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SYNTHESIS AND APPLICATION OF EPOXY-OLIGOESTERIC MIXTURES OF ED-20 EPOXY RESIN PEROXIDE DERIVATIVE DURING CROSSLINKING

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Abstract. The reaction of chemical modification of ED-20 epoxy resin with isopropylbenzene hydroperoxide has been studied. The process duration effect on the reaction between resin and hydroperoxide has been determined. The possibility to use the synthesized product as a component in the process of epoxy-oligoesteric compositions crosslinking with application of hardeners various by their nature has been studied.

Keywords: epoxy, isopropylbenzene hydroperoxide, modification, crosslinking, gel fraction, hardener.

1. Introduction

The formation of spatially crosslinked blends based on epoxy resins occurs in the presence of hardeners varied in their nature [1]. As the plasticizer of such blends the unsaturated oligoesteracrylates, specifically oligoesteracrylate TGM-3, are applied**.** The aliphatic polyamines and acids anhydrides are used as hardeners. The inability to chemically bind oligoesteracrylate with epoxy resin molecules during product molding indicates the disadvantage of the above mentioned mixture. It causes worsening of exploitation properties of the products based on such mixtures.

It has been previously shown that in order to bind the oligoesteracrylate molecules with epoxy resin molecules into a mixture, the modified by *tert*-butyl hydroperoxide epoxy resin which contains in its structure free epoxy and peroxide groups, should be additionally added. [2]. While crosslinking the epoxy-oligoesteric mixtures, the application of such compounds enables to chemically bind epoxy resin and oligoesteracrylate molecules. As a result, the epoxy resin and modified epoxy resin molecules form a structure containing free peroxide groups at room temperature in the presence of hardeners. Further heating up to 383K and above causes the labile peroxide groups decomposition with free radicals formation. The created radicals cause polymerization of oligoesteracrylate unsaturated links and graft molecules of such compounds to structural matrix based on epoxy resin.

On the other hand, the scientific sources prove [2] that the peroxides decomposition containing a fragment of isopropylbenzene hydroperoxide decomposes by an average of 20 K in comparison with peroxide containing fragments of *tert*-butyl hydroperoxide. Consequently, the epoxy-oligoesteric mixtures application as the active additive of epoxy resin, modified by isopropylbenzene hydroperoxide, allows to reduce the molding temperature of products based on the above mentioned compounds.

In addition, it is essential to determine if other substances may be the hardeners for epoxy-oligoesteric mixtures.

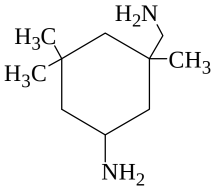
2. Experimental

2.1. Initial Substances and their Purification

The following substances were used:

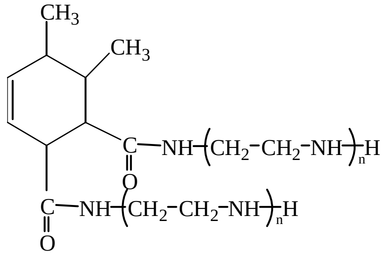
- industrial ED-20 dianic epoxy resin without additional purification with molecular weight (M_n) 400 g/mol and the epoxy groups content (*e.n.*) 20.4 %;
- isopropylbenzene hydroperoxide (IPBHP) by formula $C_6H_5C(CH_3)_2OOH$ containing 10.5 % of active oxygen $[O]_{act}$;
- benzyltriethylammonium chloride (BTEAH) by formula $[(C_2H_5)_3NCH_2C_6H_5]Cl$ with M_n 227.5, type “chemically pure”;

- potassium hydroxide (KOH) and toluene, type “chemically pure” without additional purification;
- polyethylenepolyamine (PEPA) by formula $H_2N(CH_2–CH_2–NH_2)_n$ H, where n = 3, 4 and 5, type “pure”;
- isophorenediamine (IFDA) by formula:



