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CHEMICAL MODIFICATION OF ED-24 EPOXY RESIN BY ADIPIC ACID

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Abstract. The possibility of epoxy resin carboxy-containing derivative (CDER) obtaining has been studied on the basis of dianic epoxy resin ED-24 and adipic acid (AA). The synthesized CDER contains epoxy and carboxy groups at the same time. Used catalysts were benzyltriethylammonium chloride (BTEACH); 1,4-diazobicyclo[2,2,2]octane; *N,N*-dimethylaminopyridine; 18-Crown-6, potassium hydroxide, triethylamine and 18-Crown-6+ZnCl₂ catalytic system. The effect of the catalyst nature and amount, reagents ratio, process temperature and time on the reaction proceeding between ED-24 and AA has been determined. The structure of CDER synthesized in the presence of BTEACH and its characteristics were confirmed by IR-spectroscopy. Using industrial dianic epoxy resin ED-20 the cross-linking of polymeric composites containing 10, 20 and 30 mass parts of CDER has been investigated at 413 K in the presence of polyethylenepolyamine.

Keywords: epoxy resin, acid, catalyst, quaternary ammonium salt, kinetics, IR-spectroscopy, cross-linking, gel-fraction, hardness, films.

1. Introduction

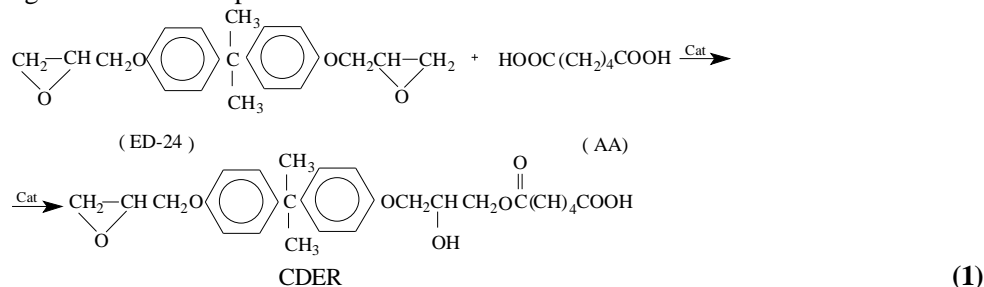
Epoxy resins are widely used as the basis of compositions for the production of anticorrosive and chemically stable coatings, hermetics, glues, *etc.* [1-3]. The reason is that the wares based on epoxy resins are characterized by good physico-mechanical, protective and dielectric properties. The epoxy coatings protect steel wares from corrosive damage under atmospheric

conditions; they are characterized by high hardness and toughness [4]. Among the defects there is the decrease of coating adhesion to the metal surface in aqueous solutions and relatively high cost of epoxy resins.

To improve some characteristics of the wares based on epoxy resins, as well as to reduce their price, the epoxy resins are modified by such compounds [5, 6] as low-molecular compounds and polymers [1]. The compatibility between epoxy resins and high-molecular compounds with simultaneous formation of cross-linked structures is especially significant from the standpoint of creating materials with desired properties. At the same time, the exchange of epoxy group for low-molecular fragment of another compound may considerably affect both application area of epoxy resin and approach to the formation of cross-linked networks based on epoxides.

Among all low-molecular compounds applicable as modifiers for epoxy resins, the organic acids are used most often [7]. Moreover, unsaturated acids are predominantly used, namely acrylic, methacrylic and crotonic acids [7]. The result of the mentioned modification is obtaining of oligomers without epoxy group but with double end-bonds. Therefore the epoxy resins modified by unsaturated acids may be further used in those polymeric mixtures, the network formation of which takes place only according to radical mechanism [7].

In order to obtain oligomers capable to increase the films elasticity in this work we studied the chemical modification of ED-24 epoxy resin by adipic acid in accordance with the following equation:



Obtained by the reaction (1) carboxy-containing derivative of ED-24 epoxy resin (CDER) should contain free epoxy and carboxy groups compared with the known oligomers synthesized due to the epoxy resin modification by unsaturated acids. CDER application in the polymeric mixtures will give the possibility to form cross-linked networks in accordance with a condensation mechanism.

