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A. V. Kurnoskin[a]
[a] Scientific Productive Unit "Stekloplastic" Kryukovo, Moscow, Russia

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APPLICATION OF METALLIFEROUS EPOXY CHELATE POLYMERS FOR COMPOSITE PRODUCTION

A. V. KURNOSKIN

Scientific Productive Unit
"Stekloplastic"
Kryukovo, Moscow, Russia

ABSTRACT

Based on the "theory of solidity" of glass reinforced plastics (GRP), the dependence of the mechanical strength of composites containing E-glass (%: 54.0 SiO_2, 17.5 CaO, 14.0 Al_2O_3, 8.0 B_2O_3, 4.5 MgO, 0.6 K_2O, 0.2 Fe_2O_3, 0.1 F_2) reinforcement and metalliferous epoxy chelate polymers (MECP) on the mass of the chelate hardeners produced by the reactions of some organic salts of the transition metals (Cu, Co, Cd, Ni, Zn, Fe, Mn) with aliphatic amines as the ligands has been studied. It has been found that the maximal values of the coefficient of solidity (S) corresponding to the maximal mechanical strength of GRP can be reached when 1 mol diglycidyl ether or Bisphenol-A is cured by 0.14 mol of the hardeners. Analysis of the dependence of GRP strength properties on the structures of chelate hardeners showed a predominant influence of the organic salt anion and, to a lesser extent, the metal cations. To a much lesser degree, the ligands can be explained by the dependence of the adhesional strength of the "polymer–glass" system on the concentration of the polar groups (the anions and metal cations) in the polymer matrix. It has been shown that the dynamics of changing S as a result of the variation of the hardener content in the epoxy compositions is primarily dependent on the metal cation type. The maximal values of S correspond to Zn^{2+} and Cu^{2+}. The values obtained for the dependence of MECP properties on complex hardener structural fragments (anion, cation, and ligand) allows for a preliminary evaluation of the metal chelate structures and epoxy compound compositions necessary to produce GRP with a required set of properties.

INTRODUCTION

The important practical significance of the new metalliferous epoxy chelate polymers (MECP), which have been used to create heat-resistant [1, 2] and high-strength composites able to endure considerable cyclic loading [3], demands further intensive development of MECP chemistry which will undoubtedly be based on theoretical generalization of the existing experimental results.

It was established [1, 2, 4–8] that the hardening of epoxy oligomers [diglycidyl ether of Bisphenol-A (DGEBA), ED-22 grade, with an epoxy equivalent weight of 170–180, made in the USSR] with chelates of the formula

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

where M is a cation of a metal: Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, MnO^{2+}

R is a ligand: ethylene diamine (en), diethylene triamine (dien), triethylene tetramine (trien), cyanoethylated diethylene triamine (cydien) $NC-(-(CH_2)_2-NH)_3-(CH_2)_2-CN$

X is an anion of an organic acid: CH_3COO^-, $C_6H_5COO^-$, $CH_2=C(CH_3)-COO^-$, $HOC_6H_4COO^-$, $H_2NC_6H_4COO^-$, $CH=NHC_6H_4O^-$, $CH=N(CH_2)C_6H_4O^-$

n is the number of the ligands in a complex, 1 or 2

p is the metal valency, 2 or 3

results in obtaining epoxy matrixes containing coordinately bonded metal cations and allows for adjustment in a wide range of polymer properties obtained both by varying the structure of the chelates and by changing their content in the epoxy compounds.

This paper deals with an investigation of the dependence of MECP properties on the structural fragments of the complex hardeners (Eq. 1: metal cation, ligand, and anion) that is important for a preliminary evaluation of the chelate structures and epoxy compound compositions necessary to produce glass reinforced plastics (GRP) with the required set of properties.

EXPERIMENTAL

The materials, methods, and synthesis are described in the previous works of the author [1–8].

The indices of the mechanical strength of MECP were determined in accordance with established standards [9].

RESULTS AND DISCUSSION

Metal-containing epoxy chelate composites and cured polymers have the following advantages:

Simplicity in the synthesis of complex hardeners and epoxy compounds
Long pot lives at 20°C

Low hardening temperatures (80–120°C) and high cure rates (2–6 h) at these temperatures
Elevated deflection temperature (up to 163°C) and mechanical strength (tensile strength up to 100 MPa, elongation at break 5%)
The possibility of changing the MECP properties by variations in the hardener concentration of epoxy compounds
Excellent thermal and chemical resistance
Good electrical properties

Experimental data concerning these MECP properties are detailed in References 1–8.

Examination of the structure of MECP and optimization of epoxy compound compositions depend on the metal-containing hardener concentration. A change in the MECP structure requires determination of the optimum hardener mass corresponding to the maximal strength of GRP. The optimum mechanical strength of the polymer matrix corresponding to the maximal strength of the composite depends on the type and characteristics of the filler. As a model filler, E-glass (%: 54.0 SiO_2, 17.5 CaO, 14.0 Al_2O_3, 8.0 B_2O_3, 4.5 MgO, 0.6 K_2O, 0.2 Fe_2O_3, 0.1 F_2) was chosen, while the optimization of the composition of the epoxy chelate compounds will be realized on the basis of the "theory of the composite solidity" worked out by Roginskii, Kanovich, and Koltunov [10], a summary of which is given below.

The solidity of a reinforced polymer demands continuity of its components, a lack of linkage breaks along the boundaries, and uniformity of the system as a whole.

A composite remains solid until there is a failure due to the discontinuity of the reinforcing elements in reaching the ultimate stress values. If the beginning of failure in a reinforced material is related to polymer discontinuity or to a break in the links along the interface or to the loss of stability of the fibers or layers, then such material is not considered to be solid, and so the strength of the reinforcing elements is incompletely used.

Based on contemporary views of the mechanism of composite destruction, the main parameters affecting composite strength are assumed to be the strength and stiffness (the modulus of elasticity and diameter) of the reinforcement; the modulus of elasticity; deformability; tensile strength and shearing strength of the polymer matrix; and the adhesional strength of the entire system. The compressive strength and shearing strength of the composite were taken to be the output parameters when resolving the "theory of solidity."

