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SYNTHESIS AND PROPERTIES OF CARBOXY-CONTAINING PEROXY OLIGOMER

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Abstract. Carboxy-containing peroxy oligomer (CPO) has been synthesized *via* the reaction of peroxy derivative of ED-24 epoxy resin with free peroxy and epoxy groups with adipic acid in the presence of benzyl triethylammonium chloride. The effect of catalyst amount, reaction temperature and process time on the reaction rate has been determined. The effective rate constants and activation energies have been calculated. CPO synthesis procedure has been developed. CPO structure has been confirmed by chemical and IR-spectroscopic analyses. CPO was studied as an additive for the cross-linking of epoxy-oligoesteric mixtures based on ED-20 epoxy resin and TGM-3 oligo-esteracrylate. Using IR-spectroscopy the chemism of the mentioned cross-linking has been determined.

Keywords: epoxy resin, oligoesteracrylate, peroxy group, carboxy group, acid number, cross-linking, gel-fraction, film hardness, IR-spectroscopy.

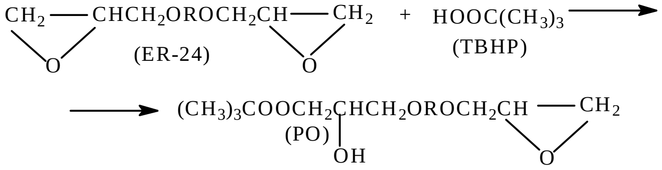
1. Introduction

It is well-known [1] that oligomers containing labile –O–O– bonds are safer and have higher stability during storage compared with low-molecular peroxides. Recently epoxy resins of various structures [2-4] have been used as initial compounds for the peroxy oligomers (PO) synthesis. In contrast to the initial compounds, PO synthesized on the basis of epoxy resins are already thermoreactive compounds. They may form free radicals at heating allowing to use them in those polymeric mixtures the cross-linking of which proceeds *via* radical mechanism [5]. At the same time it is important that PO contain other functional groups in addition to –O–O– bond. Hence the formation of three-dimensional structures *via* polycondensation mechanism will be possible.

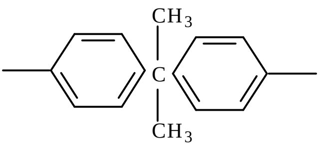
Literature data describe PO containing –O–O– bond in their structure, as well as epoxy and hydroxy groups [2], fluorine-containing and hydroxy groups [6] and others [4].

This work deals with the synthesis of PO which contain peroxy, carboxy and hydroxy groups in their structure. The presence of –O–O– bond and carboxy group in the ooligomer molecule allows to extend the area of PO application and to increase the adhesive properties of the films on their basis.

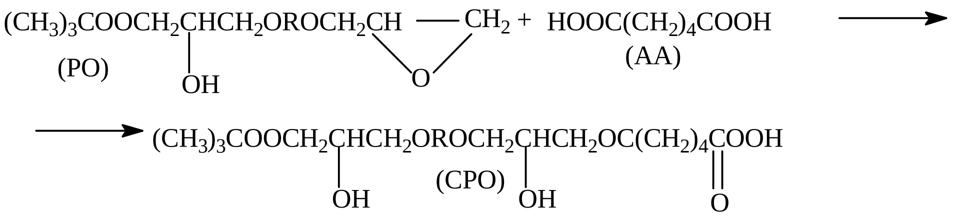
We propose to obtain carboxy-containing peroxy oligomer (CPO) by two stages, using ED-24 epoxy resin as an initial compound. At the first stage PO is synthesized in accordance with the known procedure [2]. PO contains –O–O– bond and free epoxy group:



(1)

where: R=


At the second stage PO is treated by adipic acid (AA) in accordance with the reaction (2):



$$\underset{\text{(PO)}}{(CH_3)_3COOCH_2\underset{OH}{CH}CH_2OROCH_2\underbrace{CH-CH_2}_{O}} + \underset{\text{(AA)}}{HOOC(CH_2)_4COOH} \longrightarrow \qquad (2)$$

$$\longrightarrow (CH_3)_3COOCH_2\underset{OH}{CH}CH_2OROCH_2\underset{OH}{CH}CH_2O\underset{O}{\overset{}{C}}(CH_2)_4COOH \quad \text{(CPO)}$$

CPO molecule contains peroxy, hydroxy and carboxy groups at the same time and may be used as the active component of the polymeric mixtures.

2. Experimental

2.1. Materials

We used ED-24 industrial epoxy resin ED-20 with a molecular mass (M_n) of 340 g/mol and epoxy number (*e.n.*) of 24.0 %. The adipic acid was used as received without additional purification.

PO was synthesized in accordance with [7] using ED-24 (100 g), 98%-TBHP (66.0 g) and catalytic mixture consisting of BTEACh (19.0 g) and KOH (3.9 g). It was found: M_n 420 g/mol, *e.n.* 9.0 % and active oxygen content ($[O]_{act}$) 2.9 %.

