CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 4, No. 2, 2010 Chemistry

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CHEMICAL MODIFICATION OF ED-24 EPOXY RESIN PEROXY DERIVATIVE BY $C_9H_4F_{16}O$ fLUORINE-CONTAINING ALCOHOL-TELOMER

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Received: September 23, 2009

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Abstract. The possibility of chemical modification of ED-24 epoxy resin peroxy derivative (PDER) by $C_9H_4F_{16}O$ fluorine-containing alcohol-telomer (FAT-C_9) has been shown using 18-Crown and $ZnCl_2$ catalytic system. The effect of catalyst amount, temperature and process time on the reaction rate has been studied. New peroxy oligomer containing fluorine atoms (FPO) has been synthesized and characterized. The FPO structure has been confirmed by IR-spectroscopy. It has been proposed to use FPO as an active additive to the polymeric mixes based on ED-20 industrial epoxy resin and TGM-3 oligoesteracrylate.

Keywords: epoxy resin, peroxy oligomer, fluorine-containing alcohol-telomer, 18-Crown-6+$ZnCl_2$ catalyst, modification, crosslinking, gel-fraction.

1. Introduction

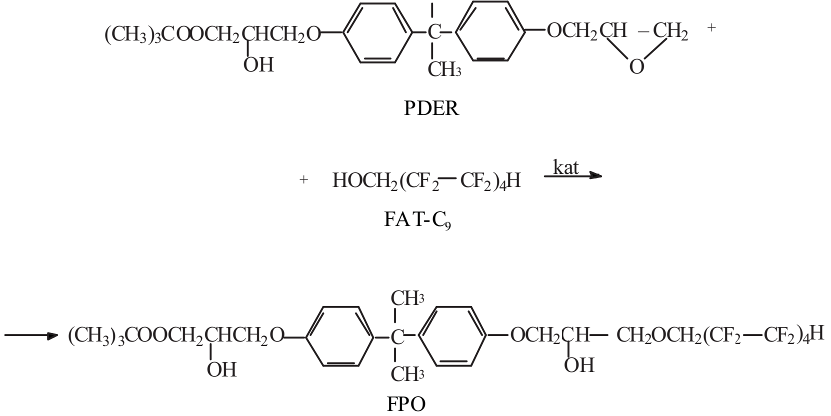
Peroxy oligomers (POs) synthesized on the basis of epoxy resins are thermoreactive products capable to form free radicals at heating [1]. Such a property allows to use them as initiating agents at polymerization and crosslinking of polymeric composites [2, 3]. On the other hand the mentioned PO may be used as modifiers for the forming processes of polymeric materials of both linear and crosslinked structure owing to the presence of dianic chain fragments in their molecules [4].

Among all known POs on the basis of epoxy resin, compounds, molecules of which contain the epoxy group in addition to a labile –O–O– bond are of the greatest interest. This peculiarity allows to use them in the forming processes of spatial-crosslinked structures by both radical and condensation mechanisms [5].

It is well-known [6-8] that compounds containing silicium [6], fluorine [7], boron [8] or other atoms are used for the improvement of operational characteristics of wares on the basis of epoxy resins. At the same time the presence of fluorine atoms in the synthesized polymer essentially improves its corrosion, heat and frost resistance [7]. On the other hand, the simultaneous presence of –O–O– bond and fluorine atom in the oligomer molecule allows to use different by nature polymers for the production of polymeric materials and improve their operational characteristics.

Oligomers on the basis of epoxy resins with simultaneous presence of –O–O– bond and fluorine atom are not described in literature.

Synthesis of peroxy oligomers which contain the peroxy group and fluorine atoms may be described as following:



PDER

FAT-C_9

FPO

2. Experimental

2.1. Starting Reagents

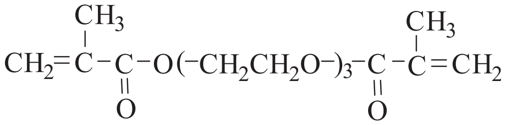
Peroxy derivative on the basis of dianic epoxy resin (PDER) was synthesized using ED-24 epoxy resin and *tert*-butyl hydroperoxide according to the procedure described in [1]. It was found: molecular mass (M_n) 344 g/mol, active oxygen content ($[O]_{act}$ 3.5 % and epoxy number (*e.n.*) 12.0 %.