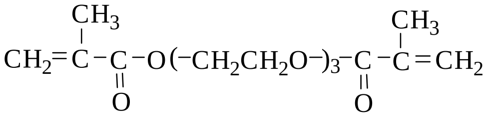
with M_n = 170.3, type “pure”;

- polyethylenepolyamide by formula:



where n = 1-2, type “pure”;

- triethyleneglycoldimethacrylate (oligoesteracrylate TGM-3) by formula



$$CH_2=\underset{}{\overset{CH_3}{C}}-\underset{O}{\underset{\|}{C}}-O(-CH_2CH_2O-)_3-\underset{O}{\underset{\|}{C}}-\overset{CH_3}{C}=CH_2$$

with M_n = 280, type “pure”.

2.2. Analytical Methods

The average molecular weight M_n of the synthesized resin was determined by cryoscopic method, using dioxane as solvent. The epoxy number (*e.n.*) was determined by back titration of hydrochloric acid solution and acetone 0.1 N with alkali solution [3]. The gel fraction content (*G*, %) was determined in the Soxhlet apparatus for 12 h at the boiling point of the solvent [4]. The hardness of the films (*T*, rel. units) was measured on the pendulum device M-3 at room temperature [5]. The hygroscopic property of the samples was determined after being kept within 97 % humidity environment [6] for 48 h.

2.3. Investigations Procedure

2.3.1. Kinetics of modified isopropylbenzene hydroperoxide epoxy resin synthesis

The synthesis of epoxy modified resin with isopropylbenzene hydroperoxide was studied in the three-necked reactor equipped with mechanical stirrer, back condenser and thermometer. The reactor was loaded with ED-20 epoxy resin, hydroperoxide, and solvent. The reaction mixture was stored in the thermostat at 323K. Under continuous stirring the 60 % aqueous catalyst solution in the amount of 15.0 mol % and 40 % aqueous KOH co-catalyst solution in the amount of 12.5 mol % per 1 g-eq. of a resin epoxy group were added. After the definite time the samples were withdrawn and the concentration of epoxy groups in the reaction mixture were determined according to the method described in [1].

2.3.2. Isopropylbenzene hydroperoxide modified by epoxy resin (ESP) obtaining

The ED-20 epoxy resin in the amount of 50 g was dissolved in 150 ml of toluene at 323K in the reactor. 50 g of isopropylbenzene, 13.3 g of 60 % BTEAH solution, and 4 g of 40 % KOH solution were added to the homogenous mass under continuous stirring. The reaction mixture was kept under stirring for 12 h at 323 K. After the end of the reaction the mixture was cooled to room temperature, transferred to a separating funnel, and the remains were washed out with the solvent. The reaction mass was settled in the funnel for over 0.5 h until two phases appeared. The lower layer with catalyst and co-catalyst was washed out and the upper one was washed with a small amount of distilled water until a neutral reaction was achieved. The organic layer was transferred to a flask to be vacuumed. The distilled water and solvent remains were taken away. The remains in the flask were precipitated with petroleum ether and dried at 318 K until constant weight was achieved.

A light-yellow product in amount of 65 g with 530 g/mol molecular weight, 2.6 % active oxygen content and 7.6 % epoxy number was obtained. The oligomeric product is soluble in the most organic solvents.

