

CARBOXY DERIVATIVE OF DIOXYDIPHENYLPROPANE DIGLYCIDYL ETHER MONOMETHACRYLATE AS AN ADDITIVE FOR COMPOSITES

Michael Bratychak^{1,}, Oksana Iatsyshyn¹, Olena Shyshchak¹,
Olena Atsakhova¹, Helena Janik²*

DOI: dx.doi.org/10.23939/chcht11.01.049

Abstract. Carboxy derivative of dioxydiphenylpropane diglycidyl ether monomethacrylate (CDE) containing the fragment of dianic epoxy resin, as well as free carboxy and methacrylic groups has been studied as a component of epoxy-oligoesteric and bitumen-polymeric mixtures. The epoxy-oligoesteric mixtures were investigated using ED-20 dianic epoxy resin, the crosslinking of which was carried out in the presence of polyethylene polyamine. Physico-mechanical properties and chemical stability of the coatings based on epoxy-oligoesteric mixtures with CDE were determined. Bitumen-polymeric mixtures with CDE were studied taking bitumen produced at JSC “Ukratnafta” (Ukraine) as an example.

Keywords: epoxy resin, carboxy and methacrylic groups, epoxy-oligoesteric and bitumen-polymeric mixtures, crosslinking, protective coatings.

1. Introduction

Modern composites are multicomponent systems containing, apart from the main component, different additives providing the improvement of operational properties. The additives used for the composites may be of organic and inorganic nature. While using inorganic additives the physical modification of the formed structure mainly takes place. If organic additives are used, the

chemical modification is possible between them and main component of the composite. The chemical modification takes place if polymer (oligomer) with different functional groups is used as an additive.

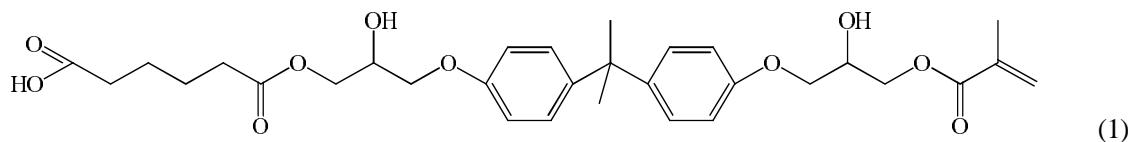
Recently a number of works has appeared concerning the creation of functional oligomers as active additives for different polymeric materials and composites [1, 2]. The main demand for such products is the presence of reactive groups capable to react with functional groups of the composite at room temperature and at heating [3, 4]. Epoxy compounds are widely used as the initial materials [5]. The reason is the presence of reactive epoxy groups in their structures, which can be converted into other reactive groups [6-10].

In this work we propose to use carboxy derivative of dioxydiphenylpropane diglycidyl ether monomethacrylate (CDE) as an additive for the composites.

2. Experimental

2.1. Materials

CDE of the formula (1) was synthesized using dioxydiphenylpropane diglycidyl ether (DDE) according to the procedure described in [11] *via* two stages.



¹ Lviv Polytechnic National University, 12, S. Bandera St., 79013 Lviv, Ukraine

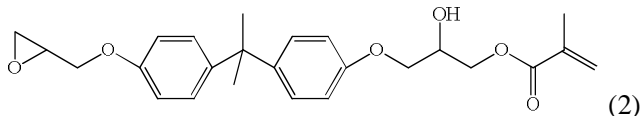
² Gdansk University of Technology, 11/12 G. Narutowicza St., 80233 Gdansk, Poland

* mbratychak@gmail.com

© Bratychak M., Iatsyshyn O., Shyshchak O., Astakhova O., Janik H., 2017

At the first stage DDE (Bisphenol A diglycidyl ether, Sigma-Aldrich, USA) reacts with methacrylic acid (Merck, Germany) in the presence of tetrabutylammonium iodide as a catalyst. Tetrabutylammonium iodide was used as received, without additional purification (Sigma-Aldrich, Germany).

