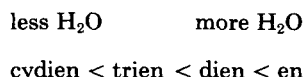# Water Resistance of Metalliferous Epoxy Chelate Polymers

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SYNOPSIS

Epoxy chelate polymers have been produced by hardening of diglycidyl ether of bisphenol-A (DGEBA) with chelates of metals and aliphatic amines, such as ethylene diamine (en), diethylene triamine (dien), triethylene tetramine (trien), and cyanoethylated diethylene triamine (cydien). The influence of structure and quantity of the hardeners on water resistance of the metal-containing polymers has been studied. Water sorption was found to be increased depending on the ligands and independently of temperature in the following series:

less H_2O more H_2O

cydien < trien < dien < en

The influence of anions is determined by ionization constants of corresponding organic acids and depends on temperature. The influence of metal cations on water resistance also depends on temperature. Maximal water resistance can be achieved by hardening of DGEBA with 0.11 mol of chelate per 1 mol of the oligomer. Strengths of the water-resistant epoxy chelate polymers have been determined. The conclusion has been drawn with respect to copper complexes application in high-strength water-resistant polymer production.

INTRODUCTION

Water sorption of epoxy polymers may result in significant deterioration of their properties, in particular, in the sharp decrease of adhesion ability.[1] That is why the investigation of water resistance of new epoxy compositions is of great importance. This point is of high priority in the case of systems containing polar particles, e.g., metal cations that are able to result in a significant change of polymer behavior in humid medium.

Epoxy composition modification by metal-containing admixtures such as chromates of lead or strontium, dithiophosphates, metals naphthionates, titanium–organic compounds,[2–8] or the hardening of epoxy oligomers with tin halides,[9–11] salts of carboxylic acids,[12–21] and phthalocyanines[22–26] is known to result in an increase in water resistance. The application of mixed-ligand chelates of iron, zinc, tin, or aluminum as the hardeners allows the curing to be conducted under water.[27–30]

The present work deals with the investigation of the water-resisting property of new metalliferous epoxy chelate polymers, i.e., bisphenol A-based epoxy oligomers hardened with mixed-ligand complexes of salts of metals and organic acids and aliphatic amines.[31–34]

EXPERIMENTAL

Materials

Diglycidyl ether of bis-phenol A (DGEBA), ED-22 grade, with an epoxy equivalent weight of 170–180, made in the USSR, was used as an epoxy oligomer. The salts of metals and organic acids were used as well as the aliphatic amines: ethylene diamine (en), diethylene triamine (dien), triethylene tetramine (trien), and bis-N,N'-(β-cyanoethyl)-diethylene triamine (cydien).

Methods

Gel time was determined by a Reotest-2 instrument. The time of gel formation was assumed to be the

time corresponding to composition viscosity η, for which $\lg \eta = 6$ (mPa s).

The properties of complex hardeners and polymers were investigated with the thermal analyzer TA 3000 (METTLER) containing a differential scanning calorimeter and a thermogravimetric cell.

Water absorption and strength of polymers were determined in accordance with the standards given in Ref. 35. Water absorption was determined on specimens with dimensions $40 \times 40 \times 2$ mm^3.
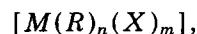
Synthesis

Complex hardeners were synthesized by direct combining of the salts with the amines used in equimolar proportions while stirring for 2–4 h at the melting points of the chelates. The compounds produced were identified by elemental analysis, and infrared spectroscopy confirmed the coordinating of the ligands with the metals through the nitrogen atom in amino groups. The properties of the hardeners are in Table I.

Metalliferous epoxy chelate polymers were made by the casting of fluid compositions into metal molds and were hardened for 11 h at 120°C.

RESULTS AND DISCUSSION

The properties of the epoxy chelate metalliferous polymers are in Table II. Since strength depends on the quantity of the hardener, the indicated indices are maximal attainable, the quantity of hardener for each of them being different. Water absorption of the polymers under different conditions as a function of hardener content is in Figures 1–8. Table II shows the values of maximal water resistance corresponding to minimal water absorption. In general terms, the structure of chelate hardener can be presented by the formula

$$[M(R)_n(X)_m],$$

where M is a metal; R, a ligand; X, an anion, and n and m, whole numbers. For this reason, let us an-

