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CHEMICAL MODIFICATION OF DIANIC EPOXY RESIN BY FLUORINE-CONTAINING ALCOHOLS

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Abstract. New epoxy resins with fluorine atoms have been synthesized *via* chemical modification of dianic epoxy resin with fluorine-containing alcohols-telomers C_7 , C_9 and C_{13} , using benzyltriethylammonium chloride and KOH as a catalyst system. Their characteristics have been examined. The structure of synthesized products has been confirmed by IR-spectroscopy. It has been shown that new epoxy resins may be used as active plasticizers for industrial epoxy resin.

Keywords: epoxy resin, fluorine-containing alcohols-telomers, quaternary ammonium salts, catalyst, modification, crosslinking, gel-fraction.

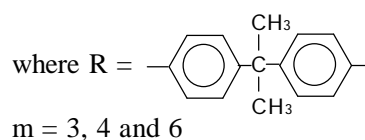
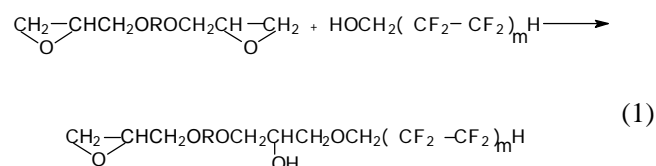
1. Introduction

Operational properties of wares based on industrial epoxy resins may be improved due to their chemical modification both by low-molecular and high-molecular compounds [1, 2]. The change of epoxy group for low-molecular carbon fragment may essentially affect the range of modified epoxy resins application, as well as the approach to the formation of wares on their basis. Aliphatic, aromatic, unsaturated and saturated acids [3, 4] are used mostly for modification and wares on their basis are used in varnish-and-paint, electrotechnical, radio, rubber-technical and other branches of industry [5, 6]. Acid anhydrides are used for the production of water- and alkaline-soluble oligomers based on epoxy resins [1, 2] and for the increase of materials thermal stability [7]. The introduction of alcohol fragments into epoxy resin improves its elastic properties [8]. Thermal characteristics of such resins may be improved due to the modification of epoxy resins by phenols [8]. The original method of epoxy resins modification by hydroperoxides and functional peroxides has been developed at Lviv Polytechnic National University [9, 10]. Peroxy derivatives of epoxy resins are widely used as crosslinking agents for polymeric compositions [11] and active additives for rubber mixtures [12].

The introduction of fluorine compound into the epoxy resin preserving epoxy group should improve, to our mind, operational characteristics of the ware and preserve the ability of epoxy compound to crosslink with industrial non-modified resin. V. Nazarov *et al.* [13] describe the polymeric system composed of dianic epoxy resin, isomethyltetrahydrophthalic anhydride as a hardener and 2,4,6-tris(dimethylaminomethyl)phenol as an accelerant. The presence of fluorine atoms in such mixture is achieved by the introduction of vat residues after production of fluorine-containing alcohols-telomers and fluorine esters.

Fluorine-containing additives in such systems are not chemically bounded with crosslinked epoxy resin, which essentially affects the operational properties of the ware [13].

This work deals with the possibility of chemical modification of dianic epoxy resin by alcohols-telomers preserving the epoxy group by the following reaction:



The reaction was studied in the medium of organic solvent using benzyltriethylammonium chloride and potassium hydroxide as a catalyst system.

2. Experimental

2.1. Starting Reagents and Their Purification

Initial dianic epoxy resin was used as received without additional purification. Its molecular mass (M_n) was 390 g/mol and epoxy number (*e.n.*) was 20.1 %.

The following fluorine-containing alcohols-telomers had the “chemically pure” label:

FTS-C₇ by HOCH₂(CF₂-CF₂)₃H formula with M_n 332;

FTS-C₉ by HOCH₂(CF₂-CF₂)₄H formula with M_n 432;

FTS-C₁₃ by HOCH₂(CF₂-CF₂)₆H formula with M_n 632.

Benzyltriethylammonium chloride (BTEAC) with M_n 227.5 had the “chemically pure” label.

Potassium hydroxide (KOH) and toluene had the “chemically pure” label and were used without further purification. Polyethylenepolyamine (PEPA) was a technical compound without additional purification.

