

OBTAINING OF COUMARONE-INDENE RESINS BASED ON LIGHT FRACTION OF COAL TAR

4. BITUMEN-POLYMER BLENDS WITH PARTICIPATION OF COUMARONE-INDENE RESINS WITH EPOXY GROUPS

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<https://doi.org/10.23939/chcht13.01.112>

Abstract. Using light fraction of coal tar (5.75 wt % of coumarone and 44.45 wt % of indene), glycidyl methacrylate and styrene, the coumarone-indene resin with epoxy groups (CIRE) has been synthesized. Monoperoxy derivative of diglycidyl ether Bisphenol A (PO) was used as an initiator. The possible formation of CIRE has been studied on the model systems consisting of PO, glycidyl methacrylate, indene or coumarone, or styrene, or mixture of mentioned compounds. The synthesized product has been investigated as a polymer additive to bitumen-polymer blends (BPB). The effect of CIRE amount, temperature and time on the BPB operational characteristics has been examined. By means of IR-spectroscopy the structures of CIRE, bitumen and BPB were determined.

Keywords: coumarone-indene resin, model systems, epoxy groups, bitumen-polymer blend, IR spectroscopy.

1. Introduction

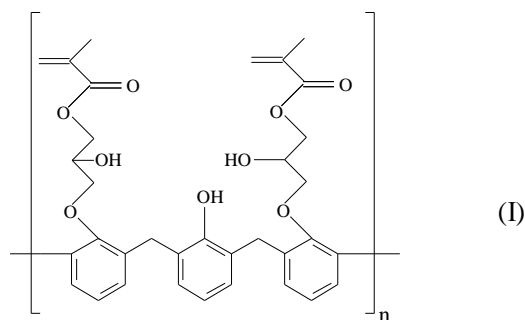
It is known [1, 2] that different additives are used to improve the operational characteristics of petroleum bitumen. Such additives today are inorganic, as well as organic compounds [1]. Significant improvement in the quality of petroleum bitumen is achieved due to the introduction of polymers [1, 2]. Moreover, according to the literature data [3], the production volume of polymer modified bitumen in Europe is above 10 % of total amount of used bituminous materials. As polymeric additives to bitumen thermoplastics (polyethylene,

polypropylene, polyvinyl chloride, *etc.*), thermosetting polymers (ethylene-propylene-diene copolymer, styrene-butadiene-styrene copolymer, *etc.*), elastomers (rubbers) and thermosetting resins (epoxy resin, polyurethane resin, *etc.*) are used [1]. Today thermoplastics and thermosetting polymers are most often used for the bitumen modification.

The addition of polyethylene increases the bitumen heat resistance [1]. When bitumen is modified with an ethylene-propylene copolymer, its elastic and adhesion properties are improved. The addition of styrene-butadiene-styrene polymer in the amount of 3 wt % allows to increase the bitumen softening temperature, to decrease the brittleness temperature by 3–7 K and to increase their ductility by 2–3 times [1, 3].

The presence of various functional groups in the polymer structure contributes to the improvement of BPB adhesion properties [1].

Over the past few years, the researchers of the Department of Chemical Technology of Oil and Gas Processing at Lviv Polytechnic National University (Ukraine) have been working on the creation of new oligomeric products containing functional groups [4–8]. Such oligomer products are studied as additives to bitumen. G. Strap *et al.* [6] proposed to use as an additive to petroleum bitumen the phenol formaldehyde oligomers modified with glycidyl methacrylate (I) and peroxide derivative of epoxy resin (II) of the general formulae:

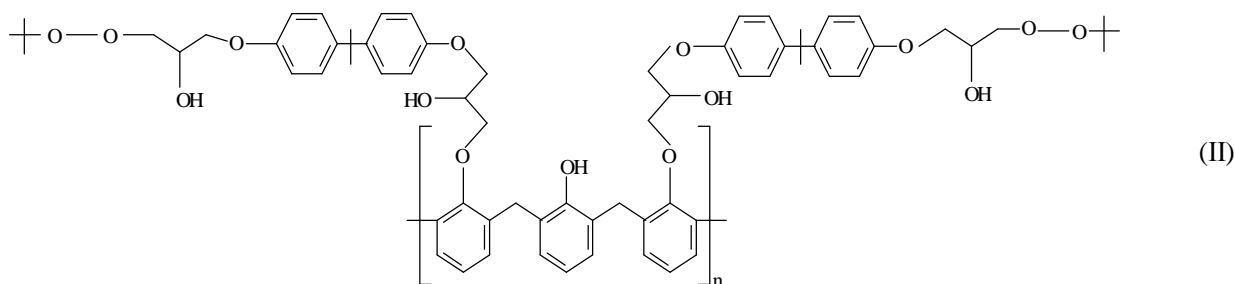


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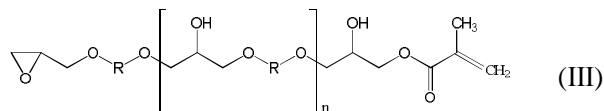
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$n = 1-2$

The introduction of oligomer I into BPB leads to the decrease in ductility and penetration of such blends, but at the same time, their adhesion is practically doubled. The optimum amount of oligomer I is 3 wt % per 100 g of initial bitumen [6]. Similar results are obtained when using oligomer II. The optimum amount of oligomer II is 1 wt %, under which the adhesion increases twice, and ductility increases as well.