Table I   Properties of Chelate Hardeners

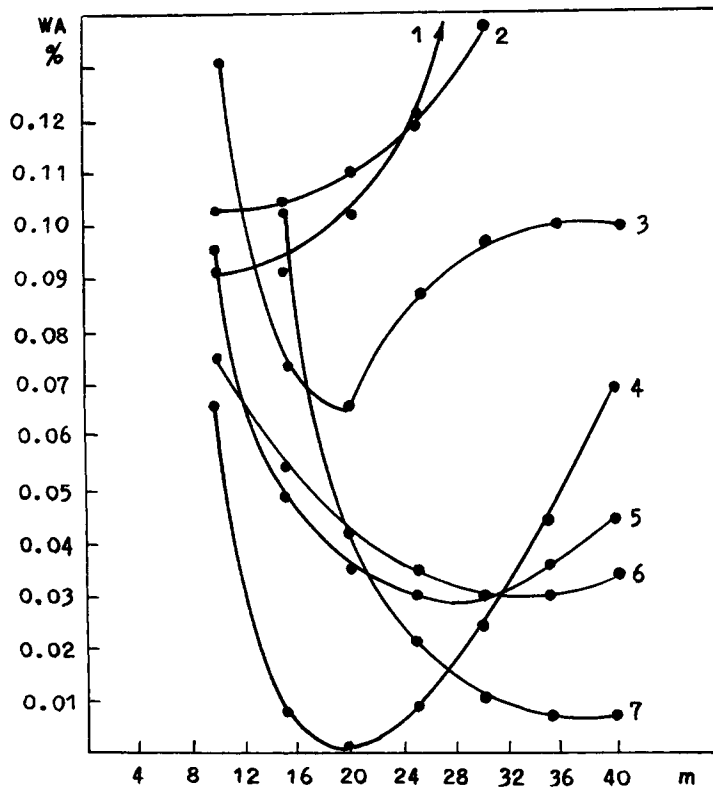| NN 1	Hardener (without Water of Crystallization) 2	Molecular Weight 3	Melting Point (°C) 4	Gel Time of DGEBA at 95°C (Min) 5	Curing Time of DGEBA at 120°C (Min) 6
1	Cu(en)$_2$(HOC$_6$H$_4$COO)$_2$	457.9	142	645	280
2	Cu(dien)(HOC$_6$H$_4$COO)$_2$	440.9	192	555	241
3	Cu(trien)(HOC$_6$H$_4$COO)$_2$	484.0	139	230	100
4	Cu(cydien)(HOC$_6$H$_4$COO)$_2$	546.9	125	492	214
5	Zn(trien)(HOC$_6$H$_4$COO)$_2$	521.9	117	221	96
6	Zn(cydien)(HOC$_6$H$_4$COO)$_2$	584.8	35	451	196
7	Co(trien)(HOC$_6$H$_4$COO)$_2$	497.4	112	451	196
8	Ni(trien)(HOC$_6$H$_4$COO)$_2$	551.3	113	180	80
9	Fe(trien)(HOC$_6$H$_4$COO)$_3$	613.5	65	205	90
10	MnO(trien)(HOC$_6$H$_4$COO)$_2$	491.4	117	148	65
11	Co(cydien)(HOC$_6$H$_4$COO)$_2$	560.3	90	942	410
12	Ni(cydien)(HOC$_6$H$_4$COO)$_2$	614.1	68	376	160
13	Fe(cydien)(HOC$_6$H$_4$COO)$_3$	676.3	47	428	186
14	Cu(trien)(HN=CHC$_6$H$_4$O)$_2$	450.1	80	70	31
15	Co(dien)(CH=N(CH$_2$)C$_6$H$_4$O)$_2$	428.4	228	35	15
16	Co(dien)(HOC$_6$H$_4$COO)$_2$	454.4	153	726	316
17	Cd(en)$_2$(H$_2$NC$_6$H$_4$COO)$_2$	504.9	135	1500	650
18	Cd(dien)(H$_2$NC$_6$H$_4$COO)$_2$	487.8	113	1200	520
19	Cd(trien)(H$_2$NC$_6$H$_4$COO)$_2$	530.9	125	450	196
20	Cd(cydien)(H$_2$NC$_6$H$_4$COO)$_2$	593.8	92	525	228
21	Cu(trien)(H$_2$NC$_6$H$_4$COO)$_2$	482.1	123	213	93
22	Zn(cydien)(C$_6$H$_5$COO)$_2$	516.7	94	433	188
23	Cu(trien)(CH$_3$COO)$_2$	345.9	55	215	93
24	Zn(cydien)(CH$_3$COO)$_2$	428.6	Below 20	410	178
25	Zn(cydien)(CH$_2$=C(CH$_3$)COO)$_2$	444.7	Below 20	415	180

Figure 1 Water absorption at 100°C for 0.5 h (*WA*) of the polymer based on DGEBA as a function of hardener content (*m*: mass $p/100$ mass p DGEBA): (1) Zn(cydien)(HOC$_6$H$_4$COO)$_2$; (2) Co(dien)(CH$=$N(CH$_2$)C$_6$H$_4$O)$_2$; (3) Fe(trien) (HOC$_6$H$_4$COO)$_3$; (4) Fe(cydien)(HOC$_6$H$_4$COO)$_3$; (5) MnO(trien)(HOC$_6$H$_4$COO)$_2$; (6) Cu(trien)(HN$=$CHC$_6$H$_4$O)$_2$; (7) Co(cydien)(HOC$_6$H$_4$COO)$_2$.

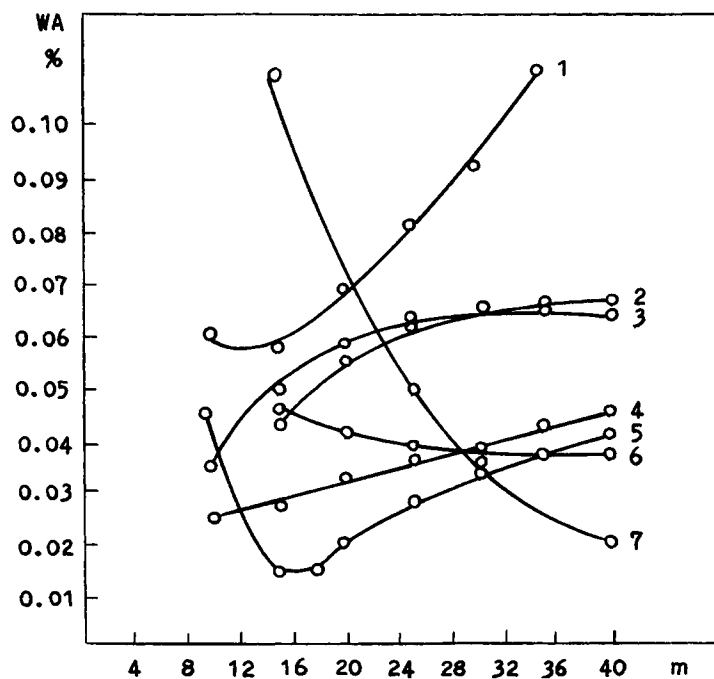**Figure 2** Water absorption at 20°C for 24 h (*WA*) of the polymer based on DGEBA as a function of hardener content (*m*: mass $p/100$ mass p DGEBA): (1) Co(dien)(CH$=$N(CH$_2$)C$_6$H$_4$O)$_2$; (2) Co(cydien)(HOC$_6$H$_4$COO)$_2$; (3) Zn(cydien) (HOC$_6$H$_4$COO)$_2$; (4) Cu(trien)(HN$=$CHC$_6$H$_4$O)$_2$; (5) Fe(cydien)(HOC$_6$H$_4$COO)$_3$; (6) MnO(trien)(HOC$_6$H$_4$COO)$_2$; (7) Fe(trien)(HOC$_6$H$_4$COO)$_3$.