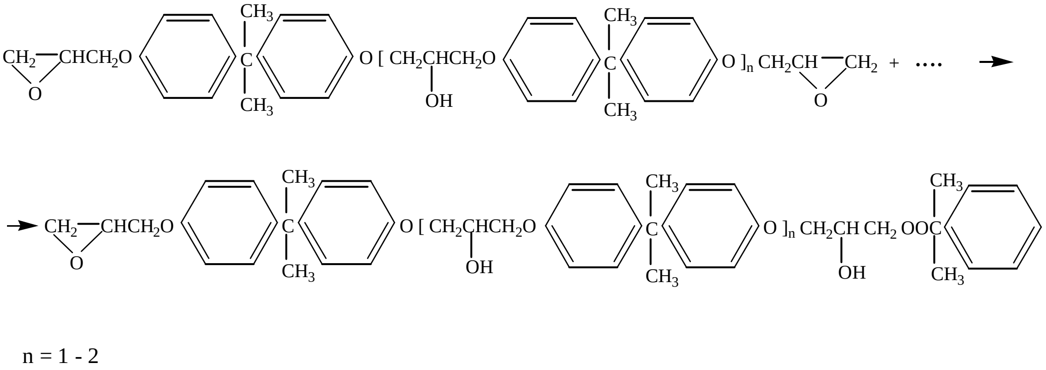
2.3.3. Epoxy-oligoesteric blends crosslinking

The mixtures based on ESP and ED-20 epoxy resin were prepared by mixing the components at room temperature or heating them to 313 K for 15–20 min with subsequent adding of hardener to the homogeneous mixtures. The mixtures were put on the standard glass or metal plates previously degreased by acetone and the compositions hardening was carried out at the temperature of 403 K for 10–50 min. The structural changes monitoring was carried out by the film hardness determined at room temperature applying the M-3 device and also by the crushed samples gel fraction content determined in the Soxhlet apparatus by acetone extraction for 10–12 h.

3. Results and Discussion

3.1. Synthesis of Epoxy Resin Modified by Isopropylbenzene Hydroperoxide (ESP)

The ESP synthesis can be represented by the following equation:



n = 1 - 2

Taking into account that a product which contains both epoxy and peroxy groups can be successfully used as an active additive of epoxy-oligoesteric mixtures, the process should proceed for the time sufficient to decrease the epoxy groups by half. The study was conducted by the method described in Subsection 2.3.1, and the result is shown in Fig. 1.

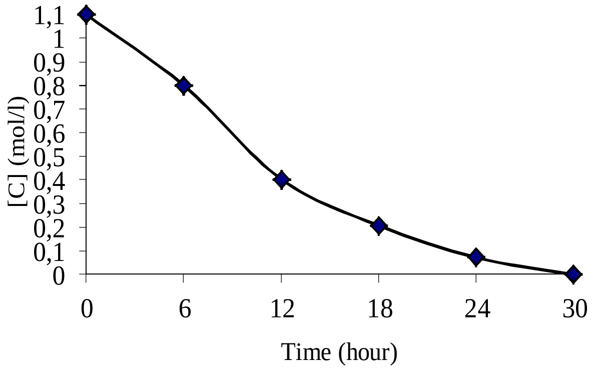


Fig. 1. The concentration dependence of epoxy groups on time at 323 K for the reaction of ED-20 resin with HPIPB at the ratio ED-20:HPIPB = 1:2 mol

During the reaction at 323K for 30 h, the epoxy groups are completely absent in the reaction mixture. This fact indicates that under present conditions there is a complete replacement of the ED-20 resin epoxy groups for the HPIPB fragments. On the other hand, it is shown that the epoxy groups concentration decrease by half can be achieved for 10–12 h. These results were used for the further development of ESP synthesis procedure which is presented in Subsection 2.3.2. The data concerning the results of the active oxygen content and epoxy numbers indicate that the synthesized product contains both free epoxy and peroxy groups. The obtained product was studied as an active additive of epoxy-oligoesteric mixtures.

3.2. Epoxy-Oligoesteric Compounds Crosslinking in the Presence of ESP

The epoxy-oligoesteric compounds crosslinking in the presence of ESP was studied by applying hardeners various by nature. The methodology of the research was described in Subsection 2.3.3.