The system of the inequalities (Eq. 2) connecting the mechanical properties of the reinforcement and polymer matrix has been obtained after examination of the mechanism of the GRP destruction and analysis of the stressed-strained state of the composites:

$$E_t/E_R \geq 0.064 \qquad \tau_a/\sigma_R \geq 0.040 \qquad (2)$$
$$\sigma_t/\sigma_R \geq 0.060 \qquad \epsilon/\epsilon_R \geq 1.500$$

where E_R = tensile modulus of reinforcing material (fiber)
σ_R = tensile strength of the fiber
ϵ_R = elongation at break of the fiber
τ_a = adhesional strength under shear of GRP

These conditions of solidity (Eq. 2) allow us to define the requirements for the polymer matrix by using known values of the strength indices of a reinforcing material; for example, when E-glass is applied:

	E-glass	Requirements for the polymer
σ_t, MPa	2350	162.5
E_t, GPa	75	4.5
ϵ, %	3.0	4.5
τ_a, MPa	—	100

(3)

Because no known epoxy polymer compositions have the values of indices (Eq. 3), an approximation of these indices to the requirements of system solidity (Eq. 2) has been estimated.

Since the specific contribution of various factors to the composite strength is different and is defined by the coefficient $\overline{\varphi}_i$, the durability of the system is determined by

$$F(\eta_i,\varphi_i) = \sum_i \eta_i\overline{\varphi}_i = S$$

where S is a coefficient of solidity

η_i is a coefficient of the polymer indices compliance with the conditions of solidity (Eq. 2):

$$\eta_E = E/E_{\text{th}}, \qquad \eta_\sigma = \sigma/\sigma_{\text{th}}, \qquad \eta_a = \tau_a/\tau_{a_{\text{th}}}$$

(the subscript "th" denotes the theoretical values of the parameters (Eq. 3) determined from the conditions of solidity)

The total contribution of the adhesional strength of the composite and of the polymer strength is equal to unity:

$$\overline{\varphi}_E + \overline{\varphi}_\sigma + \overline{\varphi}_a = 1$$

The values of the coefficients for each parameter are

$$\overline{\varphi}_E = 0.13, \qquad \overline{\varphi}_\sigma = 0.25, \qquad \overline{\varphi}_a = 0.62$$

The values of the coefficients of the polymer indices in compliance with the conditions of solidity are

$$\eta_E = \frac{E_t}{E_{t_{\text{th}}}} = \frac{E_t}{4500}\left(\frac{\text{MPa}}{\text{MPa}}\right)$$

$$\eta_\sigma = \frac{\sigma_t}{\sigma_{t_{\text{th}}}} = \frac{\sigma_t}{162.5}\left(\frac{\text{MPa}}{\text{MPa}}\right)$$

$$\eta_a = \frac{\tau_a}{\tau_{a_{\text{th}}}} = \frac{0.6\sigma_t}{\tau_{a_{\text{th}}}} = \frac{0.6\sigma_t}{100}\left(\frac{\text{MPa}}{\text{MPa}}\right)$$

Thus, the formula for the calculation of the coefficient of solidity is

$$S = \sum_i \eta_i \bar{\varphi}_i = 0.13 \frac{E_t}{4500} + 0.25 \frac{\sigma_t}{162.5} + 0.62 \frac{\sigma_t 0.6}{100}$$

if $E_t \leq 4500$ MPa. If $E_t > 4500$ MPa, it is accepted that $\eta_E = 1$.

The coefficient of solidity is a criterion of continuity and, consequently, of the mechanical strength of the composites.

When the strength properties of a chosen polymer completely comply with the conditions of solidity (Eq. 2), then $\eta_i = 1$ and $S = 1$. For real polymers, $S < 1$.

Reference 10 contains a more detailed explanation of the "theory of solidity."

The dependence of the coefficient of solidity on the content of the complex hardeners in DGEBA-based epoxy compounds has been examined by using the values of the mechanical strengths of MECP established earlier [1-8] and the above-stated method of S calculation. Figures 1-5 show that these dependences have extremes. For a metal-free polymer, S changes insignificantly, by 16% (Fig. 5, [(trien)$(HOC_6H_4COOH)_2$]); the introduction of metal cations allows S to change by using different masses of the hardeners from 1.6 to 2.5 times (Fig. 1, [Cu$(en)_2$-$(HOC_6H_4COO)_2$]; Fig. 2, [MnO(trien)$(HOC_6H_4COO)_2$]; Fig. 5, [Zn(cydien)$(C_6H_5$-$COO)_2$]) although in specific cases S changes slightly, by 13 to 23% (Fig. 2, [Ni-(trien)$(HOC_6H_4COO)_2$]; Fig. 5, [Co(dien)$(CH{=}N(CH_2)C_6H_4O)_2$]). The low values of S for epoxy compositions containing [Co(dien)$(CH{=}N(CH_2)C_6H_4O)_2$] (Fig. 5, $S_h = 0.44$) and [Cu(trien)$(CH{=}NHC_6H_4O)_2$] (Fig. 1, $S_h = 0.30$) can be explained

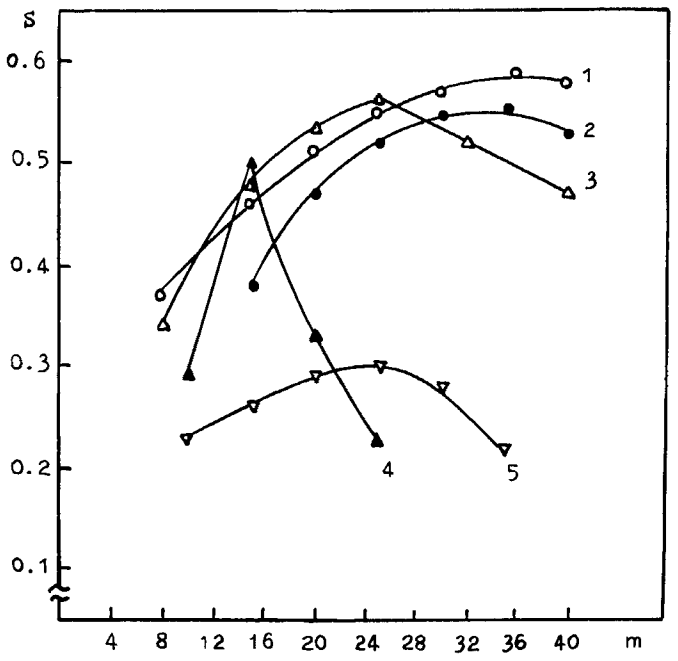

FIG. 1. Dependence of the solidarity coefficient (S) of the polymers based on DGEBA on the hardener content (m = polymer mass per 100 polymer mass of DGEBA). 1: Cu$(en)_2(HOC_6H_4COO)_2$. 2: Cu(dien)$(HOC_6H_4COO)_2$. 3: Cu(trien)$(H_2NC_6H_4COO)_2$. 4: Cu-(trien)$(CH_3COO)_2$. 5: Cu(trien)$(CH{=}NHC_6H_4O)_2$.

