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CHEMICAL MODIFICATION OF POLYGLYCIDYL PHENOL-FORMALDEHYDE OLIGOMERS BY METHACRYLIC ACID

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Abstract. A new oligomer with unsaturated double bonds in the side chains has been synthesized *via* chemical modification of polyglycidyl phenol-formaldehyde oligomer (PGPFO) by methacrylic acid (MA) using benzyltriethylammonium chloride as a catalyst. The effect of temperature and reaction time on the reaction proceeded between PGPFO and MA has been studied. The effective rate constants and activation energy of the reaction have been calculated. The structure of the synthesized oligomer has been confirmed by chemical and IR-spectroscopic analyses. The cross-linking of epoxy-oligomeric mixtures based on ED-20 epoxy resin, peroxy derivative of epoxy resin, TGM-3 oligoesteracrylate and synthesized oligomer has been examined using polyethylenepolyamine as a hardener.

Keywords: epoxy resin, methacrylic acid, quaternary ammonium salt, oligoesteracrylate, peroxide, gel-fraction.

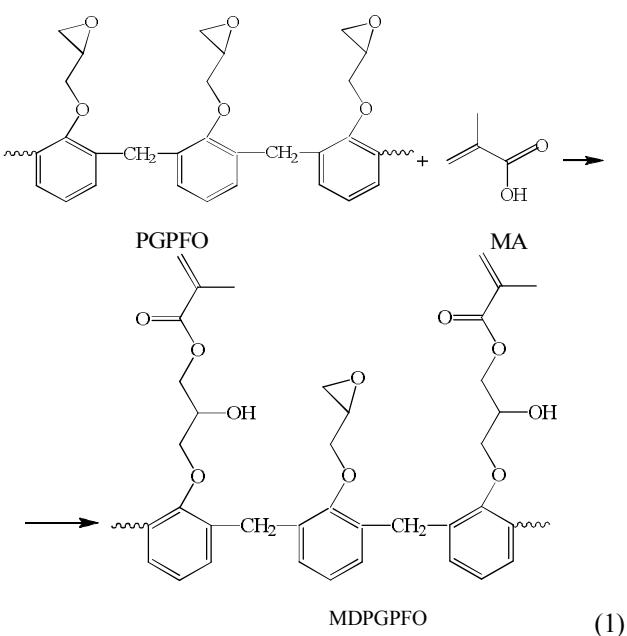
1. Introduction

Phenol-formaldehyde resins (PhFR) take a special place among known oligomers because the products based on them are characterized by a low cost and a series of positive properties [1]. In order to extend the area of their application and to improve their compatibility with other polymers, PhFR are modified by different low-molecular compounds [2]. The modification by epichlorohydrin [3], furfurylglycide ether [4], 1,2-epoxy-3-*tert*-butyl peroxypropane [5], glycidyl methacrylate and other compounds [6] were described in the literature.

V. Puchin *et al.* [5] obtained oligomers with labile –O–O– bonds in the side chains *via* PhFR modification by 1,2-epoxy-3-*tert*-butyl peroxypropane. Such oligomers are capable to form three-dimensional products while heating including those with unsaturated polymers [7]. The PhFR ability to combine with unsaturated products may be increased due to its modification by glycidyl methacrylate

[8]. So called polyglycidyl phenol-formaldehyde oligomers (PGPFO) are formed *via* PhFR modification by epichlorohydrin [9]. They are variations of epoxy resins and are able to form cross-linked products in the presence of hardeners used for dianic epoxy resins [10]. Moreover, the peculiarity of PGPFO is the presence of reactive epoxy groups in their side chains giving the possibility to use them for the further modification [11]. Thus, products with reactive peroxy and epoxy groups are synthesized *via* modification of polyglycidyl phenol-formaldehyde oligomers by hydroperoxides. Later on they may be applied to form products *via* radical or condensation mechanisms [3].

In this work taking into account the high reactivity of PGPFO we studied the formation of products on their basis which contain unsaturated double bonds and epoxy groups. Such products may be obtained due to the interaction between PGPFO and methacrylic acid (MA) according to the equation:



The synthesized methacrylic derivative of poly(glycidyl phenol-formaldehyde) oligomers (MDPGPFO) contains functional groups different by their nature and may be used as an additive to polymeric mixtures during films formation on their basis.