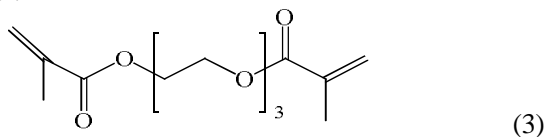
Dioxydiphenylpropane diglycidyl ether mono-methacrylate (DDEMA) was obtained [12], its formula is below. Its molecular mass (M_n) was 430 g/mol, epoxy groups content 11.2 % and bromine number 35.9 gBr₂/100g product.



At the second stage DDEMA was treated by adipic acid (DuPont, USA) in the presence of benzyltriethylammonium chloride, which was used as received, without additional purification (Sigma-Aldrich, Germany). For CDE: M_n 580 g/mol, carboxy groups content 7.2 %, bromine number 25.2 gBr₂/100g product and epoxy groups were absent.

ED-20 epoxy dianic resin (Ukraine) was used as an initial component to obtain epoxy-oligoesteric mixtures. Its M_n was 390 g/mol and epoxy groups content 20.0 %.

Oligoesteracrylate (TGM-3, Ukraine) was used as a plasticizer of epoxy-oligoesteric mixtures. Its M_n was 286 g/mol.



Polyethylene polyamine (PEPA, Ukraine) as a hardener was used as received, without additional purification.

Bitumen was supplied by JSC "Ukratnafta" (Ukraine) with the following characteristics: penetration 57×0.1 mm, ductility 79.1 cm, softening temperature according to "ball & ring" method 318.1 K and adhesion to glass 45.9 %.

2.2. Methods of Testing

Molecular masses of DDEMA and CDE were determined by cryoscopy in dioxane. Bromine number was determined according to [13]; epoxy and carboxy groups content – [14]. Film hardness (H , rel.units) was measured by M-3 pendulum device at room temperature according to the standard [15]. Gel-fraction content (G , %) was determined *via* extraction of grinded samples by acetone in a Soxhlet apparatus during 12 h [15].

Impact strength of the synthesized films was determined using U-1A device [15] and bending strength – ShG-1 device [15]. Cross-cut method [16] was used to determine the film adhesion. Chemical stability was determined by films immersion into 3 % solution of CH₃COOH, 3 % solution of H₂SO₄, 5 % solution of NaOH, 5 % solution of NaCl and distilled water.

The softening temperature of bitumen and bitumen-polymeric mixtures was determined using "ball & ring" method, ductility and penetration – according to

the methods described in [17], adhesion to glass – according to [18], content of asphaltenes, neutral resins and oils according to [19, 20].

2.3. Crosslinking of Epoxy-Oligoesteric Mixtures

The mixtures were prepared by mixing composites till homogeneous state and then PEPA was added. After applying mixtures over standard glass plates the crosslinking was conducted at room temperature and at heating. The crosslinking at heating was studied stepwise. At first the films were kept at room temperature for 24 h and then they were heated at different temperatures for 15, 30, 45, 60 and 75 min. The process of film formation was controlled by changing gel-fraction (G) and hardness (H) of resulting films.

2.4. Bitumen-Polymeric Mixtures Obtaining

Bitumen-polymeric mixtures were prepared at the laboratory plant described in [21]. The sample of bitumen (100 g) was loaded into a metal vessel and heated to 383 K under constant stirring. Then CED was added, the mixture was heated to the definite temperature and kept for a definite time. After the end of the experiment the mixture was transferred into a metal vessel and cooled to room temperature. Then the softening temperature, ductility, penetration and adhesion to glass were determined.

3. Results and Discussion

3.1. Epoxy-Oligoesteric Mixture

ED-20 based lacquered films are obtained *via* crosslinking of ED-20 resin in the presence of PEPA. TGM-3 oligoesteracrylate is added in order to decrease the strains occurred in the crosslinked structure, *i.e.* TGM-3 is like a plasticizer and is not chemically bounded with ED-20 molecules. During exploitation of the polymeric film TGM-3 is "sweated" over its surface and thus worsens film properties. So it was important to find the compound which would be the plasticizer of epoxy resin and chemically bounded with it.