Fluorine-containing alcohol-telomer (FAT-C_9) with M_n 432 g/mol had the "chemically pure" label.

The system consisting of 18-Crown-6 and zinc chloride which had the "chemically pure" label was used as a catalyst. The ratio between 18-Crown-6 and zinc chloride was 1 : 3 moles.

The following components were used for obtaining polymeric mixtures:

- ED-20 industrial dianic epoxy resin with *e.n.* 20.1 %;
- oligoesteracrylate (TGM-3) with M_n 280 g/mol by formula:



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

- polyethylenepolyamine (PEPA) was a technical compound without additional purification;
- solvents (2-propanol and acetone) had the "chemically pure" label and were used 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 a back titration of hydrochloric acid and acetone solution by 0.1 N alkali solution [9]. The active oxygen content was determined according to [10]. Films hardness and gel-fraction content were determined using the known procedure [11].

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 reaction kinetics

The kinetic investigations of PDER chemical modification by FAT-C_9 was carried out in a three-necked reactor equipped with a mechanical stirrer, thermometer and backflow condenser. PDER and FAT-C_9 solutions in 2-propanol were loaded into the reactor. Predetermined amount (to calculate for 1 g-eq of epoxy group) of the catalyst aqueous solution was added under continuous stirring. The reaction mixture was heated in the thermostat prior to the necessary temperature (313, 323 or 333 K). 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 [9]. The epoxy groups content was calculated using the formula:

$$[C]_{ep.gr.} = \frac{N \cdot K \cdot \left(V_b - (V_t - V_k)\right)}{V_s}, \text{ mol/l}$$

where $[C]_{ep.gr.}$ is a concentration of epoxy groups in the solution, mol/l;

N – normality of alkali solution, equal to 0.1N;

K – correction coefficient for 0.1N potassium or sodium hydroxide;

V_b – amount of 0.1N alkali necessary for the titration of blank test, ml;

V_t – amount of 0.1N alkali necessary for the titration of the sample, ml;

V_k – amount of 0.1N alkali necessary for the titration of the catalyst, ml

V_s –sample volume of 0.5 ml.

The obtained results were used for the construction of graphical dependencies and then effective rate constants of the reaction between PDER and FAT-C_9 were calculated. The effective activation energy was determined by interpretation of obtained results in the coordinates of Arrenius equation log (K) = f(1/T).

2.4.2. FPO synthesis

FPO was synthesized in a three-necked reactor with a mechanical stirrer, reverse condenser and thermometer. 20.0 g of PDER and 35.6 g of FAT-C_9 dissolved in 120 ml of 2-propanol as well as 25% aqueous solution with 20 mol % of 18-Crown-6 for 1 g-eq. of epoxy group and 20% aqueous solution with 60 mol % of $ZnCl_2$ for 1 g-eq. of epoxy group were loaded into the reactor. The reaction mixture was thermostated at 323 K for 18 h. Then the reaction mass was cooled to the room temperature and transferred into the separating funnel. The residues were washed with the solvent. The reaction mix was settled in the funnel for 30 min till well-defined separation. The bottom layer with catalyst aqueous solution was poured out and the upper layer was washed with distilled water. The organic layer was placed into the flask and s of the solvent was distilled under the residual pressure. Then the layer was precipitated with petroleum ether and dried. First, it was dried in the air under normal conditions and then at

318 K under the residual pressure of 133–266 Pa till the mass became constant. In synthesized oligomer we determined the content of epoxy groups and active oxygen, molecular mass and solubility in organic solvents.

2.4.3. FPO crosslinking activity

FPO crosslinking activity was studied using gel-fraction content and hardness of polymeric films. For this purpose compositions were prepared by components mixing till homogeneous viscous solutions were obtained. Then they were applied over degreased glass plates of the standard size. The crosslinking was studied by two methods. In accordance with the first one, applied films were endured under normal conditions for 10 days. Gel-fraction content and film hardness were determined after definite periods of time. In accordance with the second method the films were endured at room temperature for 1 day, and then they were heated to 403 K for 15, 30, 45, 60 and 75 minutes. After crosslinking 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 FPO Synthesis Procedure

We showed earlier [1] that 18-Crown-6+$ZnCl_2$ catalytic system may be successfully used for chemical modification of epoxy resins by compounds containing a mobile hydrogen atom. Such catalytic system with the molar ratio 1 : 3 forms stable complex capable to catalyze the reaction between the epoxy resin and hydroperoxide at low temperatures.