2. Experimental

2.1. Materials

For the synthesis we used PGPFO obtained by the procedure described in [9]. Its molecular mass (M_n) is 460 g/mol and epoxy number (*e.n.*) is 17 %. MA was used as received without additional purification. Benzyltriethylammonium chloride (BTEAC) was used as a catalyst. Toluene was a solvent. The epoxy dianic resin ED-20 used for the cross-linking has M_n 390 g/mol and *e.n.* 20.0 %. Peroxy oligomer (PO) was synthesized in accordance with the procedure described in [12] with M_n 430 g/mol, *e.n.* 9.6 % and active oxygen content $[O]_{act}$ 2.9 %. TGM-3 oligoesteracrylate has 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 (M_n) 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 0.1 N alkali solution [9]. The concentration of acid groups in the reaction medium was determined according to the formula (2):

$$[C]_{a.g.} = \frac{V_{KOH} \cdot N \cdot K}{V_s} \quad (2)$$

where V_{KOH} – amount of 0.1 N solution KOH expended for the sample titration, ml; V_s – sample volume, ml; N – normality of KOH solution; K – correction factor for titre of 0.1 N solution KOH

Film hardness and gel-fraction content were determined using the known procedures.

2.3. Spectral Methods

Infrared spectra (IR) were obtained using “Specord-80” apparatus with the relevant absorption range of 4000–400 cm⁻¹.

2.4. Experimental Procedure

2.4.1. Kinetics study

The chemical modification of PGPFO by MA was studied in a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer in the inert medium. PGPFO, MA and toluene were loaded into the reactor. The mixture was heated to 343, 353 or 358 K under constant stirring and then the catalyst (BTEAC in the form of 60%-aqueous solution) was added. The reaction proceeding was controlled by the change of carboxy groups concentration (mol/l) using formula (2):

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

2.4.2. MDPGPFO synthesis

MDPGPFO was synthesized in a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer in the inert medium. 200 g of PGPFO were dissolved in 1000 ml of toluene at 353 K. The mixture was mixed at 353 K and 35 g of BTEAC (as 60%-aqueous solution) were added. Then 68.0 g of MA were added. The reaction mixture was kept at the mentioned temperature for 6 h, then cooled and transferred to the separating funnel. The bottom layer was removed and the upper one was washed out by a small amount of water to the neutral reaction. MDPGPFO was obtained after vacuum distillation of organic layer at 323 K and residual pressure of 2.7–4.0 kPa. 264 g of the brown-colored product was obtained. Its molecular mass is 590 g/mol. The product is dissolved in the most organic solvents.

2.4.3. MDPGPFO cross-linking activity

MDPGPFO cross-linking activity was studied taking polymeric mixtures I and II (Table 1).

Table 1

Composition of epoxy-oligomeric mixtures

Component	Component content in the mixture, wt %	
	I	II
ED-20	61.5	61.5
MDPGPFO	15.4	-
PGPFO	-	15.4
PO	15.4	15.4
TGM-3	7.7	7.7
PEPA	10.0	10.0

Polymeric mixtures were prepared by mixing of the components till homogeneous viscous solution was obtained. It was applied over degreased glass plate of the standard size. The films were kept for 24 h at room temperature and then heated to 383, 403 or 423 K for 15, 30, 45, 60 and 75 min. The film formation was controlled by determination of hardness (M-3 pendulum device) and gel-fraction content (Soxhlet apparatus, 10 h, chloroform).

3. Results and Discussion

3.1. Kinetic Regularities

On the basis of literature data [13] BTEAC (60% aqueous solution) was used as the catalyst for Eq. (1). The amount of MA used for the modification was 1 mol per 1 epoxy group of above-mentioned oligomer. The catalyst amount was 0.2 mol per 1 g-eq epoxy group. Toluene was the reaction medium.

