Metalliferous epoxy chelate polymers: 1. Synthesis and properties

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A study has been made of the possible synthesis of metalliferous epoxy chelate polymers (MECPs) by hardening of the diglycidyl ether of bisphenol A (DGEBA) with the chelates of metals (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+} and Mn^{4+}) and aliphatic amines (ethylenediamine, diethylenetriamine, triethylenetetramine and cyanoethylated diethylenetriamine). The salts of the metals and organic acids have been combined with the amines to produce the chelates both in solvents (acetone, water) and in the absence of solvents. The complex hardeners were identified by elemental analysis and infra-red spectroscopy. The reactivity of the complexes in reactions with DGEBA and its dependence on the structures of the chelates have been investigated. The properties of epoxy polymers modified by metal cations have been studied. MECPs have been found to possess significant strength. The introduction of cations into the epoxy matrices increases the deformation temperature up to 163°C and tensile strength up to 100 MPa. The copper-containing polymers exhibit a significant increase in thermal oxidative stability, which becomes comparable with the heat resistance of well known epoxy–anhydride systems.

(Keywords: epoxy polymers; metal-containing polymers; synthesis; structure; properties; influence)

INTRODUCTION

Up till now, metal-containing epoxy polymers have mainly been obtained by hardening of epoxy resins with metal β-diketonates[1,2]. Poor compatibility of the β-diketonates with epoxy oligomers results in the formation of heterogeneous systems in which the full potential of polymer matrix modification with metal cations cannot be realized. The most important condition for the effectiveness of such modification is the formation of chemical bonds between the cation and the polymer chain, which can be achieved only in a homogeneous system with complete compatibility of the metal-containing hardener with the oligomer. This is obtained by using as hardeners the chelates of transition metals (Cu, Zn, Co, Fe, Ni, Mn, Cd) formed in the reaction of some metal organic salts with aliphatic amines. The new chelate hardeners are considered to be highly effective in terms of synthesis, which is not a time-consuming process and is easy to perform, and with respect to their processing and the properties of the cured epoxy oligomers, which show high strength and high thermal oxidative stability[3–6]. The above allowed the hardeners concerned to be used for manufacturing composites able to endure considerable cyclic loading[7].

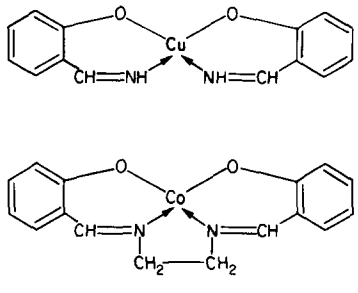
The present work deals with the investigation of the synthesis and properties of new metalliferous epoxy chelate polymers (MECPs).

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA), ED-22 grade, with epoxy equivalent weight of 170–180, made in Russia, was used as an epoxy oligomer.

Metal oxides (MnO_2, Fe_2O_3, CuO and ZnO), salicylic acid (HOC_6H_4COOH), organic salts of metals, and salicylaldimines of copper ($Cu(NH{=}CHC_6H_4O)_2$) and cobalt ($Co(CH{=}N(CH_2)C_6H_4O)_2$) were used:



as well as the following aliphatic amines: ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien) and bis-*N*,*N*′-(β-cyanoethyl)diethylenetriamine (cydien; $NC{-}((CH_2)_2NH)_3{-}(CH_2)_2{-}CN$).

Methods

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

The properties of the complex hardeners and epoxy polymers were investigated with a thermal analyser (Mettler TA 3000) containing a calorimeter and a thermogravimetric cell.

To characterize the heat resistance of the polymers, the thermogravimetric technique was used in the isothermal regime in air.

The strength indices of the polymers were determined in accordance with standards[8].

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SYNTHESIS

Synthesis of chelates by direct reaction of components

Use of aliphatic amines possessing melting points lower than 20°C allows synthesis of the chelates to be performed in the absence of solvents. The conditions necessary for the reactions to proceed are determined by the properties of the chelates produced. If the end-product is a low-viscosity fluid, e.g. the chelates $[Zn(cydien)(CH_2{=}C(CH_3)COO)_2]$ and $[Zn(cydien)(CH_3COO)_2]$, the reactions are conducted with stirring of the components for 1–2 h at 50–70°C. In the case when the end-product is a hard substance, e.g. $[Co(dien)(CH{=}N(CH_2)C_6H_4O)_2]$ or $[Cu(en)_2(HOC_6H_4COO)_2]$, the syntheses are carried out for 2–4 h at the melting points of the chelates.

The synthesis of the complexes could be carried out using metal oxides as the initial components. The latter are reacted with the aliphatic amines and organic acids for 1–6 h at 100–160°C to form the chelates:

$$CuO + 2HOC_6H_4COOH + H_2NRNH_2 \rightarrow [Cu(H_2NRNH_2)(HOC_6H_4COO)_2] + H_2O$$

where R is an organic radical. The chelates of iron and manganese have been synthesized in the following way:

$$Fe_2O_3 + 6HOC_6H_4COOH + 2\,trien \rightarrow 2[Fe(trien)(HOC_6H_4COO)_3] + 3H_2O$$

$$MnO_2 + 2HOC_6H_4COOH + trien \rightarrow [MnO(trien)(HOC_6H_4COO)_2] + H_2O$$

Synthesis of chelates in solvents

Because the aliphatic amines have high solubility, the synthesis of chelates with these ligands can be performed in certain solvents. Since synthesis via direct reaction of the components demands higher temperature and prolonged time, the possibility of hardener production in acetone solutions is thus of great practical importance. In the latter case the solution obtained can be used without intermediate hardener segregation in the production of binder intended for the impregnation of reinforcing materials.

