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EPOXY RESINS CHEMICAL MODIFICATION BY DIBASIC ACIDS

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Abstract. Kinetic regularities of epoxy resins chemical modification by aliphatic and aromatic dibasic acids have been studied. The commercial dianic resins ED-20 and ED-24 were used as epoxy resins. Oxalic, malonic, succinic, sebacic, maleic, terephthalic and isophthalic acids were used as dibasic carboxylic acids. The effective rate constants and activation energies of the reactions between epoxy resin and acids by different nature have been calculated. The synthesis method for oligomers with epoxy and carboxy groups has been suggested. The structure of synthesized oligomers was confirmed by chemical analyses and IR-spectroscopy.

Keywords: epoxy resin, carboxylic acid, kinetic investigations, effective rate constant, activation energy, IR-spectroscopy.

1. Introduction

It is well-known that epoxy resins modification allows to increase the resin functionality and improve their chemical and physico-mechanical properties [1-3]. The introduction of various functional groups into the epoxy resin molecule increases its reactivity and resins acquire new properties which are non-typical of them before modification [4-5]. Among low-molecular compounds used for modification the carboxylic acids are the most widely used and prospective ones [6]. The presence of carboxy group in the structure increases a chemical and thermal stability, hardness, elasticity, adhesion, tensile and impact strength [7-9]. Moreover, epoxy resins with carboxy end groups show better ability to structurize the epoxy-oligomeric mixtures based on them and leads to additional crosslinking of such systems [10].

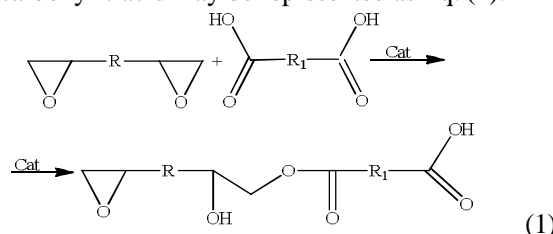
Earlier we studied modification of ED-24 dianic epoxy resin by the adipic acid [11]. It was found that such modification is prospective and improves the resin properties, therefore it is advisable to study epoxy resin modification by carboxylic acids in details.

The aim of this work is to investigate the kinetic regularities of epoxy resins modification by various dibasic carboxylic acids (aliphatic, aromatic, unsaturated ones) and suggest the synthesis method for oligomers with free epoxy and carboxy groups.

2. Experimental

2.1. Materials

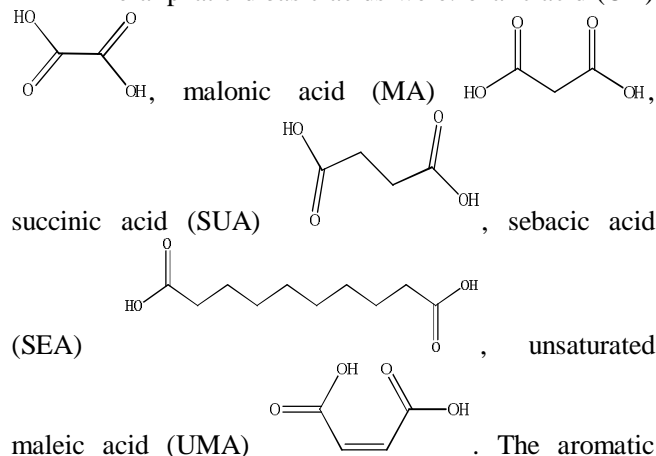
Generally the reaction between epoxy resin and dibasic carboxylic acid may be represented as Eq. (1):

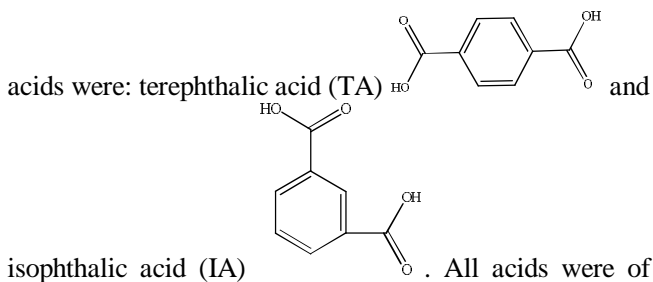


where R is a fragment of dianic epoxy resin; R₁ is a fragment of dicarboxylic acid

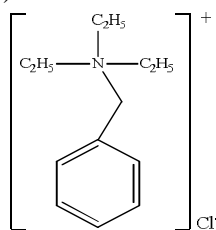
The molecular mass of the initial epoxy resins ED-20 and ED-24 was 430 and 340 g/mol, respectively; their epoxy number (*e.n.*) was 20 and 24 %, respectively.