2.2. Analytical Methods

The number-average molecular masses M_n of the synthesized resins were determined by cryometry using dioxane as the solvent. The epoxy number (*e.n.*) was determined using back titration of hydrochloric acid acetone solution by 0.1 N alkali solution [14]. The gel-fraction content (6 %) was determined by weighing the extracted samples for 14 h in Soxhlet apparatus [15]. Films hardness (*H*, rel.units) was determined using M-3 pendulum device at room temperature.

2.3. Spectral Methods

Infrared spectra (IR) were obtained using a dispersive Perkin-Elmer apparatus with the relevant absorption range in 4000–400 cm⁻¹ region.

2.4. Experimental Procedure

2.4.1. The procedure for studying reaction kinetics between epoxy resin and fluorine-containing alcohol-telomer

The chemical modification of epoxy resin by fluorine-containing alcohol-telomer in the presence of catalytic system composed of BTEAC and KOH was carried out in a three-necked reactor equipped with a mechanical stirrer, thermometer and backflow condenser. 30 g of epoxy resin, 200 ml of toluene and 24 g of FTS-C₇ were loaded into the reactor. The reaction mixture was heated in the thermostat prior to 343 K. Then 4.8 g of BTEAC (60%-aqueous solution) and 1 g of KOH (40% aqueous solution) were added under the continuous stirring.

The reaction proceeding was controlled by the change of epoxy groups concentration in the reaction medium. For this purpose samples of 0.5 ml were taken in certain equal interval and analyzed by the procedure described in [14]. The epoxy groups content was calculated using formula

$$[C]_{ep.gr.} = \frac{N \cdot K \cdot (V_1 - V_2)}{V_s}, \text{ mol/l}$$

where $[C]_{ep.gr.}$ is a concentration of epoxy groups in the solution; N – normality of potassium hydroxide solution, equal to 0.1N; K – correction coefficient for 0.1N potassium hydroxide; V_1 – amount of 0.1N potassium hydroxide necessary for the titration of blank test, ml; V_2 – amount of 0.1N potassium hydroxide necessary for the titration of the sample, ml; V_s – sample volume of 0.5 ml.

2.4.2. The crosslinking procedure of dianic epoxy resin in the presence of fluorine-containing resin

The industrial dianic resin was mixed with fluorine-containing epoxy resin at room temperature till the homogeneous mixture was obtained. PEPA was added under stirring. Then the mixture was poured over glass plates with standard size. The hardness and gel-fraction content were determined using above-mentioned methods.

3. Results and Discussion

3.1. Determination of Reaction Time

Chemical modification of dianic epoxy resin with fluorine-containing alcohols-telomers by the reaction (1) is based on the well-known reaction between compounds containing active hydrogen atom and the resin with epoxy group. Non-organic bases, acids, Lewis acids and quaternary ammonium salts may be catalysts of the mentioned reaction [1, 2]. Quaternary ammonium salts are effective catalysts for the reaction, when hydroperoxides are used as compounds containing active hydrogen atom [17]. In order to increase the reaction rate of hydroperoxide with epoxy ring we suggested earlier [18] to use catalytic system consisting of quaternary ammonium salt and potassium hydroxide. Moreover, the amount of quaternary ammonium salt should be 15.0 mol % and KOH – 12.5 mol % to calculate for 1g-eq of the resin epoxy group [18]. Toluene should be used as a reaction medium. Taking into account that quaternary ammonium salts are catalysts for interphase transfer, quaternary ammonium salt and potassium hydroxide were used as aqueous solutions (60% solution of the salt and 40% solution of KOH). The obtained results were used for the chemical modification of epoxy resin by fluorine-containing alcohol-telomers.

In order to establish the reaction time necessary for the proceeding of the reaction (1), we made experiments using the procedure, described in Subsection 2.4.1. The obtained results are presented in Fig. 1.

One can see from Fig. 1 that the change of the half of epoxy groups for fluorine fragments demands the reaction time of nearly 10 h at 343 K. Incomplete changes of epoxy groups for fluorine atoms give the possibility to preserve reactivity of modified resin in the crosslinking. The obtained results are the basis for the development of synthesis procedure for modified epoxy resins.