The conditions for chelate hardener formation are shown in *Table 1*. The reactants were placed in a reactor with a mechanical stirrer at a rotation rate of 50 rev min^{-1}.

Analysis of the data shows that the reaction rate of complex formation depends on the structural fragments of the chelates (metal cation, ligand and anion) and decreases in the following order:

Ligand trien ~ cydien > dien > en

Anion $HOC_6H_4COO^- > C_6H_5COO^- > CH_3COO^- > H_2NC_6H_4COO^- > NH{=}CHC_6H_4O^-$

Metal $Cu^{2+} > Co^{2+} > Fe^{3+} > Ni^{2+} > Zn^{2+}$

The formation of complexes of the copper salts (in particular, salicylate) is an exothermic process and is accompanied by a rise in reaction mixture temperature up to 90°C, which is why the solvent boils when acetone is used.

The trends in the reactivity change are explained by the fact that trien and cydien are more dentate in comparison with dien and en, as well as by the high coordination power of the copper, forming the strongest complexes with nitrogen ligands. The anion reactivity series is a direct function of the strength of the organic acids, which is confirmed by its comparison with their ionization constants:

	HOC_6H_4COOH	C_6H_5COOH	CH_3COOH	$H_2NC_6H_4COOH$
pK_a	3.00	4.18	4.75	4.95

Thus the syntheses of the chelates of copper, $[Cu(trien)(HOC_6H_4COO)_2]$ and $[Cu(cydien)(HOC_6H_4COO)_2]$, via the reactions of copper salicylate with trien and cydien in acetone for a few minutes at 20°C are considered to be the most technological regarding conditions.

The properties of the chelate hardeners synthesized by means of the different methods are shown in *Table 2*.

Synthesis of polymers

MECPs were made by casting of the compounds into metal moulds and were hardened for 11 h at 120°C.

Table 1 Synthesis of chelates in two solvents, water and acetone

		Water			Acetone		
Salt	Ligand	Temperature (°C)	Time of stirring (min)	Yield (%)	Temperature (°C)	Time of stirring (min)	Yield (%)
$Cu(HOC_6H_4COO)_2$	en	20	60	68	20	60	34
	dien	20	30	73	20	60	63
	trien	20	5	100	20	5	100
	cydien	20	5	95	20	5	100
$Zn(HOC_6H_4COO)_2$	cydien	80	60	14	50	60	25
$Zn(C_6H_5COO)_2$	cydien	80	60	10	50	60	20
$Zn(CH_3COO)_2$	cydien	80	60	12	50	60	4
$Cu(CH_3COO)_2$	trien	20	5	100	50	60	5
$Cu(H_2NC_6H_4COO)_2$	trien	80	60	56	50	60	3
$Cu(NH{=}CHC_6H_4O)_2$	trien	80	60	35	50	60	0.2
$Cd(H_2NC_6H_4COO)_2$	trien	95	60	38	50	60	12
$Co(HOC_6H_4COO)_2$	trien	50	30	93	20	30	78
$Fe(HOC_6H_4COO)_3$	trien	90	30	71	50	30	56
$Ni(HOC_6H_4COO)_2$	trien	65	60	77	50	60	34
$Zn(HOC_6H_4COO)_2$	trien	80	60	16	50	60	19

Table 2 Production and properties of chelate hardeners

No.	Hardener	Method of production[a]	Molecular weight	Appearance[b]	Colour	Melting point (°C)	Solubility in acetone at 20°C (g/100 g of acetone)	Parameters of curing of epoxy oligomer (0.1 mol of hardener per 1 mol of DGEBA)				
								Temperature at beginning of reaction (°C)	Gel time at 95°C (min)	Maximum temperature of reaction (°C)	Heat change of reaction ($J g^{-1}$)	Curing time at 120°C (min)
1	$Cu(en)_2(HOC_6H_4COO)_2$	1	457.9	cr.	violet	142	13.8	87	645	183	335	280
2	$Cu(dien)(HOC_6H_4COO)_2$	1, 2	440.9	cr.	blue	192	75.5	88	555	167	334	241
3	$Cu(trien)(HOC_6H_4COO)_2$	1, 2, 3	484.0	cr.	blue	139	362.5	89	230	138	332	100
4	$Cu(cydien)(HOC_6H_4COO)_2$	1, 2, 3	546.9	r.	blue	125	197.3	92	492	137	328	214
5	$Cd(en)_2(H_2NC_6H_4COO)_2$	1	504.9	cr.	brown	135	5.8	70	1500	193	389	660
6	$Cd(dien)(H_6NC_6H_4COO)_2$	1	487.8	pd.	grey	113	23.6	72	1200	181	384	520
7	$Cd(trien)(H_2NC_6H_4COO)_2$	1	530.9	cr.	yellow	125	24.1	76	450	154	366	196
8	$Cd(cydien)(H_2NC_6H_4COO)_2$	1	593.8	cr.	grey	92	27.7	76	525	149	364	228
9	$Co(dien)(HOC_6H_4COO)_2$	1	454.4	cr.	black	153	64.5	83	726	154	368	316
10	$Co(trien)(HOC_6H_4COO)_2$	1, 2	497.4	cr.	violet	112	71.4	86	451	145	360	196
11	$Co(cydien)(HOC_6H_4COO)_2$	1, 2	560.3	cr.	violet	90	76.8	91	942	144	350	410
12	$Zn(trien)(HOC_6H_4COO)_2$	1, 3	521.9	pd.	yellow	117	11.5	83	221	147	341	96
13	$Zn(cydien)(HOC_6H_4COO)_2$	1, 3	584.8	r.	yellow	35	20.4	86	451	145	340	196
14	$Ni(trien)(HOC_6H_4COO)_2$	1	551.3	pd.	violet	113	10.1	87	180	140	334	80
15	$Ni(cydien)(HOC_6H_4COO)_2$	1	614.1	r.	violet	68	11.8	90	376	139	330	160
16	$Fe(trien)(HOC_6H_4COO)_3$	1, 2, 3	613.5	r.	red	65	70.5	85	205	144	337	90
17	$Fe(cydien)(HOC_6H_4COO)_3$	1, 2, 3	676.3	r.	red	47	68.8	88	428	142	333	186
18	$MnO(trien)(HOC_6H_4COO)_2$	3	491.4	r.	black	117	10.4	81	148	149	345	65
19	$Cu(trien)(H_2NC_6H_4COO)_2$	1	482.1	cr.	blue	123	12.7	81	213	146	367	93
20	$Cu(trien)(CH_3COO)_2$	1	345.9	r.	blue	55	12.8	87	215	144	346	93
21	$Cu(trien)(HN{=}CHC_6H_4O)_2$	1	450.1	pd.	black	80	insoluble	80	70	157	367	31
22	$Zn(cydien)(CH_3COO)_2$	1	428.6	r.	colourless	below 20	5.3	83	410	150	344	178
23	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	1	444.7	r.	orange	below 20	insoluble	80	415	149	342	180
24	$Zn(cydien)(C_6H_5COO)_2$	1	516.7	cr.	yellow	94	45.6	84	433	147	341	188
25	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	1	428.4	cr.	brown	228	insoluble	82	35	173	376	15