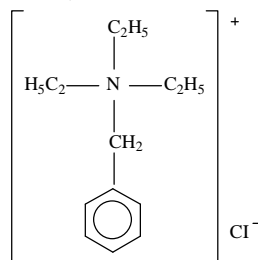
2. Experimental

2.1. Materials

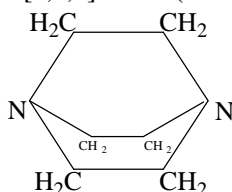
We used ED-24 industrial epoxy resin with a molecular mass (M_n) 340 g/mol and epoxy number (*e.n.*) 24 %. The adipic acid was used as received without additional purification.

The following compounds were used as the catalyst:

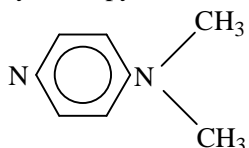
- Benzyltriethylammonium chloride (BTEACH)



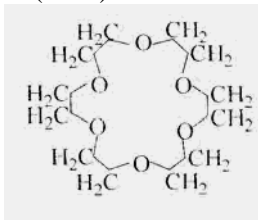
- 1,4-Diazobicyclo[2,2,2]octane (DABCO)



- *N,N*-dimethylammonopyridine (DMAP)



- 18-Crown-6 (O-18)



- Potassium hydroxide (KOH)

Triethylamine (TEA) and zinc chloride ($ZnCl_2$) were used as received without additional purification.

Isopropyl alcohol and toluene (analytical grade) were used as solvents.

The epoxy dianic resin ED-20 used for cross-linking was characterized by M_n 390 g/mol and *e.n.* 20.4 %.

Polyethylenepolyamine (PEPA) was used as received without additional purification

2.2. Analytical Methods

The number-average molecular mass M_n of the synthesized product was determined by cryometry using dioxane as the solvent. The epoxy number was determined using a back titration of hydrochloric acid and acetone solution by 0.1N alkali solution [8]. The content of carboxy groups was calculated according to the procedure described in [9]. Film hardness and gel-fraction content were determined using the known procedures.

2.3. Spectral Methods

Infrared spectra (IR) were obtained using "Specord-80" apparatus with the relevant absorption range in 4000–400 cm^{-1} region.

2.4. Experimental Procedure

2.4.1. The procedure for reaction kinetics

The chemical modification of ED-24 dianic epoxy resin by adipic acid was studied in a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer. ED-24 epoxy resin, adipic acid and isopropyl alcohol were loaded into the reactor. The mixture was heated to 333, 343 or 353 K under constant stirring and then the catalyst was added. The reaction proceeding was controlled by the change of carboxy groups concentration (C_{COOH}). For this purpose 1 ml of the solution was taken off every 15 minutes and 5 ml of isopropyl alcohol were added. The concentration was calculated using the formula:

$$[C]_{COOH} = \frac{V_1 \cdot N}{V_2}$$

where $[C]_{COOH}$ – concentration of carboxy groups, mol/l; V_1 – amount of 0.1 N alkali solution for titration, ml; V_2 – amount of withdrawn sample, ml; N – 0.1 N alkali solution.

The obtained results were used for the construction of graphical dependencies and then the effective rate constants for the reactions between CDER and AA were calculated. The effective activation energy was determined by interpretation of obtained results in the coordinates of Arrhenius equation $\log(K) = f(1/T)$.

2.4.2. CDER synthesis

60 g of ED-24 epoxy resin and 200 ml of toluene were loaded into a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer.

The mixture was heated to 343 K under constant stirring. Then 11.4 g of benzyltriethylammonium chloride dissolved in 10 ml of water were added. After this 24.4 g of adipic acid dissolved in 200 ml of isopropyl alcohol were added dropwise for 2.5 h. The reaction mass was kept at 343 K for additional 1 h. Then 500 ml of benzene were added and the reaction mixture was transferred to the dividing funnel. After demixing the bottom aqueous layer was removed and the upper layer was washed out by water till the catalyst was separated. CDER was purified using vacuum distillation of the solvents. 71.8 g of the product were obtained (yield 85.7 %). The content of carboxy and epoxy groups, and molecular mass of the product were determined.

2.4.3. CDER cross-linking activity

CDER cross-linking activity was studied using gel-fraction content and hardness of polymeric films. For this purpose the compositions were prepared by components mixing till homogeneous viscous solutions were obtained. Then they were applied over degrease glass plates of the standard size. The films were kept at room temperature for 24 h and then heated to 413 K for 15, 30, 60 and 75 min. After cross-linking the film hardness was determined using M-3 pendulum device at room temperature. Grinded samples were extracted in a Soxhlet apparatus with acetone for 10 h and gel-fraction content was determined.