In connection with this fact and in order to develop the FPO synthesis procedure it was necessary to determine the effect of a catalyst amount, temperature and process time on chemical modification of PDER by FAT-C_9. The results of investigations are represented in Fig. 1.

One can see from Fig. 1 that noticeable rate of PDER–FAT-C_9 reaction is observed when 18-Crown-6 amount is more than 20 mol %. Rate constants determined from Fig. 1 are represented in Table 1.

Taking into account that there is a slight difference between reaction rates depending upon 18-Crown-6 amount (40 and 20 mol %), the amount of 20 mol % was chosen as an optimum amount.

Investigating the effect of temperature on the reaction (Fig. 2) it was established that the increase of temperature increases the effective rate constant (Table 1).

But taking into account the presence of –O–O– labile bonds in the molecules of both PDER and FPO, the temperature of 323 K was chosen as an optimum. The increase of temperature to 333 K results in a partial decomposition of peroxy groups as it was mentioned in the literature [1]. Obtained results have been used for establishing the process time. The experiments were carried out using the procedure described in 2.4.1. The experimental results are presented in Fig. 3.

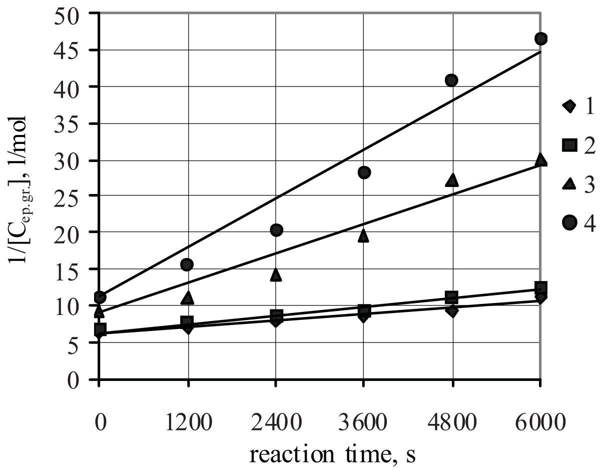


Fig. 1. Kinetic anamorphoses in 1/C–t coordinates for the reaction between PDER and FAT-C_9 at 323 K in 2-propanol medium. 18-Crown-6+$ZnCl_2$ catalytic system with the molar ratio 1 : 3. The amount of 18-Crown-6 is (mol %): 5 (1), 10 (2), 20 (3) and 40 (4) to calculate for 1 g-eq. of PDER epoxy group. The amount of FAT-C_9 is 1 mole for 1 g-eq. of PDER epoxy group

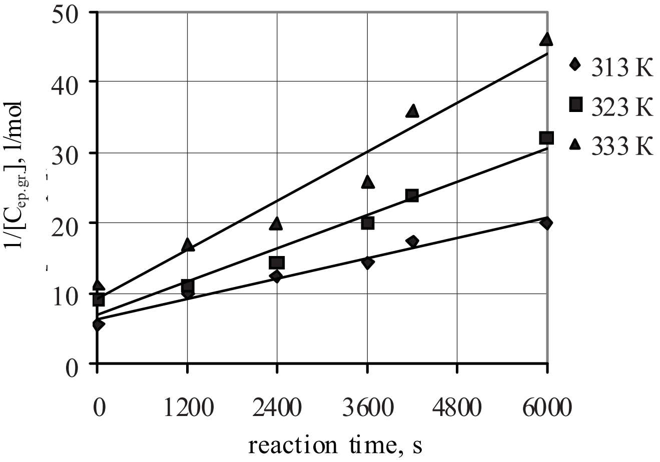


Fig. 2. Kinetic anamorphoses of epoxy groups concentration in 1/C–t coordinates for the reaction between PDER and FAT-C_9 in 2-propanol medium. The amount of FAT-C_9 is 1 mole for 1 g-eq. of PDER epoxy group. The molar ratio of 18-Crown-6+$ZnCl_2$ catalytic system is 1 : 3. The amount of 18-Crown-6 is 20 mol % to calculate for 1 g-eq. of PDER epoxy group

