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STRUCTURE AND APPLICATION OF ED-20 EPOXY RESIN HYDROXY-CONTAINING DERIVATIVES IN BITUMEN-POLYMERIC BLENDS

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Abstract. New hydroxy-derived resin with primary hydroxy and epoxy groups has been synthesized on the basis of ED-20 epoxy resin and PolyTHF-2000 oligoether. The structures of the synthesized derivative and the product based on ED-20 epoxy resin and 1,4-butanediol which was synthesized by us earlier have been confirmed by IR- and NMR spectroscopy. The synthesized derivatives were investigated as polymeric components for bitumen-polymeric blends.

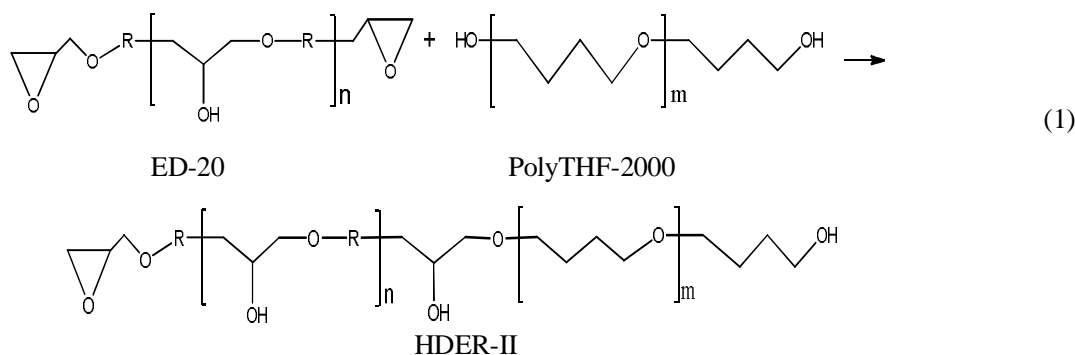
Keywords: epoxy resin, 1,4-butanediol, oligoether, PolyTHF-2000, IR- and NMR-spectroscopy, bitumen-polymeric blend.

1. Introduction

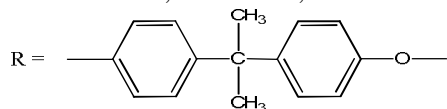
The modification of epoxy resins by different low-molecular and high-molecular compounds [1] allows to improve the operational properties of the goods on their basis and to extend their application, namely for bitumen-

polymeric blends production [2]. The reason is that modified epoxy resins contain an epoxy group and unsaturated double bonds [3] or free carboxy groups [4] allowing to react them with functional components of the blend. So, the adhesion of bitumen-polymeric blends increases. Sometimes such increase is not accompanied by the improvement of other properties, for instance, ductility. Therefore we made attempts to modify epoxy resins by glycols [5].

On the basis of ED-20 and 1,4-butanediol we synthesized an oligomeric product with a free epoxy group, fragment of ED-20 epoxy resin and aliphatic fragment of butanediol with primary hydroxy end group [5]. To our mind such oligomer contains insufficient amount of aliphatic chains capable to improve the ductility of bitumen-polymeric blends. Therefore we proposed to use the product with higher molecular mass with primary hydroxy end groups, such as PolyTHF-2000, as a modifier. The reaction between oligoether and resin may be represented as following:



where $n = 0-2$; $m = 26-28$;



The aim of the work is to study the structure of the previously synthesized oligomer [5] based on epoxy resin and 1,4-butanediol and oligoether obtained by Eq. (1).

2. Experimental

2.1. Materials

The industrial product with the molecular mass (M_n) of 390 g/mol and epoxy number (*e.n.*) of 20.0 % was used as an initial ED-20 resin. We also used 1,4-butanediol (Merck KGaA, Germany) with M_n 90.12 g/mol and PolyTHF-2000 oligoether (BASF Canada Inc., Canada) with M_n 1950 g/mol, hydroxy number of 54.7 mg KOH/g and acid number of ≤ 0.05 mg KOH/g.

