

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

2. COUMARONE-INDENE RESINS WITH EPOXY GROUPS

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Abstract. Coumarone-indene resins with epoxy groups (CIRE) have been obtained using light fraction of coal tar or fraction with the distillation range of 423–463 K based on it. Styrene and glycidyl methacrylate were used as modifiers. CIRE were synthesized *via* radical cooligomerization using monoperoxide derivative of dioxyphenylpropane diglycidyl ether (PO) as an initiator. Thermal stability of PO has been studied. The effect of initiator amount, reaction temperature and time on the yield and softening temperature of CIRE has been determined. The structure of the synthesized CIRE was confirmed by IR and ¹H NMR spectroscopy.

Keywords: coumarone-indene resin, coal tar, glycidyl methacrylate, styrene, peroxide, thermolysis, infrared spectroscopy, ¹H NMR spectroscopy.

1. Introduction

Nowadays the polymeric (oligomeric) compounds are independently used for the production of various goods and as additives for the creation of composites [1, 2]. At the same time the increased requirements for the polymeric materials demand the creation of polymers (oligomers) with definite operational characteristics. This may be achieved *via* combining different by nature monomers which participate in the production of polymeric compound or *via* modifying the finished polymer by various additives [1].

Last decade a series of researches has been carried out in Lviv Polytechnic National University regarding the usage of industrial wastes for the production of new polymeric compounds [3–12]. These wastes contain

different by nature monomers capable of creating new polymeric compounds under certain conditions.

For instance, the so called C9 fraction is obtained after rectification of the product obtained during hydrocarbons pyrolysis to ethylene [3, 4]. The C9 fraction contains 40–70 % of unsaturated compounds; it is successfully used for the production of petroleum resins [3–12]. The introduction of functional groups, namely epoxy [5], carboxy [9], hydroxy [14] and other groups [12] into the resin structure allows to use the resins as additives when producing protective coatings [13], bitumen-polymeric mixtures [15] and different materials [16].

Indene-coumarone fraction (ICF) is produced from coal tar which is a by-product of coal coking [17]. It contains components capable of polymerization, and hence, may be used for the production of coumarone-indene resins (CIR) [17]. CIR obtained *via* ionic polymerization are used as polymeric components while creating bitumen-polymeric mixtures [18] but they have limited application due to the absence of functional groups in their structure.

Another by-product of a coking process is a light fraction of coal tar (LFCT). Similar to ICF it contains coumarone, indene, styrene and other unsaturated products and also may be used for the production of CIR. Previously we described CIR with free carboxy groups obtained from LFCT *via* radical polymerization with addition of styrene and methacrylic acid [19]. 2,2'-Azobis(2-methylpropionitrile) was used as an initiator, the process temperature was 353 K, time 6 h. The content of carboxy groups in the synthesized CIR was 13.8 %, the softening temperature 391–392 K and molecular weight 950 g/mol. The resins yield was 9.7 % relative to the initial mixture and 68 % – relative to the components capable of polymerization. When using chromatography it was established that only methacrylic acid completely undergoes a copolymerization reaction resulting in CIR formation. Styrene conversion was 40.8 %, coumarone – 30.6 %, indene – 45.2 % [19].

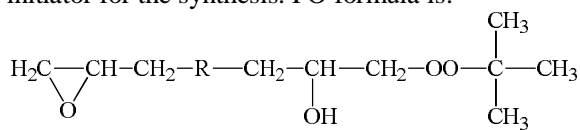
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The purpose of the present work is to obtain CIR with epoxy groups from LFCT. Glycidyl methacrylate is an additional monomer. We propose to use monoperoxide derivative of dioxyphenylpropane diglycidyl ether (PO) as an initiator for the synthesis. PO formula is:



Free epoxy group of PO is introduced into the synthesized compound and allows to obtain oligomeric products with epoxy groups. Apart from free epoxy group, PO contains labile $-\text{O}-\text{O}-$ bond. It means an additional source of free radicals stimulating the polymerization of monomers.

