

# Modification of Epoxide Resins by Functional Oligomers

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## Abstract

*Modification of epoxide resins ED-16 and ED-20 by carboxyl and epoxide polyether and also by glycediluretan oligomer has been investigated; improvement of durable, deformational, adherence and protective properties of ED-20 has been shown. Mixtures of ED-16 and glycediluretan oligomer in various ratio have been recommended as a protective coatings, hermetics, adhesives etc. hardened in natural conditions.*

**Key words:** *epoxide resin, GUO, protective coating.*

## Introduction

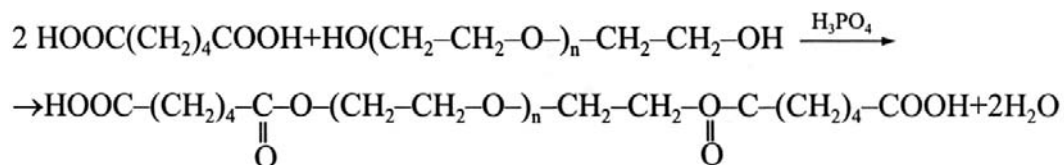
Functional epoxide and phenolphormaldehyde oligomers are widely used as the main components of the protective coatings and other polymer composition materials characterized by high adhesive strength to the surface of various substrates and increased durability to the influence of hostile environments. However, necessity of their hardening under increased temperatures and creating special conditions of covering worsens their exploitation characteristics and makes difficult application of their compositions in atmosphere-climatic conditions [1-3].

Modification of functional epoxide (EO) and phenolphormaldehyde oligomers (PFO) by polyethers, reactive high-molecular oligomers, rubbers etc. gives an opportunity to get plastified and elastified compositions, differing by high impact strength, thermal stability, wear resistance, adhesive strength and so on [4].

## Experimental Part

For modification of epoxide resins ED-16 and ED-20 we have synthesized carboxyl and epoxide oligoether (CEPE) on the basis of industrial polyether-oligooxyethyleneglycol (OEG) (Laprol-2502 with  $\overline{MM}$   $2.0 \div 2.5 \cdot 10^3$ ). The latter was carboxylized by adipic acid in the melting in the  $H_3PO_4$  presence at  $190^\circ C$  temperature in nitrogen atmosphere within 3 hours (beginning of the evolution of first water drops) in ratio with polyether, adipic and phosphorous acid – 88.9 : 10.38 : 0.72 mass.%. The number of COOH groups in reaction

mixture is:  $5.460 \cdot 10^{-10} \%$  – in 60 minutes;  $2.731 \cdot 10^{-10} \%$  – in 180 minutes, i.e. it reduced twice in 3 hours.



Carboxydated polyether (CPE,  $\overline{\text{MM}}$  -  $2.8 \cdot 10^3$ ) was copolycondensated with epoxide resin ED-16 ( $\overline{\text{MM}}$  - 510, ep. number – 16.0) or ED-20 ( $\overline{\text{MM}}$  - 60, ep. number – 20.8) in the presence of triethanolamine catalyst, in ratio of CPE, EO and  $(\text{HOCH}_2\text{CH}_2)_3\text{N}$  correspondingly 92.78 : 5.62 : 1.6 mass.% at  $140^\circ\text{C}$  within 4 hours. Triethanolamine neutralizes  $\text{H}_3\text{PO}_4$  residues and catalyzes opening of epoxide circle.

For determining of polycondensation degree – reduce of epoxide number (ED-16) samples were selected from reaction mass each half an hour and dissolved in toluene mixture: ethanol (40:60). Reducing of epoxide group content in reaction mixture for 60-240 minutes took place from 9.89 to 5.20.

Analyses of OEG, CPE and CEPE IR-spectrums showed presence of zones of absorbance in the range of  $1725\text{-}1750 \text{ cm}^{-1}$ , corresponding to compound ether groups, but application of triethanolamine promoted preserving of hydroxyl ( $3333 \text{ cm}^{-1}$ ) and epoxide ( $1042 \text{ cm}^{-1}$ ) groups in synthesized oligomers (fig.1-3).