Table II Properties of Epoxy Chelate Polymers Based on DGEBA

Hardener: X = Property Value, m = Hardener Quantity Responding to Property Value (mol per 1 mol of DGEBA) 1		Properties					
		Deflection Temperature (°C) 2	Tensile Strength (MPa) 3	Tensile Modulus (GPa) 4	Elongation at Break (%) 5	Water Absorption (%)	
						At 20°C for 24 h 6	At 100°C for 0.5 h 7
Cu(en)$_2$(HOC$_6$H$_4$COO)$_2$	X:	110	97	3.1	5.0	0.096	0.145
	m:	0.150	0.268	0.150	0.296	0.058	0.058
Cu(dien)(HOC$_6$H$_4$COO)$_2$	X:	100	89	3.3	5.0	0.107	0.170
	m:	0.231	0.269	0.231	0.231	0.078	0.078
Cu(trien)(HOC$_6$H$_4$COO)$_2$	X:	130	65	3.1	3.5	0.052	0.077
	m:	0.170	0.146	0.146	0.146	0.105	0.105
Cu(cydien)(HOC$_6$H$_4$COO)$_2$	X:	115	90	7.6	5.0	0.013	0.065
	m:	0.061	0.218	0.187	0.187	0.061	0.092
Zn(trien)(HOC$_6$H$_4$COO)$_2$	X:	130	92	3.7	4.6	0.034	0.069
	m:	0.228	0.099	0.228	0.099	0.065	0.065
Zn(cydien)(HOC$_6$H$_4$COO)$_2$	X:	130	91	3.4	5.0	0.034	0.092
	m:	0.146	0.116	0.173	0.116	0.058	0.058
Co(trien)(HOC$_6$H$_4$COO)$_2$	X:	108	79	3.4	3.8	0.049	0.044
	m:	0.170	0.102	0.170	0.102	0.068	0.170
Ni(trien)(HOC$_6$H$_4$COO)$_2$	X:	95	55	4.4	2.1	0.078	0.036
	m:	0.092	0.092	0.248	0.153	0.092	0.092
Fe(trien)(HOC$_6$H$_4$COO)$_3$	X:	92	63	3.9	1.8	0.020	0.066
	m:	0.112	0.054	0.221	0.054	0.221	0.112
MnO(trien)(HOC$_6$H$_4$COO)$_2$	X:	110	53	3.1	1.3	0.037	0.030
	m:	0.241	0.068	0.275	0.068	0.275	0.248
Co(cydien)(HOC$_6$H$_4$COO)$_2$	X:	100	53	4.0	3.5	0.041	0.007
	m:	0.153	0.092	0.241	0.153	0.092	0.241
Ni(cydien)(HOC$_6$H$_4$COO)$_2$	X:	92	68	4.4	2.7	0.008	0.006
	m:	0.082	0.054	0.167	0.082	0.088	0.054
Fe(cydien)(HOC$_6$H$_4$COO)$_3$	X:	120	74	3.0	2.2	0.013	0.001
	m:	0.102	0.075	0.201	0.075	0.075	0.102
Cu(trien)(HN=CHC$_6$H$_4$O)$_2$	X:	163	39	3.5	1.3	0.024	0.030
	m:	0.190	0.190	0.228	0.190	0.075	0.228
Co(dien)(CH=N(CH$_2$)C$_6$H$_4$O)$_2$	X:	105	65	3.6	2.3	0.056	0.103
	m:	0.160	0.197	0.119	0.197	0.078	0.119
Co(dien)(HOC$_6$H$_4$COO)$_2$	X:	115	91	3.2	4.8	0.032	0.140
	m:	0.187	0.150	0.150	0.187	0.075	0.150
Cd(en)$_2$(H$_2$NC$_6$H$_4$COO)$_2$	X:	70	68	3.4	1.8	0.032	0.225
	m:	0.201	0.136	0.170	0.170	0.102	0.136
Cd(dien)(H$_2$NC$_6$H$_4$COO)$_2$	X:	103	96	4.2	3.4	0.010	0.097
	m:	0.207	0.207	0.245	0.207	0.068	0.207
Cd(trien)(H$_2$NC$_6$H$_4$COO)$_2$	X:	75	80	6.0	3.2	0.030	0.057
	m:	0.194	0.139	0.129	0.139	0.061	0.061
Cd(cydien)(H$_2$NC$_6$H$_4$COO)$_2$	X:	100	100	4.4	5.0	0.030	0.030
	m:	0.228	0.173	0.116	0.173	0.116	0.085
Cu(trien)(H$_2$NC$_6$H$_4$COO)$_2$	X:	134	88	3.0	2.5	0.045	0.110
	m:	0.163	0.163	0.163	0.163	0.085	0.085
Zn(cydien)(C$_6$H$_5$COO)$_2$	X:	97	87	4.0	2.7	0.028	0.100
	m:	0.197	0.078	0.099	0.099	0.163	0.197
Cu(trien)(CH$_3$COO)$_2$	X:	102	77	3.4	4.0	0.046	0.111
	m:	0.099	0.146	0.146	0.146	0.099	0.099

Table II   (*Continued*)

Hardener: X = Property Value, m = Hardener Quantity Responding to Property Value (mol per 1 mol of DGEBA) 1		Properties					
						Water Absorption (%)	
		Deflection Temperature (°C) 2	Tensile Strength (MPa) 3	Tensile Modulus (GPa) 4	Elongation at Break (%) 5	At 20°C for 24 h 6	At 100°C for 0.5 h 7
Zn(cydien)(CH₃COO)₂	X:	100	77	3.9	2.8	0.019	0.138
	m:	0.173	0.078	0.316	0.119	0.078	0.078
Zn(cydien)(CH₂=C(CH₃)COO)₂	X:	102	55	4.0	2.1	0.028	0.111
	m:	0.190	0.075	0.269	0.075	0.075	0.116
	$\bar{m}$					0.096	0.121
	m_{optimum}					0.110	

alyze the influence of each structural fragment of the chelate molecule (a ligand, an anion, and a cation) on water resistance.