2. Experimental

2.1. Materials

The raw materials for CIRE synthesis were light fraction of coal tar (LFCT), produced at JSC "Zaporizhokoks" (Ukraine), and indene-coumarone fraction (ICF) with the distillation range of 423–463 K based on it. The content of the components is described in [19].

To increase the CIR yield we used styrene. It was dried before the experiments with solid alkali and then purified by distillation at 323 K under residue pressure of 300–400 Pa. Its characteristics: refractive index $n_D^{20} = 1.5471$ (literature value $n_D^{20} = 1.5468$); density $d_4^{20} = 0.650$ (literature value $d_4^{20} = 0.9059$) [20]. Glycidyl methacrylate (GMA) was a monomer with $d_4^{20} = 1.042$, $n_D^{20} = 1.449$ purchased from Aldrich. Monoperoxide derivative of dioxyphenylpropane diglycidyl ether was synthesized according to the procedure described in [21]. Its characteristics: molecular weight 420 g/mol, epoxy number 10 %, active oxygen content 2.7 %. Toluene was purchased from Aldrich. The petroleum ether was a fraction with a boiling range of 313–343 K, $d_4^{20} = 0.650$.

2.2. Analytical Determination

The number-average molecular weight (M_n) of the synthesized CIR was determined using cryoscopy in dioxane. Epoxy number (*e.n.*) was determined according to the procedure described in [22]. The softening temperature of CIR was determined using a ring-and-ball method [23].

2.3. Thermal Analyses

Thermal studies were carried out to determine the decomposition temperature of PO relative to the peroxy

group using Q-1500 D derivatograph (F.Paulik–J.Paulik–L.Erdey). The samples were analyzed under dynamic mode at the heating rate of 2.5 K/min in air atmosphere. The sample was heated to the temperature of 523 K; its weight was 300 mg. The reference substance was alumina. TG sensitivity was 100 mg, DTA sensitivity 100 μV , DTG sensitivity 500 μV .

2.4. Spectral Measurements

IR spectra of CIRE were recorded using "Specord-80" spectrophotometer (Zeiss, Germany) with the relevant absorbance range of 4000–400 cm^{-1} . The samples were dissolved in acetone and obtained films were applied over the plate with KBr (layer thickness was 0.03 mm).

H NMR spectra were recorded at 353 K using a Varian Mercury Vx Spectrometer operating at Larmor frequencies of 400 MHz. The spectral width was 6402.0 Hz, acquisition time 1.998 s and the number of recorded scans 64.

2.5. Synthesis Procedure

LFCT or ICF cooligomerization was carried out in metal ampoules by the capacity of 100 ml. The ampoules were loaded with the corresponding mixture, blown with an inert gas, closed and placed into a thermostat. After finishing the process the ampoules were cooled to room temperature and the matter was precipitated using petroleum ether. The precipitated product was dried in a vacuum oven at 313 K till the weight became constant. The yields relative to the initial reaction mixture (X_1) and main resin-formed components (styrene, indene, coumarone, GMA) (X_2) were calculated according to the formulae (1) and (2), respectively:

$$X_1 = \frac{m_r}{m_{in}} \cdot 100\% \quad (1)$$

$$X_2 = \frac{m_r}{m_{st} + m_{in} + m_{cm} + m_{GMA}} \cdot 100\% \quad (2)$$

where m_r – weight of the resulted resin, g; m_{in} – weight of the initial reaction mixture, g; m_{st} , m_{in} , m_{cm} , m_{GMA} – weights of styrene, indene, coumarone and GMA, respectively.

3. Results and Discussion

3.1. PO Thermal Stability

In order to use PO as the initiator, it is necessary to know about its thermal stability, *i.e.* the temperature under which the $-\text{O}-\text{O}-$ bonds are decomposed and free radicals are formed. The results of thermal studies are represented in Fig. 1.