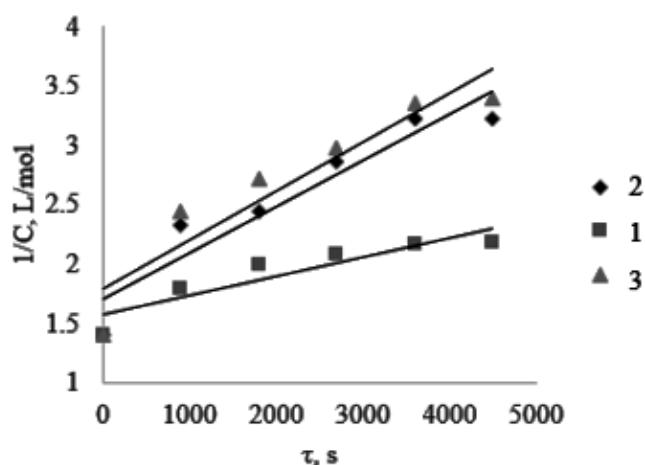


Fig. 1. Kinetic anamorphoses in $1/C - t$ coordinates for the reaction between PGPFO and MA in toluene medium at different temperatures (K): 343 (1); 353 (2) and 358 (3). BTEAC amount is 0.2 mol; MA content is 1 mol per 1 epoxy group of PGPFO

While studying the effect of temperature on the reaction rate (Fig. 1) we found that the increase in temperature to 353 K essentially affects the rate of the reaction between PGPFO and MA (compared with 343 K). Moreover, the further increase in temperature by only 5 K slightly affects the reaction rate. The calculated effective rate constants (K_{ef} , l/(mol·s)) are: 0.0002 ± 0.000004 at 343 K; 0.00039 ± 0.000005 at 353 K and 0.00041 ± 0.000004 at 358 K. The interpretation of obtained results in the Arrhenius coordinates allows to determine the effective activation energy equal to 56.89 ± 1.03 kJ/mol (Fig. 2).

The effect of reaction time on the reaction proceeding is represented in Fig. 3. After 6 h the carboxy groups are exhausted. The obtained results are used for the development of MDPGPFO synthesis procedure represented in Subsection 2.4.2.

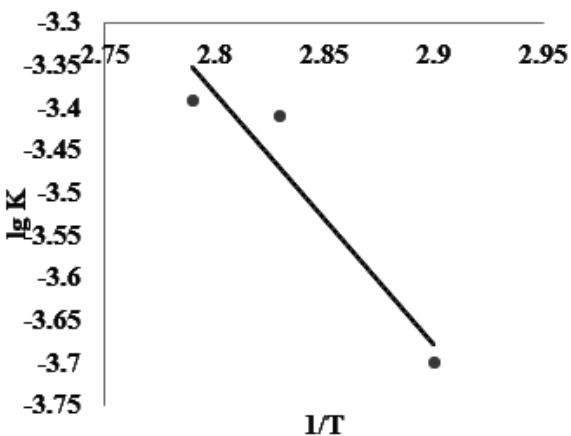
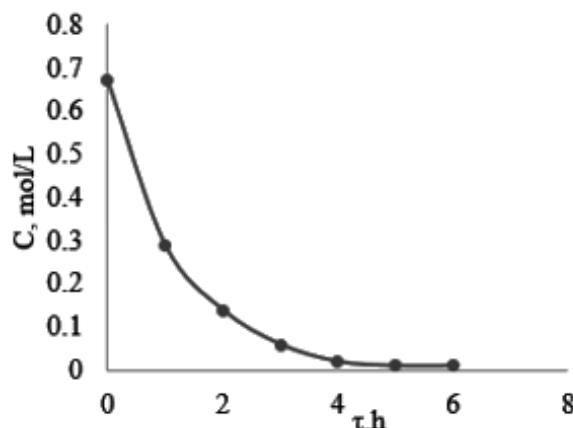


Fig. 2. Dependence of lgK on $1/T$ for the reaction between PGPFO and MA in toluene medium. BTEAC amount is 0.2 mol; MA content is 1 mol per 1 epoxy group of PGPFO

Fig. 3. Dependence of carboxy groups concentration on the reaction time at 353 K. BTEAC amount is 0.2 mol; MA content is 1 mol per 1 epoxy group of PGPFO; toluene is the reaction medium