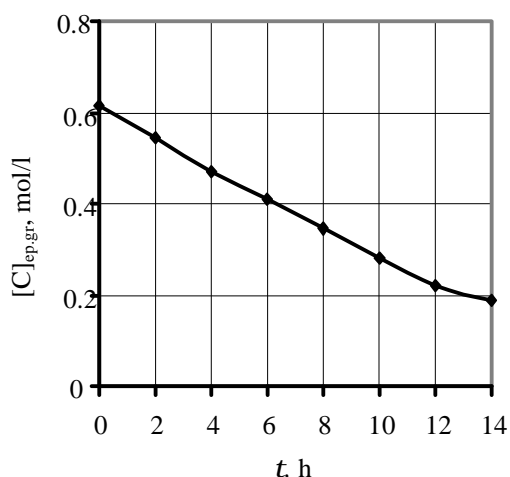


Fig. 1. Change of epoxy groups concentration for the reaction between epoxy resin and FTS-C₇ at 343 K in toluene. FTS-C₇ content is 1.0 mol to calculate for 1 g-eq of the resin epoxy group

3.2. Synthesis Procedure for Fluorine-Containing Epoxy Resins (FER)

In order to develop the synthesis procedure for modified resins we have used above-mentioned results, as well as the data from literature. The process temperature is 343 K. Reaction time is 10–14 h. FER synthesis was carried out in a three-necked reactor equipped with a mechanical stirrer, thermometer and backflow condenser. Epoxy resin, fluorine-containing alcohol and solvent were loaded into the reactor. The reaction mixture was thermostated prior to 343 K, then 60% aqueous solution of BTEAC (15 mol %) and 40% aqueous solution of KOH (12.5 mol %) were added under stirring. At the end of the reaction the mixture was cooled to room temperature and placed into the funnel. The residues were washed away by toluene. The reaction mass was settled for 0.5 h up to the moment the clear phase separation appeared. The lower layer with aqueous solutions of catalysts was thrown away and the upper one was washed with distilled water until the reaction became neutral. The organic layer was vacuumed till 1/3 of the solvent volume. The residue was precipitated with petroleum ether and dried at room temperature first, then – in vacuum oven at 353 K and residual pressure 133–266 Pa till the mass became constant. The obtained resin was analyzed to determine its molecular mass and the content of epoxy groups in it.

FER-1 resin was synthesized using 30 g of dianic epoxy resin and 24 g of FTS-C₇. The products were dissolved in 200 ml of toluene. The reaction mass was thermostated to 343 K, then 4.8 g of 60% BTEAC solution and 1.0 g of 40% KOH solution were added to the reactor. The reaction time was 10 h. All further operations are described above. 40.2 g of viscous light-yellow resin was obtained (the yield was 75 %). The resin is soluble in acetone, dioxane and other organic solvents.

FER-II resin was synthesized on the basis of epoxy resin and FTS-C₇. The amounts of resin, alcohol, solvent and catalysts were the same as in the previous case. The reaction time was 14 h. 44.8 g (the yield was 84 %) of the resin soluble in organic solvents was obtained.

FER-III resin was synthesized using the analogous procedure. The difference was that the amount of FTS-C₇ was 1.0 mol to calculate for 1 epoxy group of the resin. 65.1 g (the yield was 85 %) of the viscous, soluble in organic solvents product was obtained.

FER-IV resin was synthesized in the same way as FER-I or FER-III using 30.0 g of epoxy resin and 30.3 g of FTS-C₉. The BTEAC amount was 4.8 g, KOH amount was 1.2. The reaction time was 14 h. 49.5 g (the yield was 82 %) of the viscous, soluble in organic solvents product was obtained.

FER-V resin was synthesized using 30 g of epoxy resin, 60.6 g of FTS-C₉ dissolved in 250 ml of toluene. The amount of the catalysts was the same as for FER-IV synthesis. 75.2 g (the yield was 83 %) of the viscous, soluble in organic solvents product was obtained.

FER-VI resin was synthesized using 30 g of dianic epoxy resin, 44.3 g of FTS-C₁₃ dissolved in 200 ml of toluene. The amount of the catalysts was the same as for FER-V synthesis. 66.9 g (the yield was 90 %) of the white powder was obtained.

The characteristics of synthesized products are represented in Table 1.

One can see from Table 1 that the increase of FTS-C_n amount in the mixture considerably decreases the epoxy groups amount and increases resin molecular mass. Using 0.5 mol of alcohol-telomer for one epoxy group, *i.e.* one mole for one mole of initial dianic epoxy resin, we may change one epoxy group of the resin for fluorine-containing fragment saving at the same time the second epoxy group (*vide* Eq. 1).

The structure of fluorine-containing dianic epoxy resins was confirmed by IR-spectroscopy.