The following compounds were used as the catalyst:

– Benzyl triethylammonium chloride (BTEACh)

– Potassium hydroxide (KOH)

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

ED-20 epoxy dianic resin was used for cross-linking and characterized by M_n 390 g/mol and *e.n.* 20.1 %.

Oligoesteracrylate TGM-3 as the technical one was used with M_n 280 g/mol.

Polyethylenepolyamine (PEPA) was used as received without additional purification.

2.2. Analytical Methods

The number-average molecular mass of the synthesized products were 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 alkaline solution [8]. The active oxygen content was determined in accordance with [9]. The content of carboxy groups was calculated according to the procedure described in [8]. Film hardness and gel fraction content were determined using the known procedures [10].

2.3. Spectral Methods

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

IR-spectroscopic investigations of the epoxy-oligomeric mixtures were carried out using Therma Electron Corporation-Nicolet 8700 device in the spectroscopic laboratory of Gdansk Technical University (Poland). The device is equipped with an adapter Specac Golden Gate with ATR diamond crystal.

The epoxy-oligomeric mixtures prepared by the procedure described above are applied by a thin layer over the plate with KBr. The film is pressed by other plate with KBr using the mechanical instrument and IR-spectrum is recorded. The plates with the films are placed in a desiccator and sustained at room temperature for 24 h. Then the following spectrum is recorded. After heating at 423 K IR-spectra are recorded every 30 min.

2.4. Experimental Procedure

2.4.1. The procedure for reaction kinetics

Kinetic investigations of the reaction between PO and AA were carried out in the three-necked reactor equipped with a mechanical stirrer, thermometer and back condenser. PO solution and AA in isopropanol were loaded into the reactor. The catalyst was added under constant stirring. Then the mixture was thermostated till the necessary temperature and samples (0.5 ml by volume) were withdrawn after definite time intervals. The concentration of carboxy groups in the samples was determined using the formula:

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

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

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

2.4.2. CPO synthesis

The solution of PO (30 mg) dissolved in 150 g of isopropanol was loaded into the three-necked reactor equipped with a mechanical stirrer, back condenser and thermometer. The mixture was heated under stirring to 333 K. Then 12.0 g of adipic acid and 3.7 g of benzyl triethylammonium chloride dissolved in 3.3 ml of water were added. The reaction mass was sustained at 333 K under stirring for 20 h. Then 150 ml of toluene was added and the mixture was carried into a dividing funnel. The bottom layer is not used and the upper one was washed by water till the catalyst was removed. After vacuum distillation 39.6 g of CPO was obtained (yield 94.2 %).

2.4.3. Cross-linking of epoxy-oligomeric mixtures

Epoxy-oligomeric mixtures were prepared and cross-linked according to the procedure described in [11].

2.4.4. Determination of acid number in cross-linked samples

Acid number (*a.n.*) in cross-linked samples was determined according to the procedure described in [11].

3. Results and Discussion

3.1. CPO Synthesis

To develop the CPO synthesis method by Scheme (2) it is necessary to study the effect of catalyst amount, temperature and process time on the reaction rate.

While analyzing literature data [12] it was found that the best proceeding of the reaction between organic acid and compound with epoxy ring takes place in the presence of BTEACh as a catalyst. The results of the catalyst effect on the reaction between PO and AA are represented in Fig. 1.

Fig. 1 shows that in case of 5 mol % of BTEACh the reaction between PO and AA does not proceed. The increase of catalyst amount to 10 mol % and higher allows the reaction to proceed in accordance with Scheme (2). Under the economic reasons and obtained results we consider that 20 mol % of BTEACh for 1 g-eq of PO epoxy group is sufficient to obtain CPO. The effective rate constants of the reaction between PO and AA are calculated from Fig. 1 and given in Table 1.

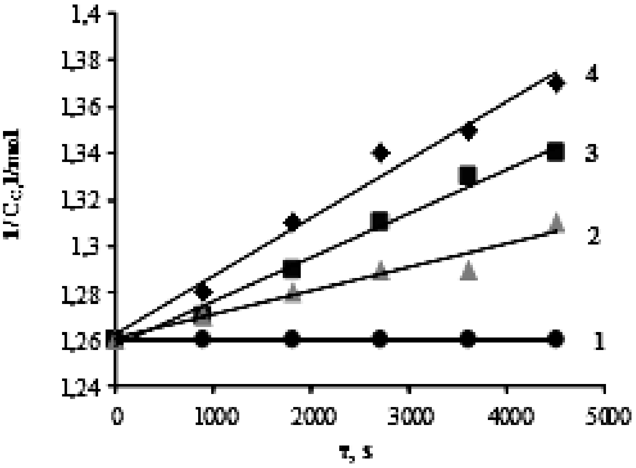


Fig. 1. Kinetic anamorphoses in 1/C$_c$ *vs* τ coordinates for the reaction between PO and AA at 333 K in the medium of isopropanol. AA amount is 1.0 for 1 g-eq. of PO epoxy group; BTEACh amount (mol %/g-eq. of PO epoxy group): 5 (1); 10 (2); 20 (3) and 30 (4)

