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MODIFIED PHENOL-FORMALDEHYDE RESINS AND THEIR APPLICATION IN BITUMEN-POLYMERIC MIXTURES

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Abstract. Phenol-formaldehyde resins (PhFR) with reactive methacrylate fragments or labile peroxy bonds in the side branches used as a polymeric component of bitumen-polymeric mixtures have been investigated. Taking into account that PhFR with peroxy fragments based on epoxy resin does not described in literature, its synthesis procedure has been developed. The kinetic regularities of the reaction between peroxy derivative of epoxy resin (PDER) and phenol group of PhFR were studied taking the reaction of PDER with phenol as an example. The structure of PhFR with peroxy groups (PhFRP) has been confirmed by IR-studies. Bitumen-polymeric mixtures with PhFRP or PhFR with unsaturated fragments (PhFRU) in the amount of 1, 3, 5 or 7 mass parts per 100 g of petroleum bitumen were examined at 443, 463 or 483 K for 0.5, 1.0 or 2.0 h. The composition of bitumn-polymeric mixtures has been determined using the group analysis.

Keywords: phenol-formaldehyde resin, modification, peroxide, unsaturated bond, kinetics, IR-spectroscopy, bitumen-polymeric mixtures, group analysis.

1. Introduction

Petroleum bitumen is a mixture of various high-molecular hydrocarbons and heteroatomic compounds containing atoms of oxygen, sulphur, nitrogen and different metals (vanadium, iron, sodium, nickel *et al.*) [1]. Oils, resins, asphaltenes, asphaltogenic acids and other components presented in the bitumen structure affect the bitumen properties. Oils decrease hardness and softening temperature and increase its flowability. Resins improve bitumen plasticity and stretching. Asphaltenes increase hardness and brittleness. Asphaltogenic acids and their anhydrides favor the stabilization of bitumen colloidal structure [1].

The main quality indexes of the commercial petroleum bitumen are penetration, softening temperature, ductility and others [1, 2]. Moreover, adherence is a very important property of road bitumen [3]. The operational properties of the commercial bitumen may be improved by introducing polymers to its structure [4].

To create the bitumen-polymeric mixtures the following polymers are used nowadays: elastomers [5, 6], thermoplastics [7], thermoplastic elastomers [6], thermoreactive resins and others [4].

In this work we studied the possibility of bitumen properties improvement *via* creation of bitumen-polymeric mixtures based on modified phenol-formaldehyde resins (PhFR). The compounds of the structure given below were used as modified PhFR.

The modified PhFR contain reactive methacrylate fragments or labile peroxy bonds in the side branches. The unsaturated double bonds may enter the polymerization reaction at heating and form more compound structures. Peroxy groups which are present in the resin structure will decompose at heating above 393 K and form free radicals. Due to the radicals recombination they react with the components of bitumen-polymeric mixture and between each other forming the products with more compound structure.
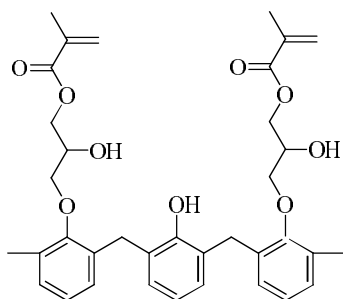
PhFR with methacrylate fragment (PhFRU) was synthesized by us and described in [8, 9]. PhFR with labile peroxy groups in the side branches (PhFRP) is not described in literature and its synthesis is represented in this work.

