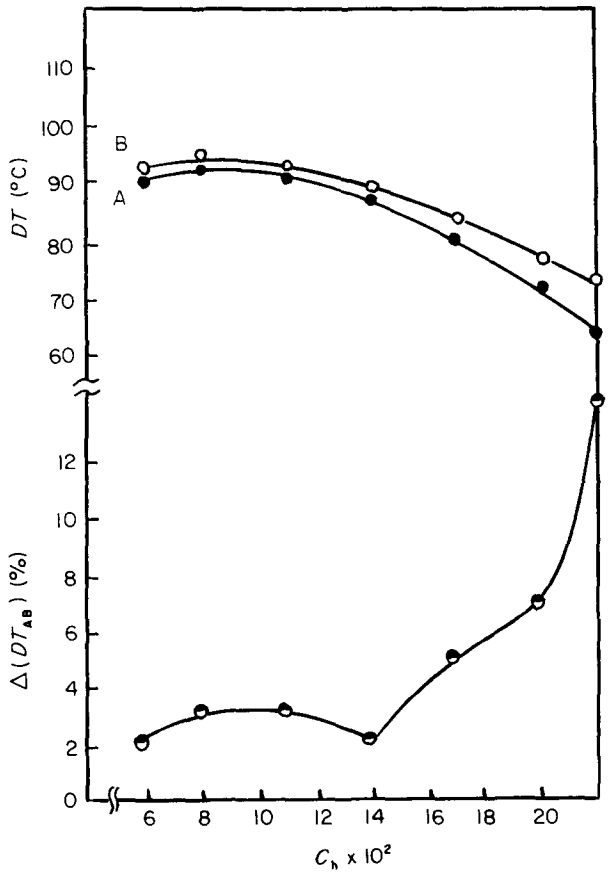

Figure 1 Deformation temperature DT and change of deformation temperature $\Delta(DT_{AB})$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)$(HOC_6H_4COO)_2$]; B, [Ni(trien)$(HOC_6H_4COO)_2$]

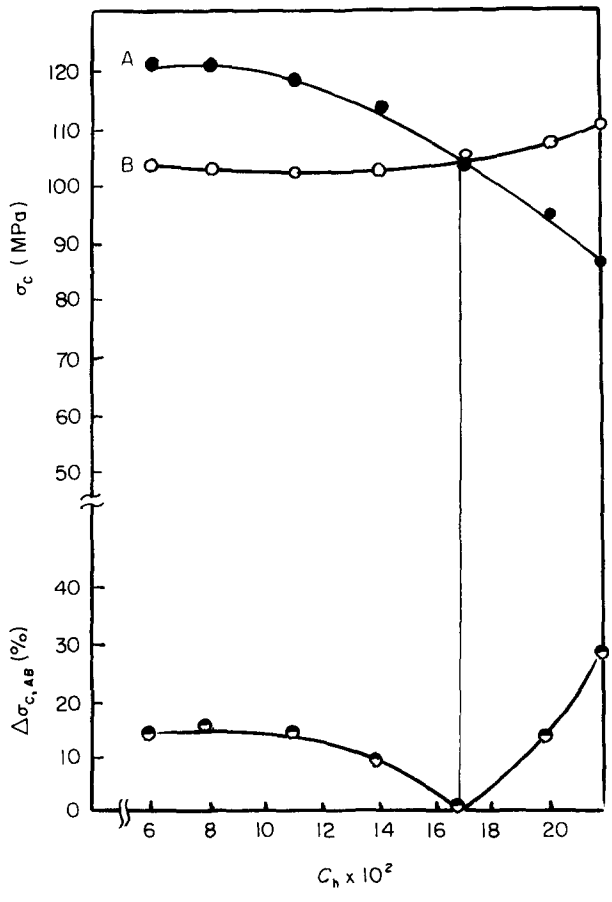

Figure 2 Compressive strength σ_c and change of compressive strength $\Delta\sigma_{c,AB}$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)$(HOC_6H_4COO)_2$]; B, [Ni(trien)$(HOC_6H_4COO)_2$]

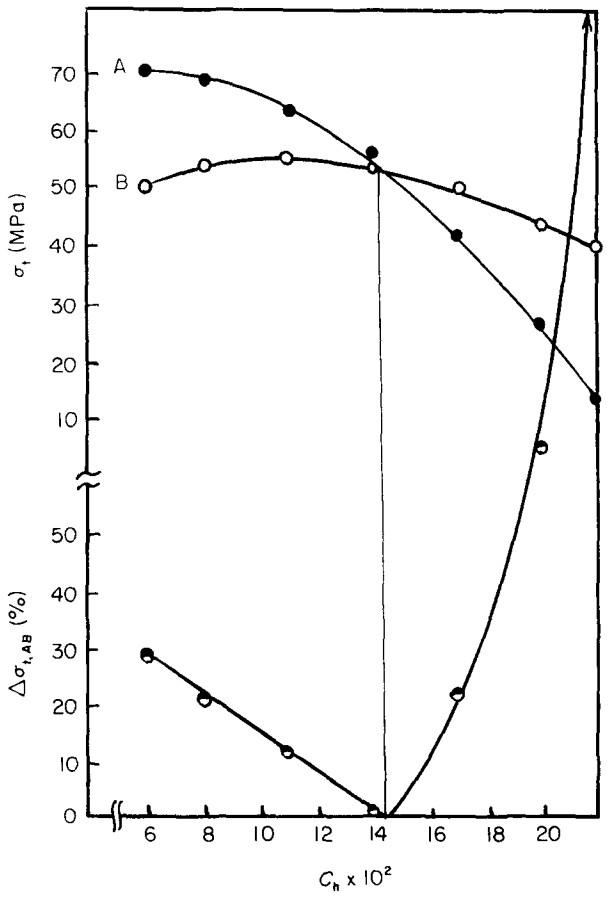

Figure 3 Tensile strength σ_t and change of tensile strength $\Delta\sigma_{t,AB}$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)$(HOC_6H_4COO)_2$]; B, [Ni(trien)$(HOC_6H_4COO)_2$]