Table 1

Effective rate constants of the reaction between PO and AA

Reaction temperature, K	BTEACh amount, mol %	$K_{ef}\cdot10^4$, l/mol·s
333	5	does not proceed
	10	0.11 ± 0.01
	20	0.18 ± 0.01
	30	0.24 ± 0.01
323	20	0.11 ± 0.01
343	20	0.27 ± 0.01

Note: isopropanol is a reaction medium; BTEACh is as 53 % aqueous solution

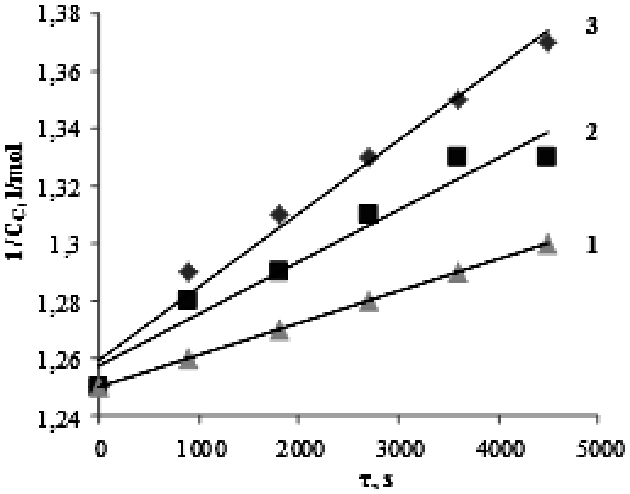


Fig. 2. Kinetic anamorphoses in 1/C$_c$ *vs* τ coordinates for the reaction between PO and AA in the medium of isopropanol at 323 (1); 333 (2) and 343 (3) K. BTEACh amount is 20 mol %; AA amount is 1.0 mol for 1 g-eq. of PO epoxy group

20 mol % of BTEACh increases the reaction rate twice compared with 10 mol % and slightly differs from K_{ef} obtained while using 30 mol % of the catalyst.

The effect of temperature on the proceeding of the reaction between PO and AA is represented in Fig. 2.

The effective rate constants are calculated from Fig. 2 and given in Table 1. Then the calculated values were used to plot the linear dependence in $\lg K_{ef}$ coordinates as the function of $1/T$ (Fig. 3).

The activation energy of the reaction between PO and AA was found from Fig. 3 to be 42 kJ/mol.

Besides the catalyst amount and reaction temperature the reaction time also affects the reaction proceeding. For this purpose the studies were carried out which established the time of complete depletion of epoxy groups in the reaction.

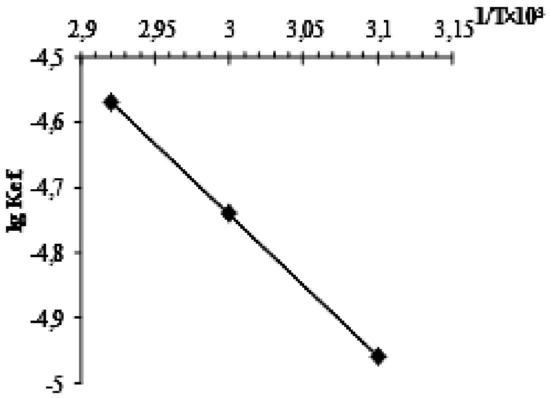


Fig. 3. Dependence of $\lg K_{ef}$ on $1/T$ for the reaction between PO and AA in the medium of isopropanol. BTEACh amount is 20 mol %, AA amount is 1.0 mol for 1 g-eq. of PO epoxy group

Fig. 4 shows that almost all epoxy groups are depleted for 20–21 h.

Thus the following conditions were chosen for the reaction between PO and AA:

- BTEACh catalyst in the amount of 20 mol % for g-eq. of PO epoxy group;
- reaction temperature of 333 K, because at higher temperatures the partial decomposition of peroxy groups in both initial and end products is possible;
- the reaction time is about 20 h;
- reaction medium is isopropanol, *i.e.* solvent which dissolves both initial and end products.

The obtained results were the basis for CPO synthesis procedure described in Subsection 2.4.2.

The synthesized CPO is an amorphous product of white color with the molecular mass of 560 g/mol, active oxygen content of 2.0 % and carboxy groups content 8.8 %. Epoxy groups are absent in the product. CPO is soluble in dioxane, chloroform, toluene+isopropanol mixture (ratio 1:1) and other organic solvents.