M. Bratyshak *et al.* [8] investigated the dianic epoxy resin modified with methacrylic acid (III) as an additive to bitumen. Its formula is:



where $n = 0-1$, $R = -C_6H_4C(CH_3)_2C_6H_4-$

The introduction of oligomer III in the amount of 3 wt % per 100 g of the initial bitumen increases the softening temperature and adhesion of the resulting mixture and decreases both ductility and penetration. Bitumen-polymer blends with oligomer III (the same as in the case of using oligomers I and II), were prepared at 463 K for 1 h. The improvement of BPB operational characteristics was caused by the transition of oils into resins and asphaltenes.

The coumarone-indene resins with free epoxy groups (CIRE), which were described earlier in [9], may be also referred to the polymers with functional groups. Such resins are obtained *via* radical polymerization of monomers of the light fraction of coal tar in the presence of peroxy derivative of dioxydiphenylpropane diglycidyl ether (PO) [9]. CIRE are characterized by the softening temperature of 336 K, the molecular weight of 1400 g/mol and the content of epoxy groups 2.3 %. The presence of free epoxy groups in CIRE allows to consider them as active additives to various mixtures. Thus, the aim of this paper is to study the possibility of using CIRE as additives to petroleum bitumen to create bitumen-polymer blends.

2. Experimental

2.1. Materials

The raw material for CIRE synthesis was light fraction of coal tar (LFCT) produced at JSC "Zaporizhkoks" (Ukraine). The LFCT composition is given in Table 1.

Table 1

Components content in LFCT

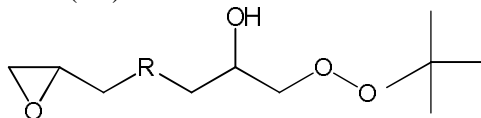
Component	Content, wt %
Benzene	0.98
Toluene	1.23
Ethylbenzene	0.32
<i>m</i> + <i>p</i> -Xylenes	8.10
<i>o</i> -Xylene	2.61
Styrene	6.73
<i>o</i> -Ethylbenzene	4.35
Pseudocumene	7.71
Hidrindane	2.64
Coumarone	5.75
Indene	44.45
Naphthalene	6.96
<i>b</i> -Methylnaphthalene	0.31
<i>a</i> -Methylnaphthalene	0.13
Other hydrocarbons	7.73
Total	100.0

Indene and coumarone were purchased from Ukrorgsyntez (Ukraine) with n_D^{20} 1.5765, d_4^{20} 0.9966 and n_D^{20} 1.5648, d_4^{20} 1.0776, respectively.

Styrene was dried before the experiments with solid alkali and purified by distillation at 323 K under residual pressure of 300–400 Pa. Its characteristic: n_D^{20} 1.5471 (literature value 1.5468); d_4^{20} 0.902 (literature value 0.9059) [10].

Glycidyl methacrylate was purchased from Aldrich (USA) with n_D^{20} 1.449, d_4^{20} 1.042.

Monoperoxy derivative of diglycidyl ether Bisphenol A (PO) was used as an initiator:



where $R = -OC_6H_4C(CH_3)_2C_6H_4O-$

PO was synthesized according to the modified method, taking into account the results presented in [11]. A three-necked reactor equipped with a mechanical stirrer, backflow condenser and thermometer, was loaded with 100 g of Bisphenol A diglycidyl ether and 100 ml of toluene. Separately a mixture was prepared consisting of 84.0 g of 70% aqueous solution of *tert*-butyl hydroperoxide dissolved in 100 ml of toluene, 19.1 g of benzyl triethyl ammonium chloride and 3.9 g of crystalline KOH. The solution of the diglycidyl ether in toluene was heated to 323 K under stirring and a mixture containing hydroxides and catalysts was added to it through a dropping funnel. Then the mixture was kept at 323 K for 6 h, cooled to room temperature and transferred to a separating funnel. After washing the catalysts, the organic layer was vacuumized at 323–333 K. The residue was re-precipitated in petroleum ether and dried under vacuum to a constant weight. 120.8 g of the resulted product was obtained; its molecular weight was 420 g/mol, active oxygen content – 2.5 % and content of epoxy groups – 8.4 %.