3.2.1. Mixtures crosslinking with polyethylenepolyamine (PEPA)

PEPA is a traditional hardener for the mixtures containing epoxy resin as the main component. During the research of epoxy-oligoesteric mixtures containing ESP it was essential to determine the effect of ESP and oligoesteracrylate TGM quantity on the gel fraction content and the hardness of films structured in the presence of PEPA. The composition of epoxy-oligoesteric mixtures with PEPA as the hardener is presented in Table 1, and the investigation results – in Table 2.

Based on the results of Table 2 and taking into account the fact that the ESP resin is more expensive product than ED-20 resin, we could assume that the optimum amount of ESP product in the epoxy-oligoesteric composition is 10 wt parts per 90 wt parts of ED-20 resin (mix III).

The obtained results were used to determine the effect of oligomer TGM-3 quantity on the gel fraction content and the polymer films hardness. The quantities of TGM-3 in mixtures were 8, 16, 24, and 32 wt parts (Table 1). The investigations demonstrate (Table 3) that the values of gel fraction content and film hardness while decreasing unsaturated oligoester content to 8 wt parts in the mixture at 403 K slightly differ from those of the mixture with 16 wt. parts (mix III). The further increase to 24 and 32 wt. parts of TGM-3 leads to gel fraction content and films hardness decrease in the mixtures. Therefore, the TGM 3 optimum amount is 16 wt parts in the crosslinking process up to 403 K.

Table 1

Composition of epoxy-oligoesteric mixtures with PEPA

Component	Component content, wt parts						
	I	II	III	IV	V	VI	VII
ESP	-	5	10	15	10	10	10
ED-20	100	95	90	85	90	90	90
TGM -3	16	16	16	16	8	24	32

Note**:** PEPA content in all compositions was 16 wt parts.

Table 2

Gel-fraction content and hardness dependence on ESP quantity and crosslinking time at 403 K

Mixture by Table 1	Gel fraction content, %					Hardness by M-3, rel. units				
	10 min	20 min	30 min	40 min	50 min	10 min	20 min	30 min	40 min	50 min
I	73	74	76	78	80	0.61	0.65	0.67	0.70	0.71
II	80	83	87	90	94	0.71	0.73	0.78	0.82	0.88
III	82	85	90	93	95	0.72	0.75	0.82	0.85	0.89
IV	82	86	92	93	96	0.72	0.76	0.83	0.85	0.90

Table 3

Gel fraction content and hardness dependence on TGM-3 quantity and crosslinking time at 403 K

Mixture by Table 1	Gel fraction content, %					Hardness by M-3, rel. units				
	10 min	20 min	30 min	40 min	50 min	10 min	20 min	30 min	40 min	50 min
V	82	84	91	92	94	0.72	0.74	0.82	0.83	0.88
III	82	85	90	93	95	0.72	0.75	0.82	0.85	0.89
VI	69	72	81	85	86	0.54	0.60	0.71	0.75	0.77
VII	58	60	67	74	76	0.42	0.50	0.58	0.60	0.61

3.2.2. Mixture crosslinking with isophorenediamine hardener

It is known from the literature data [8] that amount of isophorenediamine (IFDA) used as epoxy resins hardener should be 32g / 100g of ED-20 resin. Therefore, the content of IFDA in all compositions was 32 wt parts per 100 wt parts of ED-20. The same as in Subsection 3.2.1, the compositions consist of industrial ED-20 resin, ESP, and oligoesteracrylate TGM-3. The compositions were prepared by the method described in Subsection 2.3.2. Epoxy-oligoesteric mixture composition is given in Table 4, and the research results are represented in Tables 5 and 6.

At first we studied the mixtures with different contents of ESP – 5, 10, and 15 wt parts. As can bee seen from Table 5, the content of insoluble products is greater in those compositions in which the modified peroxide resin is present (mix. IX-XI) The polymer films hardness also reveals this fact. For 50 min at 403 K the mixture without ESP (mix. VIII) shows gel fraction content of 78 % and hardness of 0.7 rel. units in comparison with 84–86 % and 0.73–0.75 (mix. IX-XI), respectively. Since the content of gel fraction and film hardness in the mixtures IX, X, and XI are not significantly changed and reach the average values of 85 % and 0.74 rel. units, respectively, from the economic standpoint the mix. IX (containing 5 wt. parts of ESP) is the optimum one.