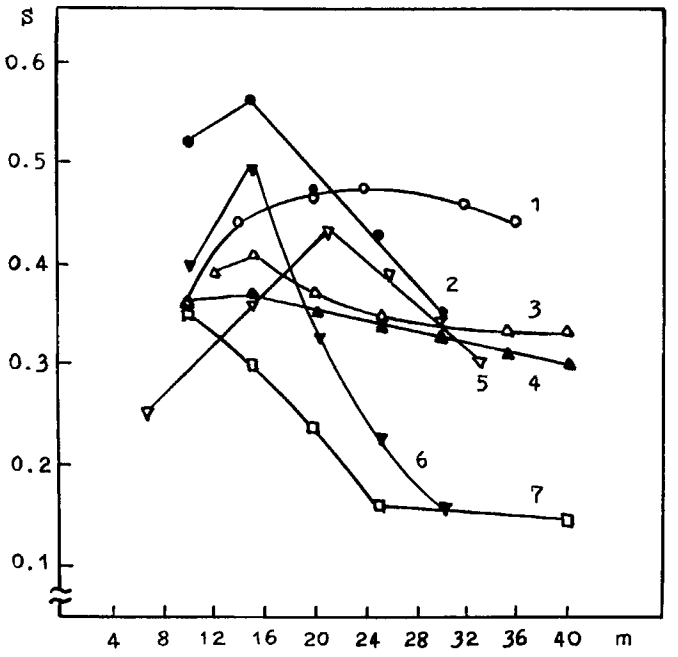

FIG. 2. Dependence of the solidarity coefficient (S) of the polymers based on DGEBA on the hardener content (m = polymer mass per 100 polymer mass of DGEBA). 1: $Cu(trien)_2(HOC_6H_4COO)_2$. 2: $Zn(trien)(HOC_6H_4COO)_2$. 3: $Fe(trien)(HOC_6H_4COO)_3$. 4: $Ni(trien)(HOC_6H_4COO)_2$. 5: $Cu(trien)(HOC_6H_4COO)_2$. 6: $Co(trien)(HOC_6H_4COO)_2$. 7: $MnO(trien)(HOC_6H_4COO)_2$.

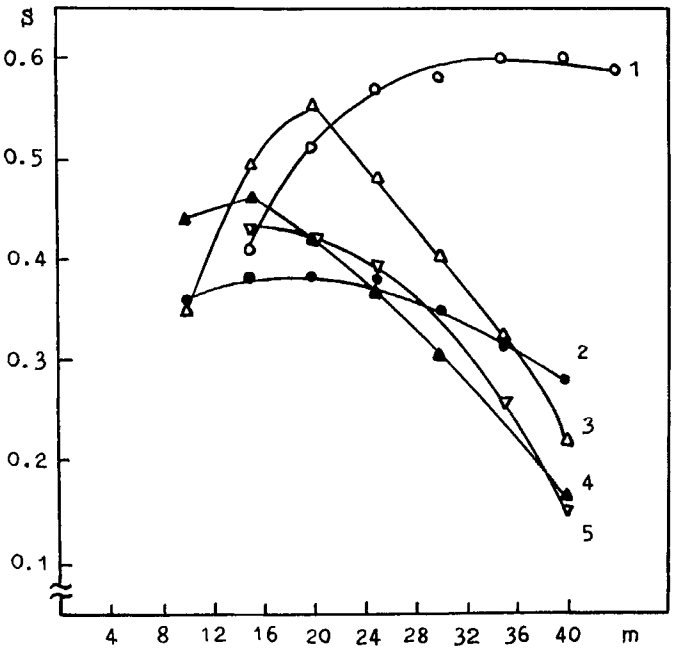

FIG. 3. Dependence of the solidarity coefficient (S) of the polymers based on DGEBA on the hardener content (m = polymer mass per 100 polymer mass of DGEBA). 1: $Cu(cydien)(HOC_6H_4COO)_2$. 2: $Co(cydien)(HOC_6H_4COO)_2$. 3: $Zn(cydien)(HOC_6H_4COO)_2$. 4: $Fe(cydien)(HOC_6H_4COO)_3$. 5: $Ni(cydien)(HOC_6H_4COO)_2$.

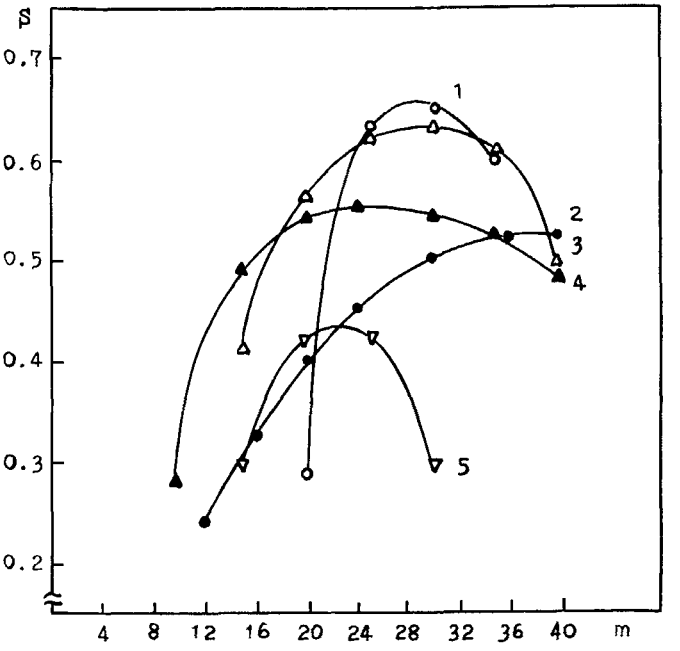

FIG. 4. Dependence of the solidarity coefficient (S) of the polymers based on DGEBA on the hardener content (m = polymer mass per 100 polymer mass of DGEBA). 1: Cd(cydien)$(H_2NC_6H_4COO)_2$. 2: Cd(dien)$_2(H_2NC_6H_4COO)_2$. 3: Cd(dien)$(H_2NC_6H_4COO)_2$. 4: Cd(trien)$(H_2NC_6H_4COO)_2$. 5: Cd(en)$_2(H_2NC_6H_4COO)_2$.