Bitumen BND 60/90 produced at the Kremenchug PJSC “Ukratnafta” (Ukraine) was used as petroleum bitumen for the experiments. Its characteristics are as follows: softening temperature – 319 K, penetration – $70 \cdot 10^{-4}$ m, ductility – $63 \cdot 10^{-2}$ m, and adhesion to glass – 47 %.

2.2. CIRE Synthesis

Radical co-oligomerization of LFCT was carried out in a 1.0 l metal ampoule. 200 ml (194.4 g) of LFCT, 24 ml (21.7 g) of styrene, 16 ml (18.3 g) of glycidyl methacrylate, and 10 g of PO were loaded into the ampoule. Then, the system was blown with an inert gas, closed and placed in a thermostat. Radical co-oligomerization proceeded at 393 K for 6 h. After co-

oligomerization, the ampoule was cooled to room temperature, the reaction mixture was transferred to a distillation flask and unreacted raw material was distilled under vacuum. The resulting product was dried in a vacuum-dryer at 313 K to a constant weight. 79.0 g of CIRE with a molecular weight of 850 g/mol and content of epoxy groups 1.9 % were obtained.

2.3. Analytical Determination

The number-average molecular weight (M_n) of the synthesized CIRE was determined using cryoscopy in benzene. The content of epoxy groups (epoxy number, e.n.) was determined according to the procedure described in [12].

2.4. Spectral Measurements

All FTIR spectra were measured by means of the Nicolet 8700 spectrometer (Thermo Scientific, Waltham, MA) equipped with the GoldenGate ATR accessory (Specac Ltd., Orpington, Great Britain). A single-reflection diamond crystal was used as the internal reflection element of the accessory. For each spectrum 256 scans were taken with the resolution of 4 cm^{-1} . The temperature was set at 298 K with using an electronic temperature controller (Specac Ltd., Orpington, Great Britain). All spectra were collected and analyzed using the commercially available software: OMNIC (Thermo Scientific, Waltham, MA), Matlab (MathWorks, Natic, MA).

2.5. Preparation of BPB and its Analysis

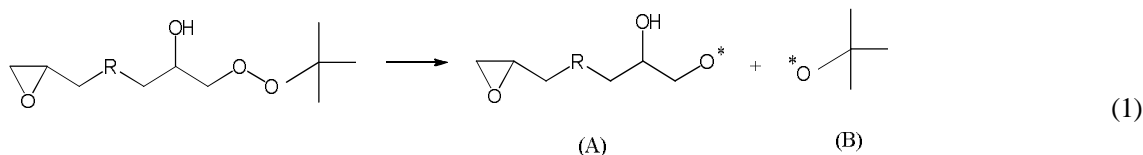
Bitumen was heated in a reactor till definite temperature, then CIRE was added and mixed ($Re = 1200$) for a definite time.

For bitumen and BPB the softening temperature (“ball and ring” method), penetration, ductility and adhesion to glass were determined according to the procedure described in [13–16]. The content of asphaltens, resins and oil were determined according to the method given in [17].

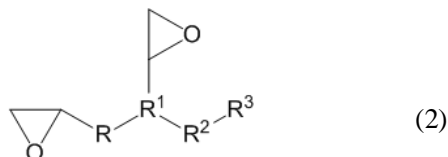
3. Results and Discussion

3.1. Copolymerization of Model Systems

The synthesized CIRE contains epoxy groups due to the presence of free epoxy and peroxy groups in the structure of initiator PO. At the polymerization temperature of 393 K the decomposition occurs and peroxy groups form two free radicals according to Eq. (1):



The radical (A) causes the copolymerization of resin-forming components of LFCT, namely indene, coumarone, styrene, as well as additionally introduced glycidyl methacrylate. Thus, we assume that the synthesized CIRE should have the following structure:



The epoxy groups in CIRE are at the ends of the molecule and in the side chains. The presence of epoxy groups in the latter ones is explained by glycidyl methacrylate copolymerization with the molecules of styrene, indene and coumarone. The epoxy group at the end of the molecule is introduced due to the initiation of components polymerization by the radical (A).

The radical (B) actually does not participate in the copolymerization reactions but converts into acetone and *tert*-butyl alcohol [18].

The composition of LFCT used in this work (Table 1) differs from that described in [18] by content of styrene, coumarone and indene (6.73 vs. 1.2; 5.75 vs. 1.3 and 44.45 vs. 3.9 wt %, respectively). Taking into account the high content of resin-forming components in LFCT it was important to determine their ability of copolymerization and formation of the structure (2). For this purpose, we prepared the model systems consisting of the initiator PO and glycidyl methacrylate (GMA) of indene, or coumarone, or styrene, or the monomers mixture (Table 2).