Hydroxy derivative of the epoxy resin HDER-I was synthesized on the basis of ED-20 epoxy resin and 1,4-butanediol according to the procedure described in [5]. Its M_n is 460 g/mol and *e.n.* 8.6 %. Hydroxy derivative of the epoxy resin HDER-II was synthesized on the basis of ED-20 epoxy resin and PolyTHF-2000 in a three-necked reactor equipped with a mechanical stirrer, back condenser and drop funnel. 40.0 g of ED-20 resin dissolved in 100 ml of isopropyl alcohol, 2.2 g of benzyltriethylammonium chloride as 60 % aqueous solution and 1.4 g of KOH as 40% aqueous solution were loaded into the reactor. The mixture was heated to 333 K under constant stirring and the solution (186 g of PolyTHF-2000 plus 300 ml of isopropyl alcohol) was added dropwise for 30 min. The mixture was sustained at above-mentioned temperature for 10 min, cooled at room temperature and neutralized by 10% solution of acetic acid. Then chloroform was added, the mixture was washed till the neutral reaction and dried under vacuum till the mass became constant. HDER-II was obtained in the amount of 220 g (yield 97%) with M_n 2280 g/mol and *e.n.* 1.9 %.

2.2. Methods of Analysis

The average molecular mass was determined by cryoscopy using dioxane as a solvent. The epoxy number was determined according to the procedure described in [6]. IR-spectroscopy was carried out using Specord M-80 spectrophotometer (Brucker, Germany). The samples were prepared as a film formed from HDER solution in chloroform and applied over KBr plates. The spectra were recorded within the range of 4000–400 cm^{-1} with the integration time of 1 s. ^1H (400 MHz) and ^{13}C (100 MHz)

NMR spectra were measured by Bruker Avance II 400 spectrometer in CDCl_3 solution at room temperature. Chemical shifts are reported in ppm on *d* scale and referenced to the solvent resonances (7.27 ppm for ^1H and 77.0 ppm for ^{13}C). For bitumen and bitumen-polymeric blend the softening temperature (“ball and ring” method), penetration, ductility and adhesion to glass were determined according to the procedure described in [7, 8]. The content of asphaltenes, resins and oils were determined in accordance with the method [9].

3. Results and Discussion

3.1. HDER Structure

3.1.1. IR-investigations

IR-investigations were carried out to confirm the structure of the synthesized HDER. The spectrum of the initial ED-20 resin was recorded for the comparison.

While comparing spectra of ED-20 and HDER-II one can see that they are non-identical (Fig. 1). The presence of epoxy groups in the initial resin is confirmed by the absorption bands at 2872 and 915 cm^{-1} , typical of epoxy ring stretching vibrations (Fig. 1a). The band at 915 cm^{-1} is absent in the spectrum of HDER-II but the new band at 2850 cm^{-1} appears. The reason is that HDER-II molecule contains only 1.9 % of epoxy groups and has a molecular mass of 2280 g/mol. ED-20 resin is characterized by the molecular mass of 390 g/mol and *e.n.* 20.0 %. In contrast to HDER-II, HDER-I is characterized by higher epoxy number (8.6 %) and molecular mass (460 g/mol) and so the presence of epoxy groups is confirmed by stretching vibrations at 916 cm^{-1} . The presence of secondary hydroxy groups in the initial and synthesized products is confirmed by stretching vibrations at 3504 cm^{-1} (ED-20), 3392 cm^{-1} (HDER-I) and 3400 cm^{-1} (HDER-II). Moreover, the presence of secondary hydroxy groups in ED-20 is confirmed by absorption band at 1035 cm^{-1} and the presence of primary hydroxy groups in HDER-II – at 1042 cm^{-1} . Etheric bond is formed while bonding glycol molecule and ED-20 molecule. The presence of this bond in HDER-II is confirmed by stretching vibrations at 1150 cm^{-1} . The presence of benzene rings is confirmed by the band at 1507 cm^{-1} for HDER-I and HDER-II and at 1510 cm^{-1} – for ED-20. In HDER-II spectrum the appearance of intensive absorption band at 750 cm^{-1} , typical of $(\text{CH}_2)_n$ bond pendular oscillations, indicates the bonding of PolyTHF-2000 molecules to ED-20 resin.