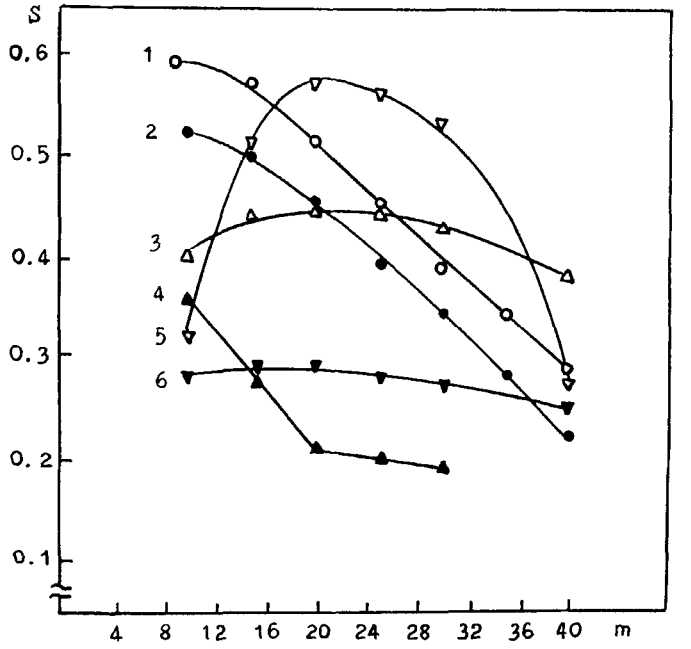

FIG. 5. Dependence of the solidarity coefficient (S) of the polymers based on DGEBA on the hardener content (m = polymer mass per 100 polymer mass of DGEBA). 1: Zn(cydien)$(C_6H_5COO)_2$. 2: Zn(cydien)$(CH_3COO)_2$. 3: Co(dien)$(CH{=}N(CH_2)C_6H_4O)_2$. 4: Zn(cydien)$(CH_2{=}C(CH_3)COO)_2$. 5: Co(dien)$(HOC_6H_4COO)_2$. 6: (trien)$(HOC_6H_4COOH)_2$.

by the structures of these chelates: the screening of the metal cations by the anions decreases the effect of the cations on the epoxy matrixes [6]. In going to anions with decreased volumes, the extent of such screening is reduced, the influence of the cations on the polymer matrix increases, and, as a consequence, S_h increases (Fig. 1, [Cu(trien)$(CH_3COO)_2$], S_h = 0.50; Fig. 5, [Co(dien)$(HOC_6H_4COO)_2$], S_h = 0.57).

The optimization of the compositions of epoxy chelate systems for the production of GRP is shown in Table 1, which presents the quantities of the chelate hardeners corresponding to the maximal values of S_h. The mean value of these quantities (0.14 mol per 1 mol DGEBA) is the optimum. It is lower than the opti-

TABLE 1. Optimization of the Solidity Coefficient of MECP

No.	Hardener	The highest value of the solidity coefficient, S_h	Hardener quantity corresponding to S_h, mol per 1 mol DGEBA
1	$Cu(en)_2(HOC_6H_4COO)_2$	0.59	0.27
2	$Cu(dien)(HOC_6H_4COO)_2$	0.56	0.27
3	$Cu(trien)(HOC_6H_4COO)_2$	0.43	0.15
4	$Cu(trien)_2(HOC_6H_4COO)_2$	0.47	0.13
5	$Cu(cydien)(HOC_6H_4COO)_2$	0.60	0.22
6	$Zn(trien)(HOC_6H_4COO)_2$	0.56	0.10
7	$Zn(cydien)(HOC_6H_4COO)_2$	0.55	0.12
8	$Co(trien)(HOC_6H_4COO)_2$	0.49	0.10
9	$Ni(trien)(HOC_6H_4COO)_2$	0.37	0.09
10	$Fe(trien)(HOC_6H_4COO)_3$	0.41	0.08
11	$MnO(trien)(HOC_6H_4COO)_2$	0.36	0.07
12	$Co(cydien)(HOC_6H_4COO)_2$	0.38	0.12
13	$Ni(cydien)(HOC_6H_4COO)_2$	0.43	0.08
14	$Fe(cydien)(HOC_6H_4COO)_3$	0.46	0.08
15	$Cu(trien)(CH{=}NHC_6H_4O)_2$	0.30	0.19
16	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	0.44	0.16
17	$Co(dien)(HOC_6H_4COO)_2$	0.57	0.15
18	$Cd(en)_2(H_2NC_6H_4COO)_2$	0.43	0.16
19	$Cd(dien)_2(H_2NC_6H_4COO)_2$	0.52	0.21
20	$Cd(dien)(H_2NC_6H_4COO)_2$	0.63	0.21
21	$Cd(trien)(H_2NC_6H_4COO)_2$	0.55	0.15
22	$Cd(cydien)(H_2NC_6H_4COO)_2$	0.65	0.17
23	$Cu(trien)(H_2NC_6H_4COO)_2$	0.56	0.18
24	$Zn(cydien)(C_6H_5COO)_2$	0.59	0.06
25	$Cu(trien)(CH_3COO)_2$	0.50	0.15
26	$Zn(cydien)(CH_3COO)_2$	0.52	0.08
27	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	0.36	0.08
	Mean value:		*0.14*

mum concentration of the hardeners necessary to attain the maximal mechanical strength of the epoxy chelate polymer matrixes (0.17 mol [4]).

Investigation of the properties of 1 mol DGEBA hardened with 0.14 mol metal chelates indicates that in this case the decrease of the strength with respect to the maximal values of the strength indices is 1.7 to 26% for certain complexes, and is an average of 11.5% (Tables 2 and 3). This is somewhat less than the decrease of these indices of the cured epoxy compositions containing 0.17 mol of the hardeners (2.5 to 28.7%, on the average 12% [4]). The calculated optimum quantity of chelate hardeners makes it possible to use the calculations for the manufacture and estimation of the properties of the epoxy chelate GRP based on DGEBA and different metal complexes. This shows promise from the viewpoint of increasing the mechanical strength of the composites since S_h of the epoxy chelate polymers reaches very

TABLE 2. Strength of the Polymers Based on 1 mol DGEBA Hardened with 0.14 mol Chelates

