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PHENOL-FORMALDEHYDE RESINS OF NOVOLAC TYPE WITH UNSATURATED SIDE BONDS

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Received: November 15, 2012 / Revised: November 18, 2012 / Accepted: December 1, 2013

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Abstract. The reaction between novolac phenol-formaldehyde resin and glycidylmethacrylate has been studied in the presence of potassium hydroxide and the synthesis procedure of phenol-formaldehyde resin with unsaturated side bonds has been suggested. The effective rates and activation energy of the mentioned reaction have been calculated. The structure of synthesized resin was confirmed by IR-spectroscopy. The synthesized resin may be used as active component of polymeric blends based on ED-20 industrial epoxy resin, its peroxy derivative (PO) and TGM-3 oligoesteracrylate. The process was controlled by gel-fraction content and polymeric films hardness. Physico-mechanical and protective properties of the synthesized epoxy-oligoesteric mixtures have been studied.

Keywords: phenol-formaldehyde resin, glycidylmethacrylate, ED-20 dianic epoxy resin, peroxy derivative, kinetics, IR-spectroscopy, cross-linking, gel-fraction, hardness, films.

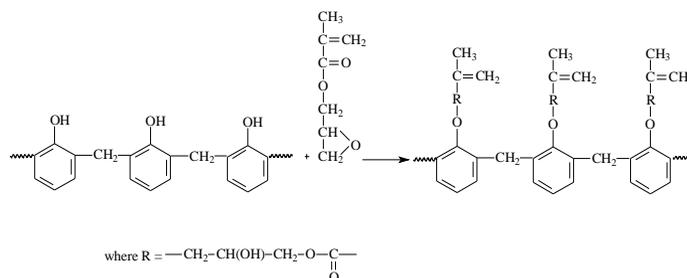
1. Introduction

Well-known phenol-formaldehyde resins (PhFR) are used in the production of press-materials, glues, protective coatings, mastics, casting blends, *etc.* [1]. Their wide application is conditioned by their high thermal stability and physico-mechanical properties [2], as well as resistance to aggressive media and organic solvents [1]. The shortco-

mings of the mentioned resins are their low adhesion and elasticity [2]. To improve the properties of the wares based on PhFR they are modified by both low- and high-molecular compounds [3]. The modification may be physical or chemical. Among a variety of chemical modifications the PhFR interaction with epoxy compounds, namely epoxy resins [4], epichlorhydrin [5], 1,2-epoxy-3-tertbutyl peroxypropane [6] and furfurylglycid ether [7] are of special attention. PhFR modification by epoxides is performed at the stage of ware forming. So-called polyglycidylphenolformaldehyde resins are obtained using epichlorhydrin. Such resins have better adhesive properties compared with the initial PhFR and that is why they are used for the production of lacquering [4]. Chemical interaction of PhFR with 1,2-epoxy-3-*tert*-butyl peroxypropane results in the products with labile –O–O– groups in the side chains. Such compounds may be combined with unsaturated polymers and elastomers [6] giving the possibility to extend PhFRs application area and to improve the operational properties of the wares based on them. PhFRs modified by furfurylglycid ether are used as the components of epoxy-oligomeric mixtures based on the dianic epoxy resin and TGM-3 oligoesteracrylate.

The chemical modification by epoxy compounds takes place due to the interaction between PhFR reactive phenol groups and epoxy groups.

In the present paper we study the possibility of novolac PhFR chemical modification by glycidylmethacrylate (GMA) in accordance with the equation:



The modified PhFR (MGMAPhFR) may be obtained due to the interaction between PhFR hydroxy groups and GMA epoxy groups.

2. Experimental

2.1. Materials

For the synthesis we used PhFR obtained by the procedure described in [8]. Its molecular mass (M_n) is 350 g/mol. GMA was used without additional purification. Its epoxy number (*e.n.*) is 28 %. Potassium hydroxide was a catalyst and isopropyl alcohol was a solvent. Both components were of P.A. purity. The epoxy dianic resin ED-20 used for the crosslinking, has M_n 390 g/mol and *e.n.* 20.0 %. TGM-3 oligoesteracrylate has M_n 280 g/mol. PO oligomer was synthesized in accordance with the procedure [9] with M_n 420 g/mol, *e.n.* 9.5 % and active oxygen content 2.9 %. Polyethylenepolyamine (PEPA) was used without additional purification.