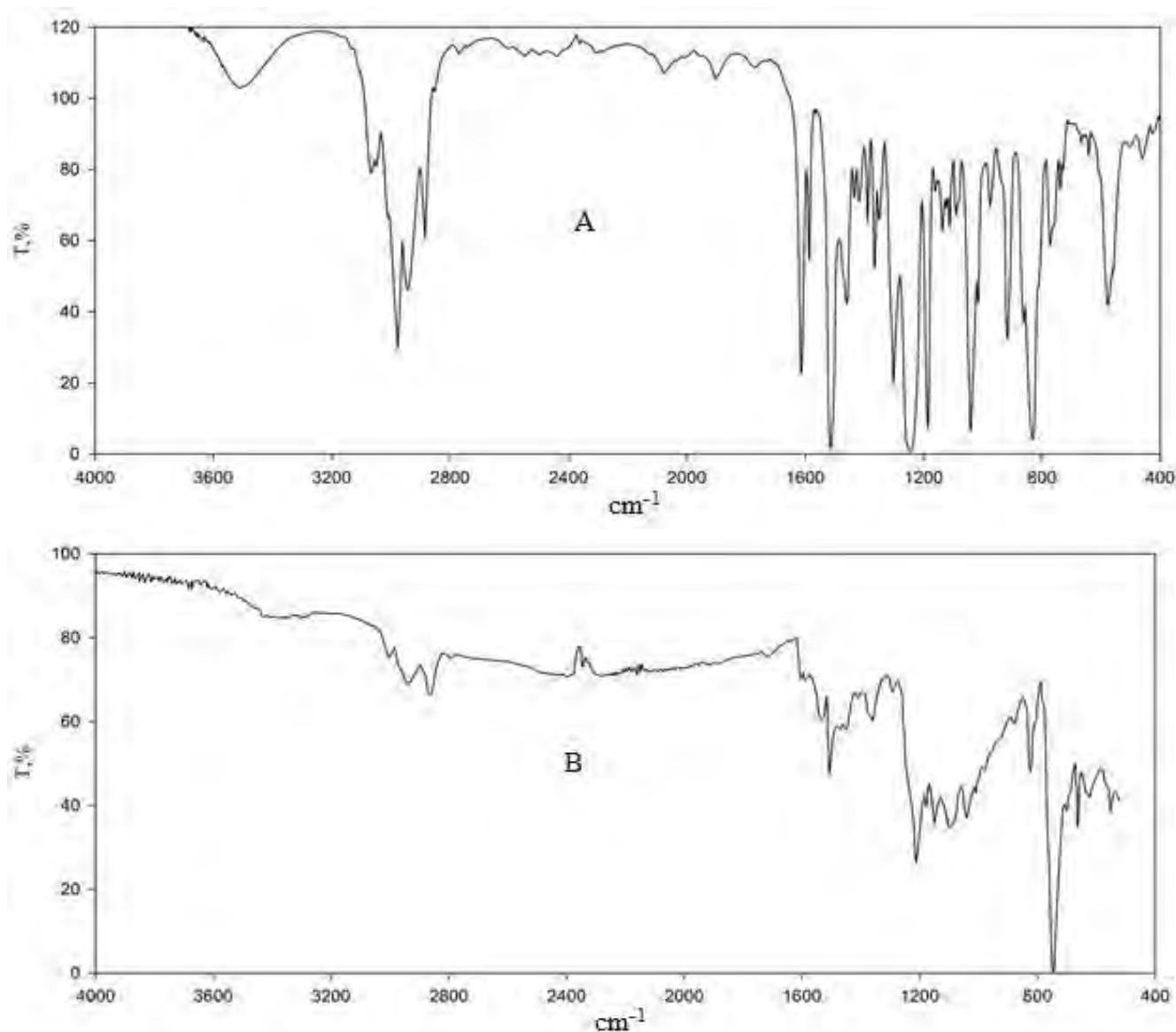


Fig. 1. IR-spectra of ED-20 (a) and HDER (b)

3.1.2. NMR-spectroscopic investigations

To confirm the structure of the synthesized products we conducted NMR-spectroscopic investigations similar to those mentioned above (Subsection 2.2). NMR-spectra of ED-20 initial resin were recorded for the comparison. The obtained results are represented in Figs. 2 and 3 and their interpretation is given in Tables 1 and 2.