One can see from Fig. 2 that absorbance bands appear at 1212, 1180 cm⁻¹ typical of vibrations of difluorine-substituted compounds [19]. The decrease of absorption band intensity at 915 cm⁻¹ typical of epoxy ring stretching vibrations reveals the chemical modification of epoxy resin by alcohol-telomer. At the same time the presence of epoxy group in the resin molecule is confirmed by absorption bands at 3056 and 3040 cm⁻¹, characteristic of stretching vibrations of (ν_{as} CH₂) ~ CH₂ group in epoxy ring, as well as at 1280–1240 cm⁻¹ typical of symmetric stretching vibrations (ν_s) of epoxy group. Also the intensity of vibrations specific for hydroxyl group is observed. The presence of hydroxyl groups is confirmed by stretching vibrations bands at 3432 cm⁻¹ and deformation vibrations bands (δ_{OH}) at 1041 cm⁻¹. These bands indicate the opening of epoxy ring, the addition of fluorine-containing alcohol molecule to it and formation of secondary hydroxyl group.

Table 1

Characteristics of synthesized resins

Fluorine-containing alcohol-telomer		Reaction time, h	Characteristics of modified resins			
Alcohol-telomer symbol	Amount (in moles) for 1 epoxy group of ED-20 resin		Resin symbol	M_n	<i>e.n.</i> , %	Yield, %
FTS-C ₇	0.5	10	FER-I	640	11.5	75
FTS-C ₇	0.5	14	FER-II	820	8.8	84
FTS-C ₇	1.0	14	FER-III	1270	2.8	85
FTS-C ₉	0.5	14	FER-IV	880	7.2	82
FTS-C ₉	1.0	14	FER-V	1750	3.8	83
FTS-C ₁₃	0.5	14	FER-VI	1050	8.9	90