We can see from formula (1) that CDE molecule contains the fragment of dianic epoxy resin, free carboxy and methacrylic groups. We assume that such a compound may be used for the creation of lacquered film instead of TGM-3. To study ED-20 crosslinking we prepared epoxy-oligoesteric mixtures, the compositions of which are represented in Table 1. The epoxy-oligoesteric mixture with TGM-3 is represented for the comparison.

Table 1

Compositions of epoxy-oligoesteric mixtures

| Component | Component content, wt % | | | | |
|-------------------|-------------------------|----|-----|----|----|
| | I | II | III | IV | V |
| ED-20 epoxy resin | 90 | 90 | 95 | 80 | 70 |
| CDE | – | 10 | 5 | 20 | 30 |
| TGM-3 | 10 | – | – | – | – |
| PEPA | 14 | 14 | 14 | 14 | 14 |

Table 2

Dependence of film gel-fraction content and hardness on the mixture composition and crosslinking time at room temperature

| Number of mixture accord. Table 1 | Index | Index values for crosslinking time, days | | | | | |
|-----------------------------------|----------|--|------|------|------|------|------|
| | | 1 | 2 | 3 | 4 | 7 | 10 |
| I | <i>H</i> | 0.29 | 0.31 | 0.35 | 0.38 | 0.41 | 0.43 |
| | <i>G</i> | 71.7 | 72.8 | 73.2 | 74.8 | 77.5 | 79.9 |
| II | <i>H</i> | 0.64 | 0.65 | 0.66 | 0.67 | 0.70 | 0.73 |
| | <i>G</i> | 81.5 | 82.6 | 83.2 | 84.9 | 86.5 | 88.3 |

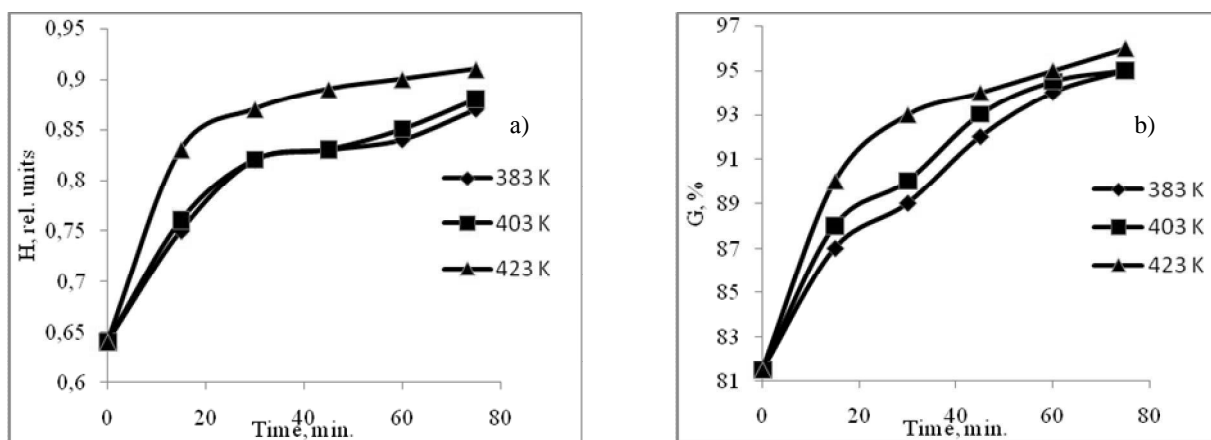


Fig. 1. Dependence of film hardness (a) and gel-fraction content (b) on crosslinking time and temperature for mixture II