The presence of epoxy groups in the molecules of the synthesized oligomers and the initial ED-20 resin is confirmed by chemical shifts of protons at 2.75 and 3.35 ppm (Fig. 2, Table 1). The primary and secondary hydroxy groups are confirmed by the chemical shifts at 3.40–4.20 ppm. Moreover, the intensity of peaks for

HDER-I and HDER-II increases compared with those of ED-20. It means that molecules of butanediol and PolyTHF-2000 bond with ED-20 molecule (Fig. 2). While bonding PolyTHF-2000 molecule to ED-20 one (Eq. (1)) the opening of epoxy ring occurs and the secondary hydroxy group is formed. The glycol bonding leads to additional introduction of the primary hydroxy groups into the structure of the synthesized oligomer. Finally it is accompanied by the increase in hydroxy groups amount and as a result – by the increase of peak intensity of chemical shift typical of hydroxy group protons. The introduction of butanediol and PolyTHF-2000 fragments into the structure of ED-20 resin increases CH₂-groups amount. This fact is confirmed by the increased signals at

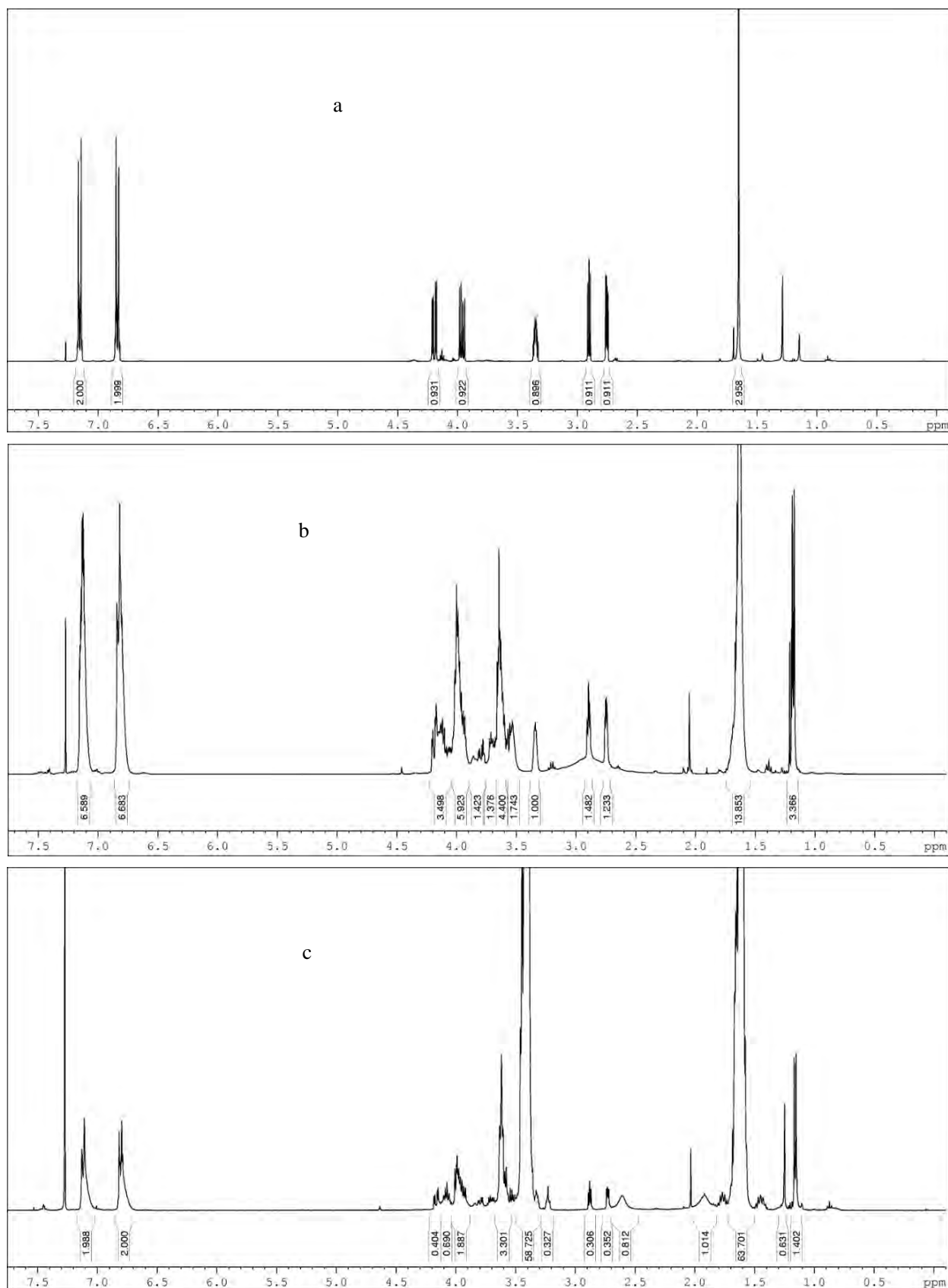


Fig. 2. ^1H NMR-spectra of ED-20 (a), HDER-I (b) and HDER-II (c)

