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## MONOMETHACRYLATE DERIVATIVE OF ED-24 EPOXY RESIN AND ITS APPLICATION

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**Abstract.** Resin derivative containing methacrylic fragment and free epoxy group at the same time has been synthesized *via* chemical modification of ED-24 epoxy dianic resin by methacrylic acid. The structure of the synthesized product has been confirmed by IR-spectroscopic investigations. Derivatography was used to determine the thermal stability of the synthesized compound. It has been suggested to use methacrylate derivative of ED-24 epoxy resin as a component of epoxy-oligoesteric and bitumen-polymeric mixtures.

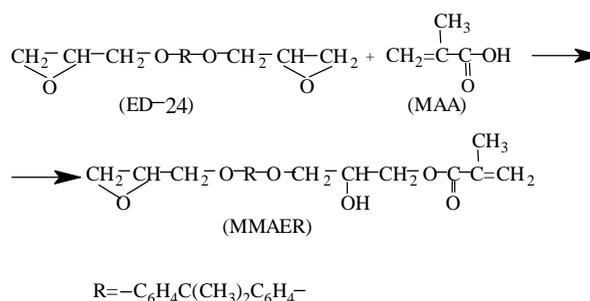
**Keywords:** epoxy resin, methacrylic acid, chemical modification, IR-study, derivatography, epoxy-oligomeric and bitumen-polymeric mixture, group analysis.

### 1. Introduction

Oligomers with different by their nature functional groups are used as active additives to various composites [1]. Epoxy resins may be used as a raw material for the synthesis of compounds with different functional groups. The presence of reactive epoxy groups in the molecules of mentioned resins allows to obtain products with other functional groups [2] on their basis. It is known [3] oligomers with unsaturated end-bonds and hydroxy groups are obtained *via* chemical modification of epoxy resins by acryl acids. Such compounds do not contain epoxy groups and may be used in different composites which are cross-linked *via* radical mechanism [3].

In the present work we suggest to obtain the product with a methacrylate fragment, free epoxy and hydroxy groups at the same time on the basis of ED-24 epoxy resin.

The synthesis of ED-24 epoxy resin monomethacrylate derivative (MMAER) may be expressed as follows:



In comparison with known acrylate derivatives of epoxy resins MMAER contains both methacrylate fragment and epoxy groups that allows to use it in the composites cross-linking of which takes place *via* polymerization and polycondensation.

### 2. Experimental

#### 2.1. Materials

ED-24 industrial epoxy resin with a molecular mass ( $M_n$ ) of 340 g/mol and epoxy number (*e.n.*) 24 % was used. Methacrylic acid is of high purity. The catalyst is tetrabutylammonium iodide of P.A. purity. ED-20 epoxy dianic resin has  $M_n$  390 g/mol and *e.n.* 20.0 %. Molecular mass of TGM-3 oligoesteracrylate is 280 g/mol. Polyethylenepolyamine (PEPA) was used as received without additional purification. Bitumen was withdrawn at Lviv asphalt plant (Lviv, Ukraine) with the following characteristics: penetration 62 mm, ductility 75 cm, softening temperature by the "ring and ball" method 319 K, adhesion 40.5.

#### 2.2. Analysis Methods

The number-average molecular masses  $M_n$  of the initial resins and synthesized MMAER were determined

by cryometry using dioxane as the solvent. The epoxy number was determined using a procedure described in [4]. Film hardness ( $H$ , rel.units) was determined using M-3 pendulum device in accordance with a standard procedure [5]. Gel-fraction content ( $G$ , %) was determined by extraction of grinded samples with acetone in Soxhlet apparatus for 12 h using the known procedure [5].

Infrared spectra (IR) were obtained using "Specord-M40" apparatus (Bruker firm, Germany). The sample was prepared as a film formed from MMDEP solution in acetone and applied over a plate with KBr (layer thickness was 0.03 mm). Spectra were recorded in the absorption range of  $4000\text{--}400\text{ cm}^{-1}$  with integration time of 1 s.