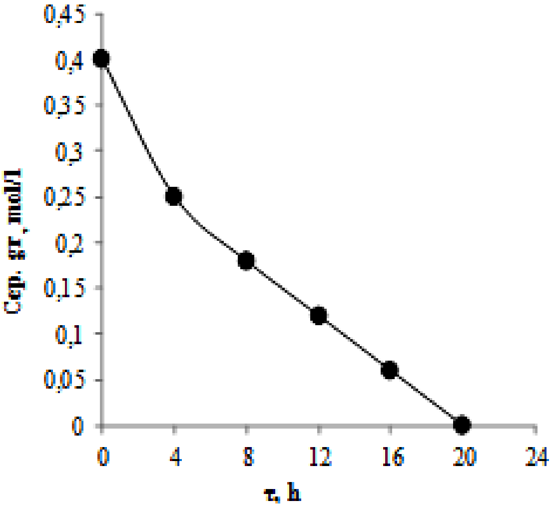


Fig. 4. Change of epoxy groups concentration for the reaction between PO and AA at 333 K in the medium of isopropanol. BTEACh amount is 20 mol %; AA amount is 1.0 mol for 1 g-eq. of PO epoxy group

3.2. IR-Spectroscopic Investigations of CPO

CPO structure is confirmed by IR-studies performed in accordance with the procedure described in Section 2.3. In CPO spectrum the absorption bands at 910 cm^{-1} are absent. It means that free epoxy groups are not present in the synthesized product. At the same time there is an absorption band at 1724 cm^{-1} typical of carbonyl group stretching vibrations in the esteric bond. It means that AA molecules join to PO resulting in the esteric bonds formation.

The presence of peroxy groups in CPO is confirmed by a slight peak at 880 cm^{-1} typical of –OO– bond stretching vibrations and by doublet of hem-dimethyl vibrations at 1380 and 1360 cm^{-1} typical of $(CH_3)_3C$– group which is a part of peroxy fragment. Free carboxy group is confirmed by stretching vibrations at 3400 and 1140 cm^{-1}; the secondary hydroxy group – at 1040 and 3360 cm^{-1}.

3.2. Cross-linking of Epoxy-Oligomeric Mixtures

The synthesized CPO was studied as an additive to the epoxy-oligomeric mixtures based on ED-20 industrial epoxy resin and TGM-3 oligoesteracrylate. Polyethylenepolyamine (PEPA) was the cross-linking agent for the mixtures.

The composition of epoxy-oligomeric mixtures with different amount of CPO is given in Table 2. The mixture without CPO was studied for the comparison (Mixture V, Table 2).

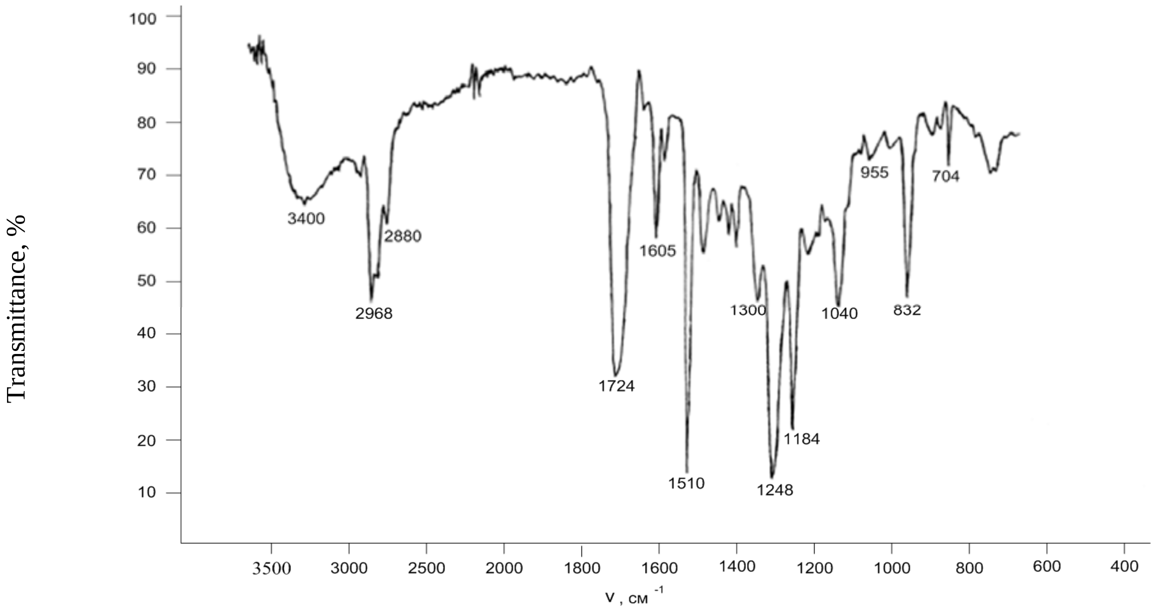


Fig. 5. IR-spectrum of CPO

Table 2

Composition of epoxy-oligomeric mixtures

Component	Component content, mass parts				
	I	II	III	IV	V
ED-20 resin	82	73	55	60	91
CPO	9	18	36	40	-
TGM-3	9	9	9	-	9
PEPA	11.5	10.2	9.1	8.4	14