The aliphatic dibasic acids were: oxalic acid (OA)





The reaction catalyst was benzyltriethylammonium chloride (BTEACH) of the formula:



Isopropyl alcohol of P.A. purity was used as a solvent.

2.2. Analytical Methods

The number-average molecular mass of the synthesized products (M_n) was determined by the isopiestic method using chloroform as a solvent and bisphenol A diglycidyl ether as a reference substance. The epoxy number was determined using a back titration of the sample in the acetone+hydrochloric acid solution by 0.1 N alkali solution [12]. The concentration of carboxy groups was determined using the procedure described in [13].

2.3. Kinetic Investigations

Kinetic investigations were carried out in a three-necked reactor equipped with a back condenser and thermometer under constant stirring according to the procedure described in [11]. The reaction was controlled by the change of carboxy groups concentration.

2.4. IR-Spectroscopy

Infrared spectra (IR) were obtained using "Spectord-80" apparatus within the range of 4000–400 cm^{-1} . The samples were prepared as films obtained from oligomer solution in chloroform and applied over KBr plates (layer thickness was 0.03 mm).

2.5. Synthesis of Functional Oligomers

Synthesis of oligomer based on ED-24 epoxy resin and OA (oligomer I)

The three-necked reactor equipped with a mechanical stirrer, back condenser and thermometer was

loaded by 90 g of ED-24 epoxy resin and 300 ml of isopropanol. The mixture was heated to 343 K and 17.1 g of BTEACH was added. Then 22.5 g of OA dissolved in 300 ml of isopropyl alcohol was added dropwise during 2.5 h. The reaction mass was sustained at 343 K under constant stirring for 1 h. Then 600 ml of benzene was added, the mixture was stirred and placed into a separating funnel. After stratification the bottom layer was separated and the upper one was washed by water to separate the catalyst. The obtained product was purified *via* vacuum distillation till the mass became constant. The product (104.5 g) with the yield of 93.0 % is soluble in acetone, isopropanol, chloroform and other organic solvents.

Synthesis of oligomer based on ED-24 epoxy resin and MA (oligomer II)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-24 epoxy resin dissolved in 300 ml of isopropanol; 17.1 g of BTEACH and 26.1 g of MA dissolved in 300 ml of isopropanol. The product (98.5 g) was obtained with the yield of 84.8 %.

Synthesis of oligomer based on ED-24 epoxy resin and SUA (oligomer III)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-24 epoxy resin dissolved in 300 ml of isopropanol; 17.4 g of BTEACH and 30.0 g of SUA dissolved in 300 ml of isopropanol. The product (102.0 g) was obtained with the yield of 96.0 %.

Synthesis of oligomer based on ED-24 epoxy resin and SEA (oligomer IV)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-24 epoxy resin dissolved in 300 ml of isopropanol; 17.1 g of BTEACH and 51.0 g of SEA dissolved in 300 ml of isopropanol. The product (88.5 g) was obtained with the yield of 94.0 %.

Synthesis of oligomer based on ED-24 epoxy resin and UMA (oligomer V)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-24 epoxy resin dissolved in 300 ml of isopropanol; 17.1 g of BTEACH and 29.1 g of UMA dissolved in 300 ml of isopropanol. The product (121.0 g) was obtained with the yield of 96.0 %.

Synthesis of oligomer based on ED-24 epoxy resin and TA (oligomer VI)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-24 epoxy resin dissolved in 300 ml of isopropanol; 17.1 g of BTEACH and 41.7 g of TA dissolved in 300 ml of isopropanol. The product (127.5 g) was obtained with the yield of 97.0 %.

Synthesis of oligomer based on ED-24 epoxy resin and IA (oligomer VII)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-24 epoxy resin dissolved in 300 ml of isopropanol; 17.1 g of BTEACH and 41.7 g of IA dissolved in 300 ml of isopropanol. The product (116.5 g) was obtained with the yield of 90.0 %.

Synthesis of oligomer based on ED-20 epoxy resin and OA (oligomer VIII)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-20 epoxy resin dissolved in 300 ml of isopropanol; 14.4 g of BTEACH and 19.0 g of OA dissolved in 300 ml of isopropanol. The product (97.5 g) was obtained with the yield of 89.4 %.