Thermographic investigations of MMAER were carried out using "Paulic-Paulic-Erdei" derivatograph Q-1500D in a dynamic mode in the air with the heating rate of 2.5 K/min. The samples weight was 300 mg. The device sensitivity was  $100\text{ }\mu\text{V}$  according to the scale of differential-thermal analysis (DTA),  $100\text{ mg}$  – to the thermogravimetric scale (TG) and  $500\text{ }\mu\text{V}$  – to the differential thermogravimetric scale (DTG). The samples were heated to 750 K. Alumina was used as a standard.

Bitumen and bitumen compositions softening temperatures were determined using the "ring and ball" method according to the procedure described in [6]; ductility and penetration – using the method described in [6]; "adherence with glass" – using the method described in [7]. The content of asphaltenes, neutral resins and oils was determined in accordance with the procedure described in [8, 9].

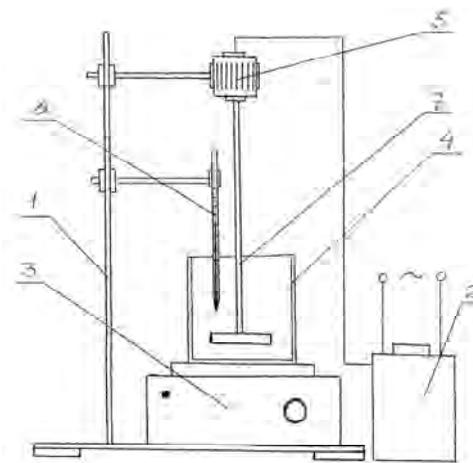
### 2.3. Investigation Procedure for Epoxy-Oligoesteric Mixtures

The compositions were prepared by components mixing with PEPA hardener 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 403 K for 75 min. The cross-linking was controlled by the change of gel-fraction content and hardness of obtained films.

### 2.4. Preparation of Bitumen-Polymeric Mixtures

Bitumen-polymeric mixtures were prepared at the laboratory plant, the scheme of which is represented in Fig. 1.

100 g of bitumen were loaded into a metal vessel (4) and heated to 383 K under stirring. MMAER (in the amount of 1–7 mass parts relative to 100 g of bitumen) was added, heated to 423–483 K and sustained for 1–3 h. Then softening temperature, ductility, penetration and adherence with glass of bitumen-polymeric mixtures were determined.



**Fig. 1.** Laboratory plant for bitumen-polymeric mixtures preparation: stand (1); power unit (2); electric heater (3); metal vessel (4); electric motor (5); thermometer (6) and stirrer (7)

## 2.5. MMAER Synthesis

MMAER was synthesized in a three-necked reactor equipped by a mechanical stirrer in the medium of inert gas. 100 g of ED-24 epoxy resin and 24.96 g of MAA dissolved in 250 ml of toluene were loaded into the reactor. Tetrabutylammonium iodide in the amount of 5.36 g was used as a catalyst. The mixture was sustained at 373 K for 1.5 h. Then it was cooled, carried into a separating funnel and the catalyst was washed out. The upper organic layer was vacuumed until  $\frac{3}{4}$  of the solvent was distilled off. The sediment was precipitated by the light petroleum and dried at 313 K and residual pressure of 133–266 Pa till the mass became constant. The MMAER yield was 87.3 %,  $M_n$  380 g/mol, *e.n.* 10.8 %. It was dissolved in toluene, 2-propanol, acetone, dioxane and other organic solvents.

## 3. Results and Discussion

### 3.1. Structure and Thermal Stability of MMAER

In order to confirm the structure of synthesized MMAER IR-investigations were carried out. The results are represented in Fig. 2.