2.2. Analytical Methods

The number-average molecular mass M_n of the synthesized product was 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 alkali solution [10]. The acidity was determined using a titration by 0.1N alkali solution. Film hardness, gel-fraction content and films chemical stability were determined using the known procedures.

2.3. Spectral Methods

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

2.4. Experimental Procedure

2.4.1. Reaction kinetics study procedure

The chemical modification of novolac phenolformaldehyde resin (PhFR) by glycidylmethacrylate (GMA) was studied in a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer in the inert medium. PhFR, GMA and isopropyl alcohol were loaded into the reactor. The mixture was heated to 323, 333 and 343 K under constant stirring and then the catalyst (KOH solution) was added. The reaction proceeding was controlled by the change of epoxy groups concentration using the formula:

$$[C]_{e.g.} = \frac{[V_{b.t.} - (V_t - V_a)] \cdot N \cdot K}{V_s}$$

where $V_{b.t.}$ – amount of 0.1 N alkali solution for blank test titration, ml; V_t – amount of 0.1 N alkali solution for withdrawn sample titration, ml; V_a – amount of 0.1 N alkali solution for the acidity determination, ml; N – solution normality; K – correction factor for the titre of 0.1N alkali solution; V_s – sample volume, ml.

The obtained results were used for the construction of graphical dependencies and calculations of the effective rate constants. The effective activation energy was determined by interpretation of the obtained results in the Arrhenius coordinates.

2.4.2. MGMAPhFR synthesis

MGMAPhFR was synthesized in a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer in the inert medium. 60 g of PhFR were dissolved in 180 ml of isopropyl alcohol at 333 K. Then 18.9 g of KOH dissolved in 60 ml of propanol were added. The mixture was mixed at 333 K and 81.0 g of GMA were added. The reaction mass was kept at the mentioned temperature for 6 h, then cooled and 360 ml of toluene were added. The mixture was transferred to the dividing funnel. After demixing the bottom layer was removed and the upper layer was washed out by a small amount of 10% acetic acid and then by water till the neutral reaction was achieved. MGMAPhFR was obtained after vacuum distillation of the organic layer at 323 K and residual pressure of 2.7–4 kPa. 73.4 g. of the product of hazel color were obtained. Its molecular mass is 640 g/mol and it is dissolved in the most of organic solvents.

2.4.3. MGMAPhFR cross-linking activity

MGMAPhFR crosslinking activity was studied taking polymeric mixtures (I-IV) given in Table 1. Mixtures V and VI with the initial PhFR were taken for the comparison.

Table 1

Composition of epoxy-oligomeric mixtures

Component	Component content in the mixture, mas %					
	I	II	III	IV	V	VI
ED-20 resin	66.7	61.5	57.1	53.3	61.5	66.7
MGMAPhFR	8.3	15.4	21.4	26.7	–	–
PhFR	–	–	–	–	15.4	8.3
PO oligomer	16.7	15.4	14.3	13.3	15.4	16.7
TGM-3	8.3	7.7	7.2	6.7	7.7	8.3
PEPA	10.8	10.0	9.3	8.7	10.0	10.8

The mixtures were prepared by components mixing till homogeneous viscous solutions were obtained. Then they were applied over degrease glass plates of the standard size. The films were kept at room temperature for

24 h and then heated to 383, 403 or 423 K for 15, 30, 45, 60, and 75 min. After cross-linking 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. Kinetic Regularities

In order to develop MGMAPhFR synthesis procedure it was necessary to study the effect of the catalyst (KOH) amount, reagents ratio, reaction temperature and time of the process proceeding. The experiments were carried out using the techniques described in Subsection 2.4.1.

The effect of potassium hydroxide amount on the rate of the reaction between PhFR and GMA is represented in Fig. 1.