Table 1

Kinetic parameters of PO thermal stability

Parameters	Values
Initial temperature of weight loss, K	393
Finishing temperature of weight loss, K	475
Maximum exoeffect, K	440
Reaction order	1.4
Z, s^{-1}	$1.33 \cdot 10^{18}$
$E, kJ/mol$	168
$k \cdot 10^2, s^{-1}$	0.89

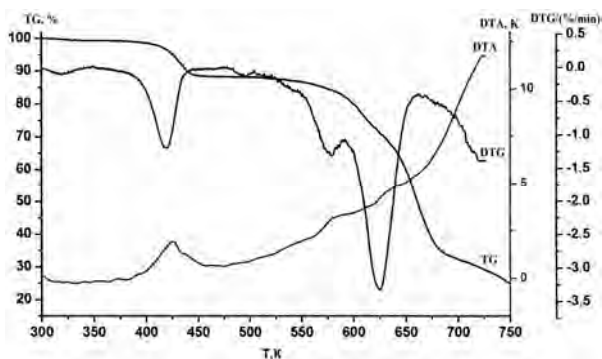


Fig. 1. TG, DTG and DTA curves for PO

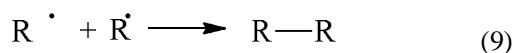
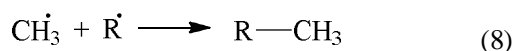
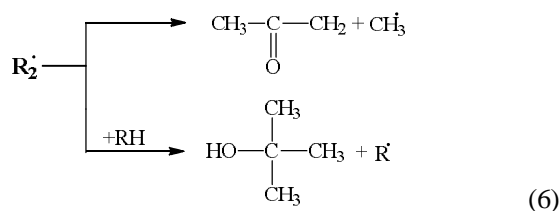
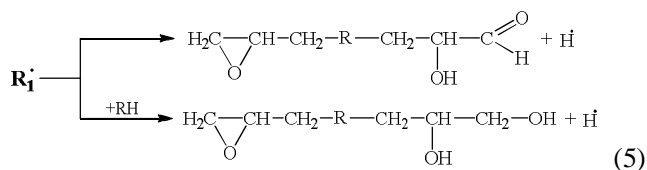
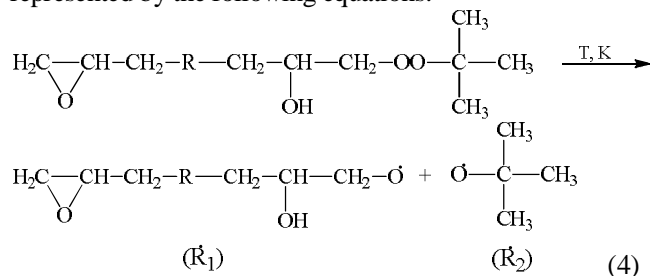
Thermolysis kinetic parameters were calculated at the stage of peroxy groups using Mathcad 2011 Professional software on the basis of the modified kinetic equation and least-squares method according to Eq. (3):

$$\ln \frac{dw}{w_k \cdot dT} = \ln \frac{Z}{q} \quad (3)$$

where w – PO weight loss at definite temperature, mg; w_k – total weight loss of PO at the definite stage, mg; Z – preexponential factor, s^{-1} ; E – activation energy, kJ/mol; R – universal gas constant ($R = 8.314 \text{ J/mol} \cdot \text{K}$); q – heating rate of PO, grad/min.

The results obtained according to Eq. (3) are represented in Table 1.

The results presented in Fig. 1 and Table 1 show that the $-\text{O}-\text{O}-$ bond in PO is decomposed already at 393 K. Moreover, the most intense decomposition with the formation of free radicals is observed at 440 K. On the basis of obtained results and literature data [24] the formation of free radicals and chemistry of PO decomposition may be represented by the following equations:



So, the PO weight loss at low temperatures occurs due to the transformation of radicals and formation of volatile products such as methane, acetone and *tert*-butyl alcohol. The formation of free radicals is observed at 393 K.

3.2. Coumarone-Indene Resins with Epoxy Groups (CIRE)

LFCT and ICF are the initial raw materials for CIRE production. To increase the resins yield we additionally used styrene. Glycidyl methacrylate (GMA) was used as a monomer to impart functionality to CIRE, *i.e.* to introduce epoxy groups into CIRE structure. PO as a 50% solution was used as an initiator for the monomers which are contained in LFCT or ICF, styrene and GMA.