3. Results and Discussion

3.1. Development of CDER Synthesis

Procedure

In order to develop CDER synthesis procedure it was necessary to study the effect of the catalyst nature and amount, reagents ratio and reaction temperature and time on the process proceeding. The experiments were carried out using the techniques described in Subsection 2.4.1. The studied catalysts were: BTEACH, DABCO, DMAP, O-18, KOH, TEA, $ZnCl_2$ and catalytic mixture O-18+ $ZnCl_2$ with a molar ratio of 1:3.

The effect of nature and amount of catalyst on the rate of the reaction between ED-24 and AA is represented in Fig. 1.

One can see from Fig. 1 that the highest rate of the reaction between ED-24 and AA is observed in the presence of DMAP, DABCO and BTEACH catalysts. In the presence of $ZnCl_2$ or O-18+ $ZnCl_2$ the reaction rate

decreases (Fig. 1, Table 1). And the reaction does not proceed in the presence of O-18, KOH and TEA.

Taking into account that effective rate constants are almost equal for the reactions in the presence of DMAP and DABCO, the effect of the catalyst amount we studied in the presence of DABCO. From Table 1 one can see that using 5 mol % of DABCO the reaction does not proceed at 353 K. The increase of such catalyst amount increases the reaction rate. On the other hand, the excessive increase of the reaction rate with the increase of DABCO amount has the limits. At the amount of 30 mol % the reaction is so fast that cross-linking of the reaction product occurs.

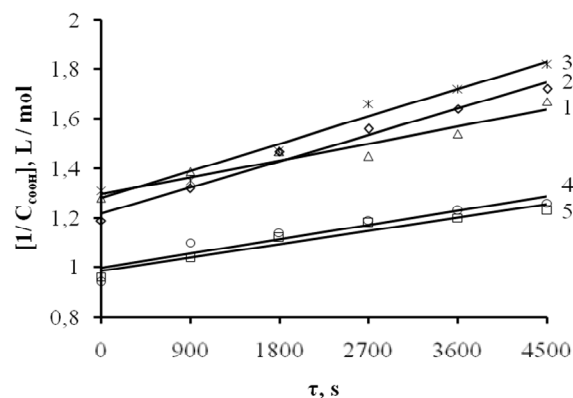


Fig. 1. Kinetic anamorphoses in the coordinates $1/C\text{-coord}$, L/mol for the reaction between ED-24 and AA at 353 K in the isopropanol medium in the presence of BTEACH (1); DABCO (2); DMAP (3); $ZnCl_2$ (4) and O-18+ $ZnCl_2$ (5) in the amount of 20 mol % to calculate for 1 g-eq of AA carboxy group. ED-24:AA = 1:1 moles

Comparing the effective rate constants which were obtained using BTEACH, DMAP and DABCO as a catalysts we observe the slight difference between values (Table 1). Therefore, taking into account the low prices and availability of BTEACH, we used it further to study the reaction between ED-24 and AA (Fig. 2, Table 1).

From the data of Fig. 2 and Table 1 it may be concluded that 30 mol % of BTEACH allows to conduct the reaction between ED-24 and AA with a sufficient rate.

The investigations of effect of ED-24:AA ratio (Fig. 3, Table 1) show that the increase of acid amount considerably decreases the reaction rate.

On the basis of obtained results and on the assumption of necessity to obtain the product with free epoxy and carboxy groups we chose ED-24:AA ratio equal to 1:1 moles.

The effect of temperature on the proceeding of the reaction (1) is given in Fig. 4.