The results were used for the further determination of the TGM-3 quantity effect on the gel fraction content and polymer films hardness. The quantities of TGM-3 in the mixtures were 8, 16, 24, and 32 wt parts (Table 4). The investigations show (Table 6) that the values of gel fraction content and film hardness while decreasing unsaturated oligoester content to 8 wt. parts in the mixture at 403 K slightly differ from those of the mixture with 16 wt. parts (mix IX). The further increase to 24 and 32 wt parts of TGM-3 leads to gel fraction content and films hardness decrease in the mixtures. In the case of mix. XIV, where oligoester content is 32 wt parts, no crosslinking is observed for 30 min heating. Therefore, the TGM 3 optimum amount is 16 wt parts in the crosslinking process up to 403 K.

3.2.3. Mixture crosslinking with polyethylenepolyamide hardener

Mixture crosslinking with the polyethylenepolyamide hardener was carried out similarly as described in the previous sections. The composition of epoxy-oligoesteric mixtures is represented in Table 7 and the results of experimental research – in Tables 8 and 9.

The same as in the previous investigations a varied content of ESP (Table 8) was studied at first. The best values of gel fraction content and films hardness were found for mix. XVIII, which contains 15 wt parts of ESP. As a result, such amount of ESP has been used to study the influence of oligoesteracrylate (Table 9). Table 9 shows mix. XX is the optimum one. TGM-3 content in it is 24 wt parts.

Table 4

Epoxy-oligoesteric mixtures composition with IFDA hardener

Component	Component content, wt parts						
	VIII	IX	X	XI	XII	XIII	XIV
ESP	-	5	10	15	5	5	5
ED-20	100	95	90	85	95	95	95
TGM-3	16	16	16	16	8	24	32

Note**:** IFDA content in all compositions was 32 wt parts.

Table 5

Gel fraction content and hardness dependence on ESP quantity and crosslinking time at 403 K

Mixture by Table 1	Gel fraction content, %					Hardness by M-3, rel. units				
	10 min	20 min	30 min	40 min	50 min	10 min	20 min	30 min	40 min	50 min
VIII	65	70	73	74	78	0.51	0.60	0.66	0.68	0.70
IX	75	78	80	83	84	0.62	0.69	0.70	0.73	0.73
X	74	78	81	83	85	0.61	0.69	0.71	0.73	0.74
XI	76	79	82	83	86	0.63	0.70	0.71	0.73	0.75

Table 6

Gel fraction content and hardness dependence on TGM-3 oligoester quantity and crosslinking time at 403 K

Mixture by Table 1	Gel fraction content, %					Hardness by M-3, rel. units				
	10 min	20 min	30 min	40 min	50 min	10 min	20 min	30 min	40 min	50 min
XII	75	79	83	83	83	0.62	0.70	0.73	0.73	0.73
IX	75	78	80	83	84	0.62	0.69	0.70	0.73	0.73
XIII	53	58	62	64	64	0.40	0.45	0.50	0.52	0.52
XIV	-	-	-	58	60	-	-	-	0.45	0.48

Table 7

Composition of epoxy-oligoesteric mixtures containing polyethylenepolyamide hardener

Component	Component content, wt. parts						
	XV	XVI	XVII	XVIII	IX	XX	XXI
ESP	-	5	10	15	15	15	15
ED-20	100	95	90	85	85	85	85
TGM-3	16	16	16	16	8	24	32

Note**:** polyethylenepolyamide content in all compositions was 25 wt parts

Table 8

Gel fraction content and hardness dependence on ESP and crosslinking time at 403 K