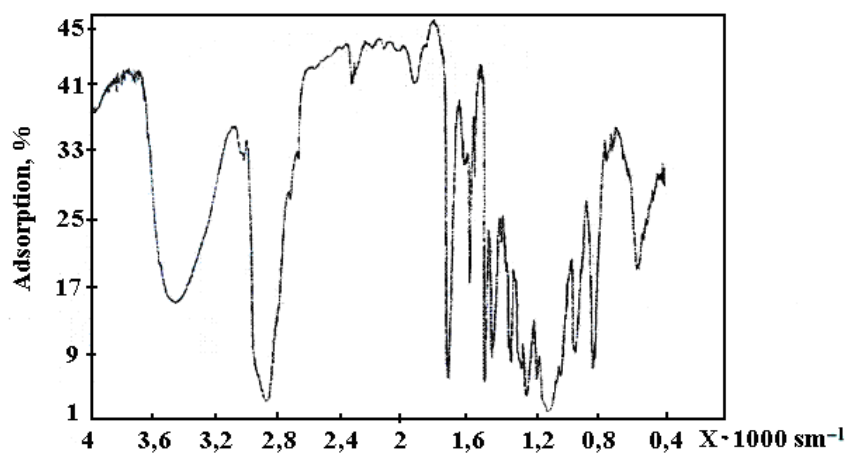


Fig. 1. IR-spectrum of oligooxyethyleneglycol

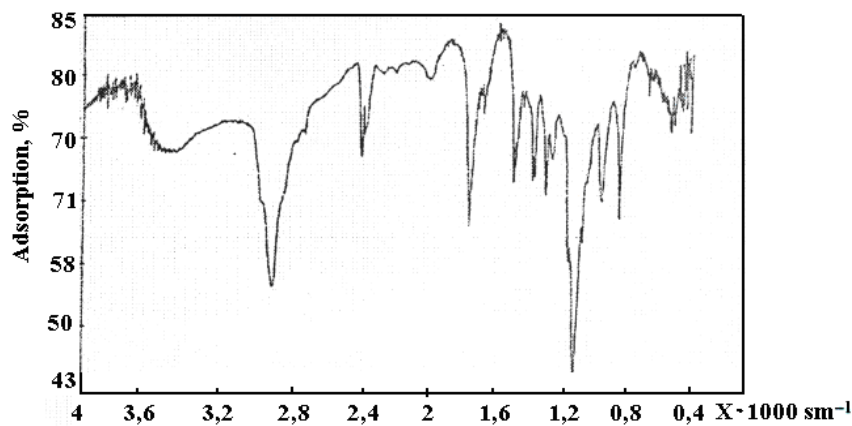


Fig. 2. IR- spectrum of carboxyle adipine acid of oligooxyethyleneglycol

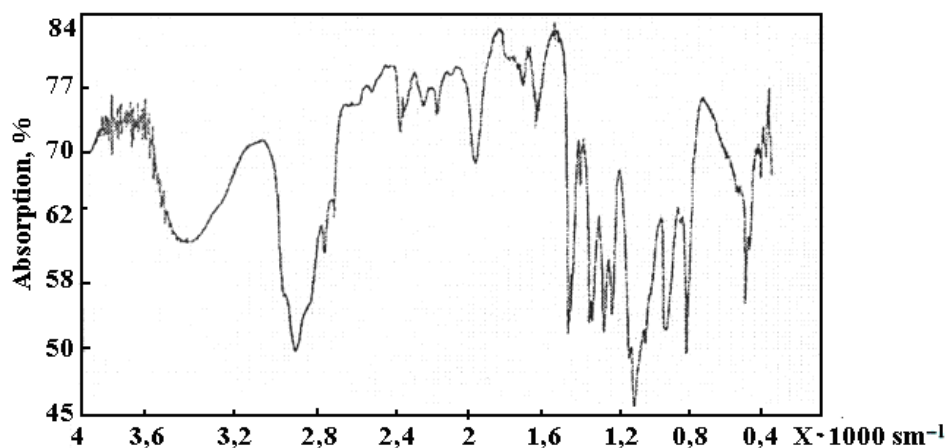


Fig. 3. IR- spectrum of carboxyle and epoxyde oligomer

As a CEPE hardener mixture of metaphenylenediamine (m-PDA) and aniline (1:1) was used. It has been determined that the hardening process proceeds along the final epoxide groups. Analysis of the obtained data shows that according to mechanical, adhesion and impact strength, resistance to hostile surroundings, heat resistant composition ED-16/CEPE (60/40) has improved indices in comparison with ED-16 (table 1).