Table 1

Effective rate constants of the reactions between ED-24 and AA

Molar ratio ED-24:AA	Catalyst and its amount (mol % for AA)	Reaction temperature, K	$K_{ef} \cdot 10^4$, l/(mol·s)
1:1	BTEACh, 5	353	Reaction does not proceed
1:1	BTEACh, 10	353	0.48 ± 0.13
1:1	BTEACh, 20	353	0.78 ± 0.13
1:1	BTEACh, 30	353	2.67 ± 0.12
1:1	BTEACh, 40	353	5.26 ± 0.12
1:1	BTEACh, 50	353	6.30 ± 0.13
1:0.5	BTEACh, 30	353	6.78 ± 0.11
1:2	BTEACh, 30	353	0.53 ± 0.09
1:4	BTEACh, 30	353	0.11 ± 0.05
1:1	BTEACh, 30	333	0.67 ± 0.11
1:1	BTEACh, 30	343	0.89 ± 0.10
1:1	O-18, 20	353	Reaction does not proceed
1:1	DMAP, 20	353	1.15 ± 0.13
1:1	ZnCl ₂ *, 20	353	0.59 ± 0.10
1:1	O-18+ZnCl ₂ ** , 20	353	0.60 ± 0.10
1:1	DABCO, 5	353	0.02 ± 0.01
1:1	DABCO, 10	353	0.52 ± 0.07
1:1	DABCO, 20	353	1.11 ± 0.12
1:1	DABCO, 30	353	Cross-linking of the reaction product
1:1	KOH, 30	353	Reaction does not proceed
1:1	TEA, 30	353	Reaction does not proceed

Notes: * ZnCl₂ as 36%-aqueous solution

** O-18+ZnCl₂ has a molar ratio of 1:3 (O-18 amount is 18–20 mol % for one carboxy group of AA)

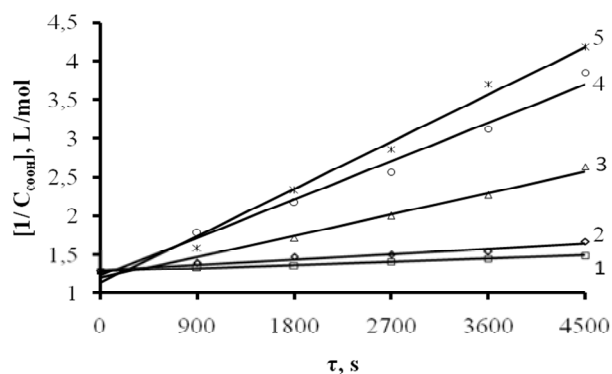


Fig. 2. Kinetic anamorphoses in the coordinates $1/C\text{-}\tau$ for the reaction between ED-24 and AA at 353 K in the isopropanol medium in the presence of 10 (1); 20 (2); 30 (3); 40 (4) and 50 (5) mol % of BTEACh to calculate for 1 g-eq of AA carboxy group. ED-24:AA = 1:1 moles

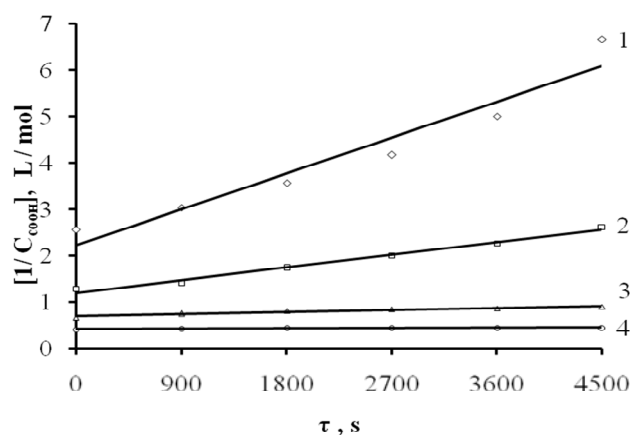


Fig. 3. Kinetic anamorphoses in the coordinates $1/C\text{-}\tau$ for the reaction between ED-24 and AA at 353 K in the isopropanol medium at different ED-24:AA molar ratios: 1.0:0.5 (1); 1:1 (2); 1:2 (3) and 1:4 (4). BTEACh amount is 30 mol % to calculate for 1 g-eq of AA carboxy group

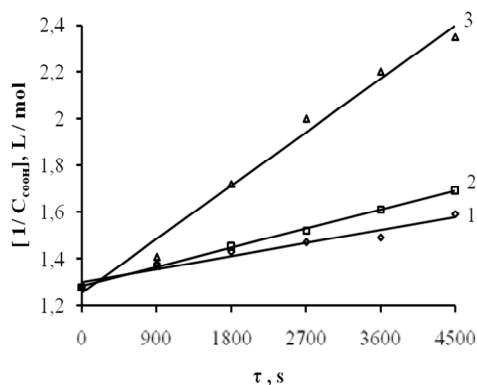


Fig. 4. Kinetic anamorphoses in the coordinates $1/C-\tau$ for the reaction between ED-24 and AA at 353 K in the isopropanol medium at different temperatures (K): 333 (1); 343 (2) and 353 (3). ED-24:AA = 1:1 moles; BTEACH amount is 30 mol % to calculate for 1 g-eq of AA carboxy group

One can see from Fig. 4 and Table 1 that the increase in temperature from 333 to 353 K increases the reaction rate 4 times. The interpretation of obtained results in the coordinates of Arrhenius equation $\log(K) = f(1/T)$ determines the activation energy. For the reaction between ED-24 and AA in the presence of BTEACH it is equal to 78.86 kJ/mol. The effect of reaction time on the carboxy groups concentration in the reaction between ED-24 and AA is represented in Fig. 5.