As is seen from *Figures 1–8* there exist values of C_h such that the ligand has no influence on the values of some indices ($\Delta X_{AB}=0$). For example: at $C_h=0.170$ mol/mol of DGEBA, $\sigma_{c,A}=\sigma_{c,B}$ and $\Delta\sigma_{c,AB}=0$ (*Figure 2*); at $C_h=0.144$ mol/mol, $\sigma_{t,A}=\sigma_{t,B}$ and $\Delta\sigma_{t,AB}=0$ (*Figure 3*); at $C_h=0.162$ mol/mol, $\sigma_{f,A}=\sigma_{f,B}$ and $\Delta\sigma_{f,AB}=0$ (*Figure 4*); and so on.

In the general form, at $\Delta X_{AB}=0$ the conditions:

$$C_{h,A}=C_{h,B} \qquad X_A=X_B \tag{3}$$

are satisfied. The concentrations of the hardeners corresponding to $\Delta X_{AB}=0$ are different for different X (*Table 1*).

The influences of the anion (*Figure 9*) and the metal (*Figure 10*) have been studied similarly to that of the ligand. The results obtained allow us to make a deduction about the abrupt changeable character of the effect of chelate structural fragments on the properties of MECPs and about the dependence of this effect on hardener concentration.

Thus, we can highlight the two approaches to the investigation of the influence of chelate structural

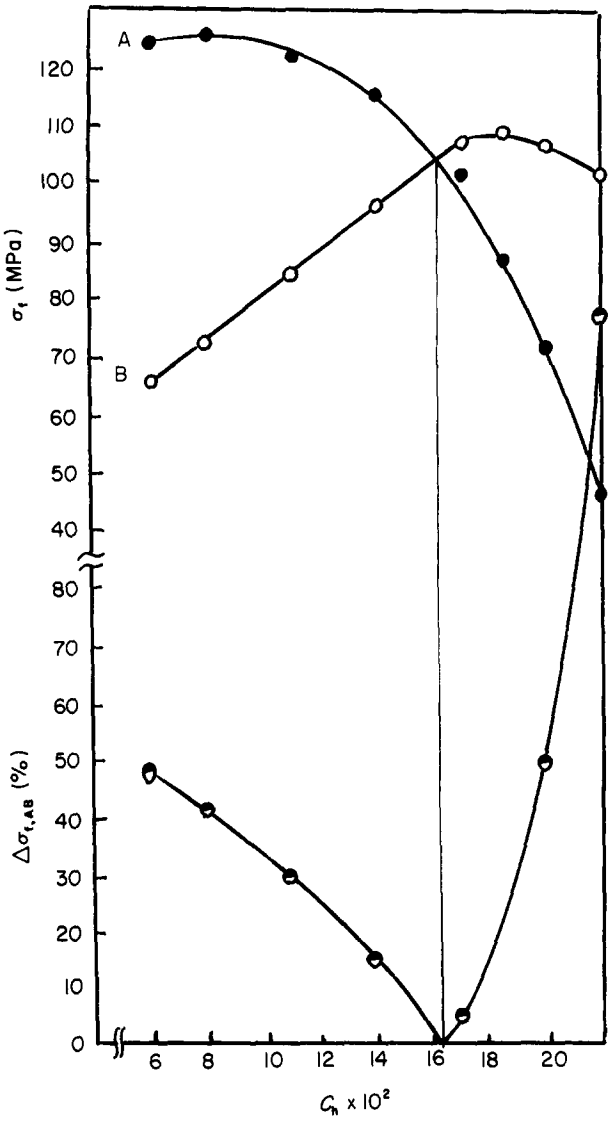

Figure 4 Flexural strength σ_f and change of flexural strength $\Delta\sigma_{f,AB}$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)$(HOC_6H_4COO)_2$]; B, [Ni(trien)$(HOC_6H_4COO)_2$]

Table 1 Hardener concentrations for $\Delta X_{AB}=0$

X	C_h (mol/mol of DGEBA)
ΔM	0.062
E_t	0.100 and 0.208
ε	0.106
σ_t	0.144
σ_f	0.162
σ_c	0.170

fragments on the properties of epoxy chelate polymers:

(i) comparison of the indices of polymers possessing similar compositions ($C_{h,A}=C_{h,B}$); and

(ii) comparison of the indices of polymers having some equal properties ($X_A=X_B$).

Let us realize the first approach here.

Polymers with maximal mechanical strength are often regarded as the most important ones from the viewpoint of practical applications. Hardening of 1 mol of DGEBA with 0.170 mol of chelate has been established to yield epoxy chelate polymers possessing the *optimal* set of indices of strength, the decrease of which with respect to the *maximal* values thereof is on average $\pm 12\%$[5]. The properties of these polymers are listed in *Table 2*. By comparing the pairs of hardeners having one changeable structural fragment, the change (decrease or increase) of the indices ΔX_{AB} of the polymers based on DGEBA and chelates A or B corresponding to the substitution of one structural fragment by another was calculated according to formula (2). For every chelate structural fragment, the mean value of $\overline{\Delta X}$ was calculated, which shows the contribution of the given fragment to the given polymer property. Proceeding from the above, we obtain the general picture of the influence of epoxy chelate matrix structural fragments on the properties of the polymers provided $C_{h,A}=C_{h,B}=0.170$ mol/mol of DGEBA (*Table 3*).

This allows us to draw the following conclusions.