One can see from the obtained results that the process time of more than 18 h is necessary to completely

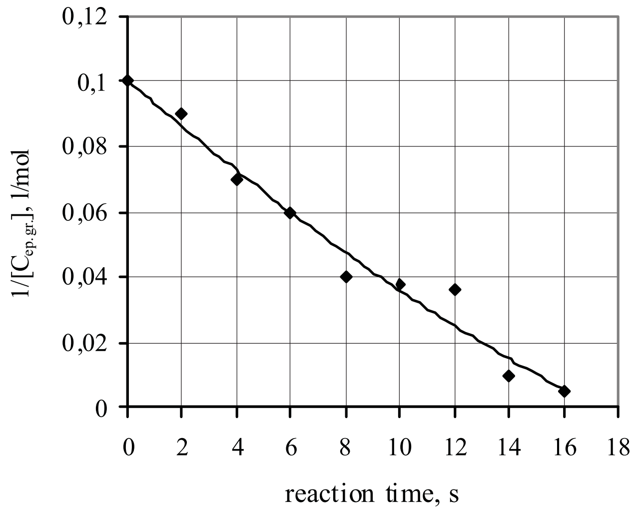


Fig. 3. Dependence of epoxy groups concentration upon the reaction time for PDER–FAT-C_9 reaction at 323 K in 2-propanol medium. The molar ratio of 18-Crown-6+$ZnCl_2$ catalytic system is 1 : 3. The amount of FAT-C_9 is 1 mole for 1 g-eq. of PDER epoxy group

replace epoxy groups for fluorine-containing fragments. Thus, the obtained results will be used for the development of synthesis procedure for oligomer containing peroxy and fluorine-containing fragments (FPO) simultaneously.

The procedure of FPO synthesis is given in Subsection 2.4.2. The synthesized FPO is a viscous product with a light-yellow color, which is soluble in acetone, isopropanol, dioxane, benzene, toluene and other organic solvents. It is found that M_n is 800 g/mol, $[O_{act}]$ is 3 % and epoxy groups are absent.

3.2. IR-Spectroscopic Investigations

FPO structure is confirmed by IR-spectroscopic investigations (Figs. 4 and 5).

One can see from Fig. 5 that the absorption band at 1212 cm^{-1} corresponding to the vibrations of difluorine-substituted compounds [12] appears in the spectrum of modified PDER. The absence of the absorption band at 920 cm^{-1} corresponding to the stretching vibrations of epoxy ring also indicates the chemical modification of epoxy resin by alcohol-telomer. The presence of peroxy groups is confirmed by the presence of deformational vibrations doublet in the absorption band at 1380–1360 cm^{-1} identifying gem-methyl vibrations of $(CH_3)_3COO–$ group in oligomer, as well as by the absorption band at 875 cm^{-1} typical for stretching vibrations of peroxy groups. The presence of hydroxyl groups is confirmed by the absorption band at 3390 cm^{-1} typical for stretching vibrations of –OH groups. The absorption band at 960 cm^{-1} corresponding to $–CH_2OCH_2–$ group appears in the spectrum of synthesized FPO.

The above mentioned results allow to state that synthesized FPO contains fluorine atoms and has greater molecular mass compared with initial PDER. It was studied as an active additive to epoxy-oligoesteric composition based on ED-20 dianic epoxy resin which contains TGM-3 oligoesteracrylate as a plasticizer.

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

In order to examine the crosslinking of dianic epoxy resin in the presence of FPO the polymeric mixture (Mix