The carboxy groups concentration decreases almost twice till 2 h. The further increase of the reaction time also decreases the concentration. It means that the interaction between free carboxy and epoxy groups takes place, *i.e.* we do not obtain the product in accordance with the Eq. (1) but observe the interaction between free epoxy groups of ED-24 resin and carboxy groups of AA with an oligomeric product formation. The sharp increase of the reaction mixture density also indicates the mentioned phenomenon.

In order to preserve the formation of oligomeric products we suggest to synthesize CDER by the Eq. (1) in such a way that we have the excess of ED-24 and the temperature of 343 K.

The synthesis procedure is described in Subsection 2.4.2. The synthesized CDER is characterized by the molecular mass of 453 g/mol, epoxy groups content 7.85 % (theoretical value 8.85 %) and carboxy group content 8.60 % (theoretical value 9.26 %).

CDER is a viscous light-yellow substance soluble in isopropanol, dioxane, acetone and other organic solvents.

3.2. IR-Spectroscopic Investigations

The presence of epoxy groups in CDER molecule is confirmed (Fig. 6) by stretching vibrations in IR-spectrum at 912 cm^{-1} , esteric groups – at 1732 cm^{-1} , free carboxy

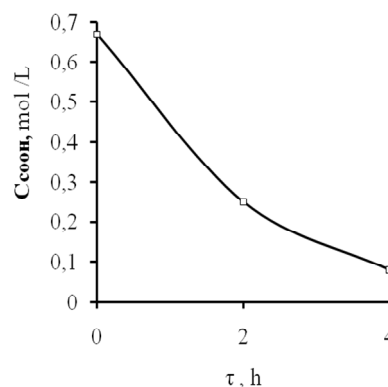


Fig. 5. Carboxy groups concentration vs reaction time. Temperature is 353 K. ED-24:AA molar ratio is 1:1. BTEACH amount is 30 mol % to calculate for 1 g-eq of AA carboxy group

groups – at 1256 cm^{-1} . The presence of hydroxy groups formed due to the epoxy ring opening at the attaching AA molecule to ED-24 molecule is confirmed by absorption bands at 3456 cm^{-1} typical for stretching vibrations of a hydroxy group.

3.3. Cross-Linking of Dianic Epoxy Resin in the Presence of CDER

In order to examine the cross-linking of dianic epoxy resin in the presence of CDER the polymeric mixtures were prepared (Table 2).

Cross-linking of polymeric mixtures was studied in accordance with the procedure described in Subsection 2.4.3. The obtained results are represented in Table 3.

One can see from Table 3 that the increase of cross-linking time increases gel-fraction content, as well as film hardness. At the same time the increase of CDER content in the polymeric mixture from 10 (Mix I) to 20 mass parts (Mix II) increases gel-fraction content but slightly decreases the films hardness. The further increase of CDER content to 30 mass parts (Mix III) leads to the further decrease of films hardness, but gel-fraction content decreases too. Moreover, gel-fraction content in Mix III is smaller than that in Mix I, where CDER content is only 10 mass parts.

The increase of gel-fraction content in cross-linked bonds with the increase of process time indicates that carboxy groups in CDER also participate in films cross-linking, *i.e.* the interaction between free carboxy groups of CDER and epoxy and hydroxy groups of ED-20 resin occurs. The decrease of films hardness with the increase of CDER amount indicates that such a compound in the polymeric mixture plays a role of a plasticizer. The part of chemical reactions proceeding between carboxy and epoxy groups at 413 K is negligible. Therefore, with the

increase of CDER amount in the polymeric mixture the total amount of insoluble products decreases but CDER role as a plasticizer increases resulting in the decrease of films hardness.