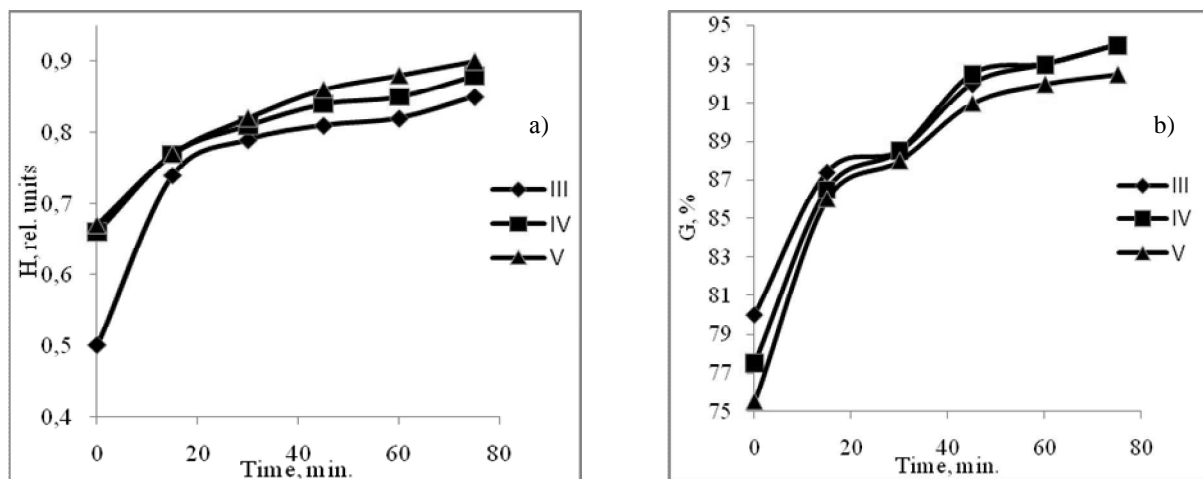


Fig. 2. Dependence of film hardness (a) and gel-fraction content (b) on crosslinking time at 403 K for mixtures III, IV and V

Films were formed according to the procedure described in Subsection 2.3 at room temperature and at heating. Crosslinking at room temperature was studied for the mixtures I and II for 1, 2, 3, 4, 7 and 10 days. Mixture I is a commercial one, consisting of 90 wt % of ED-20 dianic epoxy resin and 10 wt % of TGM-3. Mixture II consists of ED-20 and CDE. The investigation results are represented in Table 2.

After 10 days of using mixture I the protective coating is characterized by hardness of 0.43 rel.units. The standard value is 0.6 rel.units. Gel-fraction content is 79.9 %. The substitution of TGM-3 for CDE increases both values (G and H), possibly caused by the reaction between ED-20 and CDE molecules with the hardener. Further increase of crosslinking time only slightly increases the mentioned values.

The effect of temperature and time on crosslinking process for mixture II is presented in Fig. 1.

We can see from Fig. 1 that hardness and gel-fraction content of the films at 383 and 403 K depend mainly on crosslinking time. For the first 30 min the hardness achieves 0.82 rel.units and then increases very slightly. With the increase of temperature to 423 K the hardness, as well as gel-fraction content are higher (0.87 rel. units and 93.1 %, respectively) compared to those at 383 and 403 K. It means that at heating the CDE plasticizer reacts with epoxy groups of the initial resin due to the presence of free carboxy group in its structure, *i.e.* it is chemically bounded with a crosslinking matrix based on ED-20 resin. The same reaction is possible when mixture II is crosslinked at room temperature (Table 2). The reason is that ED-20 based mixture is heated at room temperature in the presence of PEPA and thus provides the interaction between the carboxy group of CDE and epoxy groups of ED-20, as well as three-dimensional polymerization of methacrylic groups of CDE.

The effect of CDE amount on gel-fraction content and film hardness is shown in Fig. 2.

The decrease in CDE amount to 5 wt % (mixture III) decreases the hardness of the films crosslinked at

room temperature (Fig. 2a) compared with mixture II containing 10 wt % of CDE (Fig. 1a). At the same time while heating at 403 K the hardness values of both films are the same (Figs. 1a and 2a). The increase in CDE amount to 20 and 30 wt % and simultaneous decrease in amount of ED-20 provide the increase in film hardness at the initial stages of crosslinking (Fig. 2a), but decrease gel-fraction content of the films crosslinked at room temperature (Figs. 2b and 1b). At heating if CDE amount in the mixtures is 5 wt % (mixture III) or 20 wt % (mixture IV), the values are almost the same achieved for mixture II. The increase in CDE amount to 30 wt % (mixture V) decreases gel-fraction content at room temperature and at heating, as well.