Note: PEPA content was calculated relative to the amount of ED-20 epoxy groups, on the assumption of 14 mass parts of PEPA per 20 g of epoxy groups

Table 3

Dependence of gel-fraction content and films hardness upon the temperature, cross-linking time and mixtures composition

T, K	Mixture in accordance with Table 2	Index	Symbol values at cross-linking time, min					
			24 h under ambient conditions	15	30	45	60	75
383	I	*G*	70.2	77.3	82.9	83.2	84.1	85.1
		H	0.25	0.50	0.63	0.66	0.77	0.85
	II	*G*	20.3	58.8	42.5	50.7	60.1	55.4
		H	Nonuniform surface					
	III	*G*	31.8	46.0	46.0	51.0	51.9	53.0
403	I	*G*	70.2	67.9	88.0	90.6	92.3	91.8
		H	0.25	0.52	0.83	0.85	0.87	0.87
	II	*G*	20.3	54.8	58.5	64.3	63.5	66.5
	III	*G*	31.8	49.6	44.1	55.1	51.9	58.2
	IV	*G*	48.0	46.0	59.1	68.6	69.6	77.6
423	I	*G*	70.2	93.1	92.4	93.2	93.3	93.3
		H	0.25	0.79	0.83	0.91	0.91	0.91
	II	*G*	20.3	39.4	51.6	51.1	65.2	75.0
	III	*G*	31.8	39.3	54.8	56.2	55.5	75.9
	IV	*G*	48.0	60.0	73.8	74.9	82.9	83.1
	V	*G*	71.7	79.1	86.6	87.6	92.1	92.1
		H	0.26	0.71	0.82	0.87	0.87	0.87

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

Table 4

Dependence of *a.n.* in Mixture III on the temperature and cross-linking time

T, K	*A.n.* values (mg KOH/g) for cross-linking time, min					
	24 h under ambient conditons	15	30	45	60	75
383	65.8	63.3	62.9	55.3	54.8	52.9
403	65.8	63.0	61.8	52.6	46.9	39.5
423	65.8	63.2	58.7	50.8	38.0	33.8