To develop the procedure for CIRE synthesis in the presence of PO it was necessary to study the effect of initiator amount, the reaction temperature and time on the CIRE yield. The investigated mixture consists of (mass parts): 45.2 of LFCT, 5.45 of styrene and 4.2 of GMA. The experiments were carried out according to the procedure described in Subsection 2.5 and the results are represented in Figs. 2-4 and Table 2.

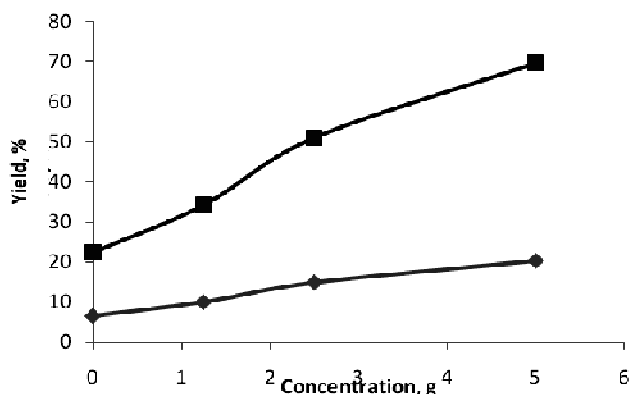


Fig. 2. The effect of PO amount on CIRE yield relative to the initial mixture (1) and resin-formed components (2) at 393 K and reaction time of 6 h. PO amount (50% toluene solution) was calculated relative to 54.85 mass parts of the initial mixture

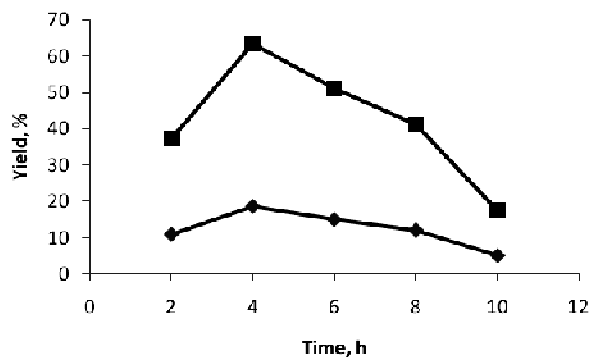


Fig. 3. The effect of process time on CIRE yield relative to the initial mixture (1) and resin-formed components (2) at 393 K. PO amount (50 % toluene solution) is 2.5 mass parts relative to 54.85 mass parts of the initial mixture

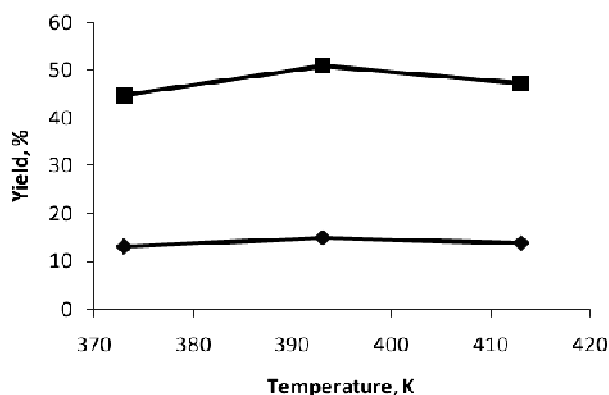


Fig. 4. The effect of process temperature on CIRE yield relative to the initial mixture (1) and resin-formed components (2) for the reaction time of 6 h. PO amount (50 % toluene solution) is 2.5 mass parts relative to 54.85 mass parts of the initial mixture

The results from Fig. 2 show that at 393 K even in the absence of PO the coumarone-indene resins are formed. It means that the monomers in the initial mixture are capable to form resins at this temperature according to the above-mentioned scheme. When using PO as the initiator, CIRE yield is increased. This fact confirms the assumption that apart from thermal polymerization of the mixture components, the initiation polymerization takes place as well due to the decomposition of PO molecules according to Eqs. (4)-(9) resulting in formation of free radicals. At the same time PO fragments are introduced into the structure of resulting resin.

