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DETERMINATION OF HYDROXY GROUPS IN THE MODIFIED EPOXY OLIGOMERS USING IR-SPECTROSCOPY

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Abstract. The use of IR-spectroscopy has been proposed to determine the content of hydroxy groups in the modified functional oligomers based on bisphenol A diglycidyl ether. Apart from hydroxy groups the investigated oligomers contain epoxy or peroxy, carboxy or acrylic groups.

Keywords: glycol, epoxide, functional oligomer, hydroxy number, IR-spectroscopy.

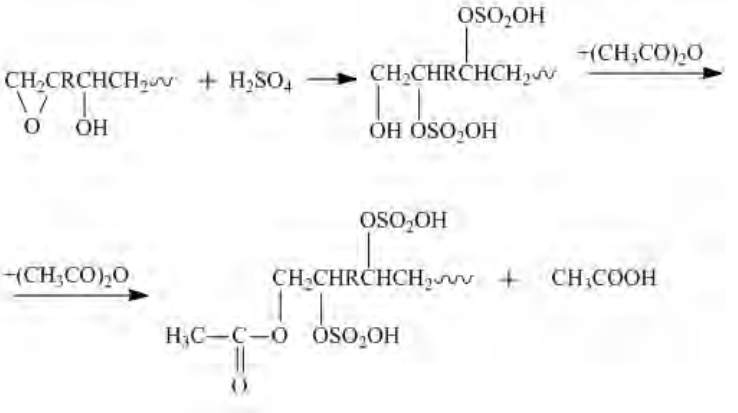
1. Introduction

Oligomers with hydroxy groups are widely used for the production of new urethane polymers [1, 2], composites with diisocyanates [3], epoxides [4], aminocompounds [5], *etc*. To date they are produced *via* polymerization of epoxides [6-8] and tetrahydrofuran [9, 10], oligomerization in the presence of functional initiators of peroxy or azodinitrile type [11, 12], thermal polymerization of monomers using hydrogen peroxide [13, 14] and polycondensation of dibasic acids with glycols [15, 16].

Recently the investigations of epoxy resins modification by hydroperoxides [17], fluorine-containing compounds [18], dibasic acids [19], methacrylic acid [20] and glycols [21] have been carried out at the Department of Petroleum Chemistry and Technology at Lviv Polytechnic National University.

In the process of chemical modifying of epoxy resins by compounds with a mobile hydrogen atom, the epoxy ring is opened and secondary hydroxy groups are formed [4]. At the same time for the majority of epoxy resins modification processes the reactions with epoxy groups preservation proceed [19, 21]. The presence of residual epoxy groups in the molecule of the synthesized oligomer complicates the determination of hydroxy groups content in it.

According to the chemical method the hydroxy groups determination in the compounds with epoxy and hydroxy groups may be expressed by Eq. (1):



(1)

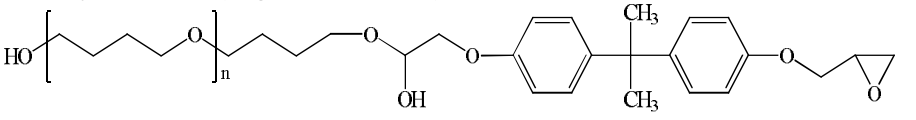
The method demands accurate determination of epoxy groups content, full opening of epoxy groups using sulfuric acid and long-run analysis. This work deals with the method based on IR-spectroscopy to determine the content of hydroxy groups in oligomers obtained *via* chemical modification of epoxy resins by various compounds with the mobile hydrogen atom.