Improvement of main physico-mechanical characteristics of the composition on the basis of ED-16/CEPE mixture is explained by increasing of  $\overline{MM}$  ED-16 as a result of copolymerization of resin with polyether and possibility of compositions hardening with hardener mixture. As a result of plasticization more elastic cross structure is formed and part of m-PDA enters hardening reaction at the highest temperatures or in exploitation of the compositions and as a result of its stability of physico-mechanical properties of the compositions has been kept for a long time.

Table 1. Physico-mechanical characteristics of ED-16 and CEPE mixture

№	Property indices	Ratio of ED-16 and CEPE, mass.h				
		100/0	60/40	50/50	40/70	30/70
1.	Limit of strength while detachment, MPa	20	32	20	14	8
2.	Limit of strength after heat aging (150°C, 10 h), MPa	9.2	17.1	–	–	–
3.	Relative extension, %	2	17	26	38	71
4.	Relative extension after heat aging (150°C, 10 h), %	16	14	–	–	–
5.	Strength of contact with steel in normal isolation, MPa	14.7	21.0	12.5	9.9	8.0
6.	Flexibility according ShG-1, mm	–	1	1	1	1
7.	Strength in impact U-1A, kg/sm	18	50	50	50	50
8.	Water absorption for 24 h. 25°C, (mass.%)	0.01	0.03	0.08	0.13	0.21
9.	Water absorption while boiling for 24 h., (mass.%)	5.2	4.8	7.4	7.9	8.1
10.	Swelling for 24 h 20°C, (mass.%)					
	H <sub>2</sub> SO <sub>4</sub>	1.10	1.0	1.2	1.5	1.9
	HCl	0.15	0.12	0.2	0.2	0.27
	NaOH	0.45	0.4	0.5	0.55	0.7
	Gasoline "Galosha"	0	0	0.1	0.7	1.2
11.	Vitality, h.	24	>72	>72	>72	>72

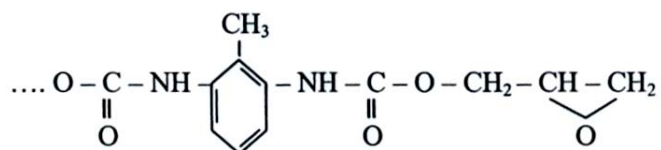
It has been shown that modified CEPE epoxide oligomers have high impact strength: in 25.5% extension on steel plate with 2 mm thickness they maintain 38 cycles during 120 minutes without damaging.

Study of electroisolation properties of the compositions in saline water showed that stability of the transition resistance value in a saturated position within 5000 h. was  $3.1 \cdot 10^7 \text{ Om} \cdot \text{m}^2$ . These data show high value of transition resistance and resistance compositions to the influence of saline water.

Introduction of 50 mass.h quantity zinc oxide into the composition causes the sharp increase of strength limit in the extension till 45MPa and reduce of relative length till 15% which is explained by intensifying influence of filler.

Prehardening of composition at 100°C within 120 min increases strength data of composition a little in comparison with such ones for compositions hardened in natural conditions within 12 hours.