Fig. 3 demonstrates the effect of the process time on the CIRE yield. The highest yield is achieved at the process time of 4–6 h (Fig. 3). Further increase in the process time decreases the yield. This fact is explained by destruction processes occurred at high temperature (393 K) and formation of low-molecular products soluble in petroleum ether and hence incapable of precipitation.

The reaction temperature also affects the CIRE yield (Fig. 4). The increase in temperature from 373 to 393 K increases the CIRE yield. Further increase to 413 K decreases the yield of the target product. The reason is deactivation of free radicals at high temperature (*vide* Eqs. (4)-(9)), and as a result, the reduction of the share of the reaction leading to the CIRE formation.

The values of the softening temperature of the synthesized CIRE are given in Table 2.

Thus, the following optimal conditions for CIRE synthesis are proposed: the reaction temperature 393 K, reaction time 6 h and PO amount (50 % toluene solution) 2.5 mass parts relative to 54.85 mass parts of the initial mixture based on LFCT.

Coumarone-indene resin with epoxy groups (CIRE-3) synthesized under optimal conditions is characterized by the yield of 14.9 and 51.1 % relative to the initial mixture and resin-formed compounds, respectively; softening temperature of 336 K; molecular weight of 1400 g/mol and epoxy number of 2.3 %.

Next we studied the effect of components ratio on the CIRE yield and the softening temperature using the fraction 423–463 K (ICF) distilled off LFCT (Table 3).

The lowest yields of the finished resin (Table 3) were found for the resin CIRE-12 synthesized in the absence of GMA in the initial mixture. At the same time the simultaneous increase in GMA amount and decrease in styrene amount increases resin yield indicating the essential influence of GMA. We cannot compare softening temperatures of the products which were synthesized using LFCT and ICF because the latter ones were viscous compounds.

Table 2

Softening temperatures of the synthesized CIRE

Synthesis conditions			CIRE symbol	Softening temperature, K
Temperature, K	Time, h	PO amount, mass parts		
393	6	0	CIRE-1	349
393	6	1.25	CIRE-2	337
393	6	2.50	CIRE-3	336
393	6	5.00	CIRE-4	376
393	2	2.50	CIRE-5	308
393	4	2.50	CIRE-6	325
393	8	2.50	CIRE-7	315
393	10	2.50	CIRE-8	–
373	6	2.50	CIRE-9	325
413	6	2.50	CIRE-10	335

Notes: The initial mixture consists of (mass parts): LFCT 45.2, styrene 5.45 and GMA 4.2. PO is used as 50 % toluene solution.

Table 3

Characteristics of CIRE based on ICF

Composition of the initial mixture, mass parts				CIRE characteristics			
ICF	Styrene	GMA	PO	CIRE symbol	Yield relative to the initial mixture, %	Yield relative to the resin-formed compounds, %	Softening temperature, K
45.2	5.45	4.20	2.5	CIRE-11	18.30	37.60	viscous compound
45.2	9.09	–	2.5	CIRE-12	6.07	12.30	viscous compound
45.2	7.27	2.08	2.5	CIRE-13	10.30	20.90	viscous compound
45.2	3.64	6.25	2.5	CIRE-14	19.40	40.00	viscous compound