[a] 1, direct reaction of amine with metal salt; 2, reaction of amine with salt in acetone; 3, reaction of amine with metal oxide and acid
[b] r., resin; cr., crystals, pd., powder

Comparative polymers were obtained by hardening of DGEBA with aliphatic and aromatic amines (4,4'-methylenedianiline (MDA); 4,4'-diaminodiphenylsulphone (DDS)) and iso-methyltetrahydrophthalic anhydride (iso-MTHPA), in well known regimes[8].

RESULTS AND DISCUSSION

Structure of chelate hardeners

The structure of the synthesized chelates was examined by considering the examples of copper and cadmium complexes. The results of the elemental analyses of the hardeners are given in *Table 3*. According to the data, the formation of side-products and partial ligand removal caused by thermolysis do not occur during the syntheses; the reactions proceed by the addition scheme:

$$M(X)_2 + NH_2RNH_2 \rightarrow [M(NH_2RNH_2)(X)_2]$$

where M is a metal, X is an anion and R is an organic radical.

The infra-red absorption spectral bands of the initial reactants and chelate hardeners presented in *Table 4* show that the stretching vibration frequencies $\nu(NH_2)$ of the complexes lie near 3250–3270 cm^{-1} and are decreased by 30–100 cm^{-1} in comparison with $\nu(NH_2)$ of the ligands, which testifies to the coordination of the amines with the metals through the amino nitrogen atoms.

The aliphatic amines used as ligands are characterized by alteration of the amino groups and methylene bridges in their molecules, which in coordinating with a metal results in the formation of a five-membered ring:

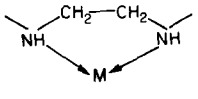


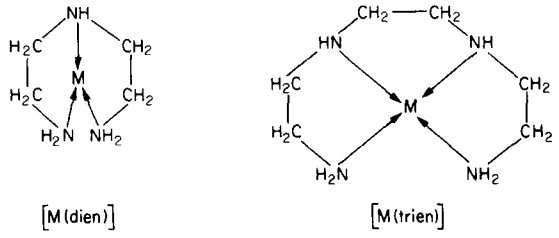
Table 3 Results of element analysis of chelates

Chelate	Calculated (%) (found)			
	C	H	N	Metal
$Cu(trien)(CH_3COO)\cdot H_2O$	34.68 (34.40)	7.51 (7.03)	16.18 (16.99)	18.50 (18.91)
$Cu(en)_2(HOC_6H_4COO)_2$	48.24 (48.71)	4.52 (5.00)	7.04 (7.00)	16.08 (16.10)
$Cu(trien)(HOC_6H_4COO)_2$	49.62 (50.02)	5.84 (6.03)	11.58 (11.21)	13.12 (13.58)
$Cu(trien)(H_2NC_6H_4COO)_2$	49.82 (50.18)	6.29 (6.71)	17.44 (17.97)	13.18 (13.40)
$Cd(cydien)(H_2NC_6H_4COO)_2$	48.50 (48.03)	5.22 (5.42)	11.79 (12.00)	18.93 (18.46)