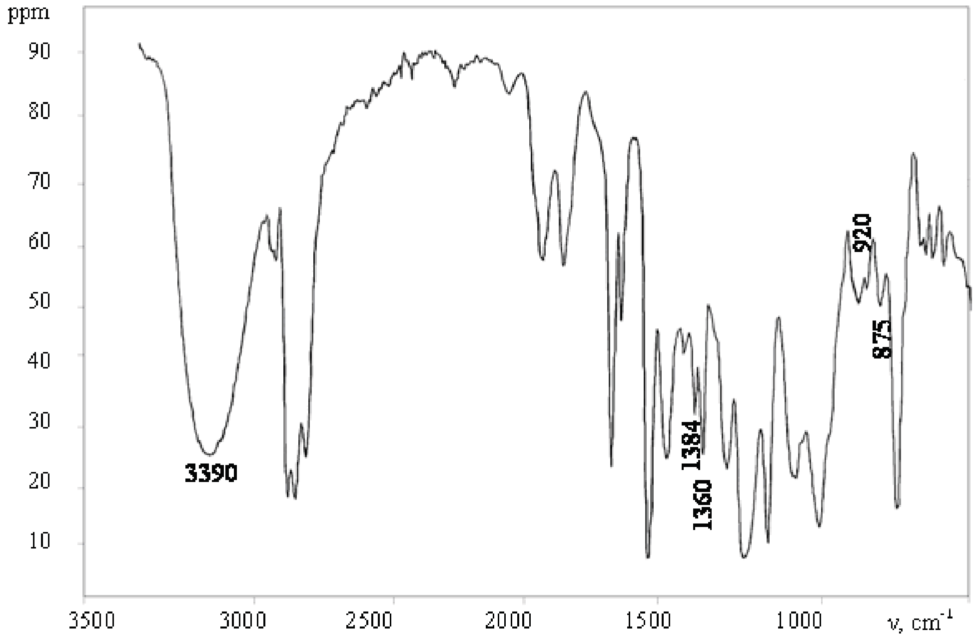


Fig. 4. IR-spectrum of PDER

I, Table 2) is prepared. The mixture with PDER (Mix II) instead of FPO is studied for the comparison. It does not contain fluorine atoms but has free peroxy and epoxy groups and lower molecular mass (Table 2).

Crosslinking of polymeric mixtures is studied in accordance with the procedure described in Subsection 2.4.3. and obtained results are represented in Tables 3 and 4.

One can see from Tables 3 and 4 that the increase of crosslinking time increases gel-fraction content, as well as films hardness. At the same time it has been established that introduction of synthesized FPO into polymeric mixture (Mix I) instead of PDER (Mix II) increases films hardness and gel-fraction content at crosslinking both at room temperature for 1 day and at 403 K. The obtained

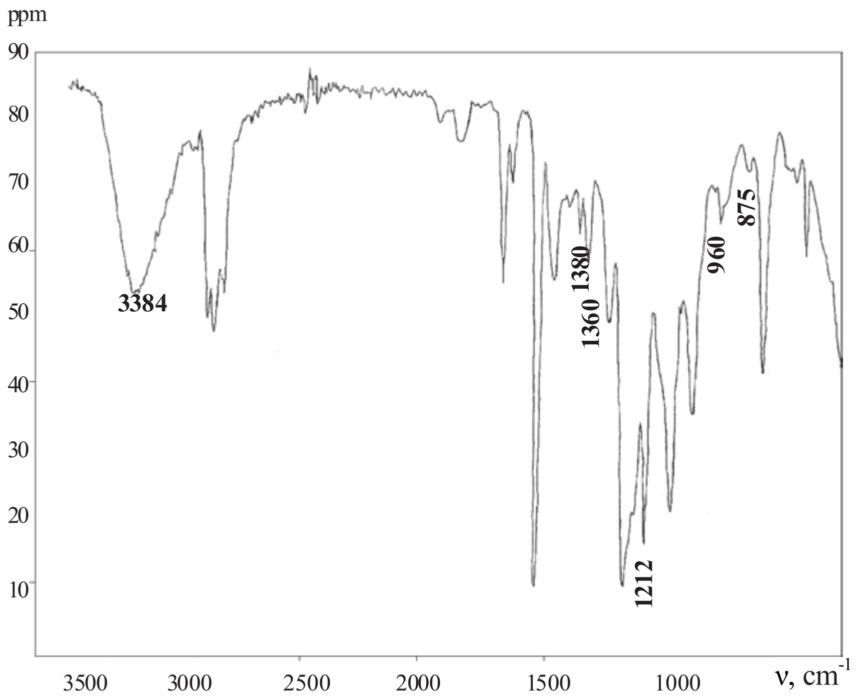


Fig. 5. IR-spectrum of FPO

Table 2

Compositions of oligoesteric mixtures

Mixture component	Component content in polymeric mixture, mas.parts	
	Mix I	Mix II
ED-20 dianic epoxy resin	90	90
FPO	10	-
PDER	-	10
TGM-3	10	10
PEPA	12.6	14.0