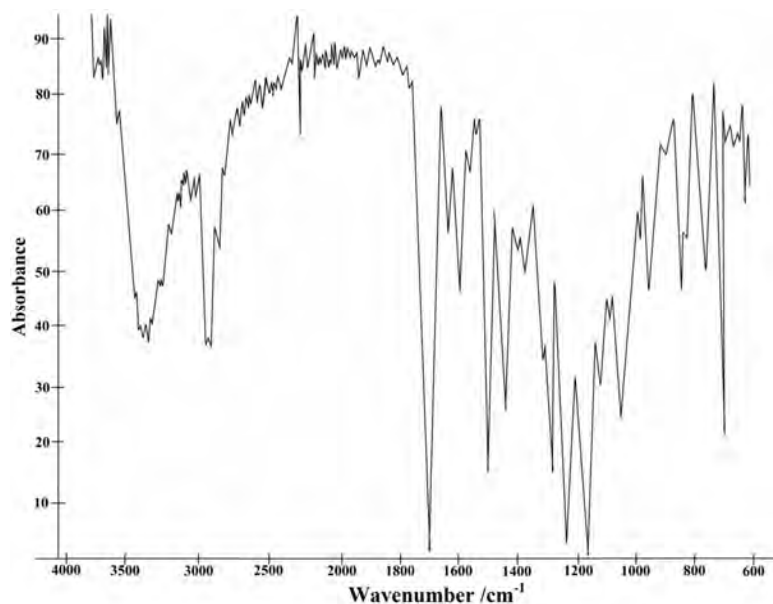


Fig. 5. IR-spectrum of CIRE-11

3.2.1. Spectroscopic Investigations

IR-spectroscopy was used to confirm the structure of the synthesized resins. The investigations were carried out according to the procedure described in Subsection 2.4. The spectra were recorded for CIRE-11. The results are represented in Fig. 5.

The presence of epoxy groups in the synthesized resin is confirmed by the absorption band at 944 cm^{-1} . The presence of OH group in coumarone-indene resin formed due to the initiation of unsaturated compounds in the initial mixture by PO is confirmed by the absorption band

at 3368 cm^{-1} . Moreover, the $\text{H}_3\text{C}-\overset{\text{H}_3\text{C}}{\underset{\text{H}_3\text{C}}{\text{C}}}-\text{CH}_3$ fragment in the resin structure is confirmed by gel-dimethyl vibrations at 1384 and 1356 cm^{-1} ; the etheric bond – at 1172 cm^{-1} ; benzene rings – at 1600 and 1512 cm^{-1} . The entering of GMA molecule with the ester bond into the resin structure is confirmed by absorption bands at 1720 , 1244 and 1046 cm^{-1} .

Thus, the investigation results confirm the presence of epoxy groups in the CIRE structure. We also observe

PO fragments in the spectra. On the other hand, taking into account Eq. (4) we may assert that epoxy groups in CIRE structure are introduced by the fragments of an initiator. The initial reaction mixture contains GMA which enters the resin structure during copolymerization and thus introduces epoxy groups as well.

To establish the role of the initiator and GMA in the process of resin formation we carried out the experiments with the mixture based on ICF. The composition of the mixture is given in Table 4.

One can see from Table 4 that the reaction mixture used for the CIRE-15 synthesis does not contain GMA. PO with epoxy groups in its composition is the initiator. In the case of CIRE-16 the reaction mixture contains GMA but the initiator is AMP without epoxy groups. According to the obtained results we assume that PO provides the presence of epoxy group in the structure of CIRE-15. As for CIRE-16, the epoxy groups may occur due to the introduction of GMA fragments into the resin structure.

To confirm the above-mentioned assumption we carried out $^1\text{H NMR}$ spectroscopic investigations with the synthesized resins CIRE-15 and CIRE-16. The results are represented in Figs. 6 and 7.

Table 4

Composition and synthesis conditions of the reaction mixture and CIRE characteristics

Composition of the initial mixture, mass parts					Copolymerization conditions		CIRE symbol	Yield relative to the initial mixture	
ICF	Styrene	GMA	PO	AMP	Temperature, K	Time, h		g	%
118	47	–	7.9	–	403	7	CIRE-15	36.6	22.2
45	15	5	–	0.6	353	8	CIRE-16	19.5	29.7

Note: PO is used as 50 % solution in toluene; AMP –2,2'-azobis(2-methylpropionitrile) as 0.2 M solution in toluene