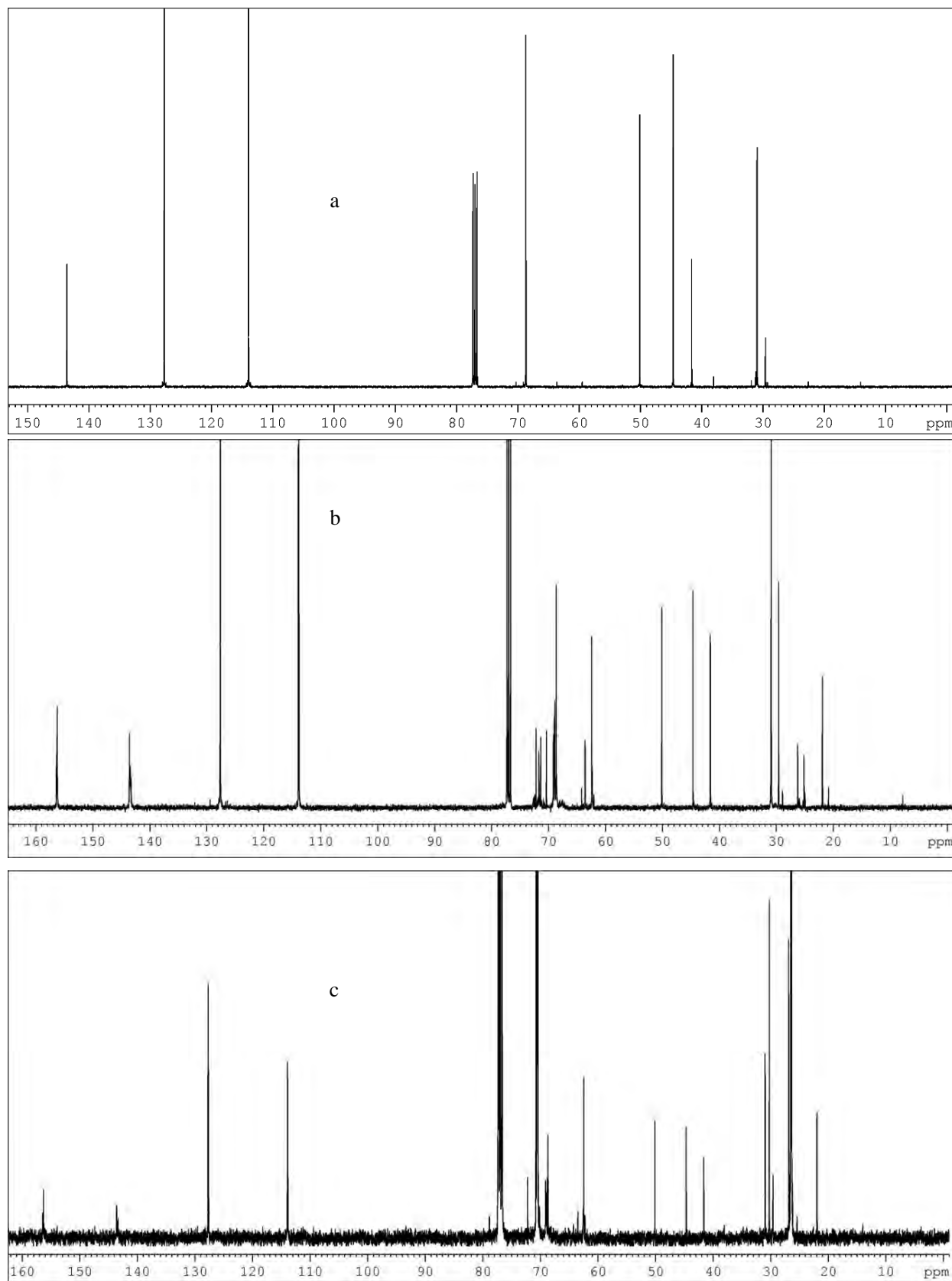


Fig. 3. ^{13}C NMR-spectra of ED-20 (a), HDER-I (b) and HDER-II (c)

Table 1

¹H NMR-spectra of ED-20 resin and products of its modification

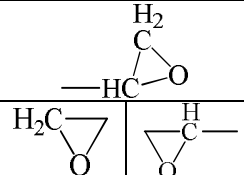
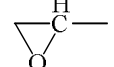
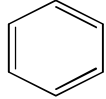
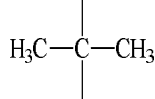
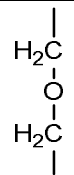

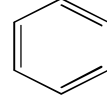
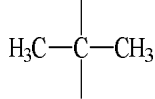
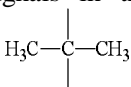
Oligomer	Chemical shift δ , ppm						
			-OH			-CH ₂ -	
ED-20	2.75	3.35	3.95–4.20	6.85–7.15	1.15	1.65	–
HDER-I	2.75	3.35	3.65–4.20	6.80–7.10	1.15	1.65	–
HDER-II	2.75	3.25	3.40–4.00	6.80–7.30	1.15	1.60–1.75	3.40

Table 2

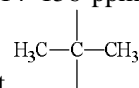
¹³C NMR-spectra of ED-20 resin and products of its modification

Oligomer	Chemical shift δ , ppm					
	-OH					-CH ₂ -
	primary	secondary				
ED-20	–	69.77	50	114–156	31–45	29–45
HDER-I	62.71	69.77	50	114–156	31–45	26–45
HDER-II	62.71	69.77	50	114–156	31–45	22–45

1.60–1.75 ppm. In contrast to ED-20 and HDER-I, the molecule of HDER-II contains etheric bonds –CH₂–O–CH₂–, which presence is confirmed by protons signal at 3.40 ppm (Fig. 2c, Table 1). The presence of benzene resins in the synthesized oligomers is confirmed by protons signals in the area of 6.80–7.30 ppm. The

fragment  is present in the synthesized oligomers and initial ED-20 resin. The proton signal at 1.15 ppm reveals this fact.

The analysis of ¹³C NMR-spectra (Fig. 3, Table 1) shows the presence of secondary hydroxy group, that is confirmed by the signals at 69.77 ppm; primary hydroxy group (which is absent in ED-20) – at 62.71 ppm; benzene rings – at 114–156 ppm; epoxy groups – at 50 ppm and

the fragment  – at 31–45 ppm. The intensity of signal of the latter fragment decreases with the increase in oligomer molecular mass. The increase in signal intensity in the area of 29–45 ppm typical of ¹³C in CH₂-group indicates butanediol and PolyTHF-2000 molecules bonding to the molecule of ED-20 resin.