Table 4 I.r. absorption spectra of chelates

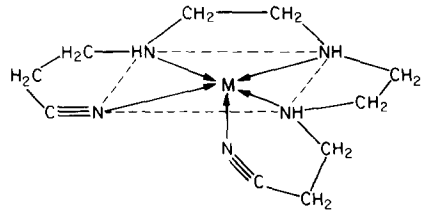
Compound	Absorption bands (cm^{-1})					
trien	1140	1350	1470	1600	2950	3300
$Cu(HOC_6H_4COO)_2$	710	760	850	860	900	1045
	1155	1260	1330	1410	1525	1580
	1610	2980	3200			
$Cd(H_2NC_6H_4COO)_2$	710	760	820	880	950	1040
	1110	1150	1240	1600	2980	3140
	3280					
$[Cu(trien)(HOC_6H_4COO)_2]$	700	760	850	1030	1250	1380
	1450	1490	1600	2850	2920	3250
$[Cu(trien)(CH_3COO)_2]$	700	1050	1100	1450	1600	2960
	3270					
$[Cd(trien)(H_2NC_6H_4COO)_2]$	720	760	860	1030	1150	1260
	1550	1620	2950	3200	3260	

In the reactions of metal salts with dien and trien in the molar ratio salt:amine = 1:1, structures are formed that have two and three bonded five-membered rings. The complexes of cydien possess two five- and two six-membered chelate rings:



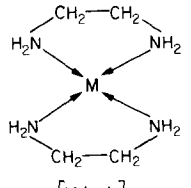
[M(dien)] [M(trien)]

(1)



[M(cydien)]

The formation of a complex of 1 mol of a metal salt with 2 mol of en yields a compound having two five-membered rings unbonded with one another:



[M(en)$_2$]

(2)

According to Chugaev's rule[9], five- and six-membered chelate rings have enhanced stability. The presence of several amino groups in a ligand is responsible for the chelate effect, i.e. an increase in stability of a metal chelate possessing a polydentate ligand in comparison with a similar complex having a monodentate ligand[10]. At the same time the stability of the chelates increases depending on the ligand in the order:

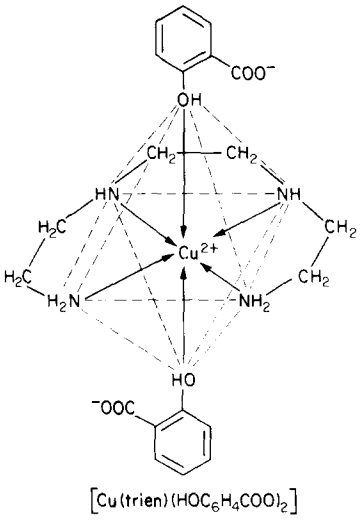
$$\text{en} < \text{dien} < \text{trien} < \text{cydien}$$

which can be explained by coordination–steric factors[10–13].

The metal cation type is no less important for chelate stability than the structure of the ligand. According to the Irving–Williams rule[14], the stability of chelate rings of bivalent metals is maximal for copper and decreases in the following order:

$$\text{Zn} < \text{Cu} > \text{Ni} > \text{Co} > \text{Fe} > \text{Mn} \qquad (3)$$

The configuration of a complex depends on the coordination number of the metal, which varies, as a rule, from 4 to 6[15]. For instance, the structure (4+2) or (4+1) is a characteristic of copper, and is considered to be a quadrilateral pyramid or bipyramid. For example:

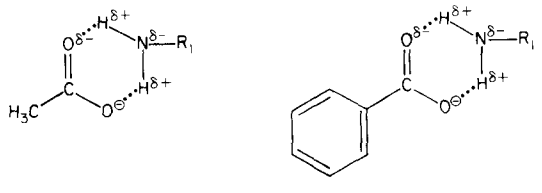


[Cu(trien)(HOC$_6$H$_4$COO)$_2$]

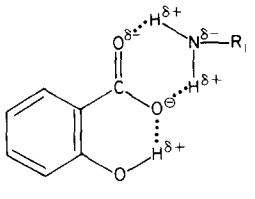
(4)

In chelate generation between metal organic salts and aliphatic amines, the anion was proved to be eliminated into the external sphere of the complex[16]. When intracomplex compounds (salicylates, anthranilates and salicylaldimines) are used for hardener synthesis, the anions preserve donor–acceptor bonds but lose direct bonds with the metals as a result of the cation coordinating with the aliphatic amines.

The spatial arrangement of the anion as well as the *ortho* isomeric arrangement of the substituents on the benzene ring encourage the formation of hydrogen bonds with the amino groups of the ligands:



(5)



where R_1 is an amine radical.

Thus, complex formation between aliphatic amines and metal organic salts leads to blocking of the nitrogen atoms of the amino groups with a metal atom, as a result of donor–acceptor bond formation, and to bonding of the hydrogen atoms of the NH_2 groups with the anions, caused by the formation of strong intramolecular hydrogen bridges.

Influence of chelate structural fragments on hardening parameters of epoxy oligomers

The deactivation of the amino groups of the ligands caused by chelate formation significantly prolongs the pot lives of the epoxy compounds based on DGEBA and the synthesized hardeners. The pot lives of these compounds at 20°C were found to be no less than 40

days, whereas the original aliphatic amines are known as hardeners for 'cold' curing that harden bisphenol A based epoxy resins at room temperature in 24 h[8].

The structural fragments of a coordination hardener (metal cation, ligand and anion) influence to a great extent the indices of the process of DGEBA hardening (*Table 2*).

Figures 1 and *2* show the dependence of the heat of reaction of DGEBA with the pure aliphatic amines (en and trien) and with the complexes $[Cu(en)_2(HOC_6H_4COO)_2]$ and $[Cu(trien)(HOC_6H_4COO)_2]$ on the temperature of hardening. The temperature at the beginning of the reactions of the epoxy oligomer with the chelate hardeners increases up to 70–92°C in comparison with the pure amines. This temperature corresponds to the beginning of complex dissociation and the formation of active particles able to react with the epoxy oligomer. As the reaction of complex dissociation is endothermic, the heat of reaction of these hardeners with DGEBA is less than that of the pure amines.