Synthesis of oligomer based on ED-20 epoxy resin and MA (oligomer IX)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-20 epoxy resin dissolved in 300 ml of isopropanol; 14.1 g of BTEACH and 21.9 g of MA dissolved in 300 ml of isopropanol. The product (107.5 g) was obtained with the yield of 96.0 %.

Synthesis of oligomer based on ED-20 epoxy resin and SUA (oligomer X)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-20 epoxy resin dissolved in 300 ml of isopropanol; 14.1 g of BTEACH and 24.6 g of SUA dissolved in 300 ml of isopropanol. The product (102.5 g) was obtained with the yield of 89.4 %.

Synthesis of oligomer based on ED-20 epoxy resin and UMA (oligomer XI)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-20 epoxy resin dissolved in 300 ml of isopropanol; 14.4 g of BTEACH and 24.3 g of UMA dissolved in 300 ml of isopropanol. The product (114.3 g) was obtained with the yield of 98.0 %.

Synthesis of oligomer based on ED-20 epoxy resin and TA (oligomer XII)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-20 epoxy resin dissolved in 300 ml of isopropanol; 14.3 g of BTEACH and 34.7 g of TA dissolved in 300 ml of isopropanol. The product (85.0 g) was obtained with the yield of 99.0 %.

Synthesis of oligomer based on ED-20 epoxy resin and IA (oligomer XIII)

The process was carried out according to the above-mentioned procedure based on 90 g of ED-20 epoxy resin dissolved in 300 ml of isopropanol; 14.4 g of

BTEACH and 34.7 g of IA dissolved in 300 ml of isopropanol. The product (124.0 g) was obtained with the yield of 96.0 %.

3. Results and Discussion

3.1. Kinetic Investigations

We noted in [11] that the reaction between ED-24 epoxy resin and adipic acid may proceed in accordance with Eq. (1) in the presence of different catalysts: BTEACH; 1,4-diazobicyclo[2,2]octane; *N,N*-dimethylaminopyridine; 18-Crown-6 (O-18); potassium hydroxide; triethylammonium; zinc chloride ($ZnCl_2$) and catalytic system of O-18 + $ZnCl_2$ with the molar ratio of 1 : 3. BTEACH was found to be the most effective catalyst among all above mentioned ones while comparing the effective rate constants of the reaction. Moreover, the increase of catalyst amount from 10 to 50 mol % per 1 g.-eq. of adipic acid carboxy group increases the effective rate constant by 13 times. At the catalyst concentration of 30 mol % the effective rate constant is already 2.67 ± 0.12 l/mol·s [11]. Therefore in current investigations we use BTEACH as the catalyst in the amount of 30 mol % per 1 g.-eq. of acid carboxy group.

To develop the synthesis procedure for oligomers with free epoxy and carboxy groups it is necessary to examine the effect of temperature on the reaction (1) proceeding. Isopropyl alcohol is a reaction medium. The amount of dibasic acid is 1 mol per 1 mol of initial epoxy resin. The kinetic investigations were carried out according to the method described in Subsection 2.3. The obtained results are represented in Figs. 1-4 and Tables 1 and 2.

The reaction between epoxy resin and dibasic carboxylic acid of aliphatic and aromatic type is described by the II order equation (Figs. 1-3). On the other hand, the effective rate constant depends on the nature of used acid. The highest rate is observed for OA (Fig. 1a, Table 1), and the lowest one – for MA (Fig. 1b, Table 1). The effective rate constants of the reactions between ED-24 and SUA, SEA or UMA have the intermediate values (Table 1). Thus, OA with its specific structure falls out the general regularity, typical of other aliphatic dibasic acids. For these acids the longer distance between carboxy groups, the higher reaction rate (Fig. 1c, Table 1). Moreover, the reaction between ED-24 and SEA is characterized by the lowest activation energy (38.8 kJ/mol, Table 1). If we compare UMA containing carboxy groups plus unsaturated double bond and SUA with the same number of carbon atoms but without double bond, we observe that UMA reacts twice quicker with ED-24 than SUA (Fig. 1d, Table 1).