So, we may conclude that CDE may be used instead of TGM-3 as a plasticizer for the mixtures containing 10 wt % of CDE and 90 wt % of ED-20 (mixture II, Table 1).

3.3. Physico-Mechanical and Chemical Properties of the Films

As it was mentioned above, the films obtained in the presence of CDE are characterized by a high content of insoluble products and high hardness, making possible their usage as lacquer coatings. For this purpose we determined some of their physico-mechanical and chemical properties. Films obtained in the presence of TGM-3 (mixture I, Table 1) were used for the comparison.

The investigations were carried out according to the methods described in Subsection 2.2 and the results are given in Table 3.

If we compare mixtures II and I (Table 3) it is obvious that mixture with CDE has better physico-mechanical properties and it is more chemically stable. These results confirm once more the participation of CDE molecules in the formation of polymeric coatings based on ED-20.

Table 3

Physico-mechanical and chemical properties of films based on epoxy-oligoesteric mixtures

| Number of mixture accord. Table 1 | G , % | H , rel.units | Impact strength, cm | Bending strength, mm | Adhesion, mm | Chemical stability, days | | | | |
|-----------------------------------|---------|-----------------|---------------------|----------------------|--------------|--------------------------|------------|------------|--------------------------------------|----------------------------|
| | | | | | | H ₂ O (dist.) | NaOH (5 %) | NaCl (5 %) | H ₂ SO ₄ (3 %) | CH ₃ COOH (3 %) |
| I* | 79.9 | 0.43 | 50 | 3 | 1 | 22 | 5 | 23 | 24 | 5 |
| I** | 89.4 | 0.80 | 40 | 5 | 2 | >45 | 34 | >45 | 38 | >45 |
| II* | 88.3 | 0.73 | 50 | 2 | 1 | 28 | 7 | 25 | 26 | 7 |
| II** | 95.3 | 0.88 | 50 | 2 | 1 | >45 | 42 | >45 | >45 | >45 |

Notes: * – crosslinking at room temperature for 10 days; ** – crosslinking at 403 K for 75 min.

Table 4

Preparation conditions and characteristics of BPM

| Temperature, K | Time, h | CDE amount per 100g of bitumen | BMP characteristics | | | |
|----------------|---------|--------------------------------|--------------------------|------------------------|------------------------------|----------------------|
| | | | Softening temperature, K | Ductility at 298 K, cm | Penetration at 298 K, 0.1 mm | Adhesion to glass, % |
| 463 | 1 | 0 | 318.1 | 79.1 | 57 | 45.9 |
| 463 | 1 | 1 | 318.9 | 64.3 | 51 | 52.4 |
| 463 | 1 | 3 | 319.7 | 54.6 | 50 | 69.1 |
| 463 | 1 | 5 | 320.4 | 38.5 | 49 | 75.7 |
| 463 | 1 | 7 | 321.2 | 33.7 | 44 | 80.9 |
| 443 | 1 | 3 | 319.0 | 52.5 | 52 | 63.6 |
| 463 | 1 | 3 | 319.7 | 54.6 | 50 | 69.1 |
| 483 | 1 | 3 | 320.1 | 63.1 | 46 | 79.0 |
| 483 | 0.5 | 3 | 319.7 | 64.6 | 48 | 67.0 |
| 483 | 1 | 3 | 320.1 | 63.1 | 46 | 79.0 |
| 483 | 2 | 3 | 321.0 | 60.3 | 42 | 83.3 |
| 373 | 1 | 7 | 320.3 | 48.5 | 45 | 63.7 |

3.4. Bitumen-Polymeric Mixtures

The analysis of the literature shows [22] that functional derivatives of epoxy resins may be used for the preparation of the so called bitumen-polymeric mixtures (BPM). Therefore, we studied the possible CDE using for this purpose. Bitumen-polymeric mixtures with CDE were obtained according to the procedure described in Subsection 2.4. It was necessary to establish the effect of CDE amount, process temperature and time on the softening temperature, ductility, penetration and adhesion to glass of obtained BPM. Some results are presented in Table 4.