For obtaining elasticized compositions of epoxide resin ED-16 it was modified by flexicohesive, functional, more highmolecular glycidil-urethane oligomer (GUO). GUO was obtained by the reaction: 1 mol polyoxypropyleneglycol with  $\overline{\text{MM}}$  - 5000 (Laprol – 5003), 2 mol toluene – 2.4 or 2.6 diisothianate at 60°C within 30 minutes till exhaustive interaction of hydroxyl groups of polyether 0.05 mol H<sub>2</sub>O and in 10-15 minutes 2 mol glycidol are introduced into the reaction mixture. The reaction continues at 65°C within 1.0÷1.5 hours till full consumption of isothianate groups. The reaction product is olygooxypropylenetriglycidil-urethane, viscous resinous liquid (liquid rubber) with  $\overline{\text{MM}}$  - 5800 and final reaction fragment of the following structure:

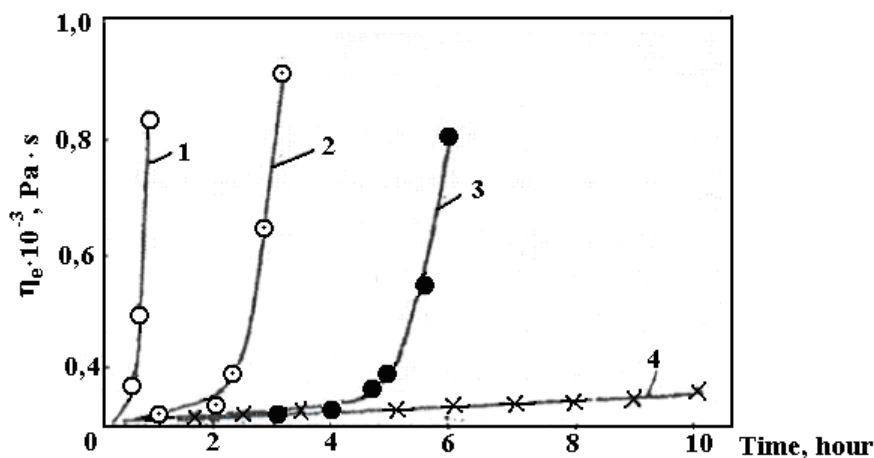


Hardening of GUO was carried out by polyethelenepolyamine (PEPA) taken in equimolar ratio of epoxide and amine groups at 20-30°C within 24 hours. Hardened GUO had the following properties: elasticity according to recoil, % – 60; strength in detachment, MPa – 16.7; relative extension, % – 162; repeated deformation of cycles –  $54 \cdot 10^3$ ; adheous strength, kg.sm – 0.25.

For studying compatibility of ED-16 and GUO a viscosimetric measurement of their mixtures in 75 : 25.50 : 50 and 25 : 75 ratio has been carried out on the device “Reotest-2” at various temperatures, deformation ( $\dot{\gamma}$  from  $0.1667 \text{ c}^{-1}$ ) and shift stress ( $\tau$  from  $2.3 \cdot 10^3 \text{ Pa}$ ). Flow curves prove anomalous (non-newton) character of viscous flow of the mixture of GUO with ED-16. Linear – non-newton zones with tangent of incline angle close to 1 and anomalous flows with big deviations are watched on flow curves as increasing of  $\dot{\gamma}$ .

Resin ED-16 at all range  $\dot{\gamma}$  and  $\tau$  at 15÷50°C did not display deviations from non-newton flow, but presence of  $\dot{\gamma}_{\text{crit.}}$  and  $\tau_{\text{crit.}}$  has been revealed. Values  $\tau_{\text{crit.}}$  for GUO and its mixture with ED-16 correspond to values  $\lg \tau_{\text{crit.}} = 5.3 \div 5.5 \text{ Pa}$ , for GUO  $\lg \tau_{\text{crit.}} = 4.9 \div 4.75$  and ED-16 –  $5.25 \div 5.2 \text{ Pa}$ . It has been shown that GUO, ED-16 and their mixtures under the influence of shift stress display anomalous-viscous flow similar to viscous flow of polymers melts. Character of the dependence curves of effective viscosity ED-16, GUO and their mixtures (50:50) at  $\tau = 2 \cdot 10^3 \text{ MPa}$  also testifies a good compatibility of olygomers. Hardening kinetics of the mixture ED-16 and GUO has been investigated according to viscosity change at 60°C.

The more hardening speed is observed during hardening by MPDA and aniline (1:1) mixture (fig.4).