3.2. Bitumen-Polymeric Blends

It is known [10, 11] that derivatives of epoxy resins may be used as a polymeric component for bitumen-polymeric blends. Above-mentioned HDERs differ from

earlier studied ones by the presence of primary and secondary hydroxy groups (HDER-I and HDER-II) and long aliphatic fragment (HDER-II). Bitumen-polymeric blends with HDER-I and HDER-II are described below.

3.2.1. Bitumen-polymeric blends with HDER-I

Bitumen-polymeric blends were studied using the methods described in Subsection 2.2. We established the effect of HDER-I amount, temperature and process time on the softening temperature, ductility, penetration and adhesion. The results are represented in Table 3.

The introduction of HDER-I into bitumen-polymeric blend decreases ductility and penetration but considerably increases adhesion (Table 3). The value of softening temperature remains constant.

With the increase in temperature to 483 K (compared with 463 K) adhesion, penetration and ductility decrease. The decrease in temperature to 443 K slightly decreases penetration and actually does not change ductility and softening temperature.

The decrease in process time to 0.5 h decreases adhesion and ductility but softening temperature and penetration are almost the same. The increase in time to 2 h leads to the similar result except ductility – its change is miserable.

Thus, the most optimal conditions for the production of bitumen-polymeric blends with HDER-I are: temperature – 443 K; HDER-I amount – 3 wt %; process time – 1 h.

Table 3

Preparation conditions and characteristics of bitumen-polymeric mixtures based on HDER-I

Sample number	HDER-I amount for 100 g bitumen	Process temperature, K	Process time, h	Characteristics of bitumen-polymeric blends			
				Softening temperature, K	Ductility at 298 K, cm	Penetration depth at 298 K, 0.1 mm	Adhesion, %
1	0	463	1.0	321	83	62	40.5
2	1	463	1.0	323	76	53	54.7
3	3	463	1.0	323	72	53	79.5
4	5	463	1.0	322	57	52	89.6
5	7	463	1.0	322	50	52	99.9
6	3	443	1.0	322	87	56	79.5
7	3	483	1.0	322	58	54	56.0
8	3	443	0.5	322	68	55	43.3
9	3	443	2.0	323	81	56	54.6

Table 4

Preparation conditions and characteristics of bitumen-polymeric mixtures based on HDER-I

Sample number	HDER-II amount for 100 g bitumen	Process temperature, K	Process time, h	Characteristics of bitumen-polymeric blends			
				Softening temperature, K	Ductility at 298 K, cm	Penetration depth at 298 K, 0.1 mm	Adhesion, %
1	0	463	1.0	319	83	62	40.5
2	1	463	1.0	322	79	57	62.0
3	3	463	1.0	321	56	58	64.9
4	5	463	1.0	321	45	61	63.5
5	7	463	1.0	321	31	63	59.3
6	1	443	1.0	322	62	57	55.6
7	1	483	1.0	321	91	57	74.8
8	1	483	0.5	322	76	58	62.5
9	1	483	2.0	321	98	57	69.4
10	0(ED-20)	483	1.0	322	41	35	75.9

Table 5

Structural-group composition of bitumen-polymeric blends with HDER-II

Sample number according to Table 4	Content of carbenes, carboids and mechanical impurities, %	Content of asphaltenes, %	Content of resins, %	Content of oils, %
1	0.12	23.82	25.85	50.21
10	0.38	23.56	25.98	50.08
11	0.55	25.61	24.23	49.61

If we compare the obtained bitumen-polymeric blends with blends without HDER-I, we see that they are characterized by the same softening temperature, higher ductility and considerably higher adhesion.

3.2.2. Bitumen-polymeric blends with HDER-II

The same as for blends with HDER-I the investigated blends were studied using the methods described in Subsection 2.2. The effect of HDER-II

amount, temperature and process time on the operational characteristics of bitumen-polymeric blends is represented in Table 4.