When the complex $[Cu(en)_2(HOC_6H_4COO)_2]$, which has two chelate rings uncombined with each other (structure (2)), is used as a hardener, the exotherm is characterized by the presence of two maxima (*Figure 1*). This can be explained by the sequential detachment of ligand molecules from the complex cation when heated:

$$[Cu(en)_2]^{2+} \rightleftharpoons [Cu(en)]^{2+} + en$$

$$[Cu(en)]^{2+} \rightleftharpoons Cu^{2+} + en$$

The complex cation $[Cu(en)]^{2+}$ formed as a result of the removal of one molecule of the amine is stronger than the original one $[Cu(en)_2]^{2+}$ and dissociates at a higher temperature. The discrete detachment of the ligand is accompanied by non-uniform heat release in the interaction of the loose amine with the epoxy oligomer.

Since trien in contrast to en forms a closed system of interconnected chelate rings (structure (1)), heating of the complex hardener based on it causes no discrete detachment of ligand molecules but is accompanied by gradual breaking of the donor–acceptor bonds of the amino groups with the metal:

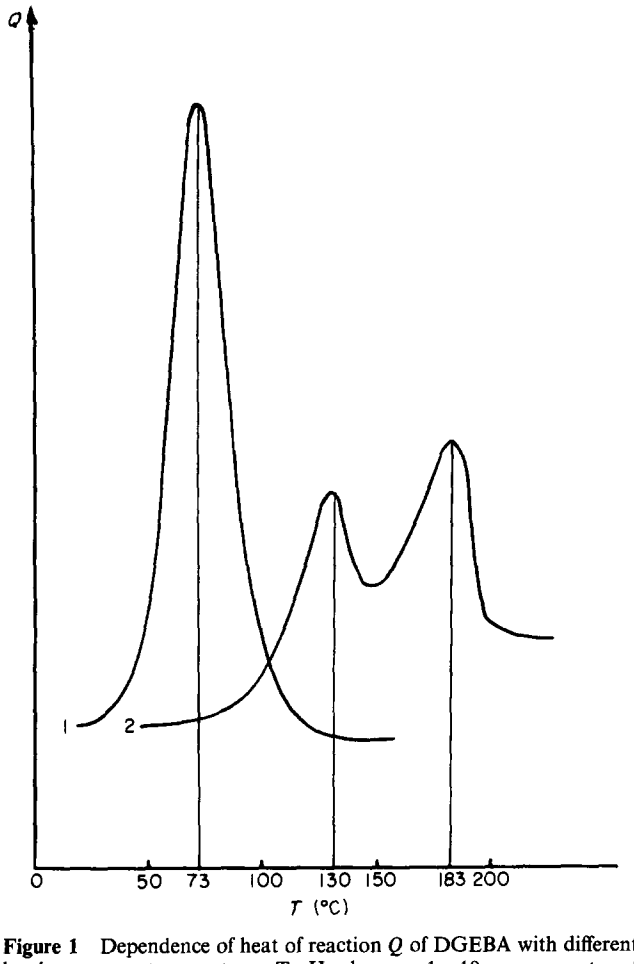


Figure 1 Dependence of heat of reaction Q of DGEBA with different hardeners on temperature T. Hardeners: 1, 10 mass parts of en; 2, 13.5 mass parts of $[Cu(en)_2(HOC_6H_4COO)_2]$ per 100 mass parts of DGEBA

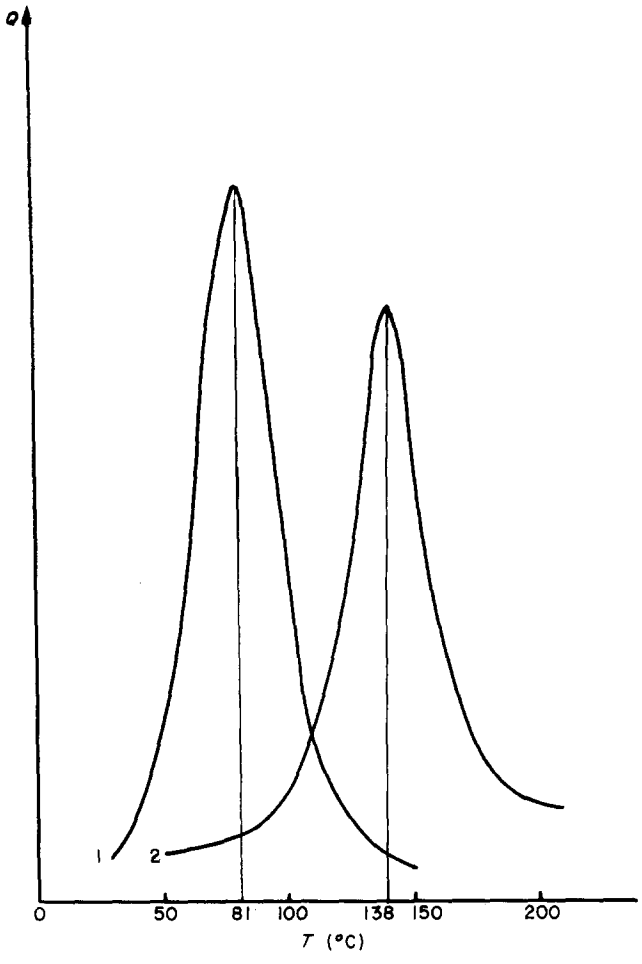
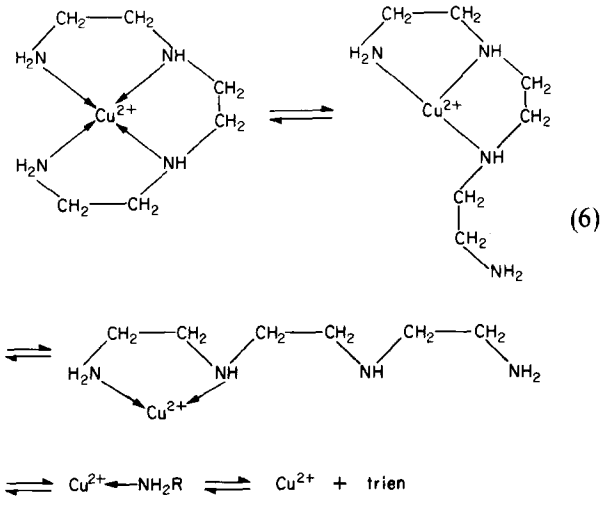