The presence of methacrylate fragment in the molecule is confirmed by the absorption band at  $1636\text{ cm}^{-1}$  corresponded to the double bond and at  $1728\text{ cm}^{-1}$  typical of stretching vibrations C=O group in esters. The presence of hydroxy group formed as a result of joining between ED-24 and methacrylic acid molecule is confirmed by the absorption band at  $3456\text{ cm}^{-1}$ . The presence of free epoxy group in MMAER molecule is confirmed by the absorption band at  $912\text{ cm}^{-1}$  and  $\text{C}(\text{CH}_3)_2$  group – by the

doublet of stretching vibrations at 1360 and 1384  $\text{cm}^{-1}$ . The stretching vibrations at 1456, 1504, 1580 and 1608  $\text{cm}^{-1}$  are typical of benzene rings in MMAER molecule.

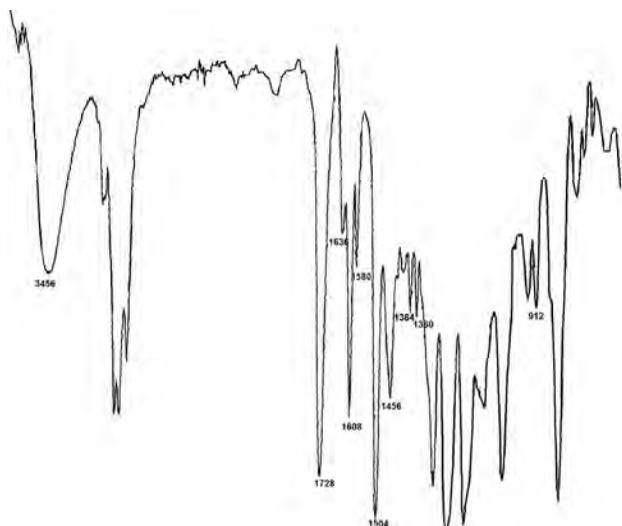


Fig. 2. IR-spectrum of MMAER

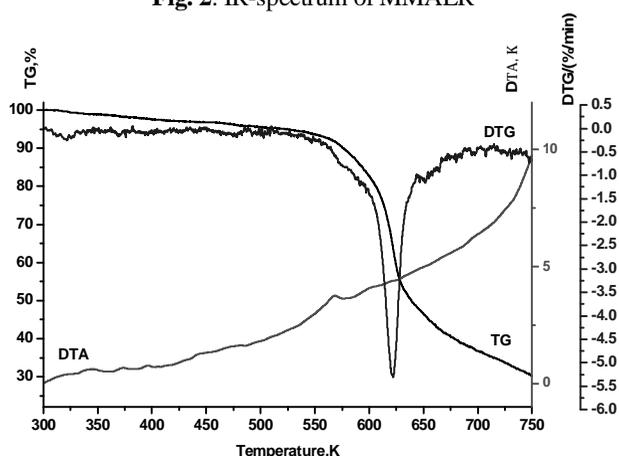


Fig. 3. TG, DTA and DTG curves for MMAER

Thus, the results presented in Fig. 2 confirm the presence of methacrylic acid unsaturated fragment and free epoxy group in the synthesized MMAER. The obtained compound is multifunctional and may be used as an active component of epoxy-oligoesteric mixtures.

To establish the thermal stability of the synthesized MMAER we carried out derivatographic investigations in accordance with the procedure described in Subsection 2.2.

The slight exothermal effect with the maximum at 568 K appears on DTA curve (Fig. 3). It is connected with the mass loss starting at 550 K and ending at 593 K. The reason is destructive processes proceeded during polymerization relative to methacrylate groups in MMAER. The obtained results show that MMAER may be used as a component of epoxy-oligoesteric mixtures without molecule decomposition at 550 K.

### 3.2. Epoxy-Oligoesteric Mixtures

The synthesized MMAER was studied as a component of epoxy-oligoesteric mixtures based on ED-20 epoxy resin and TGM-3 oligoesteracrylate. The composition of epoxy-oligoesteric mixtures is given in Table 1.

Table 1

Composition of epoxy-oligoesteric mixtures

Component	Component content, mass parts	
	I	II
ED-20 resin	80	80
TGM-3	–	10
MMAER	20	20
PEPA	14	14

The mixtures cross-linking was studied in accordance with the procedure described in Subsection 2.3. The obtained results are given in Table 2.