where R= or

R'= or
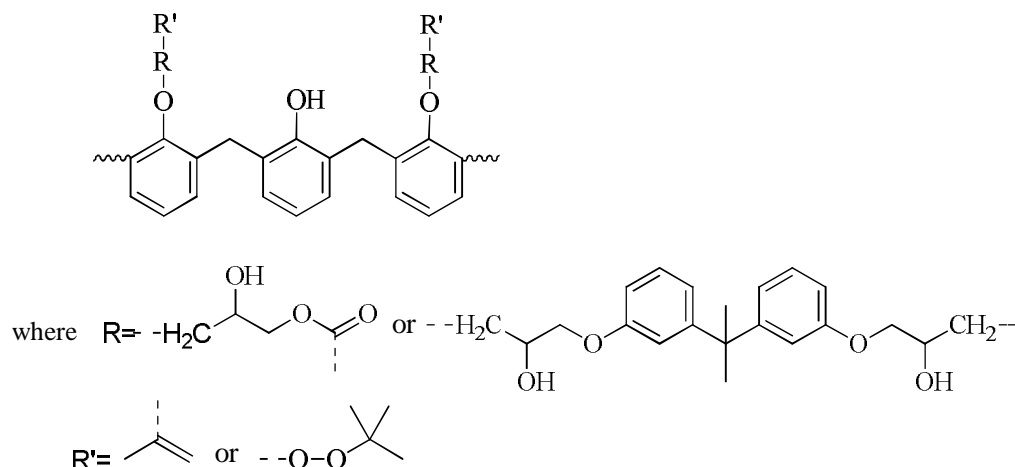
2. Experimental

2.1. Materials

PhFRU formula is:

It was synthesized from PhFR and glycidyl-methacrylate using the procedure described in [8]. Its molecular mass was found to be 640 g/mol. The presence of methacrylate fragments in PhFRU is confirmed by the presence of absorption bands at 1296, 1630 and 1712 cm^{-1} in IR-spectrum. These bands correspond to the stretching vibrations of the so-called "esteric band", double bond and carbonyl groups in esters.

PhFR used for PhFRU and PhFRP syntheses was synthesized in accordance with [10]. Its M_n is 350 g/mol. The peroxy derivative of epoxy resin used for PhFRP production was synthesized in accordance with [11]. Its M_n = 420 g/mol; epoxy number (*e.n.*) = 9.0 % and active oxygen content ($[O]_{act}$) = 2.9 %.

Phenol (Ph) used for PhFR synthesis and for the reaction with PDER was purified in accordance with the method [10]. Potassium hydroxide of PA grade was used as a catalyst. Isopropyl alcoghol was used as a reaction medium.

Bitumen was withdrawn at Lviv asphalt plant (Lviv, Ukraine) with the following characteristics: penetration 44x0.1 mm; ductility 89 cm, softening temperature by the "ring and ball" method 319 K, adherence 40.5 %.

2.2. Analyses Methods

The number-average molecular masses of PhFR and synthesized PhFRP were determined by cryometry using dioxane as the solvent. The epoxy number was determined using a procedure described in [10].

Infrared spectra (IR) were obtained using "Specord-M40" apparatus (Bruker firm, Germany). The sample was prepared as the film formed from the oligomer solution in acetone and applied over a plate with KBr (layer thickness was 0.023 mm). Spectra were recorded in the absorption range of 4000–400 cm^{-1}.

The softening temperatures of bitumen and bitumen compositions were determined using the "ring and ball" method [12]; ductility and penetration – [12]; "adherence with glass" – [1]. The content of asphaltenes, neutral resins and oils was determined in accordance with the procedure [13, 14].

2.3. Kinetics Study of the Reaction between Ph and PDER

The chemical modification of phenol with PDER was studied in a three-necked reactor equipped by a mechanical stirrer, backflow condenser and thermometer. Phenol, KOH (as a catalyst) and isopropyl alcohol were loaded into the reactor. The mixture was heated to 313, 323 or 333 K under constant stirring and then PDER was added. The reaction proceeding was controlled by the change of epoxy groups concentration (mol/l) using the formula:

$$[C]_{e.g.} = \frac{[V_{b.t.} - (V_t - V_a)] \cdot N \cdot K}{V_s} \qquad (1)$$

where $V_{b.t.}$ – amount of 0.1 N alkali solution for blank test titration, ml; V_t – amount of 0.1 N alkali solution for

withdrawn sample titration, ml; V_a – amount of 0.1 N alkali solution for the acidity determination, ml; N – solution normality; K – correction factor for the titre of 0.1N alkali solution; V_s – sample volume, ml.

The obtained results were used for the construction of graphical dependency and calculations of the effective rate constants. The effective activation energy was determined by interpretation of the obtained results in the Arrhenius coordinates.