The increase in HDER-II amount (Table 4) slightly decreases penetration and considerably decreases ductility. The value of softening temperature remains constant. Concerning adhesion, the best results are obtained at HDER-II amount of 1–5 wt %. The further increase to 7 wt % decreases adhesion. Thus, the best characteristics were found to be at 1 wt % of HDER-II.

The decrease in temperature to 443 K decreases adhesion and ductility. Other values are constant. The increase in temperature to 483 K increases adhesion and ductility. Thus, the temperature of 483 K was found to be the optimum one for bitumen-polymeric blends production.

The decrease in time to 0.5 h decreases adhesion and ductility and does not affect penetration and softening temperature. On the other hand, the increase in time to 2.0 h insignificantly increases adhesion with other constant value.

The most optimum obtaining conditions of bitumen-polymeric blends with HDER-II are: temperature – 483 K, HDER amount – 1 wt % and process time – 1 h.

The obtained bitumen blends have the same softening temperature, higher ductility and considerably higher adhesion compared with those values for bitumen without HDER-II.

We studied bitumen-polymeric blend with the initial ED-20 resin (Table 4, Sample 10) for the comparison. The blend was obtained at 483 K for 1 h and ED-20 amount of 3 wt % per 100 g of bitumen. Adhesion of the obtained blend is higher (compared with pure bitumen) but its ductility and penetration are twice lower.

To establish the reasons of some characteristics increasing/decreasing we studied the structural-group composition of HDERs. All experiments were carried out according to the procedure described in [9, 11] and results are given in Table 5.

The introduction of HDER-II into bitumen increases the content of resins, carboids and carbenes and decreases resins and asphaltenes content. If we use the initial non-modified ED-20 as a polymeric component, the content of carbenes, carboids and asphaltenes is increased in the synthesized blend, the rest indexes are decreased. Moreover, while using ED-20 (Table 4) the operational characteristics of the blend are worse. The presence of fragments with hydroxy groups in the modified ED-20 favors the conversion of oils into resins and asphaltenes into carbenes and carboids (Table 5), as well as the increase of adhesion.

4. Conclusions

Using previously developed by us the synthesis procedure based on ED-20, 1,4-butanediol and hydroxy derivative HDER-I [5], we developed the method of hydroxy derivative HDER-II synthesis based on ED-20 and oligoether PolyTHF-2000. The structures of both HDERs were confirmed by IR- and NMR-spectroscopic investigations.

HDER-I and HDER-II were studied as the components of bitumen-polymeric blends. Using HDER-I as the polymeric component in the amount of 3 wt % per 100 g of bitumen at 443 K for 1 h increases adhesion by two times and slightly increases ductility. If we use HDER-II as the component in the amount of 1 wt % at 483 K for 1 h it also increases adhesion and ductility of the blends. The presence of HDERs in the composition of bitumen-polymeric blends favors the conversion of oils into resins and asphaltenes into carbenes and carboids as well as the increase of adhesion. This fact was confirmed by structural-group analysis.

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СТРУКТУРА ТА ЗАСТОСУВАННЯ У БІТУМ-ПОЛІМЕРНИХ СУМІШАХ ГІДРОКСИЛВМІСНИХ ПОХІДНИХ ЕПОКСИДНОЇ СМОЛИ ЕД-20

Анотація. Запропонована методика синтезу на основі епоксидної смоли ЕД-20 та олігоетеру Poly THF-2000 нової гідроксилпохідної смоли з кінцевими первинною гідроксильною та епоксидною групами. Структура синтезованої похідної та раніше синтезованого нами продукту на основі епоксидної смоли ЕД-20 та 1,4-бутандіолу підтверджена з використанням ІЧ і ЯМР спектроскопії. Синтезовані похідні епоксидної смоли вивчені як полімерні компоненти бітум-полімерних сумішей.

Ключові слова: епоксидна смола, 1,4-бутандіол, олігоетер PolyTHF-2000, ІЧ і ЯМР спектроскопія, бітум-полімерні суміші.