No.	Hardener	m, g per 100 g DGEBA	DT, °C	σ_c, MPa	σ_f, MPa	σ_t, MPa	E_f, GPa	E_t, GPa	ϵ, %
1	$Cu(en)_2(HOC_6H_4COO)_2$	19.0	110	85	115	78	3.2	3.1	4.3
2	$Cu(dien)(HOC_6H_4COO)_2$	18.3	75	98	110	68	2.5	2.4	2.7
3	$Cu(trien)(HOC_6H_4COO)_2$	20.0	130	120	115	61	3.0	3.1	3.4
4	$Cu(trien)_2(HOC_6H_4COO)_2$	26.0	142	127	125	72	3.0	3.4	2.6
5	$Cu(cydien)(HOC_6H_4COO)_2$	22.6	105	108	111	79	2.8	7.0	4.8
6	$Zn(trien)(HOC_6H_4COO)_2$	21.6	115	125	123	68	3.4	3.4	2.5
7	$Zn(cydien)(HOC_6H_4COO)_2$	24.3	128	115	132	78	3.8	2.9	3.3
8	$Co(trien)(HOC_6H_4COO)_2$	20.6	108	122	96	39	3.1	3.2	4.0
9	$Ni(trien)(HOC_6H_4COO)_2$	22.8	88	103	99	53	3.3	3.3	2.1
10	$Fe(trien)(HOC_6H_4COO)_3$	25.4	87	128	79	48	3.5	3.1	1.1
11	$MnO(trien)(HOC_6H_4COO)_2$	20.3	95	128	48	30	3.1	2.8	0.8
12	$Co(cydien)(HOC_6H_4COO)_2$	23.2	93	124	114	51	3.1	3.8	3.4
13	$Ni(cydien)(HOC_6H_4COO)_2$	25.4	92	117	115	54	3.1	3.6	1.5
14	$Fe(cydien)(HOC_6H_4COO)_3$	28.0	110	123	55	48	3.5	2.8	1.5
15	$Cu(trien)(CH{=}NHC_6H_4O)_2$	18.6	120	114	82	37	3.1	2.8	1.2
16	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	17.7	95	95	121	64	3.7	3.5	2.0
17	$Co(dien)(HOC_6H_4COO)_2$	18.8	90	98	126	89	3.5	3.2	4.4
18	$Cd(en)_2(H_2NC_6H_4COO)_2$	20.9	68	123	121	68	4.5	2.5	1.7
19	$Cd(dien)_2(H_2NC_6H_4COO)_2$	24.5	107	129	103	67	3.4	3.3	1.6
20	$Cd(dien)(H_2NC_6H_4COO)_2$	20.2	89	136	130	86	2.9	3.7	2.5
21	$Cd(trien)(H_2NC_6H_4COO)_2$	22.0	61	98	96	80	3.0	6.0	3.2
22	$Cd(cydien)(H_2NC_6H_4COO)_2$	24.6	75	98	130	95	3.0	3.9	4.6
23	$Cu(trien)(H_2NC_6H_4COO)_2$	20.0	132	135	119	85	3.0	3.0	2.4
24	$Zn(cydien)(C_6H_5COO)_2$	21.4	79	125	125	76	4.2	3.2	2.1
25	$Cu(trien)(CH_3COO)_2$	14.3	98	91	130	77	2.7	3.4	4.0
26	$Zn(cydien)(CH_3COO)_2$	17.7	95	95	127	70	3.6	3.4	2.2
27	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	18.4	87	107	83	32	2.8	2.5	1.3

TABLE 3. The Decrease of the Strength and S of MECP in Comparison with the Maximal Values When 0.14 mol Chelates per 1 mol DGEBA Are Used

No.	Hardener	Decrease of the indices, %								
		S	DT	σ_c	σ_f	σ_t	E_f	E_t	ϵ	$\bar{X}_1$
1	$Cu(en)_2(HOC_6H_4COO)_2$	15.3	0	29.2	16.5	19.6	8.6	0	14.0	12.6
2	$Cu(dien)(HOC_6H_4COO)_2$	21.5	25.0	14.8	4.3	23.6	28.6	27.3	46.0	24.2
3	$Cu(trien)(HOC_6H_4COO)_2$	2.4	0	0	0	6.2	3.1	0	2.9	1.7
4	$Cu(trien)_2(HOC_6H_4COO)_2$	0	2.1	7.9	0	0	0	3.0	16.1	4.2
5	$Cu(cydien)(HOC_6H_4COO)_2$	8.4	8.7	10.0	11.8	12.2	20.0	8.0	4.0	10.7
6	$Zn(trien)(HOC_6H_4COO)_2$	16.2	11.5	2.2	7.5	26.2	0	8.1	45.7	14.4
7	$Zn(cydien)(HOC_6H_4COO)_2$	11.0	1.6	11.5	9.0	14.4	7.3	14.7	34.0	13.2
8	$Co(trien)(HOC_6H_4COO)_2$	38.9	0	0	26.2	51.3	11.4	5.9	12.8	15.4
9	$Ni(trien)(HOC_6H_4COO)_2$	5.5	7.4	12.0	9.3	3.6	19.5	25.0	0	11.0
10	$Fe(trien)(HOC_6H_4COO)_3$	17.2	5.6	2.3	5.9	23.8	16.7	20.5	38.9	16.2
11	$MnO(trien)(HOC_6H_4COO)_2$	33.3	13.6	0	7.4	43.4	24.4	9.7	38.5	19.6
12	$Co(cydien)(HOC_6H_4COO)_2$	0	7.0	1.6	2.6	3.7	8.8	5.0	2.9	4.5
13	$Ni(cydien)(HOC_6H_4COO)_2$	9.4	0	5.8	8.0	20.3	13.9	18.2	44.4	15.8
14	$Fe(cydien)(HOC_6H_4COO)_3$	28.4	8.3	1.6	50.9	35.1	5.6	6.7	31.8	20.0
15	$Cu(trien)(CH{=}NHC_6H_4O)_2$	6.8	26.4	6.6	13.7	5.1	6.1	20.0	7.7	12.2
16	$Co(dien)(CH{=}N(CH_2)C_6H_4O)_2$	0	9.5	2.1	3.2	1.5	2.6	2.7	13.0	4.9
17	$Co(dien)(HOC_6H_4COO)_2$	1.9	21.7	10.1	9.4	2.2	5.4	0	8.3	8.2
18	$Cd(en)_2(H_2NC_6H_4COO)_2$	0	2.9	1.6	1.6	0	0	26.5	5.6	5.5
19	$Cd(dien)_2(H_2NC_6H_4COO)_2$	11.6	7.0	0.8	12.1	17.1	17.1	10.8	19.0	12.0
20	$Cd(dien)(H_2NC_6H_4COO)_2$	12.1	13.5	0.7	11.6	10.3	14.7	11.9	26.5	12.7
21	$Cd(trien)(H_2NC_6H_4COO)_2$	0	18.9	0	0	0	0	0	0	2.7
22	$Cd(cydien)(H_2NC_6H_4COO)_2$	4.7	26.5	21.0	5.8	5.0	3.2	10.3	8.0	11.4
23	$Cu(trien)(H_2NC_6H_4COO)_2$	5.5	1.5	6.8	2.4	3.4	0	0	4.0	2.6
24	$Zn(cydien)(C_6H_5COO)_2$	18.2	18.8	6.0	0	12.5	6.7	20.0	21.4	12.2
25	$Cu(trien)(CH_3COO)_2$	0	3.8	31.8	0	0	19.5	0	0	7.9
26	$Zn(cydien)(CH_3COO)_2$	7.8	5.0	2.1	3.0	9.1	0	13.2	20.7	7.6
27	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	33.3	15.0	13.7	4.5	41.8	31.7	37.5	38.1	26.0
	$\bar{X}_2$	*11.5*	9.7	7.5	8.4	14.5	10.2	11.3	18.7	*11.5*

high values (up to 0.59–0.65, Table 1), exceeding the S values of epoxy compounds containing well-known hardeners (Table 4). The high values of S account for the high strength of the epoxy chelate GRP at cyclic dynamic loading caused by the increase of the composite system energy capacity in virtue of heavy metal ion introduction [11] that has been used in industry for the manufacture of composite springs [3].