It may be assumed (*vide* Table 2) that not all resin-forming components have the same activity regarding the

copolymerization with GMA and formation of the structure (2). Among all monomers, styrene has the highest activity (mixture III, Table 2). The resin yield is 99.0 % in this case. For the model systems GMA/indene or GMA/coumarone the yields are lower (mixtures I or II, Table 2). It means that indene or coumarone are not capable of the copolymerization reaction with GMA or they react in a minor quantity. The possible copolymerization of indene and coumarone described in [18] leads to the increase in resin yield for mixture IV.

To confirm our assumptions, we used IR-spectroscopy (Fig. 1). The presence of epoxy groups in the synthesized resins is confirmed by stretching vibrations at 908 and 2936 cm^{-1} . The presence of hydroxy groups introduced by the initiator PO is confirmed by stretching vibrations at 3472 cm^{-1} (mixture I, Fig. 1a), 3478 cm^{-1} (mixture II, Fig. 1b) and 3504 cm^{-1} (mixture IV, Fig. 1c). The presence of GMA fragments is confirmed by stretching vibrations of carbonyl group at 1724 cm^{-1} (mixture I, Fig. 1a) and 1728 cm^{-1} (mixture II and IV, Fig. 1b, c). Stretching vibrations at 756 cm^{-1} corresponding to 1,2-disubstituted benzene ring in the indene molecule confirm the introduction of indene fragment into the resin structure (mixture I, Fig. 1a). In the spectrum of mixture II (Fig. 1b) the band at 756 cm^{-1} corresponding to stretching vibrations of 1,2-disubstituted benzene ring and the band at 1056 cm^{-1} corresponding to etheric bond C–O–C in the coumarone molecule confirm the presence of coumarone fragment in the resin structure. The indene fragment in the resin based on mixture IV is confirmed by absorption band at 756 cm^{-1} ; stretching vibrations at 756 and 1056 cm^{-1} indicate the presence of coumarone (Fig. 1c).

Table 2

Composition of the model systems and characteristics of the synthesized resins

Mixture number	Initial monomers / quantity, g	Resins characteristics		
		Yield, %	e.n., %	M_n , g/mol
I	Indene / 50.0	74.9	15.6	550
II	Coumarone / 50.0	37.2	17.6	640
III	Styrene / 50.0	99.0	12.4	not determined
IV	Indene / 17.0 Coumarone / 17.0 Styrene / 17.0	84.8	14.4	790

Notes: the quantity of GMA in the mixtures was 50.0 g, PO – 25.0 g. Toluene (400 g) was the reaction medium. Mixture II apart from the resin dissolved in toluene contained the residue in the amount of 15.7 % with e.n. of 19.0 %.