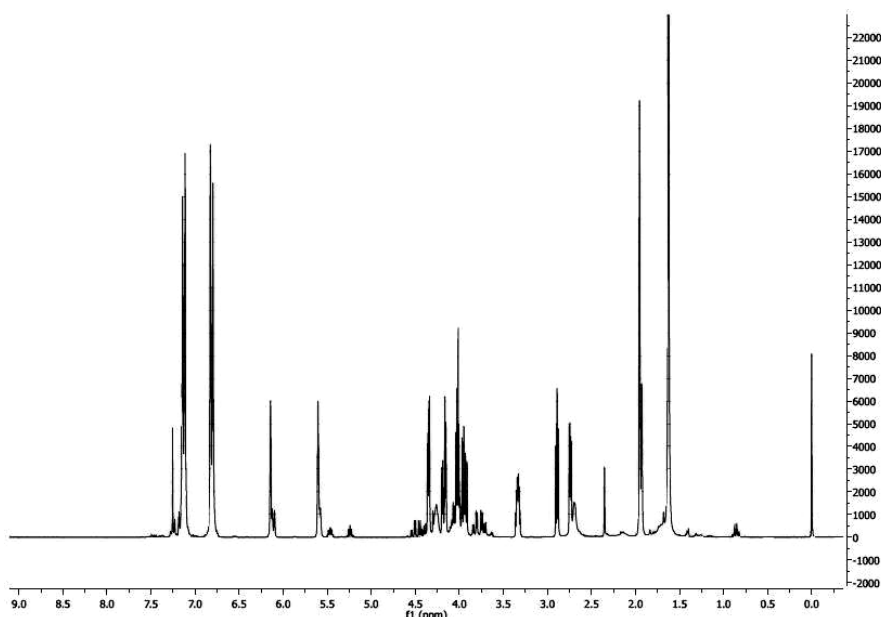


Fig. 6. $^1\text{H NMR}$ spectra of CIRE-15

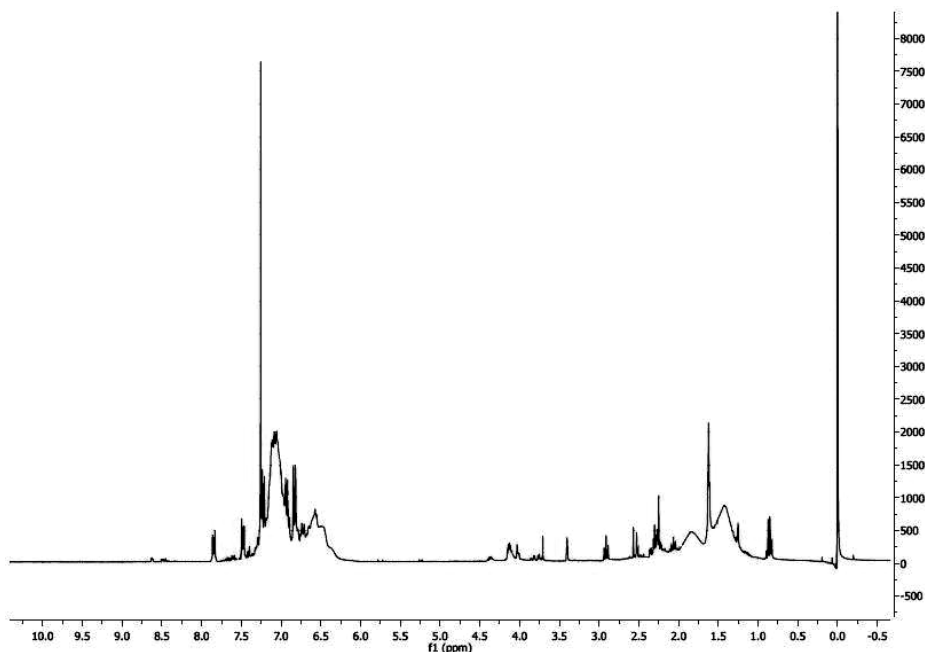

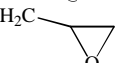




Fig. 7. ^1H NMR spectra of CIRE-16

The analysis of CIRE-15 which was synthesized using PO as the initiator in the absence of GMA shows in the spectrum (Fig. 6) the chemical shifts of protons at 2.25–2.30 ppm corresponding to  group and shifts

at 2.50–2.90 ppm typical of  group. These shifts


indicate the presence of free epoxy groups in the molecule of CIRE-15. At the same time we observe chemical shifts at 1.76 and 1.25–1.30 ppm corresponding to


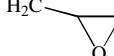
 and $(\text{CH}_3)_3\text{C}-$ groups, respectively. This fact

confirms the participation of  and $(\text{CH}_3)_3\text{CO}^\cdot$

radicals formed due to the PO decomposition in the formation of CIRE-15. The presence of $-\text{CH}_2\text{O}-$ bond introduced into the resin structure is confirmed by the signals at 3.60–4.30 ppm; aromatic rings – at 6.80–7.20 ppm. The experimental results show that PO plays a double role in a copolymerization process. On the one hand, it is the source of free radicals which initiate polymerization of unsaturated compounds contained in the initial mixture; on the other hand PO introduces epoxy groups into the resin molecule.