**Fig. 4.** Dependence of effective viscosity on duration of the testings for oligomers mixtures hardened by various hardeners: 1 – polyethylenepolyamine; 2 – methaphenylenediamin; 3 – methaphenylenediamin, aniline in correlation 1:1; 4 – aniline temperature 60°C.

Influence of mass correlation of m-phenylenediamine and aniline on physico-mechanical properties of hardened composition (table 2) has been investigated.

**Table 2.** Influence of mass ratio of m-phenylenediamine and aniline in the mixture of hardeners on the properties of hardened composition ED-16 – GUO (50:50)

№	Indices of composition properties	Ratio of m-phenylenediamine diamine and aniline in hardeners mixture		
		1.2:1	1:1	1:1.3
1.	Strength limit in extension, MPa	21.5	24.5	17.0
2.	Relative extension in detachment, %	35.0	77.5	102.5
3.	Stability of contact with steel (in normal detachment), MPa	12.8	19.0	10.8

Physico-mechanical properties of ED-16 and GUO mixtures have been determined mixtures of ED-16 and GUO has the best properties in 50:50 ratio, contact with steel, MPa – 10.3; stability limit in detachment, MPa – 24.5; relative extension, % – 77.5; impact strength, kg/sm – >50; “vitality”, hour – 40; mixtures also have high chemical strength in hostile environment (table 3).

Filling of composition by bauxite slurry (composition, % SiO<sub>2</sub> – 84; Al<sub>2</sub>O<sub>3</sub> – 10; Fe<sub>2</sub>O<sub>3</sub> – 5.4; K<sub>2</sub>O – 0.3; Na<sub>2</sub>O – 0.3) brings to the increasing of limit strength to 35MPa, but reduces relative extension to 15%. Compositions have been hardened at natural conditions at home temperature within 12 days, prehardening of composition at 100°C within 120 minutes increases strength data a little. Forming of rather developed three-dimensional structure at home temperature is obtained because of saving trace mobility of edge functional groups conditioned by the presence of elastic fragments of olygoether in the composition of formed macromolecular chain including also epoxide resin macromolecules. In the lack of GUO in the composition playing the role of flexybilizator the ability of the composition to form developed three-dimensional structure at home temperature is lost but increasing  $\overline{MM}$  ED-16 as a result of its interaction with amine diffusion resistance of hardening reaction takes place in consequence of system transition into gaseous state.

ED-16 and GUO mixtures in various ratios give opportunity to obtain compositions with wide range of data of physico-mechanical properties which allows to recommend them as protective coating, sealants, adhesives and others.

Table 3. Properties of ED-16 mixtures with glycidilurethane oligomer

№	Name of indices	Compound and properties of compositions based on ED-16 GUO mixtures		
		75/25	50/50	25/75
1.	Stability of contact with steel in normal detachment, MPa	9.81	10.3	8.7
2.	Limit of strength in detachment at 220°C	21.6	24.5	20.2
3.	Relative extension in detachment, %	60	77,5	170
4.	Flexibility on ShG-1 scale	1	1	1
5.	Impact strength, determined on the U-1A device, kg/sm	>50	>50	>50
6.	Water absorption within 24 hours at 24°C, mass. %	0.30	0.31	0.41
7.	Swelling in hostile environment within 24 hours at normal temperature, mass. % :			
	Sulphuric acid, 30%	0.80	0.90	0,97
	Hydrochloric acid, 30%	0.12	0.20	0,31
	Alkali (NaOH), 30%	0.40	0.15	0,42
	Gasoline	0	0	0
8.	Vitality, h	48	40	37

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## Modificarea rășinilor epoxidice folosind oligomeri funcționali

### Rezumat

A fost investigată modificarea rășinilor epoxidice ED-16 și ED-20 prin polieterul carboxil și epoxidic, precum și prin oligomerul glicediluretan, iar îmbunătățirea proprietăților de durabilitate, deformare, aderență și protecție ale ED-20 a fost dovedită. Amestecuri în diferite proporții ale ED-16 cu oligomerul glicediluretan au fost recomandate ca acoperiri protective, de etanșare, adezive etc.