2. Experimental

2.1. Materials

The content of hydroxy groups was determined for the following oligomers:

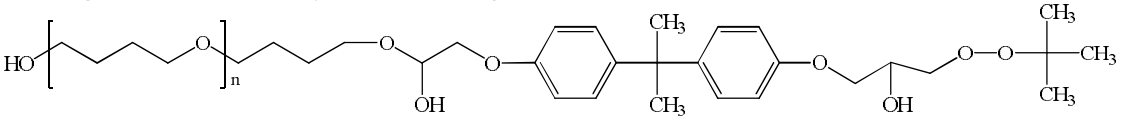
I. Oliogmers obtained *via* chemical modification of bisphenol A diglycidyl ether (DGEBA) by 1,4-butanediol (BD) (oligomer HDEO-I) or PolyTHF-2000 (oligomer HDEO-II) of the formula:



where n = 0 (HDEO-I) or n = 26–28 (HDEO-II)

HDEO-I and HDEO-II were synthesized according to the procedure described in [21]. It was found for HDEO-I: molecular weight (M_n) 420 g/mol; epoxy number (*e.n.*) 11.2 %. For HDEO-II: M_n 2280 g/mol; *e.n.* 3.3 %.

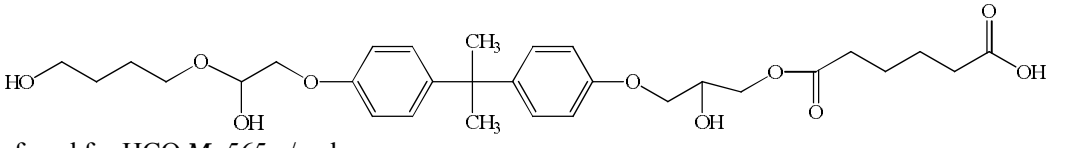
II. Oligomers synthesized *via* reaction between DGEBA peroxy derivative (PO) obtained by the method described in [23] and BD (oligomer HPO-I) or PolyTHF-2000 (oligomer HPO-II) of the formula:



where n = 0 (HPO-I) or n = 26–28 (HPO-II)

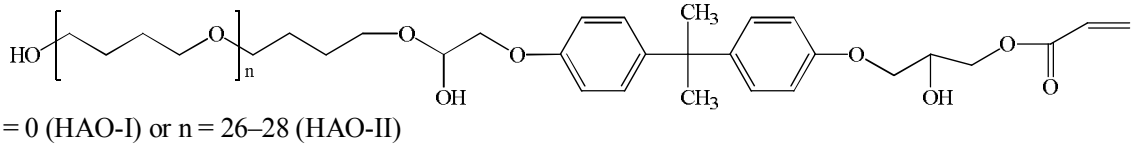
The synthesis procedure for HPO-I is described in [24], HPO-II – [25]. It was found for HPO-I: M_n 507 g/mol; active oxygen content ($[O]_{act}$) 1.91 %. For HPO-II: M_n 2370 g/mol; $[O]_{act}$ 1.03 %.

III. Oligomer HCO was obtained *via* chemical modification of HDEO-I by adipic acid according to the procedure developed by us:



It was found for HCO M_n 565 g/mol.

IV. Oligomers synthesized *via* the reaction between HDEO-I or HDEO-II and acrylic acid (oligomers HAO-I and HAO-II, respectively):

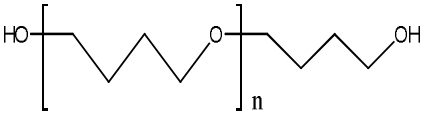


where n = 0 (HAO-I) or n = 26–28 (HAO-II)

It was found for HAO-I M_n 495 g/mol; for HAO-II – 2350 g/mol.

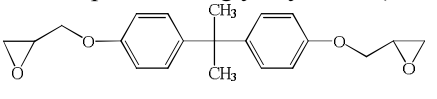
V. Butanediol (BD) produced by Merck KGaA, Germany:
It was found for BD M_n 90.12 g/mol; hydroxy number (*h.n.*) 1230 mg KOH/g.