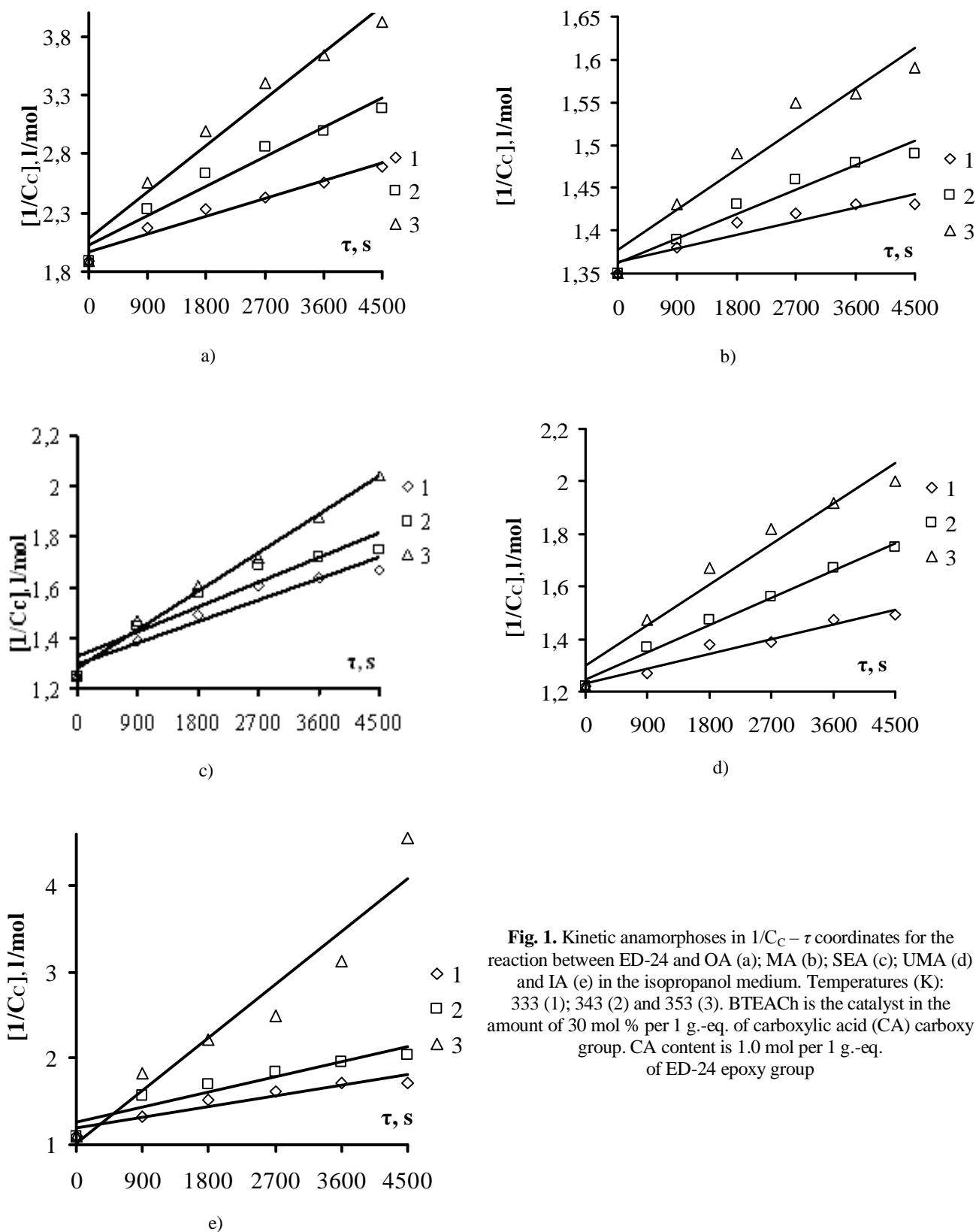


Fig. 1. Kinetic anamorphoses in $1/C_c - \tau$ coordinates for the reaction between ED-24 and OA (a); MA (b); SEA (c); UMA (d) and IA (e) in the isopropanol medium. Temperatures (K): 333 (1); 343 (2) and 353 (3). BTEACH is the catalyst in the amount of 30 mol % per 1 g.-eq. of carboxylic acid (CA) carboxy group. CA content is 1.0 mol per 1 g.-eq. of ED-24 epoxy group

Fig. 2. Dependence of $\lg K_{ef}$ on $1/T$ for the reaction between ED-24 and OA in isopropanol medium. BTEACH is the catalyst in the amount of 30 mol % per 1 g.-eq. of OA carboxy group. OA content is 1.0 mol per 1 g.-eq. of ED-24 epoxy group.