Table 5 contains the highest (S_h) and the smallest (S_s) values of the coefficients of solidity and those corresponding to the use of 0.14 mol chelates per 1 mol DGEBA ($S_{0.14}$) and the coefficients of influence (k_i) of the structural fragments of the complexes (Eq. 1: ligand, anion and cation) on S necessary to analyze the structure of MECP in terms of the influence of the structures of the hardeners on the values of S. It follows from Eq. (4) that when $k_i = 0$, there is no influence of the structural fragments ($S_{max} = S_{min}$). The wider the interval of the values of the coefficients of solidity S_{min}–S_{max}, the higher is the value of k_i and the stronger is the effect of the chelate structure on the solidity of the composites.

It follows from the data of Table 5 that the hardener structural fragments can be arranged in a series according to their influence on S:

	Anion	> Cation	> Ligand
$k_{i_{S_{0.14}}}$	0.89–1.04	0.62–0.92	0.31–0.44
$k_{i_{S_h}}$	0.64–0.87	0.56–0.58	0.40–0.51

The obtained dependence of S on the structures of the complexes confirms the basic importance of the adhesional strength in the system "polymer–glass fiber" which primarily depends on the polar fragments, viz., the anions and metal cations.

The increase of the significance of the anion type in comparison with the metal type in the production of epoxy chelate composites is accounted for the steric arrangement of these structural fragments in the chelate molecules: The anions are in the external sphere of the complexes; therefore, when the anions contact the surface of a glass-filler, they determine the adhesional strength.

A comparison of the coefficients of solidity with the type of the anions (i.e., with the strength of the corresponding organic acids) is made in Fig. 6. The dependence of S on the ionization constants of the acids is different for various complex cations: The maximal values of S correspond to the benzoate anion in case of $[Zn(cydien)]^{2+}$ usage and to the anthranilate if the $[Cu(trien)]^{2+}$ is used.

TABLE 4. Solidity Coefficients of Well-Known Polymers Based on DGEBA [8]

Hardener	σ_t, MPa	E_t, GPa	S
dien	43	3.5	0.33
trien	63	4.0	0.45
m-PDA	56	3.2	0.39
4,4′-DADPS	63	2.5	0.40
MDA	67	3.2	0.45
Phthalic anhydride	84	3.2	0.53

TABLE 5. Influence of the Chelate Hardener Structure on the Solidity Coefficient

No.	Hardener	S			Interval of S, S_{min}–S_{max}, for		Coefficient of influence, $k_{i_S} = \frac{S_{max}}{S_{min}} - 1$ (4), for	
		$S_{0.14}$	S_h	S_s	$S_{0.14}$	S_h	$S_{0.14}$	S_h
		I. The Influence of Ligand						
1	$Cu(en)_2(HOC_6H_4COO)_2$	0.50	0.59	0.37				
	$Cu(dien)(HOC_6H_4COO)_2$	0.44	0.56	0.38				
	$Cu(trien)(HOC_6H_4COO)_2$	0.42	0.43	0.25				
	$Cu(trien)_2(HOC_6H_4COO)_2$	0.47	0.47	0.36				
	$Cu(cydien)(HOC_6H_4COO)_2$	0.55	0.60	0.41	0.42–0.55	0.43–0.60	0.31	0.40
2	$Cd(en)_2(H_2NC_6H_4COO)_2$	0.43	0.43	0.30				
	$Cd(dien)(H_2NC_6H_4COO)_2$	0.55	0.63	0.41				
	$Cd(dien)_2(H_2NC_6H_4COO)_2$	0.46	0.52	0.24				
	$Cd(trien)(H_2NC_6H_4COO)_2$	0.55	0.55	0.28				
	$Cd(cydien)(H_2NC_6H_4COO)_2$	0.62	0.65	0.29	0.43–0.62	0.43–0.65	0.44	0.51

		II. The Influence of Anion						
1	$Cu(trien)(HOC_6H_4COO)_2$	0.42	0.43	0.25				
	$Cu(trien)(H_2NC_6H_4COO)_2$	0.53	0.56	0.34				
	$Cu(trien)(CH{=}NHC_6H_4O)_2$	0.28	0.30	0.22				
	$Cu(trien)(CH_3COO)_2$	0.50	0.50	0.23	0.28–0.53	0.30–0.56	0.89	0.87
2.	$Zn(cydien)(HOC_6H_4COO)_2$	0.49	0.55	0.22				
	$Zn(cydien)(C_6H_5COO)_2$	0.48	0.59	0.29				
	$Zn(cydien)(CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}COO)_2$	0.24	0.36	0.19				
	$Zn(cydien)(CH_3COO)_2$	0.48	0.52	0.22	0.24–0.49	0.36–0.59	1.04	0.64
		III. The Influence of Cation						
1	$Cu(trien)(HOC_6H_4COO)_2$	0.42	0.43	0.25				
	$Zn(trien)(HOC_6H_4COO)_2$	0.46	0.56	0.35				
	$Co(trien)(HOC_6H_4COO)_2$	0.29	0.49	0.15				
	$Ni(trien)(HOC_6H_4COO)_2$	0.34	0.37	0.30				
	$Fe(trien)(HOC_6H_4COO)_3$	0.34	0.41	0.33				
	$MnO(trien)(HOC_6H_4COO)_2$	0.24	0.36	0.15	0.24–0.46	0.36–0.56	0.92	0.56
2	$Cu(cydien)(HOC_6H_4COO)_2$	0.55	0.60	0.41				
	$Zn(cydien)(HOC_6H_4COO)_2$	0.49	0.55	0.22				
	$Co(cydien)(HOC_6H_4COO)_2$	0.38	0.38	0.28				
	$Ni(cydien)(HOC_6H_4COO)_2$	0.38	0.43	0.15				
	$Fe(cydien)(HOC_6H_4COO)_3$	0.34	0.46	0.17	0.34–0.55	0.38–0.60	0.62	0.58