Note: *a.n.* was determined before extraction with acetone

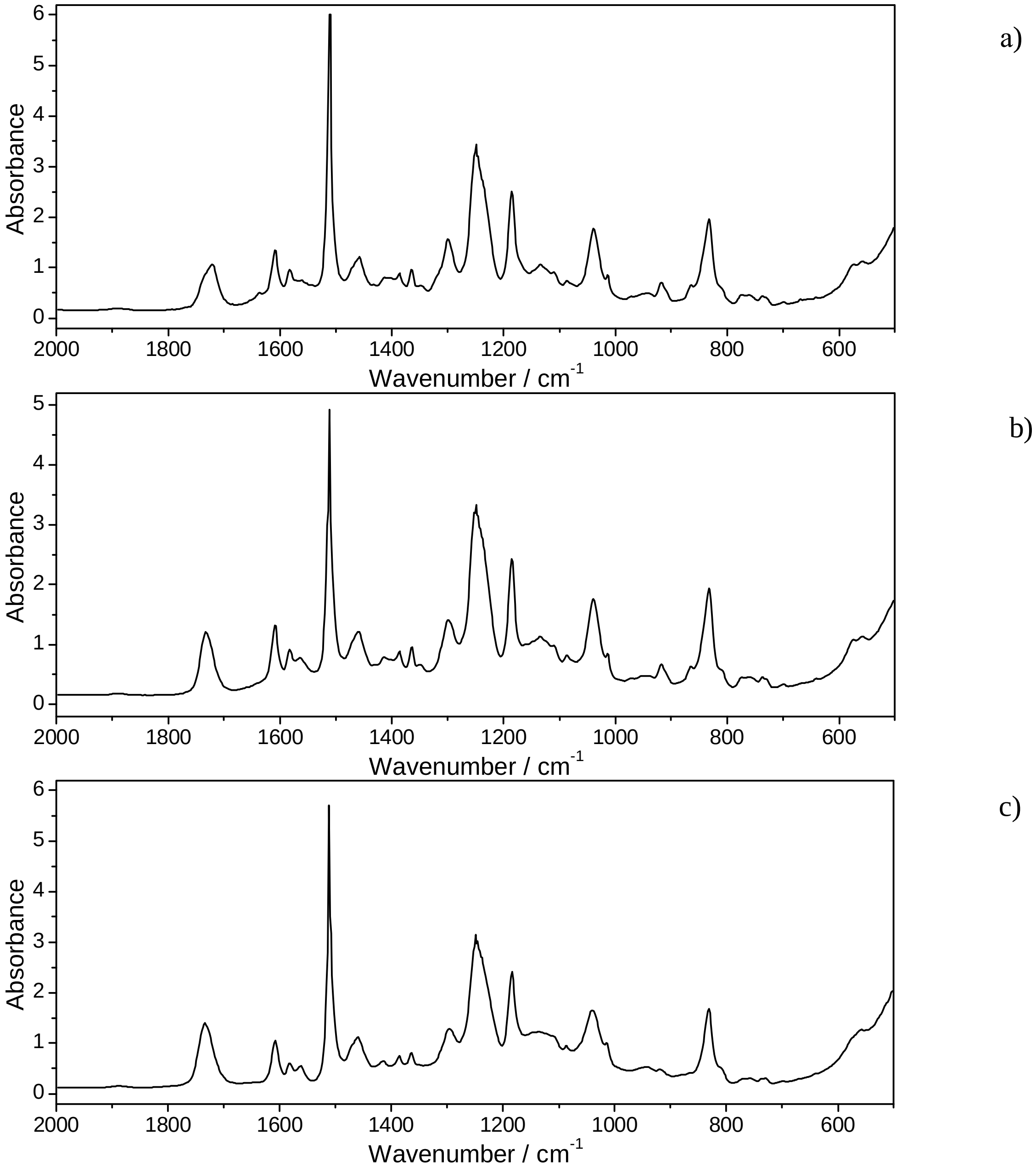


Fig. 6. IR-spectra of Mixture III: after mixture preparation (a); after cross-linking at room temperature for 24 h (b) and after heating to 423 K for 1.5 h (c)

The cross-linking of the mixtures given in Table 2 was studied in accordance with the procedure [11] first at room temperature for 24 h and then at heating to 383, 403 or 423 K for 15, 30, 45, 60 and 75 min. The obtained results are represented in Table 3.

One can see that gel-fraction content in the cross-linked samples and hardness of the obtained films depend on CPO amount, cross-linking temperature, as well as time of films forming.

It should be noted that the increase in CPO amount to 18 mass parts and more leads to the formation of nonuniform surface of the polymeric film. Thus it is difficult to determine film hardness by means of pendulum device M-3. The reason is that peroxy groups concentration increases with the increase of CPO amount in the epoxy-oligoesteric mixtures. The peroxy groups decompose at heating and form radicals and low-molecular products, namely *tert*-butanol and acetone [9]. On the one hand the formed oligomeric radicals may participate in the formation of three-dimensional structure due to the cooligomerization of TGM-3 molecules, on the other hand they are capable to recombine and form linear structures which are soluble in the organic solvents. Low-molecular products due to the rapid formation of three-dimensional compounds do not have time to evaporate. Hence the nonuniform surface of the film is formed.

In the mixtures with CPO content of 18, 36 and 40 mass parts (Mixtures II, III and IV, Table 3) the amount of insoluble products decreases. The same results are obtained for the mixtures II, III and IV owing to the increase of cross-linking temperature to 403 and 423 K. The temperature increase accelerates the peroxy groups decomposition in CPO molecules and favors the recombination reaction. All above-mentioned does not concern Mixture I, CPO content of which is 9 mass parts. This Mixture is the most optimum and obtained films are characterized by sufficient indexes of hardness and gel-fraction content.

Comparing the results obtained for Mixtures I and V (Mixture V is without CPO) one can see that the presence of CPO (9 mass parts) increases both film hardness and gel-fraction content already for 15 and 30 min of cross-linking at 423 K.

To establish the role of CPO carboxy group in the cross-linking of epoxy-oligomeric mixtures we determined the acid number (*a.n.*) in the cross-linked samples in accordance with the procedure described in [11]. The results obtained for Mixture III are represented in Table 4.

The samples are characterized by ***a.n.*** at room temperature as well as at heating. Moreover, the heating for 15–75 min decreases values of acid number. The obtained results show that ***a.n.*** determined in the cross-linked samples is in accordance with the reaction (3):

$$\sim\!\sim COOH + KOH \rightarrow \sim\!\sim COOK + H_2O \qquad (3)$$

The results from Table 4 allow to assert that at room temperature carboxy groups of CPO do not interact with hydroxy and epoxy ones of ED-20 resin. Moreover, the part of epoxy groups reacted with PEPA is insignificant (Figs. 6 and 7).