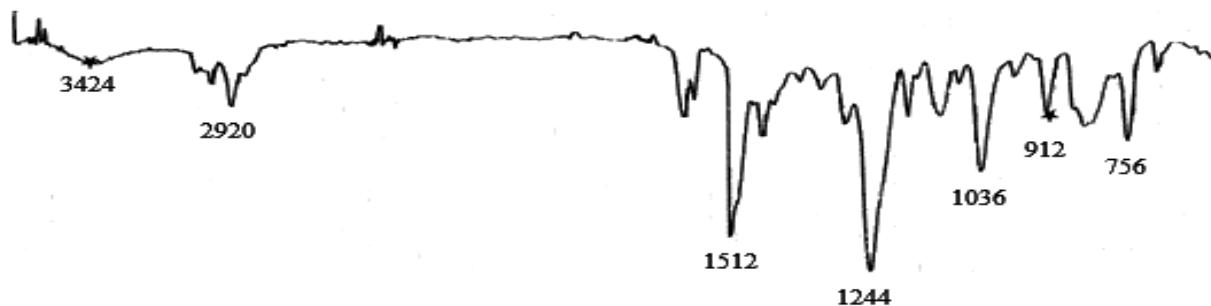


Fig. 4. IR-spectrum of MDPGPFO

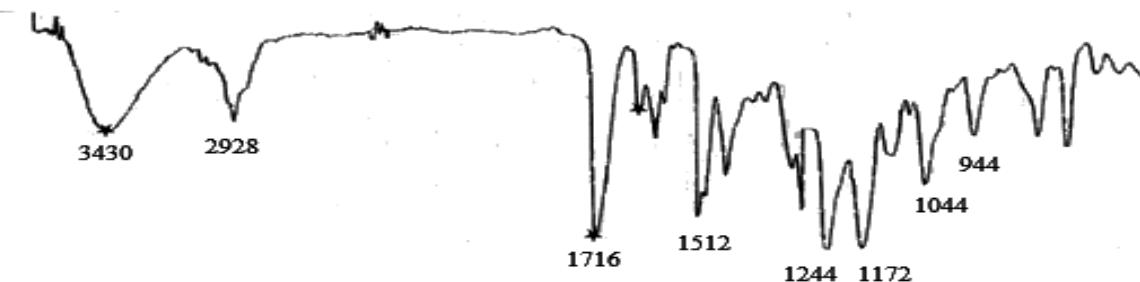


Fig. 5. IR-spectrum of PGPFO

3.2. IR-Spectroscopic Investigations

IR-spectroscopic investigations were carried out to confirm the structure of the synthesized MDPGPFO. The spectrum of the initial PGPFO is given for the comparison. The obtained results are given in Figs. 4 and 5.

It is obvious from Figs. 4 and 5 that spectra are non-identical. We observe the significant increase in the absorption band intensity at 3430 cm⁻¹ in IR-spectrum of MDPGPFO (Fig. 4). This band is typical of hydroxyl group stretching vibrations. The increase means that MA molecule bonds with PGPFO due to the interaction between carboxy groups of unsaturated acid and epoxy groups of PGPFO. Such interaction results in the opening of PGPFO epoxy ring with formation of secondary hydroxyl groups (Eq. (1)). The decrease in the absorption band intensity at 912 cm⁻¹ indicates the interaction between carboxy and epoxy groups (Fig. 4). This band is typical of epoxy ring stretching vibrations. The appearance of the absorption band at 1716 cm⁻¹ also indicates the MA bonding with PGPFO. This band is typical of stretching vibration of carbonyl group (ν_{CO}) in esters. The double bond ($\nu_{C=C}$) in MDPGPFO molecule is confirmed by the absorption bond at 1636 cm⁻¹ (Fig. 4) which is absent in PGPFO spectrum (Fig. 5).

3.3. Cross-linking of Epoxy-Oligomeric Mixtures in the Presence of MDPGPFO

The epoxy-oligomeric mixtures were cross-linked in the presence of MDPGPFO according to the procedure described in Subsection 2.4.3. The mixture used for the investigations (Table 1) contains MDPGPFO, ED-20 epoxy resin, peroxy oligomer PO and TGM-3 oligoesteracrylate. PEPA was a hardener. The mixture with PGPFO instead of MDPGPFO was taken for the comparison.