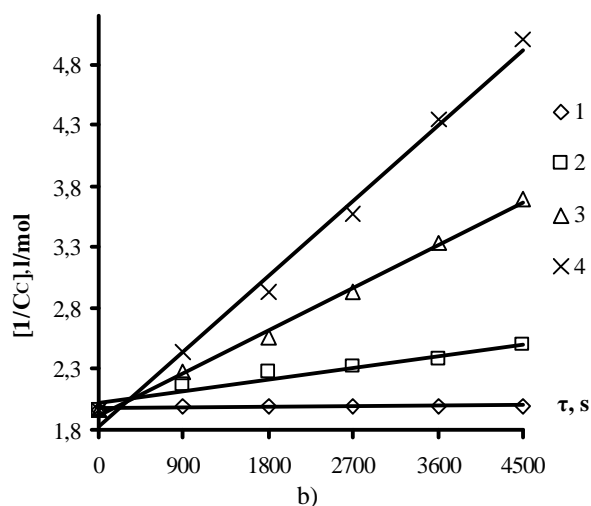
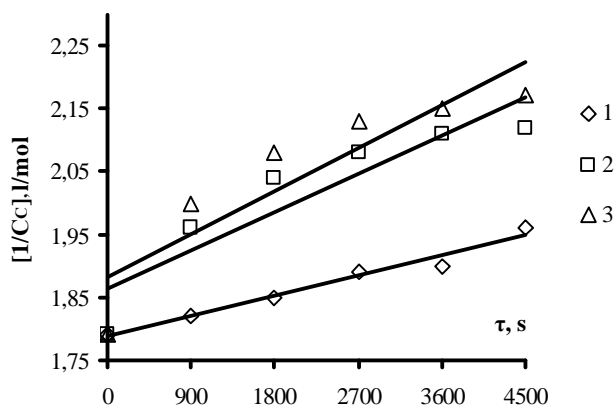
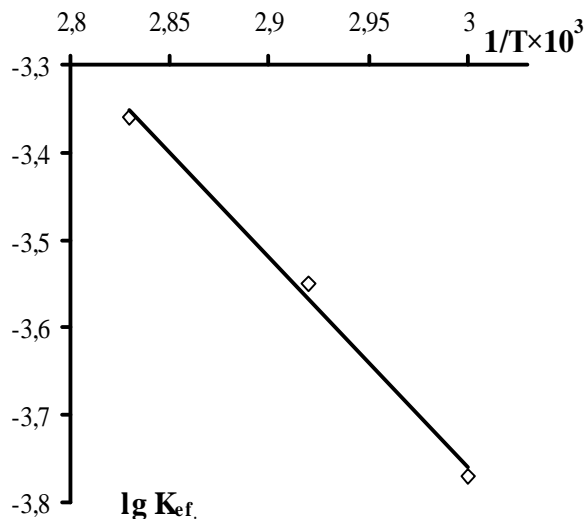


Fig. 3. Kinetic anamorphoses in $1/C_C - \tau$ coordinates for the reaction between ED-20 and SUA (a) and TA (b) in the isopropanol medium. Temperatures (K): 333 (1); 343 (2) and 353 (3). BTEACH is the catalyst in the amount of 30 mol % per 1 g.-eq. of carboxylic acid (CA) carboxy group. CA content is 1.0 mol per 1 g.-eq. of ED-24 epoxy group.

Fig. 4. Dependence of $\lg K_{ef}$ on $1/T$ for the reaction between ED-20 and TA in the isopropanol medium. BTEACH is the catalyst in the amount of 30 mol % per 1 g.-eq. of TA carboxy group. TA content is 1.0 mol per 1 g.-eq. of ED-24 epoxy group.

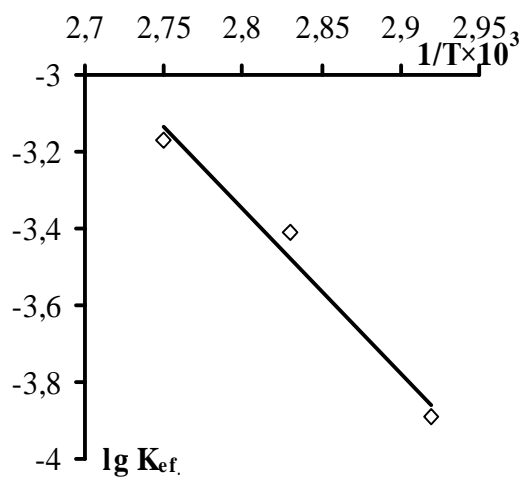


Table 1

Effective rate constants of the reaction between ED-24 and dibasic carboxylic acids