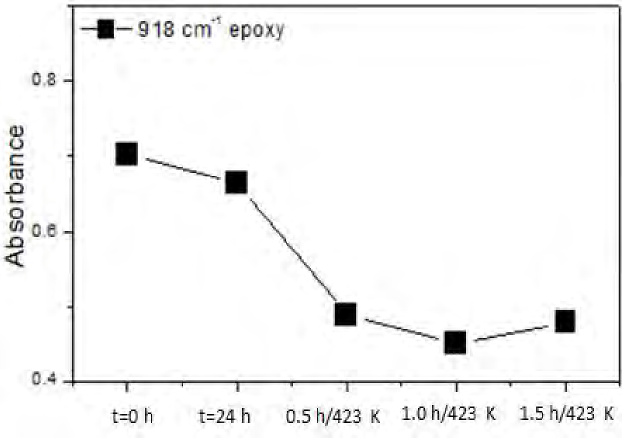
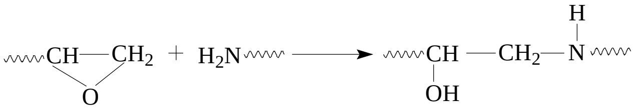
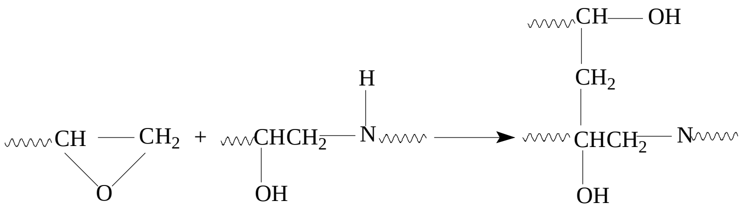


Fig. 7. The change of absorption band intensity at 918 cm^{-1} in Mixture III during cross-linking

The heating of Mixture III to 423 K for 30 min (Fig. 7) sharply decreases the absorption bands typical of epoxy group. It means that under mentioned conditions the epoxy group of ED-20 resin intensively reacts with PEPA amine groups accordingly to the reactions (2) and (3):



$$\sim\!\underset{\diagdown\,O\,\diagup}{CH-CH_2} + H_2N\!\sim \longrightarrow \sim\!\underset{OH}{\underset{|}{CH}}-CH_2-\overset{H}{\overset{|}{N}}\!\sim \qquad (4)$$



$$\sim\!\underset{\diagdown\,O\,\diagup}{CH-CH_2} + \sim\!\underset{OH}{\underset{|}{CH}}CH_2-\overset{H}{\overset{|}{N}}\!\sim \longrightarrow \sim\!\underset{OH}{\underset{|}{CH}}CH_2-\overset{\sim CH-OH}{\overset{|}{\overset{CH_2}{\overset{|}{N}}}}\!\sim \qquad (5)$$

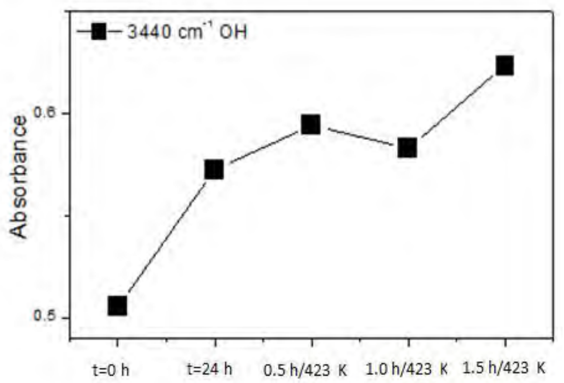


Fig. 8. The change of absorption band intensity at 3440 cm^{-1} in Mixture III during cross-linking

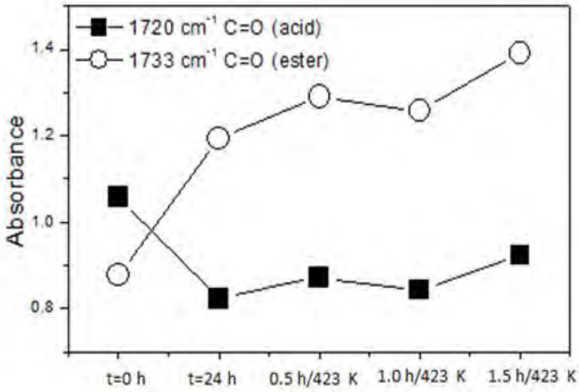
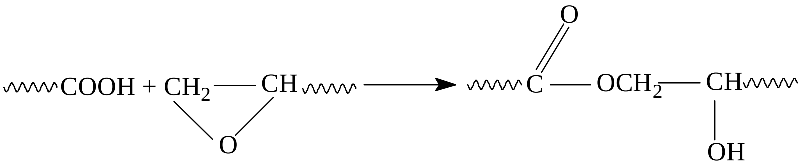


Fig. 9. The change of intensity of carboxy group absorption band at 3440 cm^{-1} in the acid and at 1733 cm^{-1} in the ester in Mixture III during cross-linking

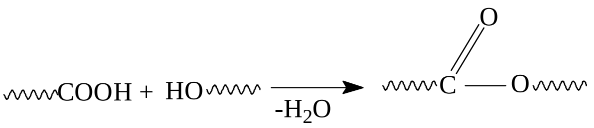
The increase of absorption band intensity at 3440 cm^{-1} typical of stretching vibrations of hydroxy group (Figs. 6 and 8) reveals the proceeding of the reactions (2) and (3).