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

depending on ligand

$$E_t > \varepsilon > \Delta M > \sigma_t > DT > \sigma_f \sim \sigma_c \gg E_f$$

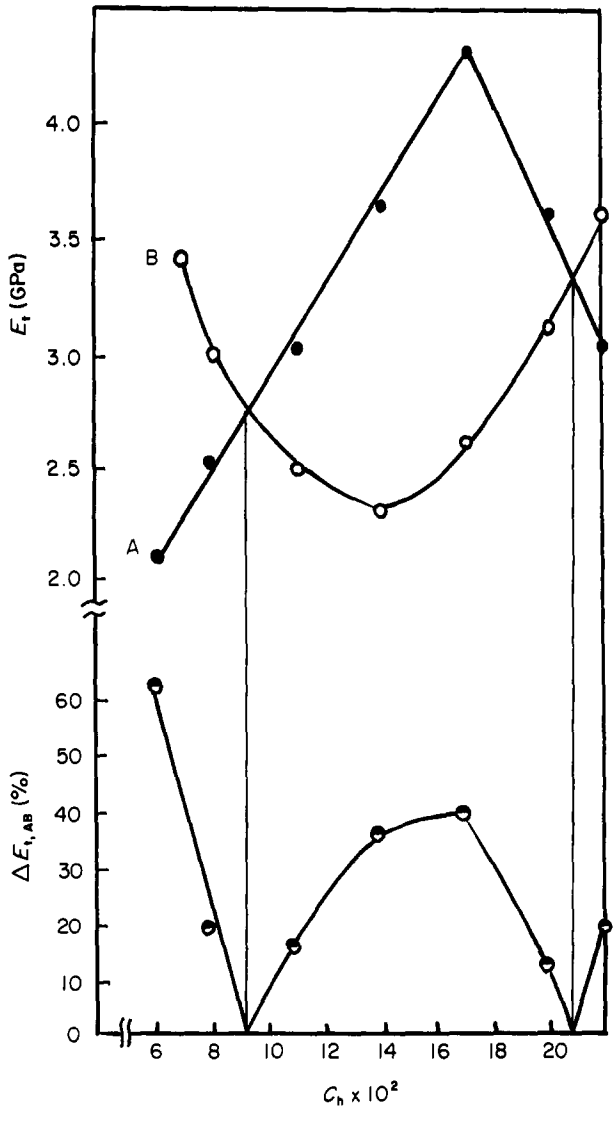

Figure 5 Tensile modulus E_t and change of tensile modulus $\Delta E_{t,AB}$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)$(HOC_6H_4COO)_2$]; B, [Ni(trien)$(HOC_6H_4COO)_2$]

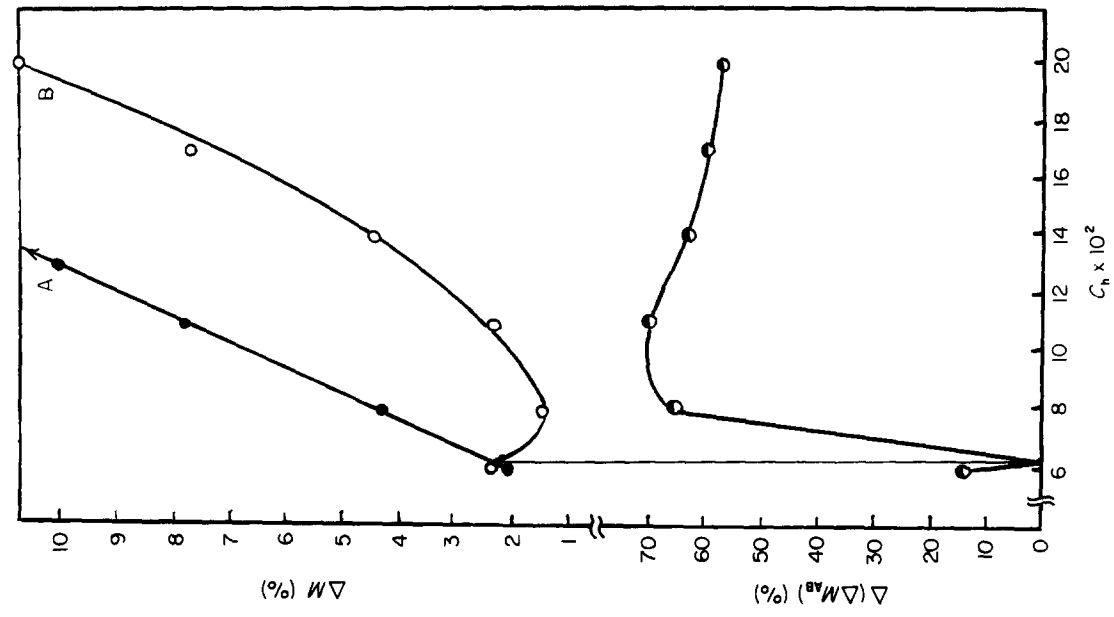

Figure 8 Mass loss ΔM and change of mass loss $\Delta(\Delta M_{AB})$ of the polymers based on DGEBA and the chelates A and B after thermal treatment in air for 10 h at 280°C as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)(HOC$_6$H$_4$COO)$_2$]; B, [Ni(trien)(HOC$_6$H$_4$COO)$_2$]