The introduction of CDE into bitumen increases the softening temperature and adhesion but decreases penetration and ductility. Taking into account the operational characteristics of the modified bitumen the optimum amount of CDE was found to be 3 wt % per 100 g bitumen. In comparison with non-modified bitumen BPM is characterized by higher adhesion (69.1 %) and ductility of 54.6 cm.

The decrease in preparation temperature to 443 K considerably decreases ductility and adhesion to glass. The higher the temperature, the higher the values of ductility and adhesion. The increase in preparation time insignificantly increases the softening temperature and adhesion but decreases ductility. So, the following conditions were chosen as optimal ones: temperature – 483 K, time – 1 h and CDE amount – 3 wt %. Under such conditions BPM is characterized by the softening temperature 320 K, ductility 63.1 cm, penetration 46x0.1 mm and adhesion to glass 79.0 %. The obtained values are higher compared to non-modified bitumen, especially adhesion, that influences bitumen application.

To establish the CDE role in BPM and structural changes in it we studied a structural-group composition of

obtained BPM (Table 5) according to standard methods [19, 20].

Table 5

Structural-group analysis of BPM with 3 wt % of CDE

| Amount, wt % | | | |
|---------------------|-------------|-------|--------|
| Carbenes + carboids | Asphaltenes | Oils | Resins |
| 0.04 | 23.62 | 51.37 | 24.97 |
| 0.08 | 24.69 | 46.97 | 28.26 |

Note: mixtures were prepared at 483 K for 1 h

The improvement of BPM operational characteristics is achieved due to the conversion of oils into resins and asphaltenes. This is due to the chemical interaction of carboxy groups in CDE with functional groups presented in the initial bitumen.

4. Conclusions

Carboxy derivative of dioxydiphenylpropane diglycidyl ether monomethacrylate (CDE) containing the free carboxy and methacrylic groups has been studied as an active additive for epoxy-oligoesteric mixtures based on ED-20 industrial dianic epoxy resin and bitumen-polymeric mixtures. The amount of CDE was 5, 10, 20 and 30 wt % per 95, 90, 80 and 70 wt % of epoxy resin, respectively. The mixture consisting of 10 wt % of TGM-3 oligoesteracrylate and 90 wt % of ED-20 was studied for the comparison. The mixture crosslinking was studied at room temperature for 10 days and stepwise (first at room temperature for 24 h and then at heating for 15, 30, 45, 60 and 75 min) in the presence of polyethylene polyamine as a hardener. The epoxy-oligoesteric mixtures with CDE

which were crosslinked both at room temperature and heating are characterized by higher gel-fraction content and better physico-mechanical and chemical properties compared with those values for the mixture with TGM-3. The obtained results show the chemical interaction between ED-20 molecules and CDE. When using CDE as a component of bitumen-polymeric mixture in the amount of 1–7 wt % per 100g bitumen, the improvement of adhesive properties is observed. The reason is a conversion of bitumen oil fractions into resins and asphaltenes.