CIRE-16 was obtained using AMP as the initiator; GMA was a carrier of epoxy groups (Table 4). We observe in the spectrum (Fig. 7) no chemical shifts at 1.25–1.30 and 1.60–1.75 ppm, indicating the absence of

$(\text{CH}_3)_3\text{C}$ and  fragments, respectively. At the

same time the spectrum of CIRE-16 contains the proton signals at 2.30 and 2.40–2.80 ppm corresponding to the protons in  and  groups, respectively.

These signals indicate the presence of free epoxy groups which are introduced into the resin structure due to the entering of GMA molecules. The proton signals at 3.65–4.30 ppm typical of $-\text{CH}_2\text{O}-$ group also confirm this fact. The presence of aromatic rings is proved by the proton signals at 6.80–7.20 ppm.

The obtained results specify that when we use PO as the initiator for copolymerization of the mixture consisting of LFCT or ICF, styrene and GMA we obtain CIRE with epoxy groups at the ends of the molecule and in the side branches.

4. Conclusions

New coumarone-indene resins with epoxy groups (CIRE) were obtained using the light fraction of coal tar (LFCT) or the fraction with the distillation range of 423–463 K (ICF), with the addition of styrene and glycidyl methacrylate (GMA), in the presence of monoperoxide derivative of dioxyphenylpropane diglycidyl ether (PO) as the initiator. Thermogravimetric investigations prove the decomposition of peroxy groups in PO at 393 K. We propose the chemistry of PO decomposition followed by

the formation of radicals and their deactivation. On the basis of studied effect of the initiator amount, the reaction temperature and time the conditions for CIRE synthesis were determined: the temperature of 393 K, time 6 h and PO amount 2.5 mass parts as 50% toluene solution relative to 54.85 mass parts of the initial mixture. The mixture consists of (mass parts): LFCT 45.2; styrene 5.45; GMA 4.2. CIRE obtained under optimal conditions has the following characteristics: the yield of 14.9 % relative to the initial mixture, the yield of 51.1 % relative to the resin-formed components, softening temperature of 336 K, epoxy number of 2.3 % and molecular weight of 1400 g/mol. The presence of epoxy groups in the synthesized resins is confirmed by IR-spectroscopy (absorption band at 944 cm⁻¹). ¹H NMR spectroscopy demonstrates that the synthesized resins have epoxy groups at the ends of oligomeric chain and side branches.

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ОДЕРЖАННЯ ІНДЕН-КУМАРОНОВИХ СМОЛ З ЛЕГКОЇ ФРАКЦІЇ КАМ'ЯНО-ВУГІЛЬНОЇ СМОЛИ

2. ІНДЕН-КУМАРОНОВІ СМОЛИ З ЕПОКСИДНИМИ ГРУПАМИ

Анотація. З використанням легкої фракції кам'яно-вугільної смоли та отриманої на її основі фракції, що википає за температур 423–463 K з додаванням стиролу і гліцидилметакрилату розроблений метод одержання інден-кумаронових смол з епоксидними групами (ІКСЕ). ІКСЕ отримані за радикальною колігомеризацією з використанням як ініціатор монопероксидної похідної дигліцидилового етеру діоксидифенілпропану (ПО). Вивчена терміна стабільність ПО. Встановлено вплив кількості ініціатора, температури та тривалості реакції на вихід та температуру розм'якшення ІКСЕ. Структура синтезованих ІКСЕ підтверджена ІЧ- та ¹H ЯМР спектроскопічними дослідженнями.

Ключові слова: інден-кумаронова смола, кам'яно-вугільна смола, стирол, малеїновий ангідрид, гліцидилметакрилат, пероксид, термоліз, ІЧ-спектроскопія, ¹H ЯМР-спектроскопія.