The influence of ligand on water resistance was examined considering the example of the hardeners:

$$[M(R)_n(X)_2],$$

where M = Cu^{2+}, Cd^{2+}; X = $HOC_6H_4COO^-$, $H_2NC_6H_4COO^-$; and R = en (n = 2); dien, trien, cydien (n = 1).

Direct comparison of water-resistance indices presented in Table II does not provide us with unambiguous knowledge of the regularities related to ligand change. For example, in case of application
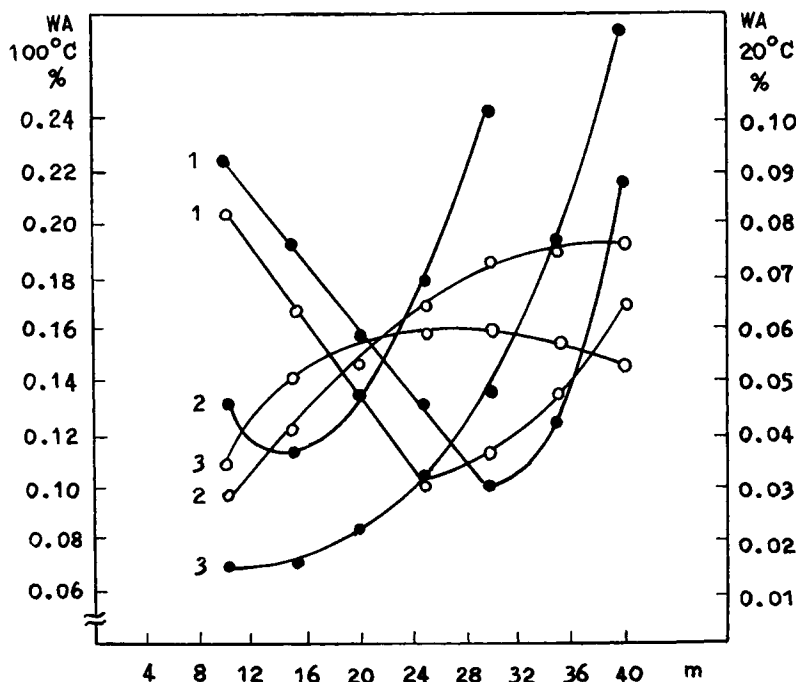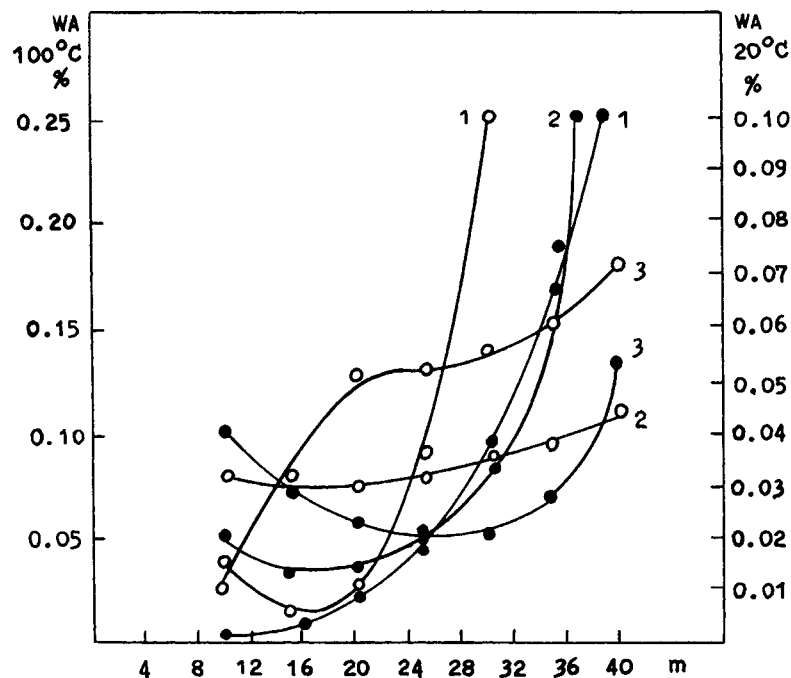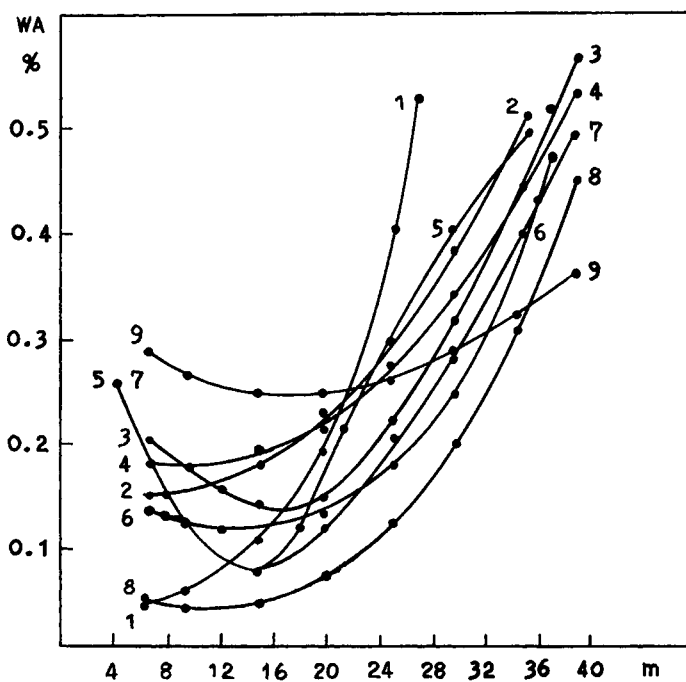