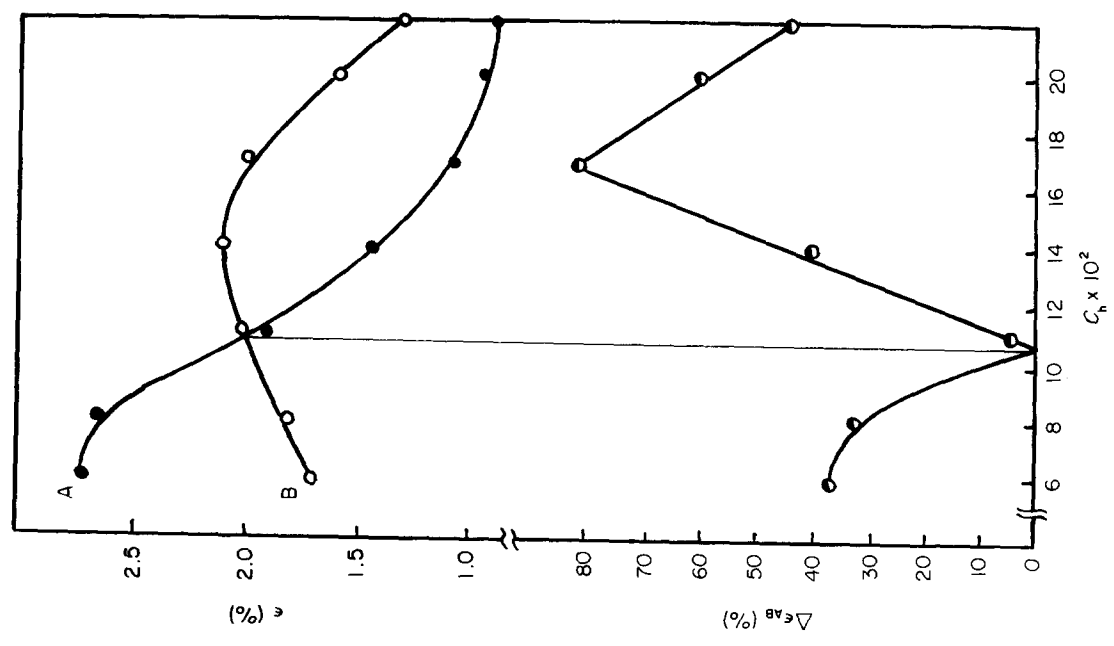

Figure 7 Elongation at break ε and change of elongation at break $\Delta\varepsilon_{AB}$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)(HOC$_6$H$_4$COO)$_2$]; B, [Ni(trien)(HOC$_6$H$_4$COO)$_2$]

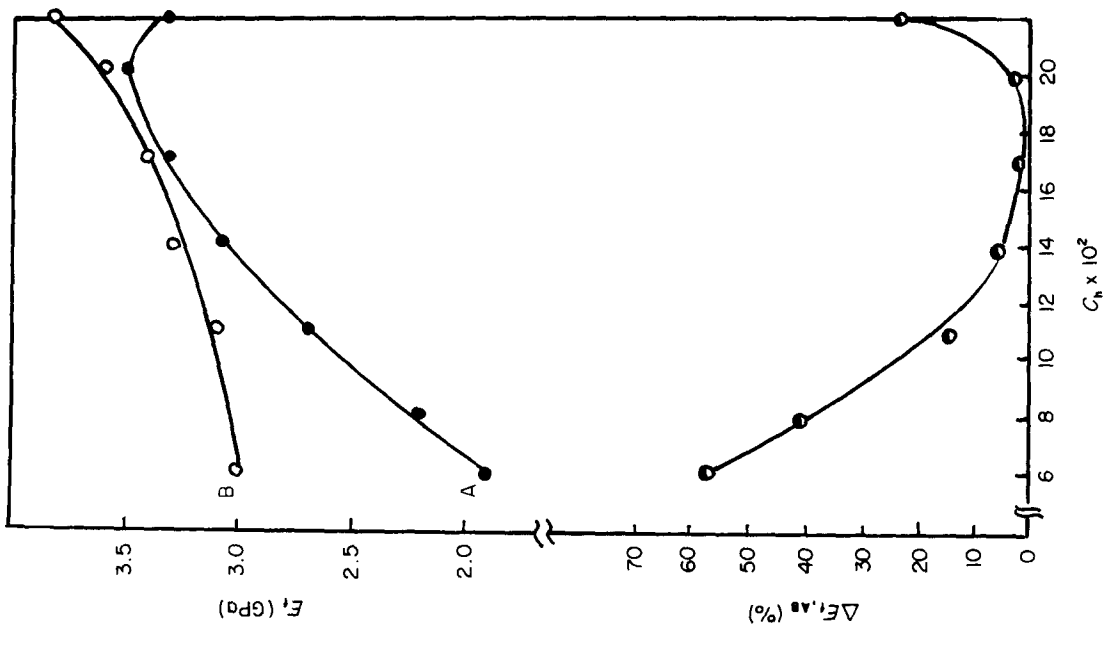

Figure 6 Flexural modulus E_f and change of flexural modulus $\Delta E_{f,AB}$ of the polymers based on DGEBA and the chelates A and B as functions of hardener concentration C_h (mol/mol of DGEBA): A, [Ni(cydien)(HOC$_6$H$_4$COO)$_2$]; B, [Ni(trien)(HOC$_6$H$_4$COO)$_2$]

Table 2 Contribution of chelate hardener structural fragments to properties of polymers based on 1 mol of DGEBA and 0.17 mol of chelate hardener