Figure 2 Dependence of heat of reaction Q of DGEBA with different hardeners on temperature T. Hardeners: 1, 10 mass parts of trien; 2, 14.2 mass parts of $[Cu(trien)(HOC_6H_4COO)_2]$ per 100 mass parts of DGEBA



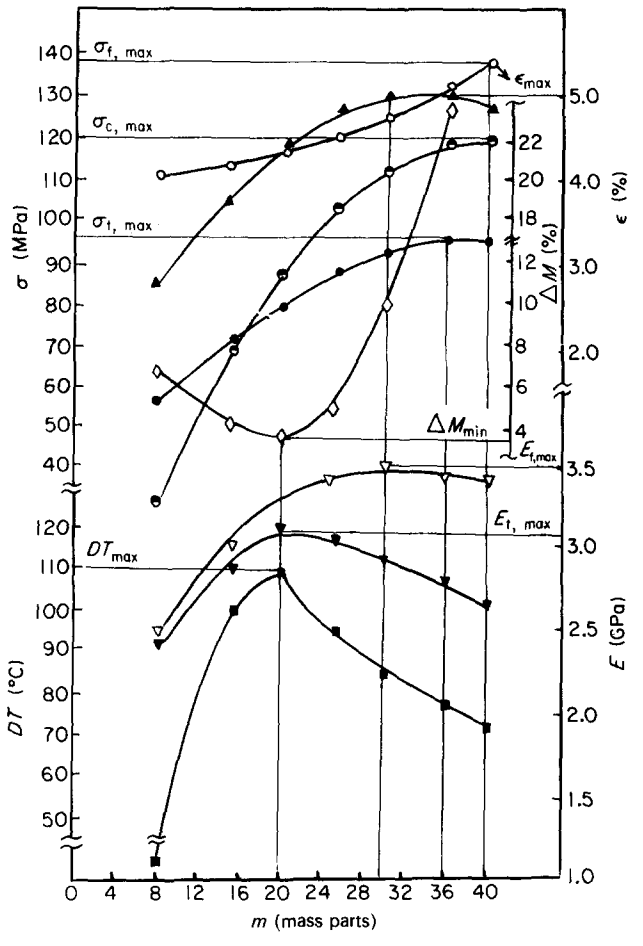


Figure 3 Dependence of properties of the polymers based on DGEBA and $[Cu(en)_2(HOC_6H_4COO)_2]$ on hardener content m (mass parts per 100 mass parts of DGEBA): (○) σ_f, (▽) E_f, (◓) σ_c, (●) σ_t, (▼) E_t, (▲) ε, (■) DT, (◇) ΔM after 10 h at 280°C in air

The temperature at the beginning of the reaction of a hardener with an epoxy oligomer depends on the initial temperature of complex dissociation, which is regarded as a two-stage process, i.e. first chelate dissociation into a complex cation and an anion, and then complex cation dissociation into a metal cation and amine. For example:

$$[Cu(trien)(HOC_6H_4COO)_2] \rightleftharpoons [Cu(trien)]^{2+} + 2HOC_6H_4COO^- \quad (7)$$
$$[Cu(trien)]^{2+} \rightleftharpoons Cu^{2+} + trien$$

The initial dissociation temperature of the complexes depends on their stability. *Table 2* shows that the temperature at the beginning of the reaction of the hardeners with DGEBA varies in the interval from 70°C (No. 5, $[Cd(en)_2(H_2NC_6H_4COO)_2]$) to 92°C (No. 4, $[Cu(cydien)(HOC_6H_4COO)_2]$) and decreases in the order:

Ligand cydien > trien > dien > en

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

Metal $Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{3+} > Zn^{2+} > Mn^{4+} > Cd^{2+}$

The first stage of chelate dissociation into a complex cation and an anion depends on the strength of the organic acid corresponding to the anion. It will be sufficient to compare the obtained dependence of the temperature at the beginning of the hardening reaction on the anions with the acid dissociation constants:

	$H_2NC_6H_4COOH$	CH_3COOH	$CH_2{=}C(CH_3)COOH$	C_6H_5COOH	HOC_6H_4COOH
pK_a	4.95	4.75	4.70	4.18	3.00

The stepwise dissociation of a complex cation (scheme (6)) depends on chelate stability, which is enhanced with the increase in the number of dentate groups of a ligand and follows the Irving–Williams rule (3).