Figure 3   Water absorption at 20°C for (○) 24 h and at 100°C for (●) 0.5 h (*WA*) of the polymer based on DGEBA as a function of hardener content (m: mass p/100 mass p DGEBA): (1) Zn(cydien)(C₆H₅COO)₂; (2) Zn(cydien)(CH₂=C(CH₃)COO)₂; (3) Zn(trien)(HOC₆H₄COO)₂;

Figure 4   Water absorption at 20°C for (○) 24 h and at 100°C for (●) 0.5 h (*WA*) of the polymer based on DGEBA as a function of hardener content (*m*: mass $p/100$ mass p DGEBA): (1) Ni(cydien) (HOC$_6$H$_4$COO)$_2$; (2) Cd(cydien)(H$_2$NC$_6$H$_4$COO)$_2$; (3) Cd(dien)(H$_2$NC$_6$H$_4$COO)$_2$.

Figure 5   Water absorption at 100°C for 0.5 h (*WA*) of the polymer based on DGEBA as a function of hardener content (*m*: mass $p/100$ mass p DGEBA): (1) Cd(trien)(H$_2$NC$_6$H$_4$COO)$_2$; (2) Cu(en)$_2$(HOC$_6$H$_4$COO)$_2$; (3) Co(dien)(HOC$_6$H$_4$COO)$_2$; (4) Cu(dien)(HOC$_6$H$_4$COO)$_2$; (5) Cu(trien)(HOC$_6$H$_4$COO)$_2$; (6) Cu(trien)(H$_2$NC$_6$H$_4$COO)$_2$; (7) Cu(cydien)(HOC$_6$H$_4$COO)$_2$; (8) Ni(trien)(HOC$_6$H$_4$COO)$_2$; (9) Cd(en)$_2$(H$_2$NC$_6$H$_4$COO)$_2$.
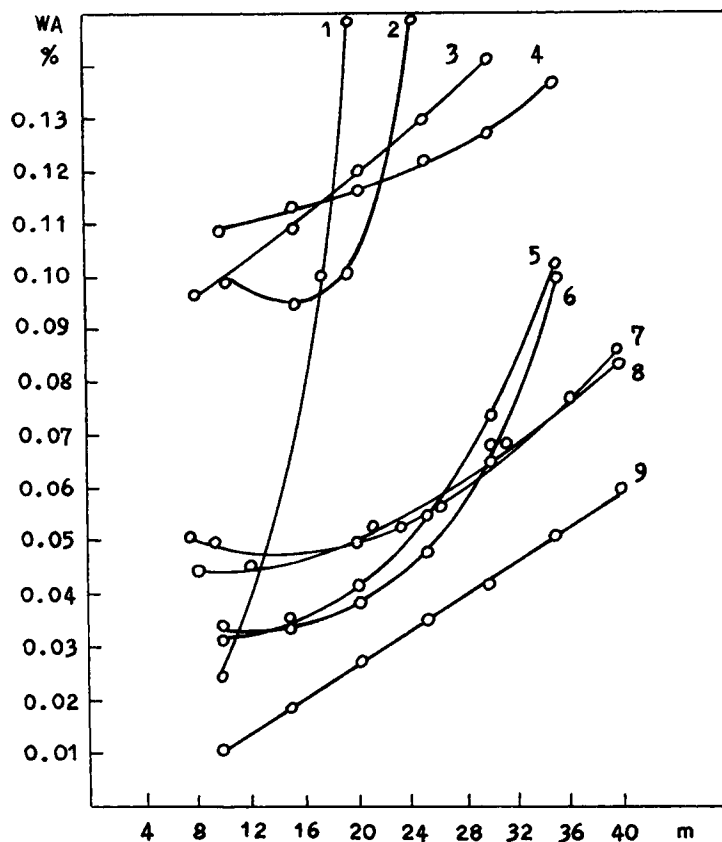
Figure 6 Water absorption at 20°C for 24 h (WA) of the polymer based on DGEBA as a function of hardener content (m: mass $p/100$ mass p DGEBA): (1) $Cd(trien)(H_2NC_6H_4COO)_2$; (2) $Ni(trien)(HOC_6H_4COO)_2$; (3) $Cu(en)_2(HOC_6H_4COO)_2$; (4) $Cu(dien)(HOC_6H_4COO)_2$; (5) $Co(dien)(HOC_6H_4COO)_2$; (6) $Cd(en)_2(H_2NC_6H_4COO)_2$; (7) $Cu(trien)(HOC_6H_4COO)_2$; (8) $Cu(trien)(H_2NC_6H_4COO)_2$; (9) $Cu(cydien)(HOC_6H_4COO)_2$.
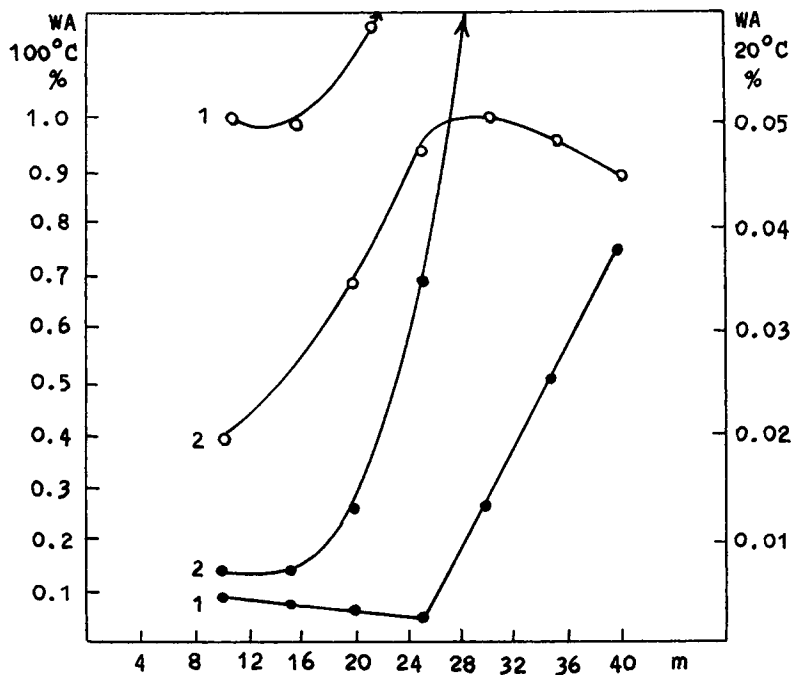