VI. Oligoether PolyTHF-2000 (BASF Canada Inc., Canada) with M_n 1950 g/mol, *h.n.* 54.7 mg KOH/g and acid number (*a.n.*) ≤ 0.05 mg KOH/g



n = 26–28

VII. Bisphenol A diglycidyl ether (DGEBA) produced by Sigma-Aldrich Co had M_n 340 g/mol; *e.n.* 24 %, *h.n.* absent.

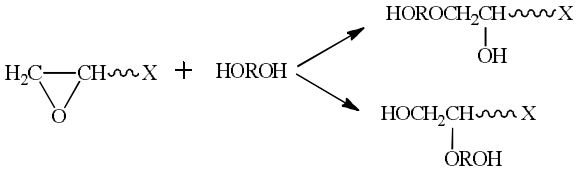


2.2. ATR-FTIR Spectra

ATR-FTIR spectra of all samples were recorded by means of Nicolet 8700 spectrometer (Thermo Electron Co.) equipped with a single-reflection diamond cell GoldenGate ATR accessory (Specac). For each spectrum 128 scans were collected with a resolution of 4 cm^{-1}. The spectrometer was purged with dry nitrogen to diminish water-vapor contamination. All spectra were additionally corrected using an advanced ATR correction algorithm (a part of OMNIC software), based on the sample and crystal material refractive indices and the angle of incident ray (45°).

3. Results and Discussion

The chemical modification of epoxy oligomers by diols may be represented by Eq. (2):



(2)

where x= -COOH, -OOC(CH$_3$)$_3$, -CH=CH$_2$, H$_2$C—CH— (O); R= -(CH$_2$)$_4$- or -(CH$_2$-CH$_2$-CH$_2$-CH$_2$-O)$_{28}$-

From the mentioned equations one can see that at modification the compounds with primary and secondary hydroxy groups (Eq. (2)) as well as the compounds with only primary hydroxy groups (Eq. (3)) are formed. On the other hand it is known [26] that according to Krasutskyi rule the chemical modification of epoxy oligomers by compounds with mobile hydrogen atom results in the reaction proceeding by both directions (Eqs. (2) and (3)). Eq. (2) predominates and leads to the formation of compounds with secondary hydroxy groups. Moreover, if we use oligoether PolyTHF-2000, the steric factor is present; hence only compounds with secondary hydroxy groups are formed. Taking all mentioned into account we may assume that used modified oligomers (see Subsection 2.1) should contain both primary (due to the introduction of glycol into the structure) and secondary hydroxy group (due to Eq. (2)).

To determine the content of hydroxy groups in the synthesized oligomers their IR-spectra were recorded. The spectra of the initial bisphenol A diglycidyl ether without hydroxy groups, 1,4-butanediol and PolyTHF-2000 were recorded for the comparison.

Some of the spectra are represented in Fig. 1.

As it is seen from Fig. 1, the hydroxy group in BD corresponds to the absorption band at 3330 cm^{-1} and in PolyTHF-2000 – at 3470 cm^{-1}. The absorption band in the area of 3400–3330 cm^{-1} typical of stretching vibrations of hydroxy groups is absent in the IR-spectrum of DGEBA. In the IR-spectrum of HDEO-I we observe the absorption band at 3380 cm^{-1} (Fig. 1), in the spectrum of HDEO-II – at 3375 cm^{-1} (Fig. 2). For HPO-I the hydroxy group corresponds to the band at 3390 cm^{-1}, for HPO-II – at 3420 cm^{-1}, for HCO – at 3375 cm^{-1}, for HAO-I and HAO-II – at 3400 and 3450 cm^{-1}, respectively (Figs. 1 and 2).

Thus, considering the obtained results and literature data [27] the hydroxy groups correspond to the absorption band in the area of 3700–3100 cm^{-1}, irrespective of group type – primary or secondary one. Thus, to calculate the area corresponded to the stretching vibrations of hydroxy group, we choose the absorption band within 3700–3100 cm^{-1}.

The BD spectrum was chosen as a standard. The value of its hydroxy number is determined *via* chemical method (Table 1). From the BD spectrum the calculated area of absorption band (S^1_{BD}) is 109.49 rel.units. This value is taken as 100 % (S^2_{BD}). It corresponds to the hydroxy number determined by a chemical method equal to 1230 mg KOH/g. Then the areas of absorption band for all samples and their hydroxy numbers were calculated. The peak area is calculated according to the formula:

$$S^2_{(i)} = \frac{S^1_{(i)}}{S^1_{BD}} \cdot 100 \qquad (3)$$

where $S^2_{(i)}$ – peak sguare of hydroxy group of the investigated oligomer, %; $S^1_{(i)}$ – peak area of hydroxy group of the investigated oligomer, rel. unit; S^1_{BD} – peak area of butanediol hydroxy group, rel. unit.