ED-24 reaction with	Reaction temperature, K	$K_{ef} \cdot 10^4$, l/(mol·s)	E_a , kJ/mol
OA	333	1.70±0.20	44.1±0.3
	343	2.80±0.20	
	353	4.40±0.21	
MA	333	0.20±0.14	42.0±1.1
	343	0.30±0.14	
	353	0.50±0.14	
SUA	333	0.20±0.15	53.0±0.4
	343	0.50±0.15	
	353	0.70±0.15	
SEA	333	1.17±0.13	38.8±1.0
	343	1.56±0.13	
	353	1.74±0.13	
UMA	333	0.60±0.12	56.5±1.2
	343	1.00±0.12	
	353	2.00±0.13	
TA	333	0.60±0.25	102.5±1.4
	343	3.90±0.23	
	353	7.00±0.21	
IA	333	1.00±0.25	96.2±1.1
	343	2.00±0.13	
	353	7.00±0.12	

Note: BTEACH is the catalyst in the amount of 30 mol % per 1 g.-eq. of carboxylic acid (CA) carboxy group. CA content is 1.0 mol per 1 g.-eq. of ED-24 epoxy group. Isopropanol is a reaction medium.

Using aromatic acids (Fig. 1e, Table 1) the reaction rate is higher.

Interpretation of obtained results in Arrhenius coordinates allows to determine the effective activation energy of the reaction between ED-24 and OA (Fig. 2, Table 1). The analogous values were obtained for the reactions between ED-24 and other carboxylic acids (Table 1). The activation energy of the reaction between ED-24 and aliphatic acids is twice higher than that of the reaction between ED-24 and aromatic acids (Table 1).

ED-20 epoxy resin, compared with ED-24, contains free epoxy groups and secondary hydroxyl groups. The analysis of Tables 1 and 2 data indicates that epoxy resin nature does not influence the rate of the reaction with OA. The same results were obtained using SUA and UMA (Fig. 3a, Tables 1 and 2). At the same time the rate of the reaction between MA and ED-20 is twice higher and its activation energy is three times higher compared with those values of the reaction between MA and ED-24. The nature of epoxy resin also affects the rate of the reaction with aromatic acids (Tables 1 and 2). The effective rate constant

Table 2

Effective rate constants of the reaction between ED-20 and dibasic carboxylic acids

ED-20 reaction with	Reaction temperature, K	$K_{ef} \cdot 10^4$, l/(mol·s)	E_a , kJ/mol
OA	333	1.70±0.24	40.8±0.3
	343	2.80±0.24	
	353	4.00±0.25	
MA	333	0.10±0.13	124.5±1.5
	343	0.60±0.13	
	353	1.40±0.13	
SUA	333	0.40±0.18	33.3±0.1
	343	0.70±0.19	
	353	0.80±0.19	
UMA	333	0.50±0.12	88.1±0.9
	343	0.80±0.13	
	353	3.00±0.15	
TA	333	doesn't proceed	82.3±0.9
	343	1.30±0.20	
	353	3.90±0.20	
	363	6.70±0.18	
IA	333	0.10±0.14	195.4±2.6
	343	2.20±0.15	
	353	5.60±0.15	

Note: BTEACH is the catalyst in the amount of 30 mol % per 1 g.-eq. of carboxylic acid (CA) carboxy group. CA content is 1.0 mol per 1 g.-eq. of ED-20 epoxy group. Isopropanol is a reaction medium.

of the reaction between TA and ED-20 is twice lower compared with that of the reaction with ED-24.

The obtained experimental values and results described in [11] allow to suggest the synthesis conditions for oligomers with epoxy and carboxy group: temperature is 343 K, epoxy resin : dibasic acid molar ratio is 1 : 1, reaction time is 2.5 h, catalyst amount is 30 mol % per 1 g.-eq. of acid carboxy group. Isopropyl alcohol is the reaction medium which solves both initial compounds and obtained functional oligomer.

Synthesis procedure for oligomers based on different epoxy resins and dibasic carboxylic acids is given in Subsection 2.5. The characteristics of obtained oligomers are given in Table 3.

So, oligomers **I–XIII** are characterized by sufficiently high yield and contain free epoxy and carboxy groups. The content of epoxy and carboxy groups depends on the nature of the initial resin and dibasic acid. The presence of different functional groups in the epoxy oligomer molecule allows to extend the application of the mentioned compounds during formation of three-dimensional polymeric blends on their basis.