One can see from Fig. 6 that gel-fraction content in the epoxy-oligomeric mixtures (Mix. 1, Table 1) containing the synthesized MDPGPFO depends on temperature and cross-linking time.

At 383 K and cross-linking time of 75 min the gel-fraction content is below 75.8 %. The increase in temperature to 403 K considerably increases the amount of insoluble products and further temperature increase has a minor effect on it. Another situation is observed while determining the film hardness (Fig. 7).

While cross-linking at 383 and 403 K we observe the increase in hardness depending on time. While cross-linking at 423 K there is a sharp increase of hardness and after 40 min it achieves 0.8 rel.units; then it is practically constant.

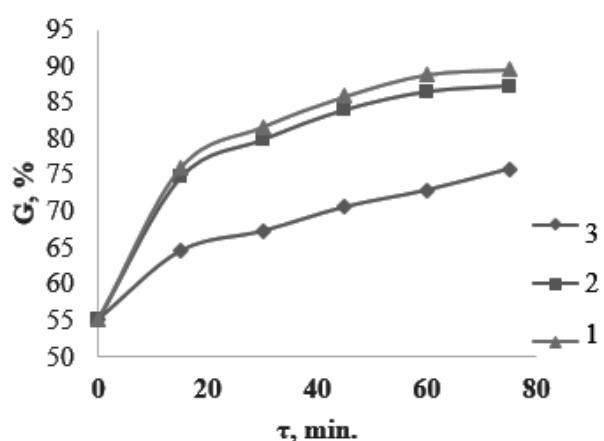


Fig. 6. Dependence of gel-fraction content in epoxy-oligomeric mixture I on temperature and cross-linking time: 383 K (1); 403 K (2) and 423 K (3)

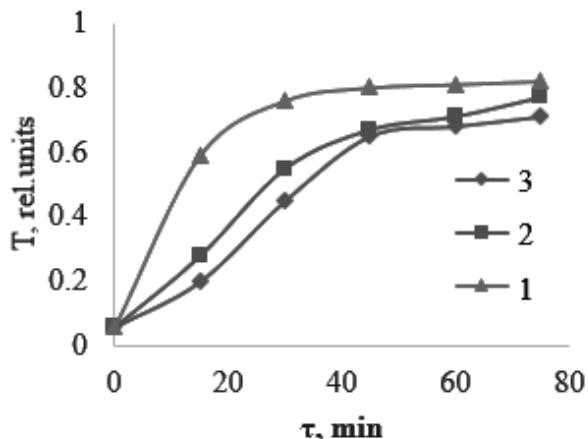


Fig. 7. Dependence of hardness on temperature and cross-linking time for epoxy-oligomeric mixture I based films: 383 K (1); 403 K (2) and 423 K (3)

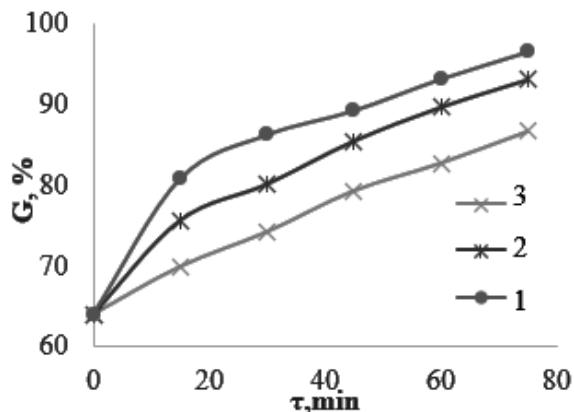


Fig. 8. Dependence of gel-fraction content in epoxy-oligomeric mixture II on temperature and cross-linking time: 383 K (1); 403 K (2) and 423 K (3)