Hence, the hydroxy number of the investigated sample in mgKOH/g is calculated from the formula (4):

$$h.n._{(i)} = \frac{S^2_{(i)} \cdot h.n._{BD}}{100} \qquad (4)$$

The hydroxy number in %:

$$h.n.^*_{(i)} = \frac{h.n._{(i)}}{33} \qquad (5)$$

The obtained results are represented in Table 1.

To check the validity of the proposed model we determined the hydroxy number by IR-spectroscopy using PolyTHF-2000. By chemical method the hydroxy number for PolyTHF-2000 was found to be 54,7 mgKOH/g or 1.6 %. Using the proposed method the hydroxy number is 51 mgKOH/g or 1.55 %. The relative error is 6.8 %.

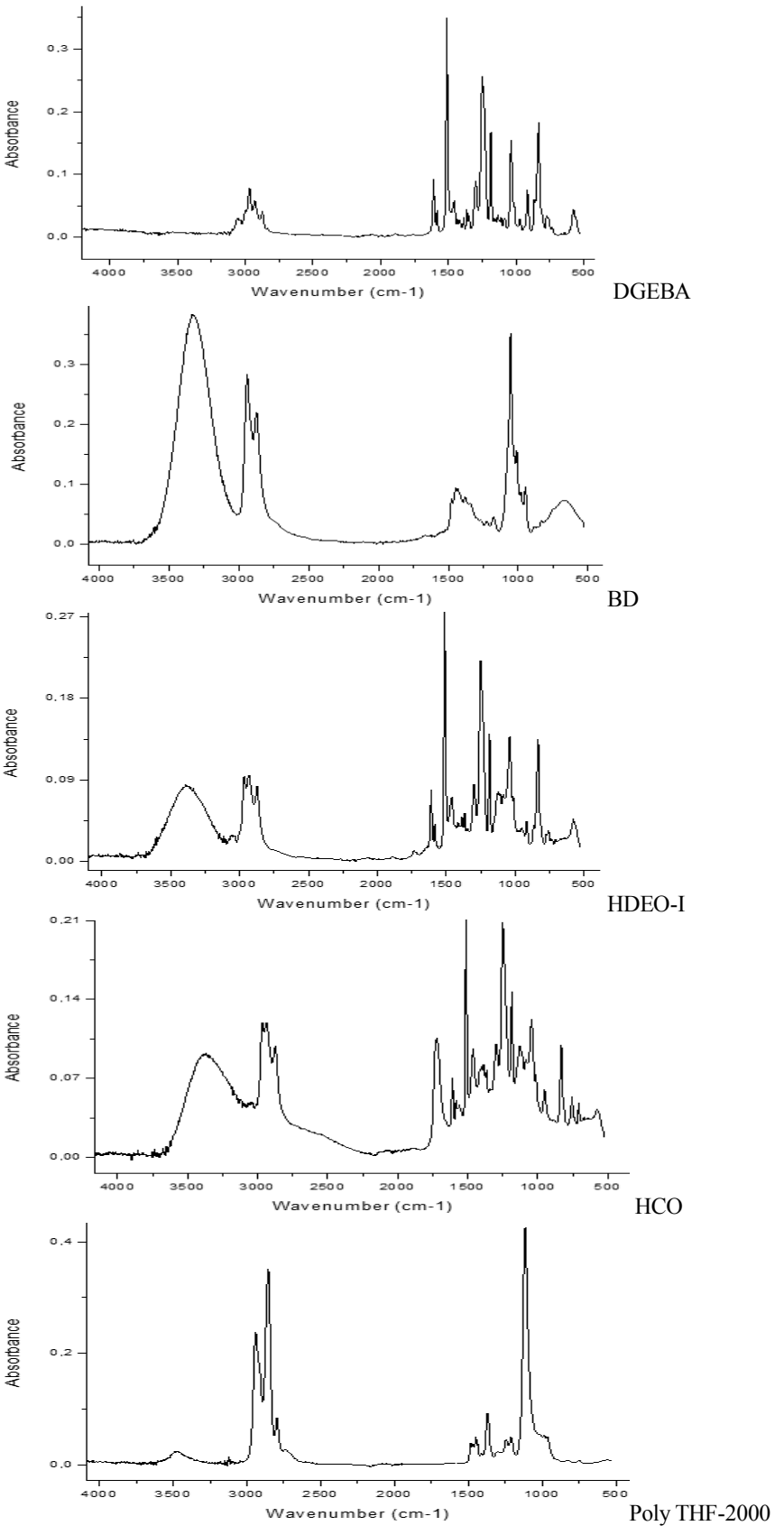


Fig. 1. IR-spectra of some samples

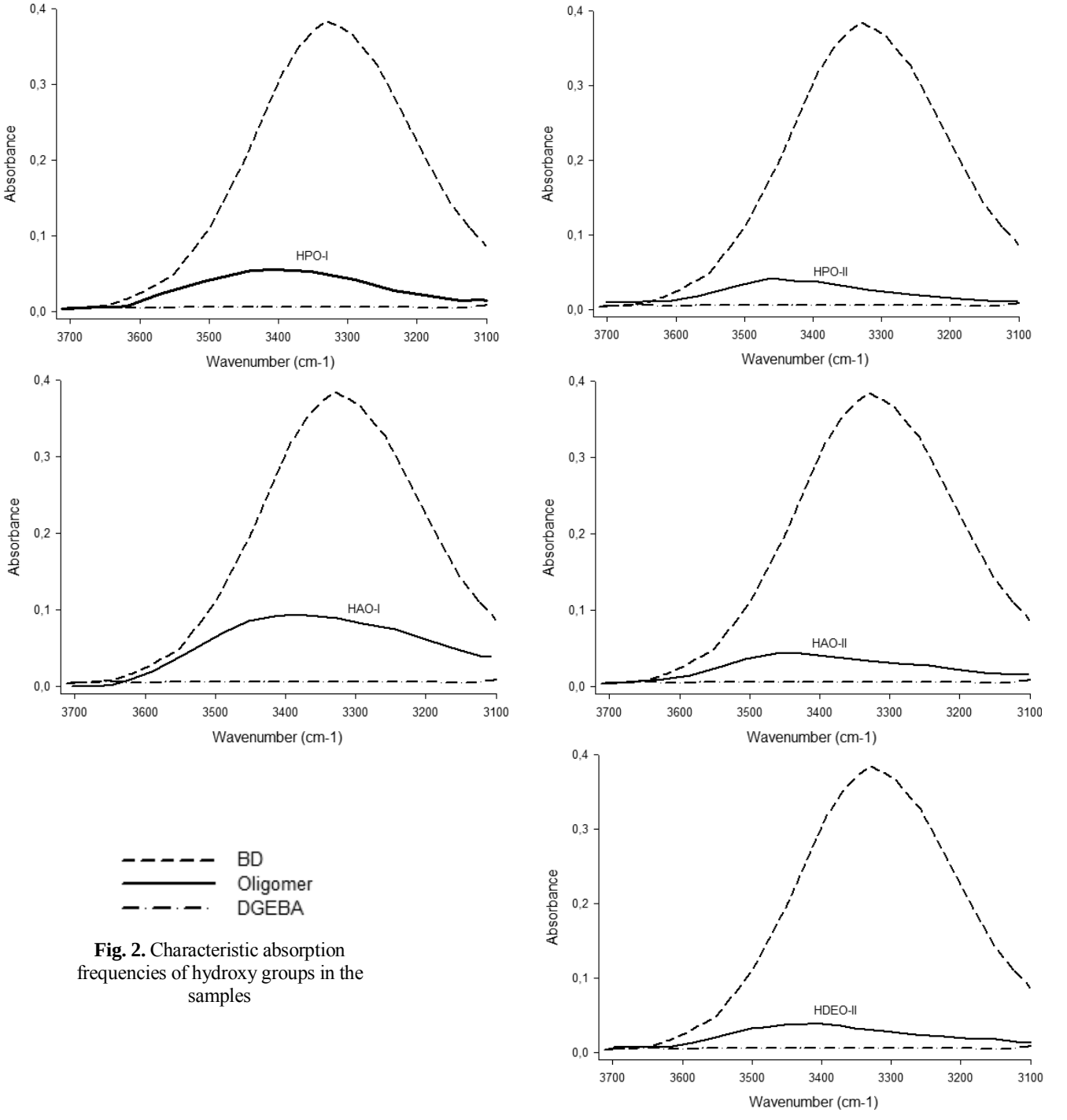


Fig. 2. Characteristic absorption frequencies of hydroxy groups in the samples

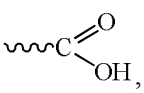
While analyzing the data from Table 1 one can see that the values obtained *via* IR-spectroscopy are in agreement with theoretical ones within the error limits. It does not concern the hydroxy number of HCO oligomer. The theoretical *h.n.