Table 3

Characteristics of functional oligomers

Oligomer	Initial compounds		Oligomer characteristics			
	Epoxy resin	Acid	Yield, %	Epoxy groups content, %	Carboxy groups content, %	M_n , g/mol
I	ED-24	OA	93.0	9.8	9.5	462
II	ED-24	MA	84.8	13.8	9.1	420
III	ED-24	SUA	96.0	10.0	8.7	468
IV	ED-24	SEA	94.0	7.8	8.0	552
V	ED-24	UMA	96.0	9.5	8.4	480
VI	ED-24	TA	97.0	8.6	9.3	497
VII	ED-24	IA	90.0	8.4	8.8	510
VIII	ED-20	OA	89.4	8.9	8.4	513
IX	ED-20	MA	96.0	7.1	7.6	580
X	ED-20	SUA	89.4	8.3	7.7	550
XI	ED-20	UMA	98.0	9.6	9.1	496
XII	ED-20	TA	99.0	6.6	7.0	630
XIII	ED-20	IA	96.0	7.4	7.2	600

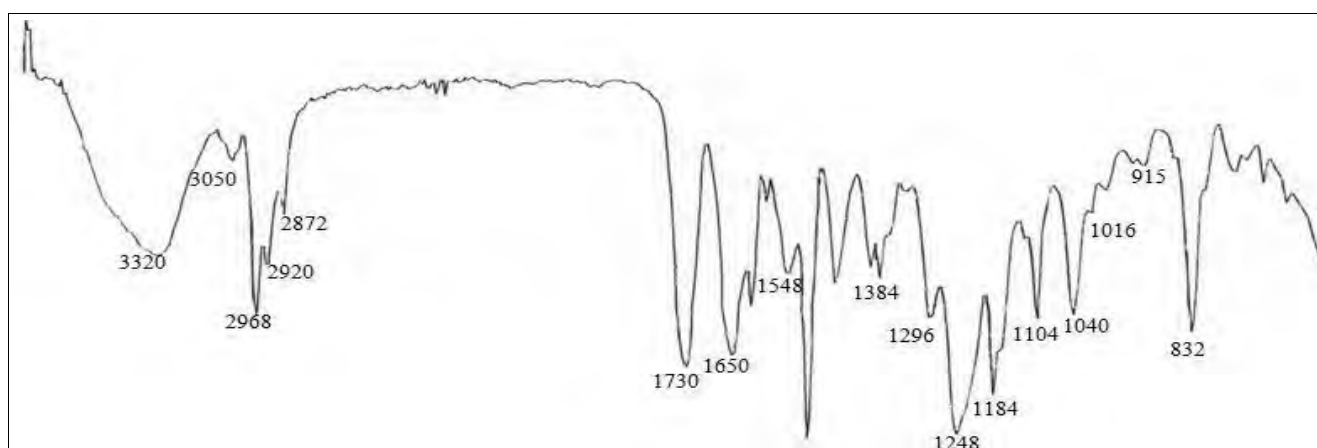


Fig. 5. IR-spectrum of oligomer V

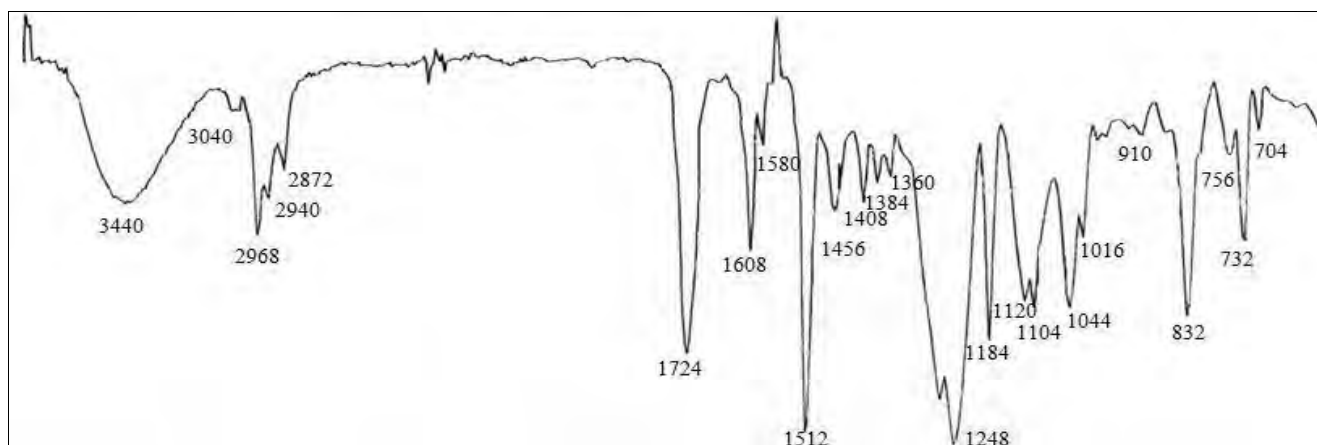
v, cm⁻¹

Fig. 6. IR-spectrum of oligomer VI

3.2. IR-Spectroscopic Investigations

IR-spectroscopic investigations were carried out to confirm the structure of the synthesized oligomers. The investigations were carried out according to the methodic represented in Subsection 2.4.

Some results are represented in Figs. 5 and 6. The presence of epoxy group in oligomer **V**, synthesized on the basis of ED-24 and UMA, is confirmed by the absorption band at 915 cm^{-1} typical of epoxy ring stretching vibrations (Fig. 5). The acid group presence is confirmed by stretching vibrations at 1348 cm^{-1} typical of hydroxy group in the carboxy group. The stretching vibrations at 3320 cm^{-1} reveals the epoxy ring opening and carboxy group attaching. The formed hydroxyl group relates to the secondary hydroxy group. The absorption band at 1296 cm^{-1} typical of this group confirms this fact. While UMA interacts with epoxy resin the esteric bond is formed that is confirmed by the presence of absorption

band at 1040 cm^{-1} typical of —C—O—C(=O)— bond and absorption band at 1730 cm^{-1} typical of carbonyl group in esters. The double bond appears due to the introduction of UMA fragments into the oligomer and its presence is confirmed by stretching vibrations at 1650 cm^{-1} .

The structure of oligomer synthesized on the basis of ED-24 epoxy resin and TA (oligomer **VI**, Fig. 6) is confirmed in the same way. The presence of epoxy group is confirmed by the absorption band at 910 cm^{-1} , free carboxy group – at 1384 cm^{-1} . The presence of hydroxy group formed due to the interaction between ED-24 and TA – by stretching vibrations at 3440 and 1248 cm^{-1} . The absorption bands at 1044 and 1724 cm^{-1} reveal the presence of esteric group and free carbonyl group in esters, respectively.