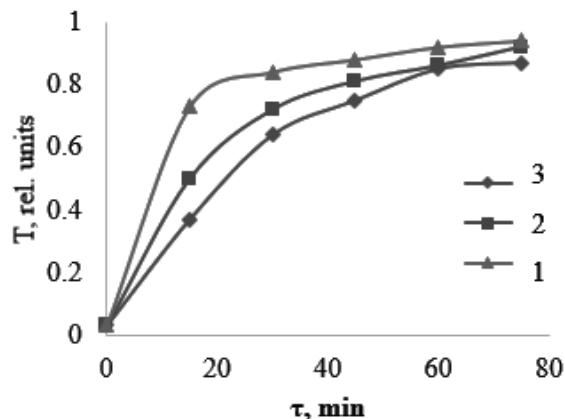


Fig. 9. Dependence of hardness on temperature and cross-linking time for epoxy-oligomeric mixture II based films: 383 K (1); 403 K (2) and 423 K (3)

If we analyze Mix. II (Table 1) with PGPFO we observe the gel-fraction content of 96.5 % at 423 K and time of 75 min (Fig. 8).

While comparing mixtures I and II there is no essential difference between cross-linking at 383 and 403 K. At the same time, there is a tendency to increase the film hardness during cross-linking at 423 K (Fig. 9).

Mix. II is characterized by higher values of gel-fraction content and film hardness compared with those of Mix. I. The reason is that Mix. I contains compounds with epoxy groups (ED-20 resin, peroxy oligomer and MDPGPFO) and compounds with unsaturated double bonds (TGM-3 and MDPGPFO). Moreover, MDPGPFO is the product mainly containing unsaturated methacrylic bonds and only 3 % of epoxy groups. PO contains peroxy and epoxy groups. PEPA is a cross-linking agent. At room

temperature ED-20 and PO molecules, as well as part of MDPGPFO molecules interact with PEPA molecules due to the presence of epoxy groups in their structures. Partially cross-linked structure is formed with inclusions of TGM-3 and MDPGPFO molecules. Such structure contains free peroxy groups due to PO molecules and free methacrylic bonds due to the partial introduction of MDPGPFO molecules into a cross-linked matrix based on ED-20 resin. Further heating of Mix. I increases both gel-fraction content and film hardness due to the interaction of epoxy groups with hydroxyl ones of the mixture components and with PEPA secondary groups as well. Besides this, the decomposition of PO peroxy groups takes place and results in grafting of MDPGPFO molecules by unsaturated double bonds and TGM-3 oligoesteracrylate molecules to the matrix.

Radicals $(CH_3)_3C^\bullet$ are formed as a result of peroxy groups decomposition in PO fragment. They cause copolymerization of MDPGPFO non-crosslinked molecules and TGM-3 oligoesteracrylate by double bonds. The latter may lead to the formation of linear (non-crosslinked) structures and network which is non-connected with the main matrix. The result is the decrease of gel-fraction content and film hardness.

In Mix. II with epoxy groups the cross-linking takes place only due to the interaction between ED-20, PGPFO and PO with PEPA. Such partially cross-linked structure contains free peroxy groups and its values of gel-fraction content and film hardness are higher already at room temperature and at the beginning of heating. While heating the peroxy groups are decomposed and as a result TGM-3 molecules graft to the main matrix and copolymerize via radical mechanism. Since the amount of compounds with double bonds in Mix. II is insignificant, the gel-fraction content and film hardness are higher for cross-linked samples.

To establish the role of every component in the cross-linking we studied epoxy-oligomeric mixtures different by their composition (Table 2).

The cross-linking of epoxy-oligomeric mixtures was studied at 403 K according to the procedure described in Subsection 2.4.3. The obtained results are represented in Table 3.

The increase of TGM-3 oligoesteracrylate content in the mixtures (Mix. III and IV, cf. with Mix. I and II, Table 1) results in the greater number of three-dimensional products. If we compare Mix. III and IV with Mix. I, the number of insoluble products in Mix. III is larger than that in Mix. I (Figs. 6 and 7) and Mix. IV (Table 3). It means that MDPGPFO molecules participate in the process of film formation. The increase in film hardness in Mix. III also indicates the proceeding of copolymerization between MDPGPFO and TGM-3. The absence of PO in the mixture, which is a source of free radicals while heating, results in a sharp decrease of cross-linked products number in Mix. VI containing PGPFO.

We do not observe significant decrease in gel-fraction content in Mix. V that confirms once more the possibility of chemical interaction between synthesized MDPGPFO and TGM-3. Such interaction is obvious comparing Mix. VII and VIII. The increase in MDPGPFO content increases both gel-fraction content and the film hardness.