* for HCO is 292 mgKOH/g and calculated by formula (4) – 373 mgKOH/g. This difference may be explained based on HCO formula. Apart from primary and secondary hydroxyl groups the HCO contains free carboxy group  , consisting of carbonyl and hydroxy groups. Moreover, the stretching vibrations of –OH of carboxy group are within the range of 3500–3580 cm^{-1} which is overlapped by hydroxy groups [27]. It means that in such a case the calculated hydroxy number is the sum of absorption bands typical of stretching vibrations of hydroxy group and –OH of carboxy group.

Table 1

Hydroxy numbers for initial and modified compounds

Compound	S^1, rel.units	S^2, %	Hydroxy number					
			IR-spectroscopy		Chemical method		Theoretical value	
			mgKOH/g	%	mgKOH/g	%	mgKOH/g	%
DGEBA	0	0	0	0	0	0	0	0
BD	109.49	100	1230	37.3	1230.0	37.3	1245	37.7
HDEO-I	24.66	22.52	277	8.4	–	–	261	7.9
HPO-I	16.81	15.35	189	5.7	–	–	215	6.5
HCO	33.21	30.33	373	11.3	–	–	292	8.9
HAO-I	31.25	28.54	351	10.6	–	–	335	10.2
Poly THF-2000	4.58	4.18	51	1.55	54.7	1.6	57	1.7
HDEO-II	4.72	4.31	53	1.61	–	–	49	1.5
HPO-II	7.34	6.7	82	2.49	–	–	72	2.2