Figure 7 Water absorption at 20°C for (○) 24 h and at 100°C for (●) 0.5 h (WA) of the polymer based on DGEBA as a function of hardener content (m: mass $p/100$ mass p DGEBA): (1) $Co(trien)(HOC_6H_4COO)_2$; (2) $Zn(cydien)(CH_3COO)_2$.
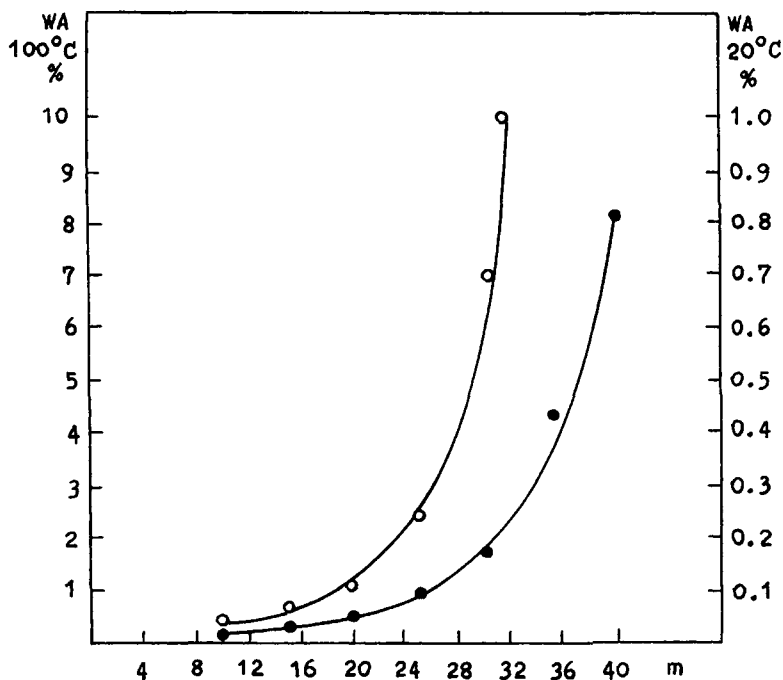
Figure 8 Water absorption at 20°C for (○) 24 h and at 100°C for (●) 0.5 h (WA) of the polymer based on DGEBA as a function of hardener [Cu(trien)(CH$_3$COO)$_2$] content (m: mass p/100 mass p DGEBA).

[Cu(R)$_n$(HOC$_6$H$_4$COO)$_2$], water sorption decreases at 20°C and 100°C in the following series:

more H$_2$O		less H$_2$O
cydien > trien > en > dien		

and for [Cd(R)$_n$(H$_2$NC$_6$H$_4$COO)$_2$], water sorption decreases at 20°C for 24 h and 100°C for 0.5 h in the following series, respectively:

more H$_2$O		less H$_2$O
dien > trien ~	cydien > en
cydien > trien	> dien > en

For this reason, the notion of unitized water absorption (UWA) of the metalliferous polymers has been introduced to solve the problem of the influence of the hardener structural fragments on the water resistance of these polymers. The magnitude of UWA is defined as the arithmetic mean of the water-sorption values of the polymers possessing the common structural fragment under investigation. When the ligand effect is examined, the common structure fragment is considered to be the ligand. For instance, in case of en application, UWA will be determined by the formula

$$\text{UWA} = \frac{WA_1 + WA_2}{2},$$

where WA_1 is the water sorption of DGEBA hardened with the chelate [Cu(en)$_2$(HOC$_6$H$_4$COO)$_2$] and WA_2 is the water sorption of DGEBA hardened with the chelate [Cd(en)$_2$(H$_2$NC$_6$H$_4$COO)$_2$]. When $dien$ is the ligand, UWA will be determined by the same formula, but WA_1 is the water sorption of DGEBA hardened with [Cu(dien)(HOC$_6$H$_4$-COO)$_2$], WA_2 is the water sorption of the oligomer hardened with [Cd(dien)(H$_2$NC$_6$H$_4$COO)$_2$], and so on. As a result, we obtain the following dependence of UWA on the ligand:

UWA (%)	en	dien	trien	cydien
at 100°C for 0.5 h	0.200	0.134	0.067	0.043
at 20°C for 24 h	0.064	0.059	0.041	0.022

i.e., water sorption increases in the following series:

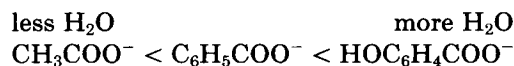| less H$_2$O	more H$_2$O
cydien < trien < dien < en	

The above phenomenon can be explained by the increase of prime amino groups content in the complex hardeners (there are two molecules of ethylene diamine in a molecule of a chelate).

The influence of anion on water resistance of the epoxy chelate polymers was investigated considering the example of the hardeners:
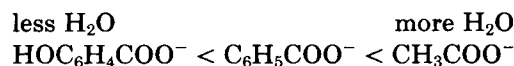
$$[M(R)(X)_2],$$

where $M = Cu^{2+}$, Zn^{2+}; R = trien, cydien; and X = CH_3COO^-, $C_6H_5COO^-$, $H_2NC_6H_4COO^-$, $HOC_6H_4COO^-$, $HN = CHC_6H_4O^-$, $CH_2 = C(CH_3)COO^-$.