Mixture by Table 1	Gel fraction content, %					Hardness by M-3, rel. units				
	10 min	20 min	30 min	40 min	50 min	10 min	20 min	30 min	40 min	50 min
XV	50	51	52	54	56	0.14	0.15	0.18	0.20	0.25
XVI	58	63	64	66	67	0.20	0.22	0.24	0.28	0.28
XVII	61	66	68	68	69	0.26	0.27	0.30	0.30	0.30
XVIII	70	71	72	72	73	0.34	0.35	0.36	0.37	0.38

Table 9

Gel fraction content and hardness dependence on TGM-3 oligoester quantity and crosslinking time at 403 K

Mixture by Table 1	Gel fraction content, %					Hardness by M-3, rel. units				
	10 min	20 min	30 min	40 min	50 min	10 min	20 min	30 min	40 min	50 min
XIX	59	61	63	64	65	0.25	0.26	0.27	0.27	0.28
XVIII	61	66	68	68	69	0.26	0.27	0.30	0.30	0.30
XX	70	74	75	76	78	0.30	0.31	0.32	0.40	0.50
XXI	55	57	58	58	59	0.20	0.21	0.24	0.24	0.25

Table 10

Physical and chemical properties of epoxy-oligoesteric mixtures

Mixture number	I	III	VIII	IX	XV	XX
Hardness, rel. units	0.67	0.82	0.66	0.70	0.18	0.32
Gel fraction content, %	76	90	73	80	52	75
Hygroscopic property, %	2.6	0.75	1.88	0.42	0.95	0.60
Tensile strength, MPa	1.44	3.20	0.76	1.13	1.38	2.82

3.3. Physical and Chemical Properties of Epoxy-Oligoesteric Mixtures

The above described studies with different hardeners in the presence of epoxy resin modified by isopropylbenzene hydroperoxide allowed us to select the most optimum hardeners.

The physical and chemical properties of epoxy-oligoesteric mixtures are given in Table 10.

According to Table 10, the best results relative to the gel fraction content and hardness, as well as tensile strength are demonstrated by mix. III. The best hygroscopic property was demonstrated by mix. IX.

The comparison of peroxide containing and peroxide free mixtures shows their considerable difference. The best results are observed for the mixtures with epoxy resin modified by isopropylbenzene hydroperoxide. Thus, it proves the significance of ESP epoxy resin in the production of products based on epoxy-oligoesteric mixtures.

4. Conclusions

The peroxide derivative of ED-20 epoxy resin containing both free epoxy group and isopropylbenzene hydroperoxide fragment has been synthesized.

Crosslinking of oligoesteric mixtures containing different amounts of of ED-20 epoxy resin peroxide derivative at 403 K for 10, 20, 30, 40, and 50 min has been thoroughly studied.

It has been established that epoxy-oligoesteric mixture crosslinked in the presence of polyethylenepolyamine, containing 10 wt parts of the synthesized product, 90 wt parts of epoxy resin and 16 wt parts of oligoesteracrylate TGM-3 are characterized by the highest number of insoluble products and the highest tensile strength.

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СИНТЕЗ ТА ЗАСТОСУВАННЯ В ПРОЦЕСАХ СТРУКТУРУВАННЯ ЕПОКСИ-ОЛІГОЕСТЕРНИХ СУМІШЕЙ ПЕРОКСИДНОЇ ПОХІДНОЇ ЕПОКСИДНОЇ СМОЛИ ЕД-20

Анотація. *Вивчено реакцію хімічної модифікації епоксидної смоли ЕД-20 гідропероксидом ізопропілбензолу. Встановлено вплив тривалості процесу на протікання реакції між смолою та гідропероксидом. Вивчена можливість використання синтезованого продукту, як компоненту в процесах структурування епокси-олігоестерних композицій із застосуванням різних за природою затверджувачів.*

Ключові слова: *епоксидна смола, гідропероксид ізопропілбензолу, модифікація, структурування, гель-фракція, затверджувач.*