As may be concluded from the experimental data, the higher the stability of the coordination compounds, the lower the maximal temperature of the exothermic reaction and the heat of reaction. That is why the dependence of these indices on the chelate structural fragments changes to the reverse of that obtained for the temperature at the beginning of the hardening reaction. The maximal temperature of the exothermic reaction and the heat of reaction decrease in the following order of the structural fragments:

Ligand en > dien > trien > cydien

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

Metal $Cd^{2+} > Mn^{4+} > Zn^{2+} > Fe^{3+} > Co^{2+} > Ni^{2+} > Cu^{2+}$

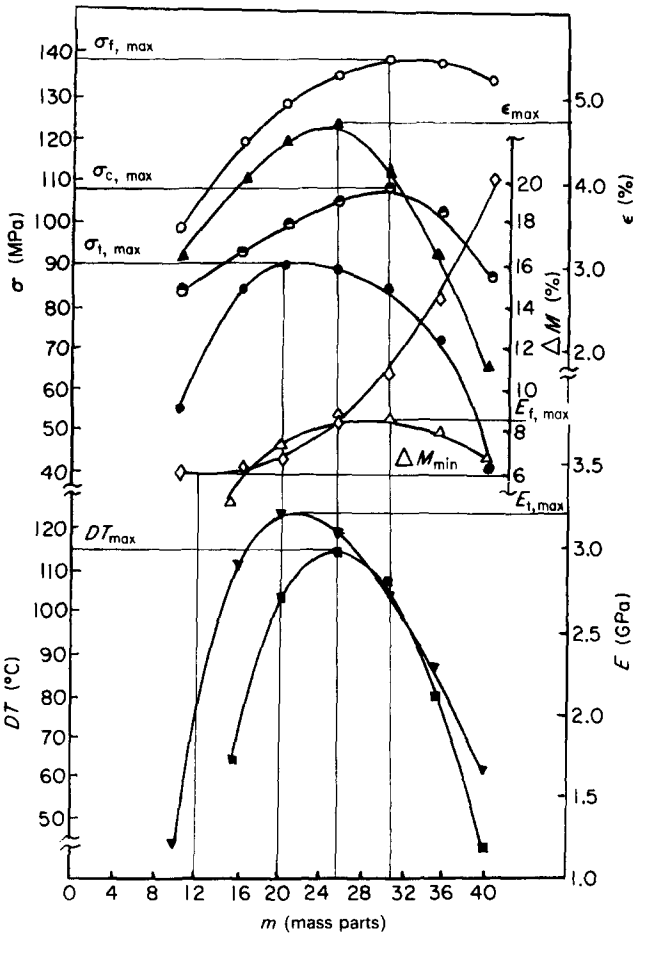


Figure 4 Dependence of properties of the polymers based on DGEBA and $[Co(dien)(HOC_6H_4COO)_2]$ on hardener content m (mass parts per 100 mass parts of DGEBA): (○) σ_f, (▽) E_f, (◓) σ_c, (●) σ_t, (▼) E_t, (▲) ε, (■) DT, (◇) ΔM after 10 h at 280°C in air

Table 5 The maximal values of the indices of the polymers based on DGEBA and different hardeners

No.	Hardener	*DT* (°C)	σ_c (MPa)	σ_f (MPa)	σ_t (MPa)	E_t (GPa)	ε (%)	ΔM after thermal treatment in air for 100 h at 260°C (%)
1	en	95	91	113	84	2.5	5.0	24.2
2	dien	91	110	117	69	2.9	2.7	24.6
3	trien	66	115	132	85	3.3	4.4	18.3
4	cydien	63	100	108	65	3.4	3.1	20.7
5	MDA	150	120	107	78	3.0	4.2	25.3
6	DDS	160	125	135	65	4.2	3.1	27.8
7	iso-MTHPA	120	115	105	52	3.7	1.4	2.8
8	$Cu(en)_2(HOC_6H_4COO)_2$	110	120	138	97	3.1	5.0	6.0
9	$Cu(dien)(HOC_6H_4COO)_2$	100	115	115	89	3.3	5.0	5.6
10	$Cu(trien)(HOC_6H_4COO)_2$	130	120	115	65	3.1	3.5	3.5
11	$Cu(cydien)(HOC_6H_4COO)_2$	115	120	126	90	7.6	5.0	3.0
12	$Cd(en)_2(H_2NC_6H_4COO)_2$	70	125	123	68	3.4	1.8	18.6
13	$Cd(dien)(H_2NC_6H_4COO)_2$	103	137	147	96	4.2	3.4	25.9
14	$Cd(trien)(H_2NC_6H_4COO)_2$	75	98	96	80	6.0	3.2	36.5
15	$Cd(cydien)(H_2NC_6H_4COO)_2$	100	124	138	100	4.4	5.0	31.3
16	$Co(dien)(HOC_6H_4COO)_2$	115	109	139	91	3.2	4.8	5.2
17	$Co(trien)(HOC_6H_4COO)_2$	108	122	130	79	3.4	3.8	6.4
18	$Co(cydien)(HOC_6H_4COO)_2$	100	126	117	53	4.0	3.5	11.9
19	$Zn(trien)(HOC_6H_4COO)_2$	130	128	133	92	3.7	4.6	15.5
20	$Zn(cydien)(HOC_6H_4COO)_2$	130	130	145	91	3.4	5.0	11.9
21	$Ni(trien)(HOC_6H_4COO)_2$	95	117	109	55	4.4	2.1	3.5
22	$Ni(cydien)(HOC_6H_4COO)_2$	92	124	125	68	4.4	2.7	6.4
23	$Fe(trien)(HOC_6H_4COO)_3$	92	131	84	63	3.9	1.8	13.9
24	$Fe(cydien)(HOC_6H_4COO)_3$	120	125	112	74	3.0	2.2	8.3
25	$MnO(trien)(HOC_6H_4COO)_2$	110	128	52	53	3.1	1.3	24.6
26	$Cu(trien)(H_2NC_6H_4COO)_2$	134	145	122	88	3.0	2.5	4.0
27	$Cu(trien)(CH_3COO)_2$	102	133	130	77	3.4	4.0	3.7
28	$Cu(trien)(HN{=}CHC_6H_4O)_2$	163	122	95	39	3.5	1.3	4.2
29	$Zn(cydien)(CH_3COO)_2$	100	97	131	77	3.9	2.8	4.7
30	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	102	124	87	55	4.0	2.1	12.8
31	$Zn(cydien)(C_6H_5COO)_2$	97	133	125	87	4.0	2.7	13.2
32	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	105	97	125	65	3.6	2.3	13.1