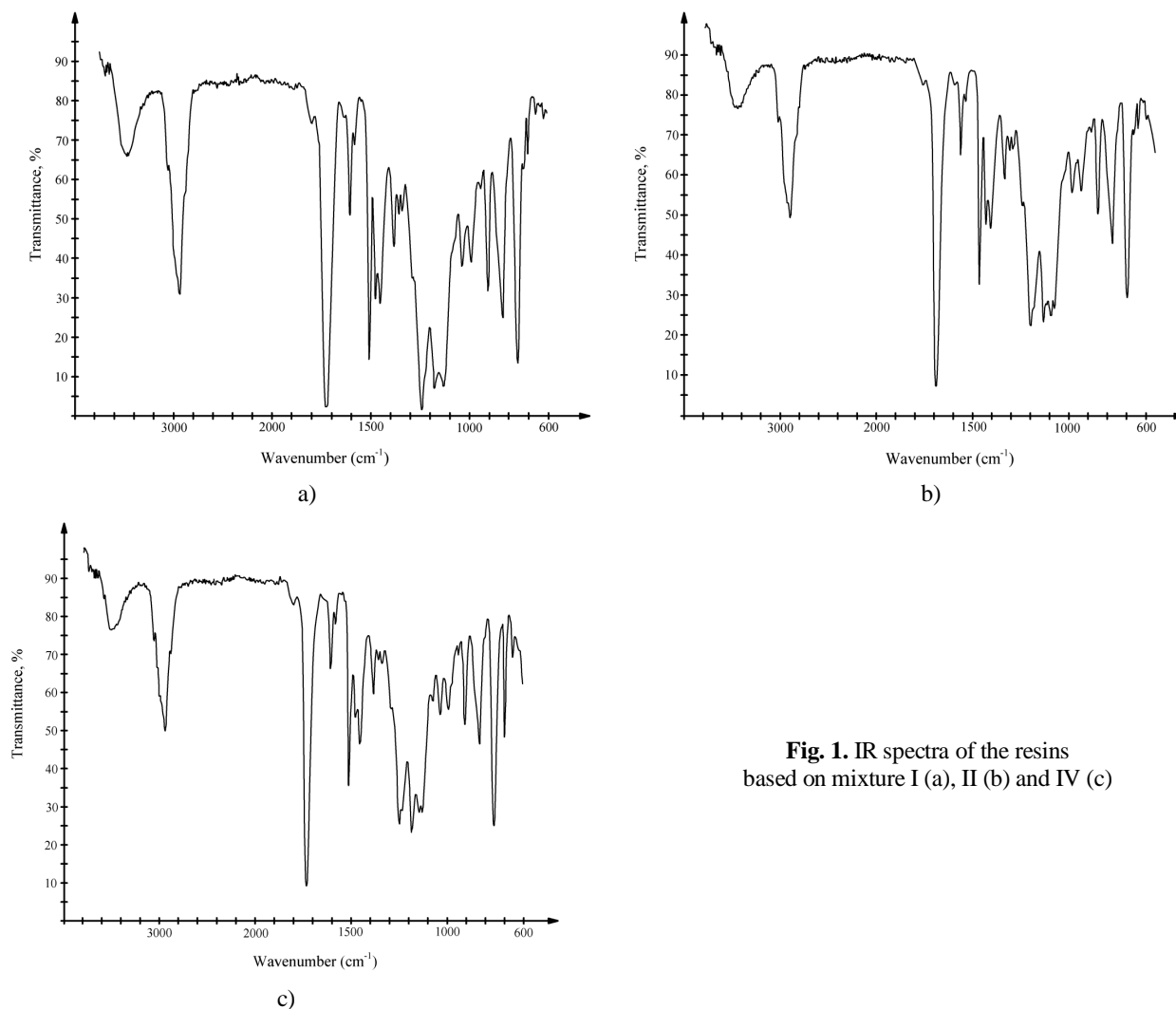


Fig. 1. IR spectra of the resins based on mixture I (a), II (b) and IV (c)

So, IR spectra confirm that all resin-forming components in LFCT, as well as GMA, participate in the formation of resin molecule. The resin yield (*vide* Table 2) depends on component activity. GMA, styrene and indene are more active, while coumarone has the lowest activity.

3.2. Bitumen-Polymer Blends (BPB)

It was shown earlier [8] that polymers (oligomers) containing free epoxy groups may be applied as additives to petroleum bitumen to improve its operational properties. The property most influenced by epoxy groups is adhesion. The group analysis shows that the introduction of epoxy component to BPB increases the content of resins, carbenes and carboids and decreases the content of oils and asphaltenes in them. In other words, oils transfer into resins and asphaltenes – into carbenes and carboids.

The synthesized CIRE are characterized by lower molecular weight and content of epoxy groups compared with the resins based on model mixtures. This fact indicates

that other components of LFCT (in addition to indene, coumarone, GMA, and styrene) also participate in CIRE formation. Moreover, CIRE synthesized *via* radical copolymerization may react with the components of LFCT. The result is the increase in molecular weight and the decrease in the content of epoxy groups due to their interaction with active hydrogen atoms.

To determine the effect of free epoxy groups on BPB properties we examined the impact of CIRE quantity, temperature and time of mixture preparation. The preparation conditions and characteristics of BPB are given in Tables 3-5.

The introduction of CIRE increases the softening temperature and decreases penetration. The increase in CIRE amount increases ductility but at CIRE content above 3 wt% this value is reduced. All blends are homogeneous except that containing 7 wt% of CIRE. In this case, the values of ductility and adhesion are essentially lower compared with other blends. The effect of CIRE amount on BPB adhesion is shown in Fig. 2.

The effect of temperature on BPB properties is represented in Table 4 and Fig. 3. The increase/decrease in temperature decreases softening temperature and ductility but increases penetration, although this value is lower compared with that for bitumen without CIRE. Adhesion also depends on temperature and the highest value was observed at 463 K. Taking into account the obtained results, the effect of preparation time on BPB characteristics was studied at 463 K.

As one can see from Table 5, the preparation time affects all values except softening temperature. The

increase in time to 120 min decreases ductility but increases penetration. At the same time, adhesion is slightly reduced. The best adhesion was found for BPB prepared for 60 min (Fig. 4).

On the basis of obtained results we can assert that CIRE as an additive for bitumen improves its characteristics, with the exception of penetration. Moreover, the adhesion of BPB is twice higher than adhesion of pure bitumen. The optimum conditions are: 99 wt % of bitumen BND 60/90 + 1 wt % of CIRE; temperature 463 K; preparation time 60 min.