Thus, IR-spectroscopic investigations allow to confirm the structure of the synthesized oligomers and indicate that such oligomers are obtained due to the chemical interaction between epoxy resins and dibasic acids of aliphatic or aromatic type. The structure of the synthesized products contains epoxy group, as well as free carboxy and secondary hydroxy groups.

4. Conclusions

1. Some kinetic regularities of the reactions between ED-24, ED-20 epoxy resins and dibasic carboxylic acids of aliphatic and aromatic type have been studied. The effective rate constants and activation energy of the mentioned reactions have been calculated.

2. On the basis of literature data and obtained kinetic regularities the synthesis procedure has been sug-

gested for the oligomers with free epoxy, carboxy and hydroxy groups. 13 new reactive functional oligomers have been synthesized and characterized.

3. The structure of the synthesized oligomers is confirmed by IR-spectroscopic investigations allowing to establish the presence of above-mentioned functional groups in the obtained oligomers.

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ХІМІЧНЕ МОДИФІКУВАННЯ ЕПОКСИДНИХ СМОЛ ДВОХОСНОВНИМИ КИСЛОТАМИ

Анотація. В роботі вивчено кінетичні закономірності хімічного модифікування епоксидних смол аліфатичними та ароматичними двоосновними кислотами. Як епоксидні смоли використовували промислові діанові смоли марок ЕД-20 та ЕД-24. В якості двоосновних карбонових кислот були використані наступні: щавлева кислота, малінова кислота, буриштинова кислота, себацінова кислота, малеїнова кислота, терефталева кислота та ізопталева кислота. Розраховані ефективні константи швидкостей реакцій та енергії активації між епоксидною смолою та різними за природою кислотами. Запропоновано методи синтезу олігомерів, що містять епоксидні і карбоксильні групи. Структура синтезованих олігомерів підтверджена хімічними та ІЧ спектроскопічними методами досліджень.

Ключові слова: епоксидна смола, карбонова кислота, кінетичні дослідження, ефективна константа швидкості реакції, енергія активації, ІЧ спектроскопія.