Figures 1 and *2* and *Table 2* show the maximal temperature of the exothermic reaction of DGEBA with the chelates to be higher than 130°C. A drop in the hardening temperature of the epoxy oligomer reduces the exothermic effect. On the other hand, a rise in hardening temperature is known to intensify the cure. Therefore, a temperature of 120°C was assumed to be the optimal one for MECP formation.

The time of gel formation and the time for complete cure of the epoxy compounds depend on the chelate dissociation rate, the amino group content in the ligand and the metal type, viz. the cation radius, cation charge, metal coordination number and geometrical configuration of the complex compound. Depending on the hardener structural fragments, the reactivity of the chelates decreases in the order:

Ligand trien > cydien > dien > en

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

Metal $Mn^{4+} > Ni^{2+} > Fe^{3+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+}$

Investigation of the completeness of hardening at 120°C has shown the time corresponding to 98% conversion of epoxy groups and to the attainment of maximal strength of the polymers to be different for various complexes (*Table 2*) and to be maximal for $[Cd(en)_2(H_2NC_6H_4COO)_2]$ (11 h). This time has been used to obtain all the MECPs, in order to provide the equality of synthesis conditions necessary for correct comparison of polymer properties. It has been found that further heating at higher temperatures (140–180°C for 2–6 h) does not increase the polymer strengths.

Properties of MECPs

It follows from the chelate dissociation schemes (6) and (7) that the reaction of an epoxy oligomer with a chelate hardener will proceed by three main mechanisms:

(i) catalytic interaction of metal cation with epoxy groups

(ii) interaction with organic acid anion, and
(iii) interaction with ligand amino groups.

A close consideration of the mechanism of epoxy chelate composition hardening is beyond the scope of the present work, but it should be mentioned that the many pathways of the reaction point to the hardener concentration in the epoxy compounds being of great importance. Theoretically, with a small content of complex in an epoxy chelate system, the concentration of the amino groups will be insufficient, and hence the oligomer–hardener reaction will proceed by the catalytic mechanism. An increase in hardener concentration will cause an increase in the content of amine and anion, and alteration of the reaction mechanism, and therefore a change in the structure and properties of the MECP.

Figures 3 and *4* present the dependence of the properties of MECPs on the content of the complexes, which was studied by considering the examples of DGEBA hardened with $[Cu(en)_2(HOC_6H_4COO)_2]$ and $[Co(dien)(HOC_6H_4COO)_2]$. The results obtained show that the maximal values of the strength, DT and thermal stability correspond to different contents of the chelates in the epoxy compounds. In most cases a decrease in the concentration of the hardeners enhances the heat resistance of the polymers, but an increase in chelate content results in the strength and DT increasing. For example, the minima of ΔM of DGEBA hardened with $[Cu(en)_2(HOC_6H_4COO)_2]$ (*Figure 3*) and $[Co(dien)(HOC_6H_4COO)_2]$ (*Figure 4*) correspond to 20 and 12 mass parts of hardener, but the maxima of σ_t of these polymers correspond to 36 and 20 mass parts respectively.

The maximal values of the strength, DT and heat resistance (the minimal mass loss of polymer after thermal treatment) of MECPs in comparison with well known DGEBA-based polymers are shown in *Table 5*. The introduction of metal cations into the epoxy matrices increases DT up to 163°C (for the chelate $[Cu(trien)(NH{=}CHC_6H_4O)_2]$), σ_c up to 145 MPa ($[Cu(trien)(H_2NC_6H_4COO)_2]$), σ_f up to 147 MPa ($[Cd(dien)(H_2NC_6H_4COO)_2]$) and σ_t up to 100 MPa ($[Cd(cydien)(H_2NC_6H_4COO)_2]$). The copper-containing epoxy polymers exhibit a significant increase in thermal oxidative stability, which becomes comparable with the heat resistance of well known epoxy–anhydride systems (the chelates $[Cu(trien)(HOC_6H_4COO)_2]$, $[Cu(cydien)(HOC_6H_4COO)_2]$ and $[Cu(trien)(CH_3COO)_2]$).

CONCLUSION

An examination of the new chelates of transition metals with aliphatic amines as hardeners of epoxy oligomers has made it possible to determine their application in the production of polymers possessing increased strength and heat resistance.

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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
m	mass of hardener in epoxy compound (g/100 g of DGEBA)
K_a	dissociation constant