Table 2

Dependence of gel-fraction content ( $G$ ) and films hardness ( $H$ ) on cross-linking time and mixtures composition at 403 K

Mixture number	Index	Index value for cross-linking time, min.					
		24 h, normal conditions	15	30	45	60	75
I	$G$	84.7	94.5	95.7	95.9	95.9	95.8
	$H$	0.61	0.69	0.73	0.73	0.74	0.74
II	$G$	87.9	92.0	92.3	92.5	92.4	93.3
	$H$	0.55	0.72	0.74	0.74	0.74	0.74

The results show that cross-linking may take place at both room temperature and heating to 403 K. The mixture without oligoesteracrylate (Mixture I) at room temperature has lower values of gel-fraction content but higher hardness compared with Mixture II. The heating of Mixture I to 403 K for even 15 min sharply increases gel-fraction content and gradually increases film hardness. In the case of Mixture II the sharp increase of film hardness is observed without essential changes. The gel-fraction content increases as well which is slightly changed at heating for 75 min. The reasons are as follows. At room temperature the three-dimensional structure is formed due to the interaction between epoxy groups of ED-20 resin and MMAER with PEPA molecules. Such interaction leads to the heating of epoxy-oligoesteric mixture followed by partial cooligomerization relative to double bonds of MMAER cross-linked molecule with TGM-3 molecules (Mixture II). Such partial cooligomerization increases gel-fraction content in Mixture II compared with Mixture I without TGM-3 molecules. Mixture II cross-linked at room temperature contains non-cross-linked

molecules of TGM-3, therefore films hardness is lower compared with that of Mixture I. At 403 K TGM-3 cooligomerization with partially cross-linked molecules of MMAER takes place already at the initial stage. The increase of heating time does not increase the content of three-dimensional structures, because polymerization of TGM-3 molecules between each other may occur instead of their cross-linking with matrix molecules (the case of Mixture I).

Polymeric films obtained on the basis of epoxy-oligoesteric mixtures with MMAER in their structure are characterized by satisfactory adhesive properties, bending strength of 3 mm and impact strength of 490.5 N/mm.

### 3.3. Bitumen-Polymeric Mixtures

We have shown earlier that functional derivatives of epoxy resins may be used for the preparation of bitumen-polymeric mixtures [10]. Bitumen-polymeric mixtures using synthesized MMAER were studied in accordance with the procedure described in Subsection 2.4. It was necessary to determine the influence of MMAER amount, temperature and process time on softening temperature, ductility, penetration and adhesion to glass of the mixtures. Bitumen-polymeric mixture with ED-24 non-modified epoxy resin instead of MMAER was studied for the comparison under optimum conditions. The obtained results are represented in Table 3.

The introduction of MMAER into the bitumen structure increases the softening temperature and bitumen

adhesion and decreases ductility and penetration. Taking into account the operating characteristics of modified bitumen the optimum amount of MMAER was found to be 3 mass parts per 100 g of the initial bitumen. Under these conditions the bitumen-polymeric mixtures are characterized by higher adhesion (47 %) and ductility of 48.0 cm compared with the initial non-modified bitumen.

The decrease of bitumen-polymeric mixture preparation temperature to 423 K decreases the ductility and adhesion. At the same time the increase of preparation temperature increases the above-mentioned values. Thus the optimum temperature was found to be 463 K. The increase of process time for the mixtures with MMAER slightly increases the softening temperature and adhesion but considerably decreases ductility.

So, the following conditions were suggested for the preparation of mixtures with synthesized MMAER: process temperature of 463 K, process time of 1 h, MMAER amount of 3 mass parts per 100 g of initial bitumen. Under mentioned conditions the bitumen-polymeric mixture is characterized by: softening temperature of 322.8 K, ductility of 51.2 cm, penetration of 54x0.1 mm and adhesion of 50.7 %. The obtained characteristics are better than those for non-modified bitumen, especially adhesion, which essentially affects the possibility of bitumen application. The introduction of ED-24 to the bitumen-polymeric mixtures instead of MMAER practically does not improve the operational properties of modified bitumen (Table 3).