No.	Hardener identification in the pair	The pair of hardeners A and B	Polymer indices (X) σ_t (MPa)	E_t (GPa)	ε (%)	σ_f (MPa)	E_f (GPa)	σ_c (MPa)	DT (°C)	ΔM (%) after: 10 h at 280°C; *50 h at 280°C; **25 h at 260°C	Comparison of polymer indices $\Delta X = \frac{\lvert X_A - X_B \rvert}{X_A} \times 100\%$ $\Delta\sigma_t$	ΔE_t	$\Delta\varepsilon$	$\Delta\sigma_f$	ΔE_f	$\Delta\sigma_c$	$\Delta(DT)$	$\Delta(\Delta M)$
I. Influence of ligand nature																		
	A	$Cu(en)_2(HOC_6H_4COO)_2$	83	3.0	4.6	118	3.4	95	109	8.9*								
1	B	$Cu(dien)(HOC_6H_4COO)_2$	78	2.8	4.0	113	3.0	100	88	14.8*	6.0	6.7	13.0	4.2	11.8	5.3	19.3	66.3
2	B	$Cu(trien)(HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	19.4*	24.1	0	32.6	0	5.9	26.3	19.3	118.0
3	B	$Cu(cydien)(HOC_6H_4COO)_2$	84	7.4	5.0	119	3.1	106	98	11.8*	1.2	146.7	8.7	0.8	8.8	11.6	10.1	32.6
	A	$Cu(dien)(HOC_6H_4COO)_2$	78	2.8	4.0	113	3.0	100	88	14.8*								
4	B	$Cu(trien)(HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	19.4*	19.2	7.1	22.5	4.4	6.7	20.0	47.7	31.1
5	B	$Cu(cydien)(HOC_6H_4COO)_2$	84	7.4	5.0	119	3.1	106	98	11.8*	7.7	164.3	25.0	5.3	3.3	6.0	11.4	20.3
	A	$Cu(trien)(HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	19.4*								
6	B	$Cu(cydien)(HOC_6H_4COO)_2$	84	7.4	5.0	119	3.1	106	98	11.8*	33.3	146.7	61.3	0.8	3.1	11.7	24.6	39.2
	A	$Cd(en)_2(H_2NC_6H_4COO)_2$	63	3.3	1.8	93	3.0	114	70	30.0**								
7	B	$Cd(dien)(H_2NC_6H_4COO)_2$	94	4.0	3.0	138	3.1	138	97	17.4**	49.2	21.2	66.7	48.4	3.3	21.1	38.6	42.0
8	B	$Cd(trien)(H_2NC_6H_4COO)_2$	80	5.9	3.1	95	3.0	98	68	24.4**	27.0	78.8	72.2	2.2	0	14.0	2.9	18.7
9	B	$Cd(cydien)(H_2NC_6H_4COO)_2$	100	4.4	5.0	132	2.9	116	77	23.8**	58.7	33.3	177.8	41.9	3.3	1.8	10.0	20.7
	A	$Cd(dien)(H_2NC_6H_4COO)_2$	94	4.0	3.0	138	3.1	138	97	17.4**								
10	B	$Cd(trien)(H_2NC_6H_4COO)_2$	80	5.9	3.1	95	3.0	98	68	24.4**	14.9	47.5	3.3	31.2	3.2	29.0	30.0	40.2
11	B	$Cd(cydien)(H_2NC_6H_4COO)_2$	100	4.4	5.0	132	2.9	116	77	23.8**	6.4	10.0	66.7	4.3	6.5	15.9	20.6	36.8
	A	$Cd(trien)(H_2NC_6H_4COO)_2$	80	5.9	3.1	95	3.0	98	68	24.4**								
12	B	$Cd(cydien)(H_2NC_6H_4COO)_2$	100	4.4	5.0	132	2.9	116	77	23.8**	25.0	25.4	61.3	38.9	3.3	18.4	13.2	2.5
											$\overline{\Delta\sigma_t}$= 22.7	$\overline{\Delta E_t}$= 57.3	$\overline{\Delta\varepsilon}$= 50.9	$\overline{\Delta\sigma_f}$= 15.2	$\overline{\Delta E_f}$= 4.9	$\overline{\Delta\sigma_c}$= 15.1	$\overline{\Delta(DT)}$= 20.6	$\overline{\Delta(\Delta M)}$= 39.0
II. Influence of anion nature																		
	A	$Cu(trien)(CH_3COO)_2$	63	3.0	3.0	110	3.3	100	98	10.1*								
13	B	$Cu(trien)(H_2NC_6H_4COO)_2$	88	3.0	2.5	122	3.0	140	134	12.0*	39.7	0	16.7	10.9	9.1	40.0	36.7	18.8
14	B	$Cu(trien)(HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	19.4*	0	0	3.3	7.3	3.0	20.0	32.7	92.1
15	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	38	3.1	1.3	85	3.2	107	140	7.4*	39.7	3.3	56.7	22.7	3.0	7.0	42.9	26.7
	A	$Cu(trien)(H_2NC_6H_4COO)_2$	88	3.0	2.5	122	3.0	140	134	12.0*								
16	B	$Cu(trien)(HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	19.4*	28.4	0	24.0	3.3	6.7	14.3	3.0	61.7
17	B	$Cu(trien)(CH{=}NHC_6H_4O)_2$	38	3.1	1.3	85	3.2	107	140	7.4*	56.8	3.3	48.0	30.3	6.7	23.6	4.5	38.3