If the process of three-dimensional structure formation by the reaction (4) takes place at room temperature, the reaction (5) proceeds at heating. The result is the increase of gel-fraction content (Table 3). At the same time the heating leads to the decrease of acid number in the cross-linked mixture (Table 4). Moreover, the decrease of intensity of carboxy group absorption band corresponding to the free acid group takes place during cross-linking already at room temperature (Figs. 6 and 9). It means that when the reactions (4) and (5) proceed, the heat evolution occurs [13] during cross-linking at room temperature. The mixture heating results in the interaction between carboxy group by both reactions (4) and (5):

The proceeding of the reaction (7) with separation of water molecules, as well as decomposition of CPO molecules followed by acetone and *tert*-butyl alcohol formation develops the nonuniform surface (as it was above mentioned, Table 3) with great amount of CPO in the mixture. The interaction between hydroxy, epoxy and carboxy groups in accordance with the reactions (6) and (7) decreases *a.n.* in the cross-linked samples (Table 4). The higher cross-linking temperature, the higher interaction with carboxy groups according to the reactions (6) and (7).

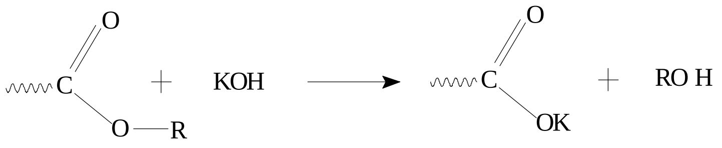


(6)



(7)

At the same time in spite of the intensity decrease of the absorption band for carboxy group in the acids (Fig. 9) we do not observe the intensive decrease of *a.n.* in the cross-linked sample (Table 4). The possible reason may be the partial usage of potassium hydroxide (necessary for *a.n.* determination) in accordance with the reaction (8):



(8)

Fragments formed by the reactions (6) and (7) as well as TGM-3 molecules may participate in the reaction (8).

Thus on the basis of experiments concerning cross-linking of epoxy-oligoesteric mixtures in the presence of CPO we may assert that interaction between ED-20 and PEPA molecules takes place at room temperature. This reaction leads to the mixture heating. Hence partial decomposition of CPO peroxy groups occurs which causes three-dimensional copolymerization of TGM-3 molecules. Moreover, partial interaction with CPO carboxy groups by the reactions (6) and (7) also takes place. Tertiary amine formed in accordane with the reaction (5) is the catalyst for the reactions (6) and (7). The mixture heating to 383 K and higher temperatures accelerates the above-mentioned reactions, namely (6) and (7). The heating increases gel-fraction content in the cross-linked samples.

4. Conclusions

1. The procedure was developed and carboxy-containing peroxy oligomer with free peroxy, carboxy and hydroxy groups was synthesized on the basis of ED-24 resin peroxy derivative (PO) and adipic acid (AA) in the presence of benzyltriethylammonium chloride. The activation energy of the reaction between PO and AA was found to be 42 kJ/mol.

2. The presence of peroxy groups in IR-spectrum is confirmed by stretching vibrations at 880 cm^{-1} and doublet of hem-dimethyl vibrations at 1380 and 1360 cm^{-1}. The band of stretching vibrations at 3400 and 1140 cm^{-1} corresponds to the free carboxy group. The presence of hydroxy group is confirmed by vibrations at 1040 and 3360 cm^{-1}.

3. We established that gel-fraction content in the cross-linked samples and hardness of the films based on ED-20 industrial epoxy resin, TGM-3 oligoesteracrylate, CPO and PEPA depend on CPO amount in the mixture, cross-linking temperature and time of films formation.

4. The cross-linking of epoxy-oligoestertic mixtures on the basis of ED-20, TGM-3 and PEPA in the presence of CPO takes place at room temperature, as well as at heating to 383, 403 and 423 K.

5. Participation of CPO carboxy groups in the cross-linking process is confirmed by IR-spectroscopy.

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СИНТЕЗ І ВЛАСТИВОСТІ КАРБОКСИЛВМІСНОГО ПЕРОКСИДНОГО ОЛІГОМЕРУ

Анотація. *За реакцією пероксидної похідної епоксидної смоли ЕД-24, що містить вільну пероксидну і епоксидну групу, з адипіновою кислотою в присутності бензилтриетиламонію хлористого вивчена можливість синтезу карбоксилвмісного пероксидного олігомеру (КПО). Встановлено вплив кількості каталізатора, температури реакції та тривалості процесу на швидкість вищевказаної реакції. Розраховано ефективні константи швидкості реакції та енергію активації. Запропонована методика синтезу КПО. Структура КПО підтверджена хімічним та ІЧ-спектроскопічним методами дослідження. КПО вивчений як додаток в процесах структурування епокси-олігомерних сумішей на основі епоксидної смоли ЕД-20 і олігоестеракрилату ТГМ-3. З використанням ІЧ-спектроскопії встановлено хімізм процесу структурування епокси-олігомерних сумішей в присутності КПО.*

Ключові слова: *епоксидна смола, олігоестеракрилат, пероксидна група, карбоксильна група, кислотне число, структурування, гель-фракція, твердість плівок, ІЧ-спектроскопія.*