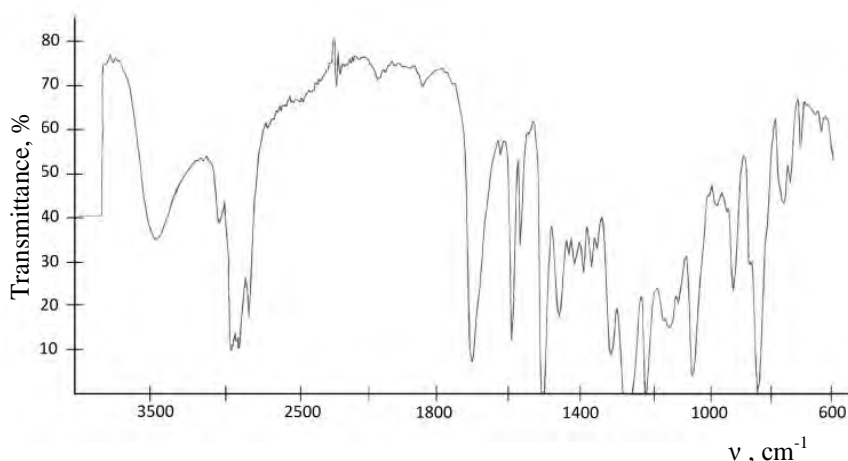


Fig. 6. IR-spectrum of CDER

Table 2

Compositions of polymeric mixtures

Mixture component	Component content in polymeric mixture, mass parts		
	Mix I	Mix II	Mix III
ED-20 dianic epoxy resin	90	80	70
CDER	10	20	30
PEPA	13.1	12.3	11.4

Table 3

Dependence of gel-fraction content and films hardness upon mix composition and cross-linking time at 413 K

Mix number	Symbol	Symbol values at cross-linking time, min					
		24 h, room temperature	15	30	45	60	75
I	G	70.9	84.0	91.5	95.0	96.5	97.0
	H	0.72	0.85	0.92	0.94	0.95	0.96
II	G	71.2	85.2	92.5	97.0	99.0	99.5
	H	0.74	0.83	0.88	0.91	0.93	0.94
III	G	69.2	80.5	88.0	92.4	93.5	94.0
	H	0.70	0.78	0.84	0.87	0.90	0.91

Note: G – gel-fraction content, %; H – films hardness, rel. units

4. Conclusions

On the basis of ED-24 dianic epoxy resin and adipic acid the product with free epoxy and carboxy groups has been synthesized and characterized. It has been established that for the reaction between ED-24 and AA benzyltriethylammonium chloride in the amount of 30 mol % to calculate for 1 g-eq of AA carboxy group may be used as a catalyst. Using 20 mass parts of CDER, 80 mass parts of ED-20 epoxy resin and PEPA as a hardener we obtained films by stepwise cross-linking: first

at room temperature for 24 h, then at the heating to 413 K for 60-75 min. The films characteristics are: hardness: 0.93–0.94 rel. units and gel-fraction content 99.0–99.5 %. The synthesized films are recommended to be used as protective coatings for a metal.

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ХІМІЧНА МОДИФІКАЦІЯ ЕПОКСИДНОЇ СМОЛИ ЕД-24 АДІПІНОВОЮ КИСЛОТОЮ

Анотація. Вивчена можливість одержання на основі діанової епоксидної смоли ЕД-24 і адипінової кислоти (АК)

карбоксильмісної похідної епоксидної смоли (КПЕС), яка одночасно містить вільну епоксидну і карбоксильну групу. Встановлено вплив природи та кількості каталізатора, зокрема бензилтриетиламонію хлористого (БТЕАХ), 1,4-діазобіцикло[2,2,2]октану, *N,N*-диметиламінопіридину, 18-Краун-6, гідроксиду калію, триетиламіну та каталітичної системи 18-Краун-6+ZnCl₂, співвідношення реагуючих речовин, температури і тривалості реакції на протікання реакції між ЕД-24 та АК. КПЕС синтезована в присутності як каталізатор БТЕАХ та охарактеризована. ІЧ-спектроскопічними дослідженнями підтверджена структура КПЕС. З використанням промислової діанової епоксидної смоли ЕД-20 вивчено при 413 К структурування у присутності поліетиленполіаміну полімерних сумішей, що містять 10, 20 і 30 мас.част. КПЕС.

Ключові слова: епоксидна смола, кислота, каталізатор, четвертинна амонієва сіль, кінетика, ІЧ-спектрокопія, структурування, гель-фракція, твердість, плівки.