HAO-II	7.48	6.83	84	2.55	–	–	71	2.1

Note: the theoretical value of hydroxy number for every sample was calculated taking into account its molecular weight and functionality.

4. Conclusions

The content of hydroxy groups was determined *via* IR-spectroscopy in the modified epoxy oligomers containing, apart from hydroxy groups, free epoxy or peroxy, carboxy or acrylic groups. The hydroxy number of investigated oligomers was found to be within 53–373 mgKOH/g. The proposed method allows to determine the content of hydroxy groups with the error lower than 10 %.

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ВИЗНАЧЕННЯ ГІДРОКСИЛЬНИХ ГРУП В МОДИФІКОВАНИХ ЕПОКСИДНИХ ОЛІГОМЕРАХ З ДОПОМОГОЮ ІЧ-СПЕКТРОСКОПІЇ

Анотація. *Запропоновано визначати вміст гідроксильних груп у модифікованих функційних олігомерах, на основі дигліциділового етеру бісфенолу А, з використанням ІЧ-спектроскопії. Використані для дослідження олігомери крім гідроксильних груп містять епоксидну або пероксидну, карбоксильні чи акрилатну групу.*

Ключові слова: *гліколь, епоксид, функціональний олігомер, гідроксильне число, ІЧ- спектроскопія.*