Table 3

Effect of CIRE content on BPB characteristics

BPB composition		BPB characteristics				
Bitumen content, wt %	CIRE content, wt %	Softening temperature, K	Ductility, cm	Penetration, 0.1 mm	Adhesion, %	Homogeneity
100.0	0	319	63	70	47	+
99.0	1.0	322	82	57	89	+
97.0	3.0	322	71	56	90	+
95.0	5.0	322	60	54	99	+
93.0	7.0	323	45	53	49	-

Notes: temperature of preparation is 463 K, time 60 min. Bitumen used is BND 60/90

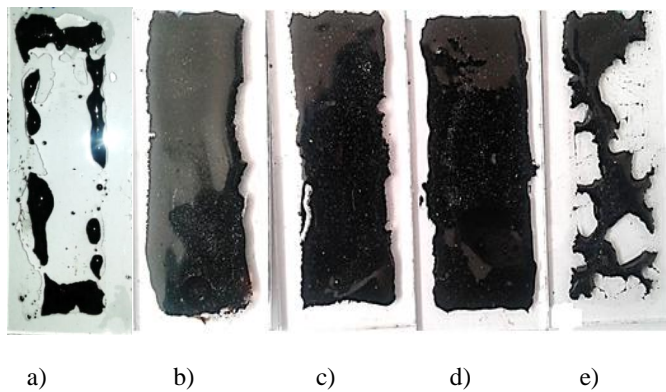


Fig. 2. BPB adhesion depending on CIRE content (wt %): 0 (a), 1.0 (b), 3.0 (c), 5.0 (d) and 7.0 (e). $T = 463\text{ K}$, $t = 60\text{ min}$

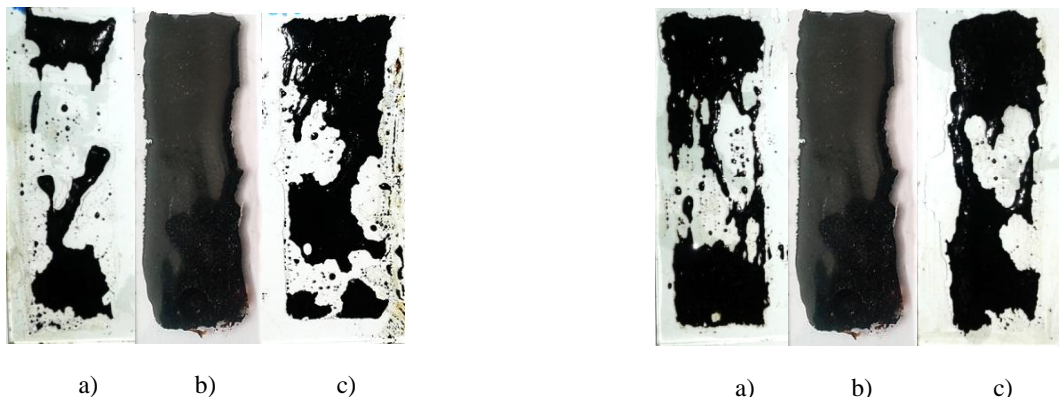


Fig. 3. BPB adhesion depending on temperature (K): 443 (a), 463 (b) and 483 (c). Bitumen: CIRE = 99:1 (w/w), $t = 60\text{ min}$

Fig. 4. BPB adhesion depending on time (min): 30 (a), 60 (b) and 120 (c). Bitumen: CIRE = 99:1 (w/w), $T = 463\text{ K}$

Table 4

Effect of temperature on BPB characteristics

Temperature, K	BPB characteristics				
	Softening temperature, K	Ductility, cm	Penetration, 0.1 mm	Adhesion, %	Homogeneity
Pure bitumen at 463 K	319	63	70	47	+
443	320	75	60	62	+
463	322	82	57	89	+
483	319	68	65	80	+

Note: BPB consists of bitumen and CIRE (99 and 1 wt %, respectively); time is 60 min

Table 5

Effect of time on BPB characteristics

Time, K	BPB characteristics				
	Softening temperature, K	Ductility, cm	Penetration, 0.1 mm	Adhesion, %	Homogeneity
Pure bitumen prepared for 60 min	319	63	70	47	+
30	322	70	67	76	+
60	322	82	57	89	+
120	320	64	71	80	+

Note: BPB consists of bitumen and CIRE (99 and 1 wt %, respectively); temperature is 463 K

Table 6

Group composition of BPB

Composition	Content, wt %			
	carbenes and carboids	asphaltenes	resins	oils
Bitumen BND 60/90, 100 %	absent	20.7	35.0	44.3
Bitumen BND 60/90 99 % + CIRE 1 %	absent	22.7	36.9	40.4

To determine the reasons for properties improvement/deterioration we studied the group composition of BPB. One can see from Table 6 that introduction of CIRE increases the quantity of asphaltenes and resins but decreases the oils content. The reason is that CIRE provides the conversion of oils into resins and then into asphaltenes. Such conversions increase adhesion, softening temperature and ductility and decrease penetration.