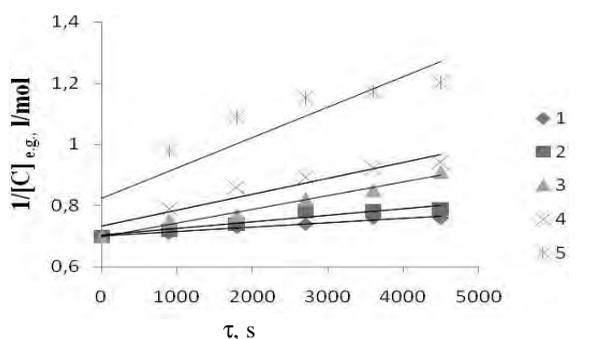


Fig. 1. Kinetic anamorphoses in the $1/C-\tau$ coordinates for the reaction between PhFR and GMA at 333 K in the isopropanol medium. KOH amount is: 0.2 (1); 0.4 (2); 0.6 (3); 0.8 (4) and 1.0 (5) moles per PhFR phenol group. GMA amount is 1.5 mol/phenol group

The lowest reaction rate is observed in the case of 0.2 and 0.4 KOH moles per PhFR phenol group (Fig. 1, Table 2). On the other hand, taking into account that at the catalyst amount of 0.6 and 0.8 moles the reaction rate is the same and further increase in the catalyst amount does not increase the reaction rate, KOH amount of 0.6 moles was chosen to be the optimum one.

The experimental results concerning the effect of the initial reagents ratio on the reaction proceeding are represented in Fig. 2 and Table 2.

The analysis of the experimental results shows that the increase of GMA amount increases the reaction rate. The effect of temperature on the reaction proceeding is given in Table 2 and Fig. 3. The increase in temperature by 10 K leads to 3–4 time increase of the effective rate

constant. The interpretation of the obtained results in the Arrhenius coordinates determines the activation energy. For the reaction between PhFR and GMA it is equal to 40.30 ± 1.05 kJ/mol.

Table 2

Effective rate constants of the reactions between PhFR and GMA

GMA amount per one phenol group, moles	KOH amount per one phenol group, moles	Reaction temperature, K	$K_{ef} \cdot 10^4$, l/(mol·s)
1.0	0.6	333	0.30 ± 0.07
1.5	0.2	333	0.10 ± 0.07
1.5	0.4	333	0.20 ± 0.07
1.5	0.6	333	0.40 ± 0.07
1.5	0.8	333	0.50 ± 0.07
1.5	1.0	333	1.00 ± 0.08
1.5	0.6	323	0.10 ± 0.06
1.5	0.6	343	1.20 ± 0.06
2.0	0.6	323	0.83 ± 0.06
2.0	0.6	333	1.43 ± 0.07
2.0	0.6	343	2.10 ± 0.07

Note: isopropyl alcohol is a medium

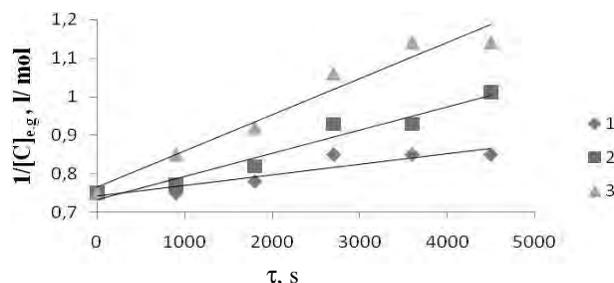


Fig. 2. Kinetic anamorphoses in the $1/C-\tau$ coordinates for the reaction between PhFR and GMA at 333 K in the isopropanol medium at KOH amount of 0.6 mol/phenol group. PhFR:GMA molar ratio is 1.0:1.0 (1); 1.0:1.5 (2) and 1.0:2.0 (3)

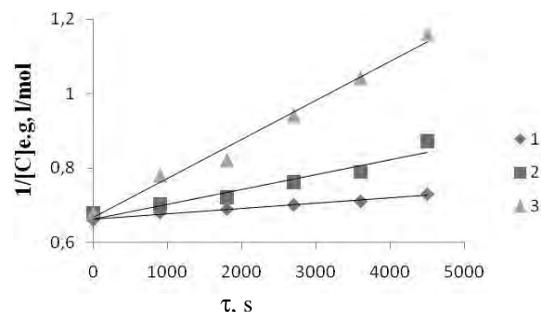


Fig. 3. Kinetic anamorphoses in the $1/C-\tau$ coordinates for the reaction between PhFR and GMA in the isopropanol medium at different temperatures (K): 323 (1); 333 (2) and 343 (3).