Table 2

Composition of epoxy-oligomeric mixtures

Component	Component content in the mixture, wt %					
	III	IV	V	VI	VII	VIII
ED-20	61.5	61.5	61.5	61.5	61.5	61.5
MDPGPFO	15.4	-	15.4	-	15.4	-
PGPFO	-	15.4	-	15.4	-	15.4
PO	15.4	15.4	-	-	-	-
TGM-3	15.4	15.4	7.7	7.7	15.4	15.4
PEPA	10.0	10.0	13.0	13.0	13.0	13.0

Table 3

Dependence of gel-fraction content and film hardness on the mixture composition and cross-linking time at 403 K

Mixture No. according to Table 1	Index	Index value for cross-linking time, min					
		24 h; room temperature	15	30	45	60	75
III	G	67.2	82.4	86.4	91.0	96.2	97.3
	H	0.03	0.37	0.55	0.69	0.82	0.84
IV	G	61.1	81.2	85.0	90.3	93.2	95.1
	H	0.05	0.44	0.61	0.72	0.76	0.80
V	G	81.00	86.2	89.3	91.2	92.4	92.8
	H	0.07	0.64	0.73	0.75	0.77	0.78
VI	G	78.1	78.97	79.8	82.6	84.9	85.9
	H	0.09	0.39	0.41	0.52	0.59	0.70
VII	G	67.3	89.5	90.7	92.0	94.2	96.9
	H	0.03	0.59	0.78	0.81	0.82	0.83
VIII	G	55.7	79.0	79.8	82.6	84.9	85.9
	H	0.04	0.14	0.20	0.43	0.59	0.63

Note: G – gel-fraction content, %; H – film hardness, rel.unit

4. Conclusions

1. A new oligomer with reactive methacrylic fragments in side chains has been synthesized via chemical modification of polyglycidyl phenol-formaldehyde oligomers by methacrylic acid using benzyltriethylammonium chloride as a catalyst.

2. The structure of synthesized oligomer has been confirmed by chemical and IR-analyses. The introduction of methacrylic fragments into the structure of polyglycidyl phenol-formaldehyde oligomer is confirmed by the presence of absorption band at 1716 cm^{-1} typical of carbonyl group stretching vibrations in esters and band at 1636 cm^{-1} referred to the double bond.

3. Synthesized oligomer has been studied during film formation based on ED-20 resin and TGM-3 oligoesteracrylate. We assume that in the presence of synthesized MDPGPFO the films are formed due to cross-linking of ED-20 and PO by PEPA molecules, as well as due to cooligomerization of TGM-3 oligoesteracrylate and MDPGPFO molecules. Such cooligomerization takes place with the assistance of free radicals formed due to the peroxy groups decomposition in PO and owing to the thermal polymerization of methacrylic groups in the air.

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ХІМІЧНА МОДИФІКАЦІЯ ПОЛІГЛІЦІДІФЕНОЛО-ФОРМАЛЬДЕГІДНОГО ОЛІГОМЕРУ МЕТАКРИЛОВОЮ КИСЛОТОЮ

Анотація. Хімічною модифікацією полігліциділфенолоформальдегідного оліогомеру (ПГФФО) метакриловою кислотою (МАК), з використанням як катализатора бензилтриетиламоній хлористого, синтезований новий оліогомер, який у бічних відгалуженнях містить ненасичені подвійні зв'язки. Вивчено вплив температури і часу на швидкість протікання реакції між ПГФФО і МАК. Розраховані ефективні константи швидкості такої реакції та розрахована енергія активації. Структура синтезованого оліогомеру, що містить у бічних відгалуженнях ненасичені подвійні зв'язки, підтверджена хімічними та ІЧ-спектроскопічними методами дослідження. Вивчено структурування епокси-оліогомерних сумішей на основі епоксидної смоли ЕД-20, пероксидної похідної епоксидної смоли, олігоестеракрилату ТГМ-3 та синтезованого оліогомеру з використанням як затвердника поліметиленполіаміну.

Ключові слова: епоксидна смола, метакрилова кислота, четвертинна амонієва сіль, олігоестеракрилат, пероксид, гель-фракція.