3.3. IR-Spectroscopic Investigations

IR spectroscopy was carried out in order to determine the role of the components in the formation of BPB. Fig. 5 represents spectra of CIRE (Fig. 5a), pure bitumen (Fig. 5b) and BPB consisting of 95 wt % of bitumen and 5 wt % of CIRE (Fig. 5c).

The presence of epoxy and hydroxy groups in CIRE (Fig. 5a) is confirmed by the absorption bands at 917 and 3400 cm^{-1} , respectively. Epoxy groups are introduced into the CIRE structure by PO molecules participated in the reaction and by GMA molecules as a result of co-oligomerization. Therefore, we suppose the CIRE molecule contains epoxy groups at the ends of the

molecule and in the side chains as well. The presence of indene molecule is confirmed by the absorption band at 755 cm^{-1} , corresponding to stretching vibrations of 1,2-disubstituted benzene. Coumarone fragment in CIRE is confirmed by absorption bands at 1050 and 755 cm^{-1} , corresponding to C–O–C bond and 1,2-disubstituted benzene, respectively.

In the spectrum of pure bitumen (Fig. 5b) we did not observe the absorption bands typical of epoxy and hydroxy groups, as well as coumarone fragments. At the same time, we observed the absorption band at 750 cm^{-1} , indicating the presence of 1,2-disubstituted benzene rings. The absorption band at 1033 cm^{-1} indicates the presence of naphthenic hydrocarbons in pure bitumen. Asymmetric stretching vibrations at 2933 cm^{-1} and symmetric deformation vibrations at 1834 cm^{-1} correspond to methyl groups in the benzene ring. The vibrations at 1603 cm^{-1} also indicate the presence of compounds consisting of benzene rings. The presence of long aliphatic fragments is confirmed by symmetric deformation vibrations of CH_2 group at 2850 cm^{-1} and asymmetric stretching vibrations of CH_3 group at 1460 cm^{-1} . The presence of substituted

benzene rings is also confirmed by stretching vibrations of CH group at 867, 816 and 748 cm^{-1} .

The identity of BPB and pure bitumen spectra (*cf.* Fig. 5c and 5b) is obvious. In the spectrum of BPB, the bands at 3400 and 917 cm^{-1} corresponding to hydroxy and epoxy groups, respectively, are absent. This indicates that at sufficiently high temperature (463 K) of BPB formation the mentioned groups react with each other and perhaps with the bitumen components, improving the properties of BPB. The band at 1050 cm^{-1} typical of coumarone is also not observed. At the same time the band at 750 cm^{-1} indicates the presence of 1,2-disubstituted fragments.

4. Conclusions

The new coumarone-indene resins with epoxy groups (CIRE) were synthesized on the basis of light fraction of coal tar and adding styrene and glycidyl methacrylate. Monoperoxide derivative of Bisphenol A

diglycidyl ether was used as a copolymerization initiator. When studying model systems, it was found that resin-forming components have different activity regarding the copolymerization with glycidyl methacrylate. The presence of indene, coumarone and styrene fragments in the synthesized resins was confirmed by IR spectroscopy.

The addition of CIRE to pure bitumen BND 60/90 significantly improves its adhesion. The optimum conditions for bitumen-polymer blends (BPB) preparation were determined: 99 wt % of bitumen BND 60/90 + 1 wt % of CIRE; the temperature of 463 K; the preparation time of 60 min. Under such condition the BPB adhesion is 89 %.

The content of asphaltenes and resins in the modified bitumen increases with the simultaneous decrease in oils content by 3.9 %. The absence of absorption bands typical of epoxy and hydroxy groups in IR spectra of BPB indicates their chemical interaction during BPB formation.