PhFR:GMA molar ratio is 1.0:1.5; KOH amount is 0.6 mol/phenol group

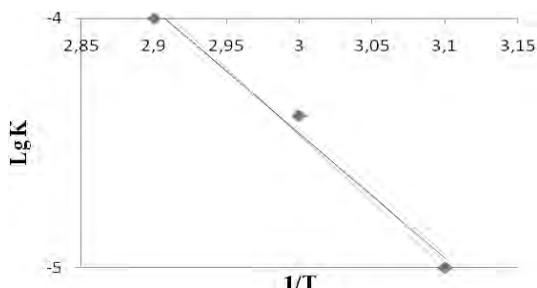


Fig. 4. Dependence of $\lg K$ on $1/T$ for the reaction between PhFR and GMA in the isopropanol medium at KOH amount of 0.6 mol/phenol group and PhFR:GMA = 1.0:1.5 mol

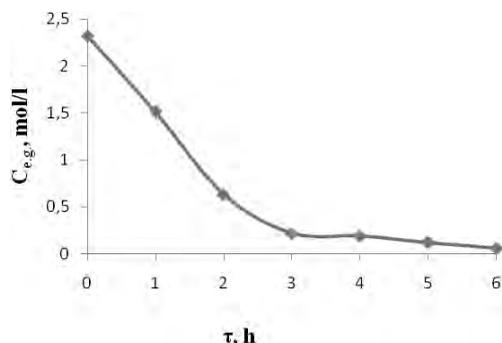


Fig. 5. Concentration change vs. reaction time at 333 K. GMA amount is 1.0 moles, KOH amount is 0.6 mol/phenol group. Isopropanol is the medium.

The effect of the reaction time is given in Fig. 5. One can see that the complete absence of epoxy groups in the reaction medium is achieved after 6 h.

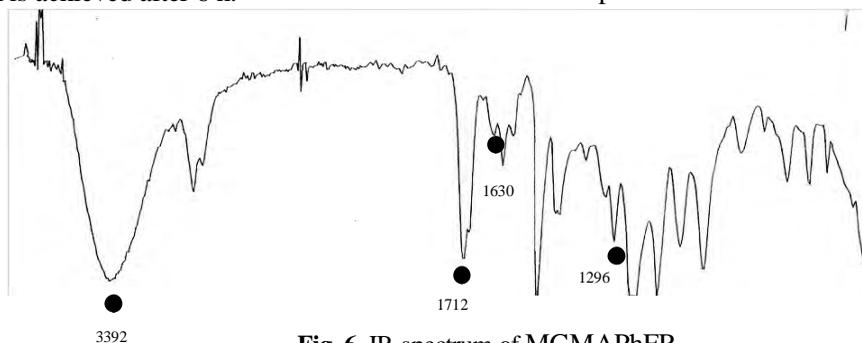


Fig. 6. IR-spectrum of MGMAPhFR

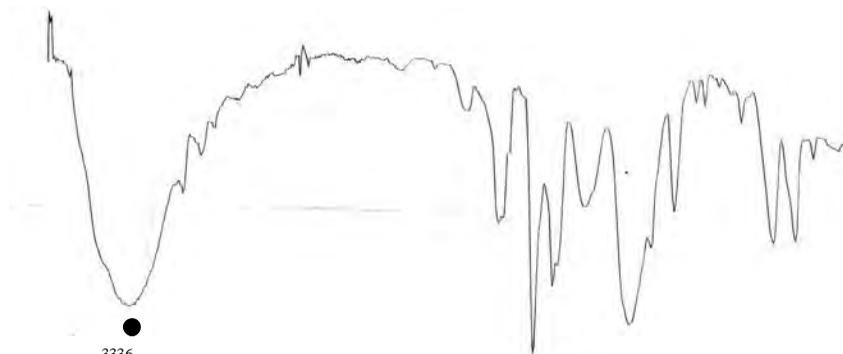


Fig. 7. IR-spectrum of PhFR

The obtained results allow to suggest the MGMAPhFR synthesis procedure described in Subsection 2.4.2.

3.2. IR-Spectroscopic Investigations

The absorption bands at 910 cm^{-1} corresponding to GMA epoxy groups are absent in IR-spectrum of MGMAPhFR (Fig. 6). The presence of epoxy groups testifies to bonding of GMA molecules to the PhFR ones. At the same time the decrease of absorption band typical of phenol OH-group (compared with the initial PhFR, see Fig. 7) and its shift toward the area of 3392 cm^{-1} is observed. It indicates partial exchange of OH-group for GMA fragments.

Moreover, the absorption bands at 1296, 1630 and 1712 cm^{-1} typical of stretching vibrations of so-called “esteric band”, double bond and carbonyl group in esters, respectively, are present in MGMAPhFR spectrum. This fact confirms the GMA bonding to PhFR.