References

- [1] Ohar H., Dolynska L. and Tokarev V.: Chem. Chem. Technol., 2013, **7**, 125.
- [2] Voronov S. and Samaryk V.: Chem. Chem. Technol., 2007, **1**, 1.
- [3] Ellis B.: Chemistry and Technology of Epoxy Resins. Blackie Academic and Professional, London 1993.
- [4] Bratychak M., Bashta B., Astakhova O. et al.: Dopov. Nats. Acad. Nauk Ukrainy, 2012, **11**, 139.
- [5] Bratychak M., Chervinsky T. and Iatsyshyn O.: Dopov. Nats. Acad. Nauk Ukrainy, 2010, **8**, 137.
- [6] Bashta B., Astakhova O., Shyshchak O. et al.: Chem. Chem. Technol., 2014, **8**, 309.
- [7] Bratychak M., Ivashkiv O. and Astakhova O.: Dopov. Nats. Acad. Nauk Ukrainy, 2014, **8**, 97.
- [8] Ivashkiv O., Namiesnik J., Shyshchak O. et al.: Chem. Chem. Technol., 2016, **10**, 587.
- [9] Bratychak M., Ivashkiv O., Astakhova O. et al.: Ukr. Khim. Zh., 2015, **81**, 59.
- [10] Bratychak M., Ivashkiv O., Bruzdziak P. et al.: Polimery, 2016, **61**, 316.
[http:// dx.doi.org/10.14314/polimery.2016.316](http://dx.doi.org/10.14314/polimery.2016.316).
- [11] Bratychak M., Iatsyshyn O., Bruzdziak P. et al.: Polimery, 2016, **61**, 766.
[http:// dx.doi.org/10.14314/polimery.2016.766](http://dx.doi.org/10.14314/polimery.2016.766).
- [12] Iatsyshyn O., Astakhova O., Shyshchak O. et al.: Chem. Chem. Technol., 2013, **7**, 73.
- [13] Siggia C. and Khana J.: Kolichestvennyi Organicheskii Analiz po Funktsionalnym Gruppam. Khimiya, Moskva 1983.
- [14] Toroptseva A., Belgorodskaya K. and Bondarenko V.: Laboratornyi Praktikum po Khimii Vysokomolekulyarnykh Soedineniy. Khimia, Leningrad 1972.
- [15] Ivanov V.: Rukovodstvo k Prakticheskim Rabotam po Khimii Polimerov. Izd-vo Leningr.Univ., Leningrad 1982.
- [16] Kinlok E.: Adgeziya i Adgezivny. Mir, Moskva 1991.
- [17] Gosudarstvennye Standarty. Nefteprodukty. Masla. Smazki. Prysadki. Izd-vo Standartov, Moskva 1987.
- [18] Hoon R.: Neftyanye Bitумы. Khimiya, Moskva 1973.
- [19] Diyarov I.: Khimiya Nefi. Khimiya, Leningrad 1990.
- [20] Isagulyanc V.: Khimiya Nefi. Khimiya, Moskva 1965.
- [21] Strap G., Astakhova O., Shyshchak O. et al.: Chem. Chem. Technol., 2013, **7**, 279.
- [22] Ivashkiv O., Astakhova O., Shyshchak O. et al.: Chem. Chem. Technol., 2015, **9**, 69.

Received: November 28, 2016 / Revised: December 18, 2016 /
Accepted: January 30, 2017

КАРБОКСИЛЬНА ПОХІДНА МОНОМЕТАКРИЛАТУ ДИГЛІЦИДІЛОВОГО ЕТЕРУ ДІОКСИДИФЕНІЛПРОПАНОУ – ДОДАТОК ДО КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ

Анотація. Карбоксильна похідна монометакрилату дигліциділового етеру діоксидифенілпропану (КПЕ), яка містить в своїй структурі фрагмент діанової епоксидної смоли та вільну карбоксильну й метакрилатну групи, вивчена як компонент епокси-олігоестерних та бітум-полімерних сумішей. Епокси-олігоестерні суміші вивчені з використанням діанової епоксидної смоли ЕД-20, структурування якої проводили в присутності поліетиленполіаміну. Визначені фізико-механічні властивості та хімічна стійкість до агресивних середовищ покриття на основі епокси-олігоестерних сумішей, що містять КПЕ. Бітум-полімерні суміші за участю КПЕ досліджено на прикладі бітумі, виробленого на ПАТ «Укртатнафта» (Україна).

Ключові слова: епоксидна смола, карбоксильні та метакрилатні групи, епокси-олігоестерні та бітум-полімерні суміші, структурування, захисні покриття.