The dependence of UWA on anion has the following form:

UWA (%)	CH_3COO^-	$C_6H_5COO^-$	$HOC_6H_4COO^-$
at 100°C for 0.5 h	0.1245	0.1000	0.0430
at 20°C for 24 h	0.0325	0.0380	0.0845

i.e., water sorption increases at 20°C in the following series:

less H_2O more H_2O
$$CH_3COO^- < C_6H_5COO^- < HOC_6H_4COO^-$$

and at 100°C, it increases in the following series:

less H_2O more H_2O
$$HOC_6H_4COO^- < C_6H_5COO^- < CH_3COO^-$$

The comparison of water resistance with ionization constants:

Acid	HOC_6H_4COOH	C_6H_5COOH	$CH_2=C(CH_3)COOH$	CH_3COOH	$H_2NC_6H_4COOH$
pK_a	3.0	4.18	4.7	4.75	4.95
UWA (%)					
Zn: 20°C	0.034	0.028	0.028	0.019	
100°C	0.092	0.100	0.111	0.138	
Cu: 20°C	0.052	0.048		0.046	0.045
100°C	0.077	0.100		0.111	0.110

shows that an increase in the ionization constant results in a water-sorption decrease at 20°C, this regularity being inversed at 100°C. With a temperature rise, the anion screening metal atom is eliminated from the coordination sphere and, as a consequence, cation hydration take place. Naturally, hydrolysis of weak acids will proceed more rapidly.

The dependence of water resistance on metal type was studied using the example of the hardeners:
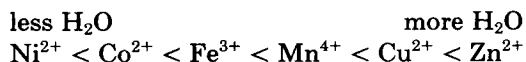
$$[M(R)(HOC_6H_4COO)_n]$$

where $M = Cu^{2+}$, Zn^{2+}, Co^{2+}, Ni^{2+}, MnO^{2+} ($n = 2$), Fe^{3+} ($n = 3$); and R = trien, cydien.

UWA of the metalliferous polymers is the following:

	Zn^{2+}	Co^{2+}	Ni^{2+}	Fe^{3+}	MnO^{2+}	Cu^{2+}
	UWA (%)					
At 100°C for 0.5 h	0.0805	0.0255	0.0210	0.0335	0.0441	0.0710
At 20°C for 24 h	0.0340	0.0450	0.0430	0.0165	0.0497	0.0325

Water sorption increases at 100°C in the following series:

less H_2O more H_2O
$$Ni^{2+} < Co^{2+} < Fe^{3+} < Mn^{4+} < Cu^{2+} < Zn^{2+}$$

Metal cations possessing high positive charges exhibit in the polymer matrix both short-range interaction with covalent bond formation and remote action to form physical bonds (van der Waals bond). Elimination and hydrolysis of the anion screening cation take place in water at 100°C. The interaction between metal and water molecules is determined by the charge and the radius of cation since the energy of attraction between particles is proportional to their dipole moment and inversely proportional to the distance between them. The above fact is confirmed by water-sorption-series changes at 20°C in the following order:

less H$_2$O   more H$_2$O

$$Fe^{3+} < Cu^{2+} < Zn^{2+} < Ni^{2+} < Co^{2+} < Mn^{4+}$$

At the same time, maximal water sorption is considered to be the characteristic of Mn^{4+} that possesses the largest charge, but, in contrast to Fe^{3+}, has two anions as do the other metals. Fe^{3+} screened by three salicylate anions imparts minimal water sorption to the polymers at 20°C.

Low water absorption of the epoxy chelate metalliferous polymers makes it possible to use them as, e.g., water-resistant coatings. There are two important aspects in the industrial application of polymers:

● strength of water-resistant polymers, and
● water-resistance of high-strong polymers.

To solve the problem of the strength of water-resistant polymers, the quantity of hardener corresponding to maximal water resistance needs to be determined (Table II).

According to the data presented in Table II, the average amount of hardener necessary for a polymer with maximal water resistance to be produced has been calculated both at 20°C and 100°C. It accounts for 0.11 mol of chelate per 1 mol of DGEBA.

The strength of DGEBA hardened with 0.11 mol of the chelates is shown in Table III. It is obvious that the majority of the water-resistant metalliferous polymers have high strength: tensile strength up to 89 MPa and deflection temperature up to 140°C.

Table III   Strength of Polymers Based on 1 Mol of DGEBA Hardened with 0.11 Mol of Chelate

NN	Hardener	Deflection Temperature (°C)	Compressive Strength (%)	Tensile Strength (MPa)	Elongation at Break (%)
1	2	3	4	5	6
1	Cu(en)$_2$(HOC$_6$H$_4$COO)$_2$	100	70	73	3.8
2	Cu(dien)(HOC$_6$H$_4$COO)$_2$	45	80	55	1.5
3	Cu(trien)(HOC$_6$H$_4$COO)$_2$	127	112	55	3.0
4	Cu(cydien)(HOC$_6$H$_4$COO)$_2$	112	112	68	3.8
5	Zn(trien)(HOC$_6$H$_4$COO)$_2$	107	121	83	4.0
6	Zn(cydien)(HOC$_6$H$_4$COO)$_2$	113	90	89	4.9
7	Co(trien)(HOC$_6$H$_4$COO)$_2$	100	120	70	1.8
8	Ni(trien)(HOC$_6$H$_4$COO)$_2$	93	102	55	2.0
9	Fe(trien)(HOC$_6$H$_4$COO)$_3$	90	124	55	1.3
10	MnO(trien)(HOC$_6$H$_4$COO)$_2$	85	127	39	1.0
11	Co(cydien)(HOC$_6$H$_4$COO)$_2$	70	123	54	1.2
12	Ni(cydien)(HOC$_6$H$_4$COO)$_2$	90	118	63	1.8
13	Fe(cydien)(HOC$_6$H$_4$COO)$_3$	120	115	62	1.9
14	Cu(trien)(NH=CHC$_6$H$_4$O)$_2$	90	119	34	1.2
15	Co(dien)(CH=N(CH$_2$)C$_6$H$_4$O)$_2$	50	95	61	1.8
16	Co(dien)(HOC$_6$H$_4$COO)$_2$	55	90	75	3.8
17	Cd(en)$_2$(H$_2$NC$_6$H$_4$COO)$_2$	63	122	58	1.0
18	Cd(dien)(H$_2$NC$_6$H$_4$COO)$_2$	77	134	65	1.8
19	Cd(trien)(H$_2$NC$_6$H$_4$COO)$_2$	40	90	73	3.2
20	Cd(cydien)(H$_2$NC$_6$H$_4$COO)$_2$	58	45	—	—
21	Cu(trien)(H$_2$NC$_6$H$_4$COO)$_2$	126	120	75	2.2
22	Zn(cydien)(C$_6$H$_5$COO)$_2$	62	132	85	2.7
23	Cu(trien)(CH$_3$COO)$_2$	103	82	77	4.0
24	Zn(cydien)(CH$_3$COO)$_2$	82	95	75	2.8
25	Zn(cydien)(CH$_2$=C(CH$_3$)COO)$_2$	70	107	41	1.7