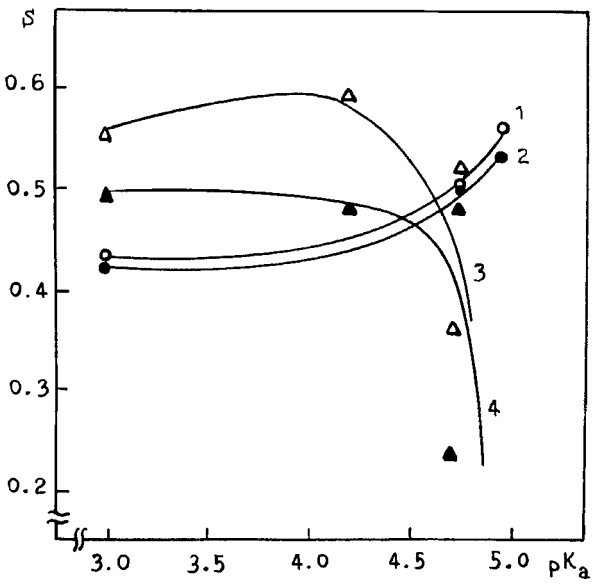

FIG. 6. Dependence of the solidity coefficient (S) of the polymers based on DGEBA on the organic acid ionization constants (K_a): (△, ○) S_h; (▲, ●) $S_{0.14}$. (○, ●: 1, 2) [Cu(trien)$(X)_2$]; X = $HOC_6H_4COO^-$, pK_a = 3.0; CH_3COO^-, pK_a = 4.75; $H_2NC_6H_4COO^-$, pK^a = 4.95. (△, ▲: 3, 4) [Zn(cydien)$(X)_2$]; X = $HOC_6H_4COO^-$, CH_3COO^-, $C_6H_5COO^-$, pK^a = 4.18; $CH_2{=}C(CH_3)COO^-$, pK_a = 4.70.

The entire change of the chelate structure is accompanied with a compensating effect on account of the interaction of the structural fragments of the triple system "metal-ligand-anion" [12]. This effect explains why metal-containing hardeners possessing different structures impart equal values of S_h to the epoxy polymers (Table 1):

$[Cu(en)_2(HOC_6H_4COO)_2]$ and $[Zn(cydien)(C_6H_5COO)_2]$ — S_h = 0.59

$[Cu(trien)(HOC_6H_4COO)_2]$ and $[Cd(en)_2(H_2NC_6H_4COO)_2]$ — S_h = 0.43

$[Zn(cydien)(HOC_6H_4COO)_2]$ and $[Cd(trien)(H_2NC_6H_4COO)_2]$ — S_h = 0.55

$[Cd(dien)_2(H_2NC_6H_4COO)_2]$ and $[Zn(cydien)(CH_3COO)_2]$ — S_h = 0.52

Calculation of the mean values of $S_{0.14}$ and S_h for the hardeners $[M(trien)(HOC_6H_4COO)_2]$ and $[M(cydien)(HOC_6H_4COO)_2]$ makes it possible to arrange the metal cations in the sequence of decreasing S values:

S_h: $Zn^{2+} > Cu^{2+} > Co^{2+} \sim Fe^{3+} > Ni^{2+} > MnO^{2+}$

$S_{0.14}$: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} \sim Fe^{3+} > MnO^{2+}$

Analysis of the dynamics of variation of the coefficient of solidity shows the considerable importance of the metal cation type (Table 6). The rate of the change of S as a result of a change of the hardener mass in the epoxy compositions is determined by differentiation of the function $S = f(m)$:

$$V = dS/dm$$

It was mentioned above that the lack of metal atoms in epoxy polymers (Fig. 5, [(trien)($HOC_6H_4COOH)_2$]) results in an insignificant change of S, the difference between the highest (S_h) and the smallest (S_s) values of the examined interval of the change of the hardener mass in this epoxy composition (Δm) being equal to $\Delta S = 0.04$. To characterize the effect of the hardener structure on V, the mean value of the rate of the change of the coefficient of solidity is used:

$$V = \Delta S/\Delta m$$

where Δm is the change of the chelate content (molar) in the epoxy composition based on 1 mol DGEBA.

By using the mean values of $\overline{V}$ for a series of chelates having one changeable structural fragment, it is possible to calculate the coefficient of the influence $k_{i_{\overline{V}}}$ that defines the extent of the effect of this structural fragment on the dynamics of the S variation. If $k_{i_{\overline{V}}} = 0$, the change of one structural fragment of the hardeners causes no change of $\overline{V}$; the value of the latter is the same for the whole series of chelates. The interval of the values of $\overline{V}_{min}$–$\overline{V}_{max}$ is wider; $k_{i_{\overline{V}}}$ is higher; and the effect of the structural fragments on the rate of S variation is stronger.

The values of $k_{i_{\overline{V}}}$ presented in Table 6 testify to the predominant role of the metal cations in changing the solidity:

	Cation	> Anion	> Ligand
$k_{i_{\overline{V}}}$:	2.31–6.72	1.43–3.03	0.71–2.21

while the extent of importance of the structural fragments is determined by the ratio

$$\frac{k_{i_{\overline{V}(\text{cation})}}}{k_{i_{\overline{V}(\text{anion})}}} \approx \frac{k_{i_{\overline{V}(\text{anion})}}}{k_{i_{\overline{V}(\text{ligand})}}} \approx 1.5\text{–}2.0$$

It was established earlier [4] that a change of the hardener mass in the epoxy compounds results in the formation of polymer matrices having different structures. The type of metal is the most important contributor to the polymerization reaction. A variation in the cation concentration changes the reaction mechanism, the structure and properties of the epoxy matrices, and, consequently, it determines the dynamics of the S variation.

CONCLUSION

Analysis of the structure and attributes of MECP show the promising character of using chelate hardeners to obtain polymers with different properties. Analysis can be accomplished by varying the composition of the metal chelates and the chelate content in the epoxy compounds, and by changing the conditions of the hardening which results in the formation of polymer matrices having different structures due to a change in the predominant mechanism for the polymerization of epoxy oligomers.