Table 3

Preparation conditions and characteristics of bitumen-polymeric mixtures

Temperature, K	Process time, h	MMAER amount, g per 100 g of bitumen	Characteristics of bitumen-polymeric mixtures			
			Softening temperature, K	Ductility at 298 K, cm	Penetration at 298 K, 0.1 mm	Adhesion, %
443	1	0	319.0	75.0	62	40.5
443	1	1	321.9	54.6	59	42.9
443	1	3	322.0	48.0	57	47.0
443	1	5	322.9	38.5	56	49.8
443	1	7	323.0	36.9	54	51.0
423	1	3	321.9	27.4	59	42.7
463	1	3	322.8	51.2	54	50.7
493	1	3	322.4	53.8	56	51.0
463	2	3	324.9	29.0	51	52.1
463	3	3	325.6	24.6	43	54.9
463	1	3*	320.0*	37.8*	60*	41.3*

\* Results obtained for bitumen-polymeric mixture with ED-24 initial resin in its structure

Table 4

Group analysis of bitumen-polymeric mixtures

Polymeric component and its amount per 100 g of bitumen	Content, mas %			
	Carbenes + carboides	Asphaltenes	Oils	Resins
absent	0.057	25.3	50.0	24.2
MMAER, 3	absent	30.6	46.6	22.8
ED-24, 3	absent	25.9	50.8	23.2

Note: Bitumen-polymeric mixtures were prepared at 463 K and time of 1 h

The above-mentioned characteristics of bitumen-polymeric mixtures depend on group composition of the modified bitumen. The group composition was studied using standard methods [8]. The obtained results are represented in Table 4.

One can see from Table 4 that the improvement of the mixtures operational properties with MMAER is achieved due to the conversion of oils and resins into asphaltenes. In the mixture with ED-24 the mentioned processes do not take place and this fact affects the obtained bitumen properties (*vide* Table 3).

#### 4. Conclusions

The production of oligomer with the free epoxy group and reactive methacrylate fragment obtained on the basis of ED-24 dianic epoxy resin and methacrylic acid has been suggested. The presence of methacrylate fragments in the molecule of the synthesized derivative was confirmed by IR-study, namely by the presence of absorption bands at  $1636\text{ cm}^{-1}$  corresponded to the double bond and at  $1728\text{ cm}^{-1}$  typical of stretching vibrations C=O group in esters. By means of derivatographic investigations the stability of the synthesized product till 550 K has been determined. The presence of unsaturated double bond and epoxy group allows to use the synthesized product as a component of epoxy-oligomeric mixtures, the cross-linking of which is carried out stepwise: first at room temperature for 24 h and then at heating to 403 K for 75 min. The obtained films are characterized by satisfactory operating properties. The application of the synthesized resin as a component of bitumen-polymeric mixture in the amount of 3 mas % per 100 g of bitumen allows to increase the film hardness, as well as its adhesion to the glass surface.

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#### МОНОМЕТАКРИЛАТНА ПОХІДНА ЕПОКСИДНОЇ СМОЛИ ЕД-24 ТА ЇЇ ЗАСТОСУВАННЯ

*Анотація.* Хімічною модифікацією епоксидної діанової смоли ЕД-24 метакриловою кислотою синтезована похідна смоли, що містить одночасно метакриловий фрагмент та вільну епоксидну групу. Структура синтезованого продукту підтверджена ІЧ-спектроскопічними дослідженнями. Дериватографічними дослідженнями встановлена термічна стабільність синтезованої сполуки. Запропоновано використовувати метакрилатну похідну епоксидної смоли ЕД-24 як компонент епокси-олігоестерних та бітум-полімерних сумішей.

*Ключові слова:* епоксидна смола, метакрилова кислота, хімічна модифікація, ІЧ-спектроскопія, дериватографічні дослідження, епокси-олігомерні та бітум-полімерні суміші, структурно-груповий аналіз бітумів.