3.3. Crosslinking of Epoxy-Oligomeric Mixtures in the Presence of MGMAPhFR

In order to examine the crosslinking of epoxy-oligomeric mixtures in the presence of MGMAPhFR the polymeric mixtures were prepared (Table 1). Crosslinking of polymeric mixtures was studied in accordance with the procedure described in Subsection 2.4.3. The obtained results are represented in Table 3.

Table 3

Dependence of gel-fraction content and films hardness upon mixtures composition, temperature and crosslinking time

Temperature, K	Mix number in accordance with Table 1	Symbol	Symbol values at crosslinking time, min					
			24 h, room temperature	15	30	45	60	70
383	II	G	74.0	79.5	81.4	87.0	87.2	88.2
		H	0.35	0.50	0.70	0.76	0.81	0.83
	V	G	64.0	77.2	81.3	83.1	84.0	84.2
		H	0.06	0.15	0.45	0.65	0.68	0.71
	VI	G	-	-	-	-	-	77.4
		H	-	-	-	-	-	0.1
403	I	G	75.5	80.1	83.2	88.1	88.3	91.4
		H	0.55	0.68	0.72	0.74	0.81	0.82
	II	G	74.0	79.8	83.2	86.9	87.4	88.5
		H	0.35	0.51	0.74	0.82	0.83	0.84
	III	G	64.9	71.5	73.1	79.8	84.1	85.3
		H	0.34	0.48	0.64	0.72	0.81	0.82
	IV	G	64.1	70.6	72.9	79.0	79.2	79.6
		H	0.28	0.47	0.51	0.69	0.75	0.82
	V	G	64.0	77.2	82.0	85.1	86.2	87.0
		H	0.06	0.18	0.55	0.59	0.69	0.77
423	II	G	74.0	84.2	88.2	89.3	91.1	91.5
		H	0.35	0.79	0.82	0.84	0.86	0.86
	V	G	64.0	80.2	85.3	86.2	88.4	90.3
		H	0.06	0.59	0.76	0.80	0.80	0.801

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

One can see from Table 3 that gel-fraction content and film hardness depend on the nature of used phenol-formaldehyde resin. The epoxy-oligoesteric mixtures containing the synthesized MGMAPhFR even at room temperature form films, which hardness is 5-6 times higher than that of the mixture with PhFR. It means that the initial PhFR at room temperature cannot interact with the components of the polymeric mixture. The formed films are sticky and rough. The same results were obtained during gel-fraction determination. Heating of films to 383 K and higher temperatures favors three-dimensional films formation for both mixtures with PhFR and synthesized MGMAPhFR. It means that reactions leading to the formation of three-dimensional structure take place at heating. In the case of the mixtures with PhFR there are reactions of phenol groups with ED-20 epoxy groups. Using the mixtures with MGMAPhFR (I-IV) with unsaturated double bonds and residual phenol groups PO partial polymerization with TGM-3 molecules takes place due to the decomposition of –O–O– groups at room temperature. Forming of films with the hardness of 0.28–0.55 rel.units confirms this fact. The increase of temperature to 383 K and higher accelerates the peroxy groups decomposition in PO molecule and increases the rate of MGMAPhFR and TGM-3 molecules copolymerization. Moreover, PO

molecules as a source of free radicals are bound with the structure formed due to MGMAPhFR and TGM-3 copolymerization. At high temperatures the additional crosslinking takes place in the mixtures with MGMAPhFR due to the interaction of phenol groups with ED-20 epoxy groups which do not react with PEPA molecules. The increase of MGMAPhFR content in the polymeric mixture decreases films hardness, as well as gel-fraction content of the samples crosslinked at room temperature but it does not practically influence the mentioned indexes of the samples heated for 75 min. The increase of temperature does not influence the gel-fraction content and films hardness. It means that the main contribution to the three-dimensional films formation (in the case of the mixtures I-IV) is introduced by the reactions of ED-20 epoxy groups and PO with PEPA, as well as MGMAPhFR copolymerization with TGM-3 due to the decomposition (by –O–O– bonds) of PO molecules partially crosslinked with ED-20. In the case of mixtures V and VI at room temperature only interaction between ED-20 and PEPA molecules takes place. PhFR and TGM-3 molecules do not participate in the crosslinking under the mentioned conditions. The heating of such mixtures leads to the partial polymerization of TGM-3 molecules by double bonds and interaction between PhFR molecules and ED-20 epoxy resin.