	A	Cu(trien)($HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	19.4*								
18	B	Cu(trien)($CH{=}NHC_6H_4O)_2$	38	3.1	1.3	85	3.2	107	140	7.4*	39.7	3.3	58.1	28.0	0	10.8	7.7	61.9
	A	Zn(cydien)($CH_3COO)_2$	65	3.2	1.8	125	3.5	95	100	8.4								
19	B	Zn(cydien)($C_6H_5COO)_2$	69	2.8	1.8	117	4.4	120	87	14.6	6.2	12.5	0	6.4	25.7	26.3	13.0	73.8
20	B	Zn(cydien)($HOC_6H_4COO)_2$	62	3.2	2.1	123	4.1	120	113	35.8	4.6	0	16.7	1.6	17.1	26.3	13.0	326.2
21	B	Zn(cydien)($CH_2{=}C(CH_3)COO)_2$	26	2.5	1.0	79	3.0	107	95	7.0	60.0	21.9	44.4	36.8	14.3	12.6	5.0	16.7
	A	Zn(cydien)($C_6H_5COO)_2$	69	2.8	1.8	117	4.4	120	87	14.6								
22	B	Zn(cydien)($HOC_6H_4COO)_2$	62	3.2	2.1	123	4.1	120	113	35.8	10.1	14.3	16.7	5.1	6.8	0	29.9	145.2
23	B	Zn(cydien)($CH_2{=}C(CH_3)COO)_2$	26	2.5	1.0	79	3.0	107	95	7.0	62.3	10.7	44.4	32.5	31.8	10.8	9.2	52.1
	A	Zn(cydien)($HOC_6H_4COO)_2$	62	3.2	2.1	123	4.1	120	113	35.8								
24	B	Zn(cydien)($CH_2{=}C(CH_3)COO)_2$	26	2.5	1.0	79	3.0	107	95	7.0	58.1	21.9	52.4	35.8	26.8	10.8	15.9	80.4
	A	Co(dien)($HOC_6H_4COO)_2$	91	3.2	4.7	130	3.6	101	113	7.1								
25	B	Co(dien)($CH{=}N(CH_2)C_6H_4O)_2$	65	3.5	2.1	118	3.6	93	104	7.9	28.6	9.4	55.3	9.2	0	7.9	8.0	11.3
											$\overline{\Delta\sigma_t}=$	$\overline{\Delta E_t}=$	$\overline{\Delta\varepsilon}=$	$\overline{\Delta\sigma_f}=$	$\overline{\Delta E_f}=$	$\overline{\Delta\sigma_c}=$	$\overline{\Delta(DT)}=$	$\overline{\Delta(\Delta M)}=$
											33.4	7.7	33.6	17.7	11.6	16.2	17.0	77.3
III. Influence of metal nature																		
	A	Cu(trien)($HOC_6H_4COO)_2$	63	3.0	3.1	118	3.2	120	130	4.2								
26	B	Zn(trien)($HOC_6H_4COO)_2$	58	3.6	1.9	110	3.4	126	121	15.9	7.9	20.0	38.7	6.8	6.3	5.0	6.9	278.6
27	B	Co(trien)($HOC_6H_4COO)_2$	25	3.4	3.1	80	3.0	121	108	5.6	60.3	13.3	0	32.2	6.3	0.8	16.9	33.3
28	B	Ni(trien)($HOC_6H_4COO)_2$	50	2.5	2.0	105	3.4	114	85	7.3	20.6	16.7	35.5	11.0	6.3	5.0	34.6	73.8
29	B	Fe(trien)($HOC_6H_4COO)_3$	45	3.5	1.1	83	4.0	128	80	9.0	28.6	16.7	64.5	29.7	25.0	6.7	38.5	114.3
30	B	MnO(trien)($HOC_6H_4COO)_2$	23	3.5	0.7	49	2.8	128	103	35.7	63.5	16.7	77.4	58.5	12.5	6.7	20.8	750.0
	A	Zn(trien)($HOC_6H_4COO)_2$	58	3.6	1.9	110	3.4	126	121	15.9								
31	B	Co(trien)($HOC_6H_4COO)_2$	25	3.4	3.1	80	3.0	121	108	5.6	56.9	5.6	63.2	27.3	11.8	4.0	10.7	64.8
32	B	Ni(trien)($HOC_6H_4COO)_2$	50	2.5	2.0	105	3.4	114	85	7.3	13.8	30.6	5.3	4.5	0	9.5	29.8	54.1
33	B	Fe(trien)($HOC_6H_4COO)_3$	45	3.5	1.1	83	4.0	128	80	9.0	22.4	2.8	42.1	24.5	17.6	1.6	33.9	43.4
34	B	MnO(trien)($HOC_6H_4COO)_2$	23	3.5	0.7	49	2.8	128	103	35.7	60.3	2.8	10.5	55.5	17.6	1.6	14.9	124.5
	A	Co(trien)($HOC_6H_4COO)_2$	25	3.4	3.1	80	3.0	121	108	5.6								
35	B	Ni(trien)($HOC_6H_4COO)_2$	50	2.5	2.0	105	3.4	114	85	7.3	100.0	26.5	35.5	31.3	13.3	5.8	21.3	30.4
36	B	Fe(trien)($HOC_6H_4COO)_3$	45	3.5	1.1	83	4.0	128	80	9.0	80.0	2.9	64.5	3.8	33.3	5.8	25.9	60.7
37	B	MnO(trien)($HOC_6H_4COO)_2$	23	3.5	0.7	49	2.8	128	103	35.7	8.0	2.9	77.4	38.8	6.7	5.8	4.6	537.5
	A	Ni(trien)($HOC_6H_4COO)_2$	50	2.5	2.0	105	3.4	114	85	7.3								
38	B	Fe(trien)($HOC_6H_4COO)_3$	45	3.5	1.1	83	4.0	128	80	9.0	10.0	40.0	45.0	21.0	17.6	12.3	5.9	23.3
39	B	MnO(trien)($HOC_6H_4COO)_2$	23	3.5	0.7	49	2.8	128	103	35.7	54.0	40.0	65.0	53.3	17.6	12.3	21.2	389.0
	A	Fe(trien)($HOC_6H_4COO)_3$	45	3.5	1.1	83	4.0	128	80	9.0								
40	B	MnO(trien)($HOC_6H_4COO)_2$	23	3.5	0.7	49	2.8	128	103	35.7	48.9	0	36.4	41.0	30.0	0	28.8	296.7