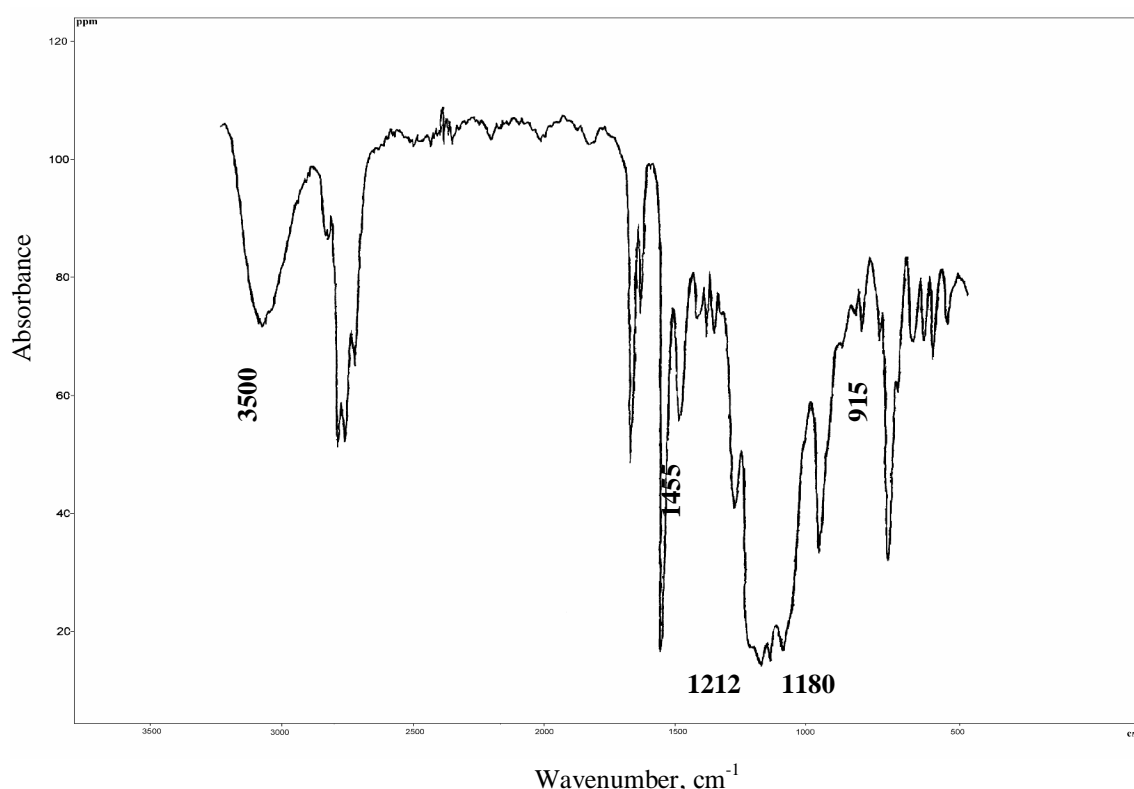


Fig. 2. IR-spectrum of FER-IV resin

Thus, synthesized molecules in comparison with the initial dianic epoxy resin are characterized by higher molecular mass and contain fluorine atoms as well as residual epoxy groups. They may be used as active additives to the mixtures based on industrial epoxy resin.

3.3. Crosslinking of Dianic Epoxy Resin in the Presence of FER

For the investigation of crosslinking of dianic epoxy resin in the presence of FER the polymeric mixtures with the compositions represented in Table 2 have been prepared.

The preparation procedure of polymeric mixtures and analysis of their crosslinking ability are mentioned in Subsection 2.4.2. The obtained results are presented in Table 3.

One can see from Table 3 that the increase of crosslinking time increases both gel-fraction content and film hardness. The introduction of small amount (10 wt. parts) of fluorine-containing epoxy resin into polymeric mixture increases gel-fraction content compared with pure epoxy resin. At the same time, the presence of resin with fluorine atoms in the mixture decreases film hardness. The increase of modified resin to 30 mas.parts decreases gel-fraction content and film hardness. The obtained results correlate with known data

Table 2

Polymeric mixtures

Number of polymeric mixture	Component amount in the mixture, wt. parts		PEPA amount, wt. parts
	Dianic epoxy resin with <i>e.n.</i> 20.1 %	FER-IV	
I	100	–	14
II	90	10	13
III	70	30	11

Table 3

Dependence of gel-fraction content and film hardness upon composition of polymeric mixtures and crosslinking time at room temperature

Number of polymeric mixture	Symbol	Symbol values at crosslinking, days					
		1	2	5	6	8	10
I	G	75.5	81.9	84.1	84.3	85.1	85.9
	H	0.58	0.69	0.77	0.82	0.85	0.88
II	G	83.3	84.8	85.6	86.9	88.2	89.8
	H	0.67	0.68	0.72	0.73	0.81	0.81
III	G	77.4	78.3	78.7	79.4	80.4	80.4
	H	0.70	0.71	0.74	0.77	0.79	0.79

Note: G is gel-fraction content and H is film hardness.

concerning the fact that the presence of fluorine atom in polymer molecule decreases the hardness of wares on polymer basis.

Thus, the use of small amount of fluorine-containing dianic epoxy resin (10 wt. parts) as an active additive for the industrial dianic epoxy resin increases amount of insoluble products in the final product and improves its operational properties, namely corrosion resistance. Moreover, fluorine-containing epoxy resin FER-IV in such mixture acts as an active plasticizer.

4. Conclusions

It has been established that catalytic system composed of benzyltriethylammonium chloride and potassium hydroxide allows the chemical modification of dianic epoxy resin by fluorine-containing alcohols-telomers. For the production of modified epoxy resins in which only half of epoxy groups are substituted by alcohol-telomer fragments it is necessary to carry out the reaction at 343 K for 14 h using one mole of fluorine-containing alcohol to calculate for one mole of initial epoxy resin.

The introduction of approximately 10 wt. parts of fluorine-containing epoxy resin into the polymeric mixture based on the industrial epoxy resin increases gel-fraction content and slightly decreases the film hardness.

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ХІМІЧНА МОДИФІКАЦІЯ ДІАНОВОЇ ЕПОКСИДНОЇ СМОЛИ ФЛУОРВМІСНИМИ СПИРТАМИ

Анотація. Хімічною модифікацією діанової епоксидної смоли з флуорвмісними спиртами-теломерами C_7 , C_9 і C_{13} з

використанням як каталітична система бензилтриетиламоній хлористий і KOH , отримано та охарактеризовано нові епоксидні смоли, що містять атоми флуору. Структура синтезованих продуктів підтверджена ІЧ-спектроскопічними дослідженнями. Показано можливість використання синтезованих смол як активних пластифікаторів промислової епоксидної смоли.

Ключові слова: епоксидна смола, флуорвмісні спирти-теломери, четвертинні солі амонію, каталізатор, модифікація, структурування, гель-фракція.