3.4. Physico-Mechanical and Protective Properties of Epoxy-Oligoesteric Mixtures

Physico-mechanical and protective properties of epoxy-oligoesteric mixtures were studied taking the mixtures I and VI (Table 1) as an example. The mixtures were prepared in accordance with the procedure described in Subsection 2.4.3. The mixtures were kept at room

temperature for 24 h and then at 383 K for 75 min. The mixture I is characterized by gel-fraction content of 83.2 % and hardness of 0.7 rel.units. For the mixture VI gel-fraction content is 77.4 % and hardness is 0.1 rel.unit. The films obtained after crosslinking of the mixture I were uniform and smooth and films formed from the mixture VI were rough (Fig. 8).

Physico-mechanical and protective properties of the films are represented in Table 4. They reveal the advantage of films with the synthesized MGMAPhFR.

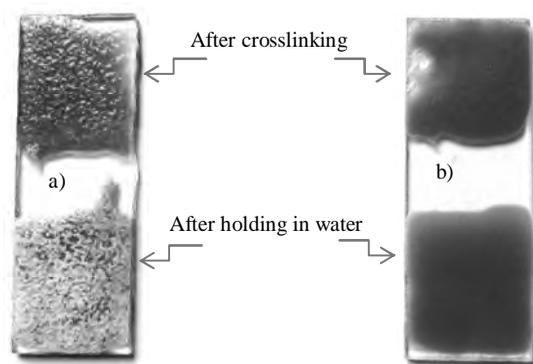


Fig. 8. Mixture VI (a) and mixture I (b) after crosslinking at 383 K for 75 min and holding in water at room temperature for 5 days

Table 4

Films physico-mechanical and protective properties

Mixture number	Physico-mechanical characteristic		Resistance to the aggressive media, h			
	Impact strength, N·m	Bending strength, mm	H ₂ O	3 % CH ₃ COOH	10 % H ₂ SO ₄	10 % NaOH
I	4.9	2	>336	>48	>48	>48
VI	3.9	10	24	2	2	2

Notes: The coatings resistance to the aggressive media was determined at room temperature. Adhesion of the film based on the mixture I was determined using “lattice notch” method and was equal to “one”.

4. Conclusions

Kinetic regularities of the chemical interaction between novolac phenol-formaldehyde resin with glycidylmethacrylate have been established in the presence of potassium hydroxide. They allow to suggest the synthesis procedure and synthesize PhFR with double unsaturated bonds in the side chains. Using IR-spectroscopy the presence of unsaturated bonds has been confirmed in the molecules of synthesized resin (stretching vibrations at 1630 cm⁻¹). The synthesized resin is an active component of epoxy-oligoesteric mixture, which increases gel-fraction content and hardness of the obtained films compared with the initial PhFR. Moreover, the obtained

films are characterized by higher impact and bending strengths and higher resistance to aggressive media.

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**ФЕНОЛО-ФОРМАЛЬДЕГІДНІ СМОЛИ
НОВОЛАЧНОГО ТИПУ ІЗ БІЧНИМИ
НЕНАСИЧЕНИМИ ЗВ'ЯЗКАМИ**

Анотація. Вивчена, в присутності гідроксиду калію, реакція взаємодії новолачної феноло-формальдегідної смоли з

гліцидилметакрилатом та запропонована методика синтезу феноло-формальдегідної смоли, яка містить бічні ненасичені зв'язки. Розраховані ефективні швидкості та енергія активації такої реакції. Структура синтезованої смоли підтверджена ІЧ- спектроскопічними методами дослідження. Показана можливість використання такої смоли як активного компоненту полімерних сумішей на основі промислової епоксидної смоли ЕД-20, її пероксидної похідної (ПО) та олігоестеракрилату ТГМ-3. Контроль за процесами структурування проводили внаслідок визначення вмісту гель-фракції та твердості полімерних плівок. Вивчені фізико-механічні та захисні властивості структурованих епокси-олігоестерних сумішей.

Ключові слова: феноло-формальдегідна смола, гліцидилметакрилат, діанова епоксидна смола ЕД-20, пероксидна похідна, кінетика, ІЧ-спектроскопія, структурування, гель-фракція, твердість, плівка.