Table 2 Continued

No.	Hardener identification in the pair	The pair of hardeners A and B	Polymer indices (X): σ_t (MPa)	E_t (GPa)	ε (%)	σ_f (MPa)	E_f (GPa)	σ_c (MPa)	DT (°C)	ΔM (%) after: 10 h at 280°C; *50 h at 280°C; **25 h at 260°C	Comparison of polymer indices $\Delta X = \frac{\lvert X_A - X_B \rvert}{X_A} \times 100\%$: $\Delta\sigma_t$	ΔE_t	$\Delta\varepsilon$	$\Delta\sigma_f$	ΔE_f	$\Delta\sigma_c$	$\Delta(DT)$	$\Delta(\Delta M)$
	A	Cu(cydien)$(HOC_6H_4COO)_2$	84	7.4	5.0	119	3.1	106	98	2.8								
41	B	Zn(cydien)$(HOC_6H_4COO)_2$	62	3.2	2.1	123	4.1	120	113	35.8	26.2	56.8	58.0	3.4	32.3	13.2	15.3	1178.6
42	B	Co(cydien)$(HOC_6H_4COO)_2$	48	3.8	3.5	104	3.1	113	98	4.6	42.9	48.6	30.0	12.6	0	6.6	0	64.3
43	B	Ni(cydien)$(HOC_6H_4COO)_2$	43	4.4	1.2	101	3.3	106	80	18.0	48.8	40.5	76.0	15.1	6.5	0	18.4	542.9
44	B	Fe(cydien)$(HOC_6H_4COO)_3$	44	2.8	1.4	50	3.4	125	101	18.2	47.6	62.2	72.0	58.0	9.7	17.9	3.1	550.0
	A	Zn(cydien)$(HOC_6H_4COO)_2$	62	3.2	2.1	123	4.1	120	113	35.8								
45	B	Co(cydien)$(HOC_6H_4COO)_2$	48	3.8	3.5	104	3.1	113	98	4.6	22.6	18.8	66.7	15.4	24.4	5.8	13.3	87.2
46	B	Ni(cydien)$(HOC_6H_4COO)_2$	43	4.4	1.2	101	3.3	106	80	18.0	30.6	37.5	42.9	17.9	19.5	11.7	29.2	49.7
47	B	Fe(cydien)$(HOC_6H_4COO)_3$	44	2.8	1.4	50	3.4	125	101	18.2	29.0	12.5	33.3	59.4	17.1	4.2	10.6	49.2
	A	Co(cydien)$(HOC_6H_4COO)_2$	48	3.8	3.5	104	3.1	113	98	4.6								
48	B	Ni(cydien)$(HOC_6H_4COO)_2$	43	4.4	1.2	101	3.3	106	80	18.0	10.4	15.8	65.7	2.9	6.5	6.2	18.4	291.3
49	B	Fe(cydien)$(HOC_6H_4COO)_3$	44	2.8	1.4	50	3.4	125	101	18.2	8.3	26.3	60.0	51.9	9.7	10.6	3.1	295.7
	A	Ni(cydien)$(HOC_6H_4COO)_2$	43	4.4	1.2	101	3.3	106	80	18.0								
50	B	Fe(cydien)$(HOC_6H_4COO)_3$	44	2.8	1.4	50	3.4	125	101	18.2	2.3	36.4	16.7	50.5	3.0	17.9	26.3	1.1
											$\overline{\Delta\sigma_t}=$ 36.2	$\overline{\Delta E_t}=$ 23.7	$\overline{\Delta\varepsilon}=$ 47.3	$\overline{\Delta\sigma_f}=$ 29.1	$\overline{\Delta E_f}=$ 14.0	$\overline{\Delta\sigma_c}=$ 7.1	$\overline{\Delta(DT)}=$ 18.1	$\overline{\Delta(\Delta M)}=$ 239.4

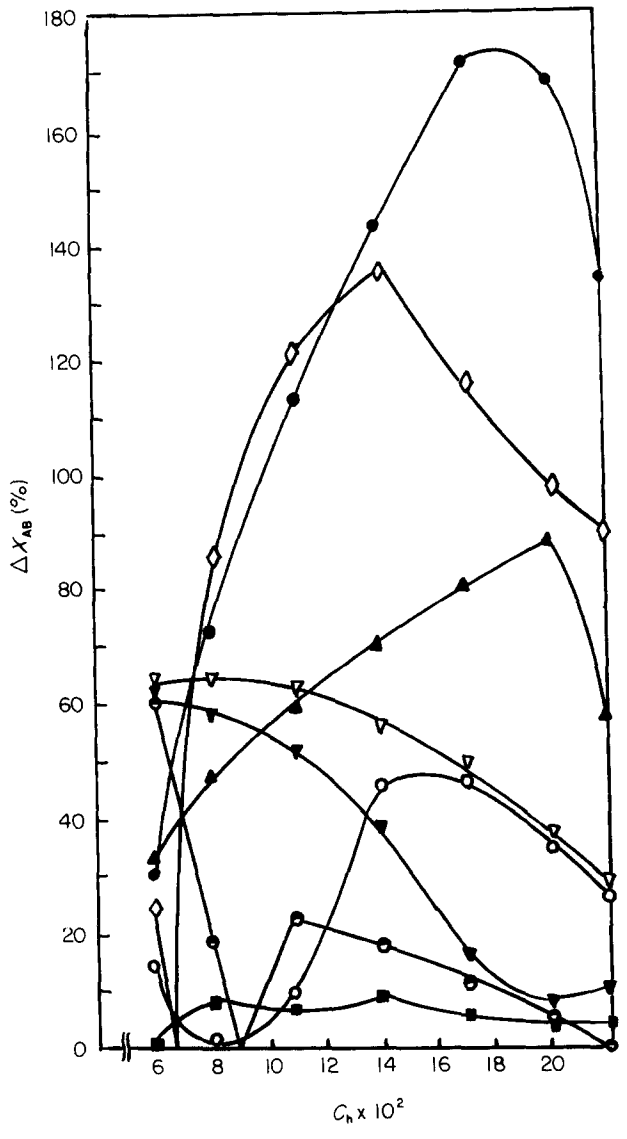

Figure 9 Change of indices ΔX_{AB} of the polymers based on DGEBA, [Zn(cydien)(CH_2=C(CH_3)COO)$_2$] (A) and [Zn(cydien)(C_6H_5COO)$_2$] (B) as a function of hardener concentration C_h (mol/mol of DGEBA): (○) $\Delta\sigma_{f,AB}$, (▽) $\Delta E_{f,AB}$, (◓) $\Delta\sigma_{c,AB}$, (●) $\Delta\sigma_{t,AB}$, (▼) $\Delta E_{t,AB}$, (▲) $\Delta\varepsilon_{AB}$, (■) $\Delta(DT_{AB})$, (◇) $\Delta(\Delta M_{AB})$ after 10 h at 280°C in air