The most useful hardeners are considered to be the chelates based on trien, cydien, salicylates, and anthranylates of metals (Table I), with maximal water resistance combined with high deflection temperature and strength being caused by copper complexes (Table III).

Consideration of the problem of water resistance of the polymers possessing maximal strength show that enhanced strength can be obtained by using more hardener than in the case of optimal water-resistance achievement. A hardener content increase is followed by a content increase of polar groups and ions in polymer matrix and, hence, by a water resistance decrease.

REFERENCES

1. M. G. McMaster and S. D. Soane, *IEEE Trans. Compon. Hybrids Manuf. Technol.*, **12**(3), 373–386 (1989).
2. H. Kazufumi, Jpn. Pat. 63-142,022 (1988).
3. Toyota Central Research & Development Lab., Inc., Jpn. Pat. 60-51,712 (1985).
4. H. Naomichi, A. Tatenobu, T. Tetsuo, and S. Wataru, Jpn. Pat. 61-113,611 (1986).
5. A. F. Nikolaev, M. S. Trizno, L. V. Sidoryuk, and Z. S. Kerimbaeva, USSR Inventor's Certificate 439,502 (1975).
6. K. A. Torossian, M. Markovitz, and F. E. Cox, U.S. Pat. 4,692,499 (1987).
7. S. Shigeyuki, M. Mitsumasa, Sh. Toru, K. Yoshitsugu, T. Minoru, and K. Torio, Jpn. Pat. 61-272,262 (1986).
8. N. Kota, Yo. Yasuhiro, M. Masashi, F. Shunichi, and M. Azuma, Jpn. Pat. 61-204,220 (1987).
9. H. Ch. Yun, U. Kazuo, and T. Hisanori, U.S. Pat. 3,513,221 (1970).
10. Minnesota Mining & Manufg. Co., Br. Pat. 1,011,284 (1965).
11. A. Heslinga and P. J. Napjus, Br. Pat. 1,297,455 (1972).
12. H. Starck and F. Schlender, U.S. Pat. 2,801,228 (1957).
13. Ch. M. Andrews, Ger. Pat. 2,659,014 (1977).
14. U. Reeh and H. Denk, Ger. Pat. 3,016,097 (1981).
15. Sh. Kyoichi and G. Koichi, Jpn. Pat. 51-21,838 (1976).
16. S. Yoshikazu and G. Koichi, Jpn. Pat. 51-37,199 (1976).
17. G. Koichi, Jpn. Pat. 52-1,960 (1977).
18. I. Kyoichi and K. Hiroshi, Jpn. Pat. 55-50,504 (1980).
19. M. Taizo, I. Tamio, and N. Seiji, Jpn. Pat. 58-13,591 (1983).
20. Shin-Etsu Chemical Ind. Co., Ltd., Jpn. Pat. 62-42,927 (1987).
21. M. Sumia, S. Kenshi, and K. Shigeru, Jpn. Pat. 63-17,925 (1988).
22. H. L. Parry, U.S. Pat. 3,301,814 (1967).
23. J. V. Crivelle, U.S. Pat. 4,238,587 (1980).
24. B. N. Achar, G. M. Fohlen, and J. A. Parker, U.S. Pat. 4,537,834 (1985).
25. N. Akio and K. Toru, Jpn. Pat. 63-33,412 (1988).
26. B. N. Achar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci. Polym. Chem. Ed.*, **21**(5), 1505–1516 (1983).
27. H. Masaaki, T. Kazuyoshi, S. Hiroharu, T. Hiroshi, and K. Nobuhiro, Jpn. Pat. 60-11,728 (1987).
28. S. Hiroshi and N. Yasusi, U.S. Pat. 3,626,022 (1971).
29. Y. Masahi and I. Isamu, Jpn. Pat. 71-15,032 (1971).
30. I. Nobuo and A. Takumi, Ger. Pat. 2,335,550 (1975).
31. A. V. Kurnoskin and V. A. Lapitsky, in *Abstracts of papers, Vsesoyuznaya Konferentsija Syntez, Struktura, Svoistva Setchatykh Polimerov*, Zvenigorod, 1988, p. 55.
32. A. V. Kurnoskin and V. A. Lapitsky, *Plast. Massy*, **2**, 65–67 (1990).
33. A. V. Kurnoskin and V. A. Lapitsky, in *β-Diketonaty Metallov*, DVGU, Vladivostok, 1991, Vol. 2.
34. A. V. Kurnoskin, V. A. Lapitsky, and T. P. Malikova, *Steklyannye Volokna Stekloplastiki*, **1**, 15–20 (1990).
35. H. Lee and K. Neville. *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 6, pp. 22–44.