On the basis of the values obtained for the dependence of MECP properties on the type of structural fragments of metal complexes and the conditions of hardening, it is possible to make preliminary estimations of the compositions of both the

TABLE 6. Influence of the Chelate Hardener Structure on the Dynamics of the Solidity Coefficient Change

No.	Hardener	$\triangle S = S_h - S_s$ (Table 5)	$\triangle m = \lvert m_h - m_s \rvert$, mol per 1 mol DGEBA	$\overline{V} = \Delta S/\Delta m$, mol^{-1}	Interval of $\overline{V}$, $\overline{V}_{min}$–$\overline{V}_{max}$	Coefficient of the influence, $k_{\overline{V}} = \frac{\overline{V}_{max}}{\overline{V}_{min}} - 1$
		I. The Influence of Ligand				
1	$Cu(en)_2(HOC_6H_4COO)_2$	0.22	0.21	1.05		
	$Cu(dien)(HOC_6H_5COO)_2$	0.18	0.16	1.13		
	$Cu(trien)(HOC_6H_4COO)_2$	0.18	0.10	1.80		
	$Cu(trien)_2(HOC_6H_4COO)_2$	0.11	0.07	1.57		
	$Cu(cydien)(HOC_6H_4COO)_2$	0.19	0.13	1.46	1.05–1.80	0.71
2	$Cd(en)_2(H_2NC_6H_4COO)_2$	0.13	0.05	2.60		
	$Cd(dien)(H_2NC_6H_4COO)_2$	0.22	0.11	2.00		
	$Cd(dien)_2(H_2NC_6H_4COO)_2$	0.28	0.15	1.87		
	$Cd(trien)(H_2NC_6H_4COO)_2$	0.27	0.09	3.00		
	$Cd(cydien)(H_2NC_6H_4COO)_2$	0.36	0.06	6.00	1.87–6.00	2.21

		II. The Influence of Anion				
1	$Cu(trien)(HOC_6H_4COO)_2$	0.18	0.10	1.80		
	$Cu(trien)(H_2NC_6H_4COO)_2$	0.22	0.12	1.83		
	$Cu(trien)(CH{=}NHC_6H_4O)_2$	0.08	0.12	0.67		
	$Cu(trien)(CH_3COO)_2$	0.27	0.10	2.70	0.67–2.70	3.03
2	$Zn(cydien)(HOC_6H_4COO)_2$	0.33	0.12	2.75		
	$Zn(cydien)(C_6H_5COO)_2$	0.30	0.20	1.50		
	$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	0.17	0.15	1.13		
	$Zn(cydien)(CH_3COO)_2$	0.30	0.24	1.25	1.13–2.75	1.43
		III. The Influence of Cation				
1	$Cu(trien)(HOC_6H_4COO)_2$	0.18	0.10	1.80		
	$Zn(trien)(HOC_6H_4COO)_2$	0.21	0.10	2.10		
	$Co(trien)(HOC_6H_4COO)_2$	0.34	0.10	3.40		
	$Ni(trien)(HOC_6H_4COO)_2$	0.07	0.16	0.44		
	$Fe(trien)(HOC_6H_4COO)_3$	0.08	0.14	0.57		
	$MnO(trien)(HOC_6H_4COO)_2$	0.21	0.20	1.05	0.44–3.40	6.72
2	$Cu(cydien)(HOC_6H_4COO)_2$	0.19	0.13	1.46		
	$Zn(cydien)(HOC_6H_4COO)_2$	0.33	0.12	2.75		
	$Co(cydien)(HOC_6H_4COO)_2$	0.10	0.12	0.83		
	$Ni(cydien)(HOC_6H_4COO)_2$	0.28	0.14	2.00		
	$Fe(cydien)(HOC_6H_4COO)_3$	0.29	0.13	2.23	0.83–2.75	2.31
		IV. Without Metal				
	$(trien)(HOC_6H_4COOH)_2$	0.04	0.16	0.25		

chelate hardeners and the epoxy chelate compounds necessary to achieve adequate operational indices of polymers and composites needed for the manufacture of high-strength thermally stable products.

SUMMARY

The establishment of the dependence of complex hardener structure effects on GRP properties on the basis of the "theory of solidity" indicates that the type of organic acid anions is of prime importance for the production of high-strength epoxy chelate composites.

SYMBOLS

For Polymers

σ_c	compressive strength
σ_f	flexural strength
σ_t	tensile strength
E_f	flexural modulus
E_t	tensile modulus
ϵ	elongation at break
DT	deflection temperature
X	index of a polymer (σ, E, ϵ, DT)
m	mass of a hardener in the composition based on DGEBA
Δm	change of the chelate content in the composition based on DGEBA (mol per 1 mol DGEBA)

For Reinforcing Fiber

σ_R	tensile strength
E_R	tensile modulus
ϵ_R	elongation at break

For Composite

τ_a	adhesional strength under shear
S	coefficient of solidity
S_h	the highest value of the solidity coefficient reached in the case of the same hardener used
S_s	the smallest value of the solidity coefficient reached in the case of the same hardener used for the investigated interval of the chelate content change
$S_{0.14}$	value of the solidity coefficient for the polymer based on 1 mol DGEBA hardened with 0.14 mol of a chelate
ΔS	change of the solidity coefficient corresponding to the change of the hardener content in the epoxy composition by the quantity Δm
S_{max}	the maximum solidity coefficient in the series of several chelates possessing two identical and one variable structural fragments

S_{min} the minimum solidity coefficient in the series of several chelates possessing two identical and one variable structural fragments

V rate of the change of the solidity coefficient corresponding to the change of the chelate content in the epoxy composition

$\overline{V}$ the mean value of the rate of change of the solidity coefficient

k_{i_s} coefficient of the influence of the chelate structural fragments on the solidity coefficient

$k_{i_{\overline{V}}}$ coefficient of the influence of the chelate structural fragments on the mean value of the rate of change of the solidity coefficient

REFERENCES

[1] A. V. Kurnoskin, *Polym.-Plast. Technol. Eng.*, *30*(7), 737–750 (1991).
[2] A. V. Kurnoskin, *Polym. Degrad. Stab.*, *37*(1), 51-59 (1992).
[3] A. V. Kurnoskin, M. Z. Kanovich, V. M. Il'in, L. L. Gusev, and V. V. Bekeshko, *Inf. Bull. Khim. Prom.*, *6*, 25–29 (1990).
[4] A. V. Kurnoskin, *J. Macromol. Sci.—Pure Appl. Chem.*, *A29*(6), 483 (1992).
[5] A. V. Kurnoskin, *Polym. Eng. Sci.*, *32*(14), 956-963 (1992).
[6] A. V. Kurnoskin, *Polym.-Plast. Technol. Eng.*, *31*(5&6), 441–450 (1992).
[7] A. V. Kurnoskin, *Ibid.*, *31*(5&6), 505–525 (1992).
[8] A. V. Kurnoskin, *J. Appl. Polym. Sci.*, In Press.
[9] H. Lee and K. Neville, in *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 6, pp. 22–44.
[10] S. L. Roginskii, M. Z. Kanovich, and N. A. Koltunov, in *Vysokoprochniye Stekloplastiki*, Khimiya, Moscow, 1979.
[11] A. V. Kurnoskin and M. Z. Kanovich, *Plast. Massy*, *5*, 54–55 (1991).
[12] V. V. Lukachina, in *Ligand-Ligandnoye Vzaimodeistviye, Ustoichivost Raznoligandnykh Kompleksov*, Naukova Dumka, Kiev, 1988.

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