Table 3

Dependence of gel-fraction content and films hardness upon mix composition and crosslinking time at 403 K

Mix number	Symbol	Symbol values at crosslinking time, min.					
		24 h at room temperature	15	30	45	60	75
I	G	82.0	98.1	99.3	99.6	99.7	99.7
	T	0.33	0.91	0.93	0.94	0.94	0.96
II	G	73.5	81.7	82.1	83.0	85.4	-
	T	0.27	0.55	0.60	0.72	0.78	-

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

Table 4

Dependence of gel-fraction content and films hardness upon mix composition and crosslinking time at room temperature

Mix number	Symbol	Symbol values at crosslinking time, days						
		1	2	3	4	6	8	10
I	G	82.0	90.1	91.2	92.1	92.3	92.4	92.9
	T	0.33	0.50	0.57	0.64	0.68	0.69	0.75

results may be explained by the fact that the presence of fluorine atoms in FPO molecule favors the decomposition of peroxy groups in a synthesized oligomer. Formed oligomeric free radicals cause three-dimensional polymerization of TGM-3 oligoesteracrylate presented in the polymeric mix. When Mix II is crosslinked at room temperature, grafting of PDER epoxy groups to ED-20 dianic epoxy resin takes place by means of PEPA. Such a structure contains free peroxy groups which are sometimes inaccessible for TGM-3 oligoesteracrylate. Therefore, free radicals formed due to decomposition while heating and modified into crosslinked structures do not cause TGM-3 three-dimensional polymerization in most cases but recombine between each other. As a result only some TGM-3 molecules form three-dimensional polymeric net, the rest of them are dissolved. This is the reason for the decrease of gel-fraction content and films hardness compared with the mixtures containing synthesized FPO.

At the same time the presence of fluorine atoms in Mix I increases films resistance to aggressive media, to alkali and acid solutions, in particular.

4. Conclusions

1. It has been established that 18-Crown-6 + $ZnCl_2$ catalytic system with the molar ratio 1 : 3 may be used for the chemical modification of dianic epoxy resin with peroxy groups by $C_9H_4F_{16}O$ fluorine-containing alcohol telomer. It is necessary that the amount of 18-Crown-6 should be no less than 20 mol % to calculate for 1 g-eq. of resin epoxy group.
2. The chemical modification of dianic epoxy resin with peroxy groups by $C_9H_4F_{16}O$ fluorine-containing alcohol telomere has to be carried out at 323 K for 18 h.
3. The introduction of 10 mas. parts of fluorine-containing peroxy oligomer into the polymeric mixture based on ED-20 industrial epoxy resin and TGM-3 oligoesteracrylate allows to increase the content of insoluble products and films hardness compared with non-modified PDER mixtures, as well as to obtain polymeric films with sufficiently high operational properties.

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ХІМІЧНА МОДИФІКАЦІЯ ПЕРОКСИДНОЇ ПОХІДНОЇ ЕПОКСИДНОЇ СМОЛИ ЕД-24 ФЛУОРВМІСНИМ СПИРТОМ-ТЕЛОМЕРОМ $C_9H_4F_{16}O$

Анотація. *Показана можливість хімічної модифікації пероксидної похідної епоксидної смоли ЕД-24 (ППЕС) флуорвмісним спиртом-теломером $C_9H_4F_{16}O$ (ФСТ-C_9) з використанням каталітичної системи 18-краун-6 та $ZnCl_2$. Вивчено вплив кількості каталізатора, температури та тривалості процесу на швидкість реакції між ППЕС і ФСТ-C_9. Синтезовано та охарактеризовано новий пероксидний олігомер, що містить атоми флуору (ФПО). Структура ФПО підтверджена ІЧ–спектроскопічними дослідженнями. Запропоновано використовувати ФПО як активний додаток до полімерних сумішей на основі промислової епоксидної смоли ЕД-20 та олігоестеракрилату ТГМ-3.*

Ключові слова: *епоксидна смола, пероксидний олігомер, флуорвмісні спирти-теломери, 18-краун-6 + $ZnCl_2$, каталізатор, модифікація, структурування, гель-фракція.*