Table 3 Values of $\overline{\Delta X}$ (%)

	$\overline{\Delta\sigma_t}$	$\overline{\Delta E_t}$	$\overline{\Delta\varepsilon}$	$\overline{\Delta\sigma_f}$	$\overline{\Delta E_f}$	$\overline{\Delta\sigma_c}$	$\overline{\Delta(DT)}$	$\overline{\Delta(\Delta M)}$
Ligand	22.7	57.3	50.9	15.2	4.9	15.1	20.6	39.0
Anion	33.4	7.7	33.6	17.7	11.6	16.2	17.0	77.3
Metal	36.2	23.7	47.3	29.1	14.0	7.1	18.1	239.4

depending on anion

$$\Delta M \gg \varepsilon \sim \sigma_t > \sigma_f \sim DT \sim \sigma_c > E_f > E_t$$

depending on metal

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

(the signs > and ≫ show the contribution of the preceding fragment to be increased 1.1–1.5 times and more than 2 times, respectively, relative to the next fragment).

The metal and anion are considered to be qualitatively close to each other in terms of the effects they have on the properties of the polymers. This can be explained by differences in the formation of the epoxy chelate matrix structure: if the interaction of an epoxy oligomer with a ligand takes place, amino group chemical bonds are formed by the nitrogen atoms, while the interaction with the anion or the cation catalytic effect causes the formation of stronger chemical bonds with the oxygen atoms. This is exactly the reason why the metal and anion affect greatly the heat resistance of MECPs (ΔM).

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

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

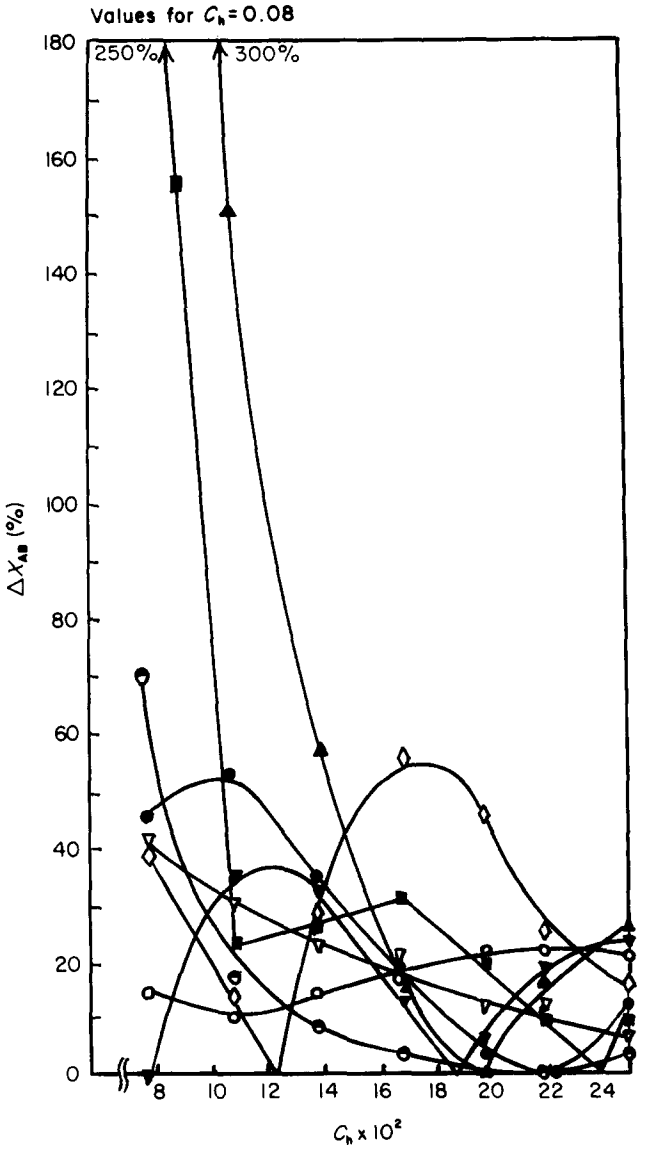

Figure 10 Change of indices ΔX_{AB} of the polymers based on DGEBA, [Cu(dien)(HOC_6H_4COO)$_2$] (A) and [Co(dien)(HOC_6H_4COO)$_2$] (B) as a function of hardener concentration C_h (mol/mol of DGEBA): (○) $\Delta\sigma_{f,AB}$, (▽) $\Delta E_{f,AB}$, (◓) $\Delta\sigma_{c,AB}$, (●) $\Delta\sigma_{t,AB}$, (▼) $\Delta E_{t,AB}$, (▲) $\Delta\varepsilon_{AB}$, (■) $\Delta(DT_{AB})$, (◇) $\Delta(\Delta M_{AB})$ after 10 h at 280°C in air

The analysis of the trends obtained shows that the most important with respect to the properties of MECPs are the metal cation, which greatly influences the heat resistance, and the ligand, which determines *DT*. The anion is considered to be less important. Proceeding from conclusion (i), the heat resistance of MECPs is influenced by the anion more strongly than are the other indices. Meanwhile, of the structural fragments, the metal has been acknowledged to be the most important with regard to the heat resistance. Therefore, the quantitative effect of the anion on the strength of the polymers is far less than that of the metal cation (the metal is the most important fragment for σ_t, σ_f and E_f, the anion only for σ_c), although a qualitative similarity has been mentioned to exist between the effects of these fragments (see the order of the indices depending on the anion and metal in conclusion (i)). This suggests that the epoxy chelate metal-containing polymer matrix contains mainly chemical bonds formed due to polymerization by the catalytic mechanism (the influence of cation) and due to the interaction with the ligand amino groups. At the same time the number of chemical bonds formed due to the interaction with the anion is far less.

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NOMENCLATURE

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