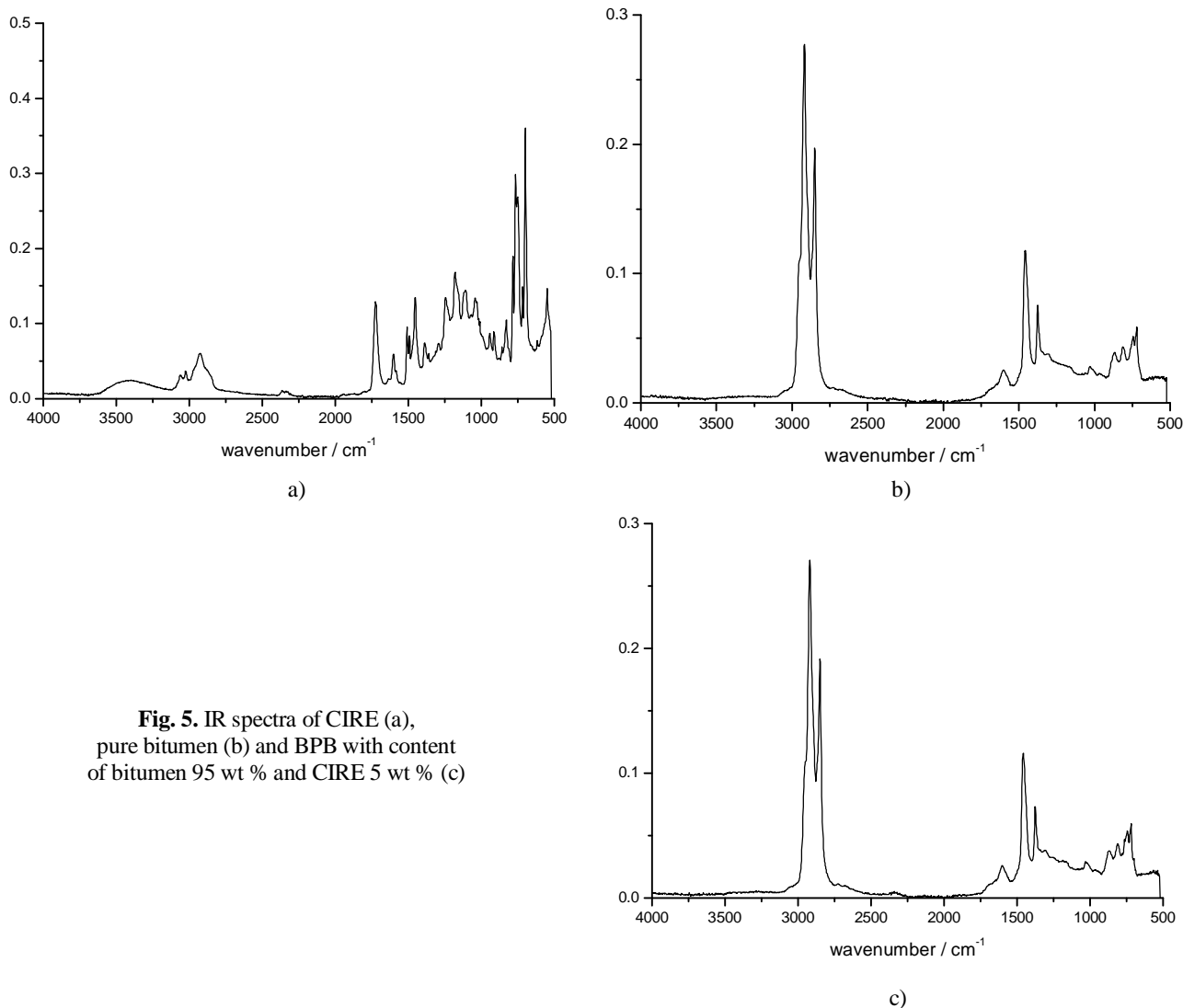


Fig. 5. IR spectra of CIRE (a), pure bitumen (b) and BPB with content of bitumen 95 wt % and CIRE 5 wt % (c)

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Acknowledgments

The work was carried out under financial support of the grant DB/Bitum No. 0117 U 004451 of the Ministry of Education and Science of Ukraine.

Received: September 02, 2018 / Revised: September 20, 2018 / Accepted: November 05, 2018

ОДЕРЖАННЯ ІНДЕН-КУМАРОНОВИХ СМОЛ З ЛЕГКОЇ ФРАКЦІЇ КАМ'ЯНОВУГІЛЬНОЇ СМОЛИ. 4. БІТУМ-ПОЛІМЕРНІ СУМІШІ ЗА УЧАСТЮ ІНДЕН-КУМАРОНОВОЇ СМОЛИ З ЕПОКСИДНИМИ ГРУПАМИ

Анотація. З використанням легкої фракції кам'яно-вугільної смоли, яка містить у своєму складі 5,75 % мас. кумарону та 44,5 % мас. індену, з додаванням гліцидилметакрилату та стиролу, з використанням як ініціатор монопероксидної похідної діглициділового етеру Бісфенол А (ПО) отримана інден-кумаронова смола з епоксидними групами (CIRE). На модельних системах, що складаються з ПО, гліцидилметакрилату, індену, або кумарону, або стиролу, або суміші вищезазначених компонентів вивчена можливість формування CIRE. CIRE вивчена як полімерний додаток до бітум-полімерних сумішей (БПС). Встановлено вплив кількості CIRE, температури та тривалості на експлуатаційні характеристики БПС. Досліджено структурно-груповий склад БПС. З використанням ІЧ-спектроскопії встановлена структура CIRE, нафтового бітуму та БПС.

Ключові слова: інден-кумаронова смола, модельні системи, епоксидні групи, бітум-полімерна суміш, ІЧ-спектроскопія.