2.4. PhFRP Synthesis

For the synthesis the same laboratory plant was used. PhFR, KOH and isopropyl alcohol were loaded into the reactor. The mixture was heated to 323 or 333 K under constant stirring and then PDER was added. The reaction mixture was transferred into a dividing funnel, neutralized by weak solution of acetic acid and washed by water. The obtained product was vacuumed and dried. The epoxy number (%) and content of active oxygen (%) were determined in accordance with the formulas (2) and (3):

$$e.n. = \frac{[V_{b.t.} - (V_t - V_a)] \cdot 0.0043 \cdot K \cdot 100}{g} \quad (2)$$

where $V_{b.t.}$ – amount of 0.1 N alkali solution for blank test titration, ml; V_t – amount of 0.1 N alkali solution for sample titration, ml; V_a – amount of 0.1 N alkali solution for the acidity determination, ml; 0.0043 – amount of epoxy groups corresponded to 1 ml of 0.1 N alkali solution; K – correction factor for the titre of 0.1N alkali solution; g – PDER mass, g.

$$[0]_{act} = \frac{(V - V_{b.t.}) \cdot 0.08 \cdot K \cdot 100}{m} \quad (3)$$

where V – amount of 0.1 N sodium thiosulphate solution necessary for the sample titration, ml; $V_{b.t.}$ – amount of 0.1 N sodium thiosulphate solution for blank test titration, ml; 0.08 – amount of oxygen corresponded to 1 ml of 0.1 N sodium thiosulphate solution; m – sample mass, g; K – correction factor for the titre.

A three-necked reactor equipped with a mechanical stirrer, backflow condenser and thermometer was loaded by 50 g of PhFR dissolved in 100 ml of isopropyl alcohol. The mixture was heated to 323 K under constant stirring. Then 10.46 g of KOH dissolved in 40 ml of isopropyl alcohol were added. The homogeneous solution was obtained and 111.64 g of PDER dissolved in 150 ml of isopropyl alcohol were added to it under stirring. The reaction mixture was sustained for 6 h at 323 K under stirring, cooled and 500 ml of toluene was added. After this the mixture was transferred into a dividing funnel where it was washed with 10%-aqueous solution of acetic acid and then by water till the neutral reaction. PHFRP was obtained after vacuumization of the organic layer at 320 K and residual pressure of 2.7–4 kPa till the mass

becomes constant. We obtained 136.8 g of hazel-colored oligomeric product. Its $M_n = 750$ g/mol and $[O]_{act} = 1.2$ %. It is soluble in the majority of organic solvents.

## 2.5. Preparation of Bitumen-Polymeric Mixtures

Bitumen-polymeric mixtures were prepared at the laboratory plant, the scheme of which is described in [15].

100 g of bitumen were loaded into a metal vessel and heated to 383 K under stirring. PhFRP in the amount of 1–7 mass parts relative to 100 g of bitumen was added, heated to 423–483 K and sustained for 1–3 h. The softening temperature, ductility, penetration and adherence with glass of bitumen-polymeric mixtures were determined.

3. Results and Discussion

3.1. Kinetic Regularities of the Reaction between Ph and PDER

Taking into account that kinetics study of the reaction between PhFR and PDER causes difficulties, it was examined taking the reaction between Ph and PDER as an example:
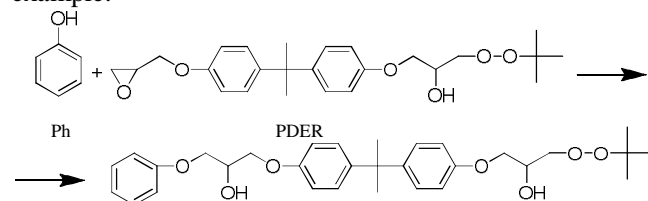
The investigations were carried out in accordance with the technique present in Subsection 2.3. The obtained results are represented in Figs. 1-3 ad Table 1.
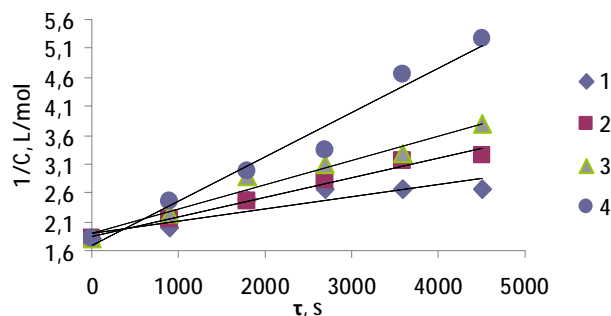

Fig. 1. Kinetic anamorfozes in the 1/C–τ coordinates for the reaction between Ph and PDER at 333 K in the isopropanol medium. KOH amount is: 0.2 (1); 0.4 (2); 0.6 (3) and 0.8 (4) moles per Ph phenol group. PDER amount is 1.0 mol/phenol mol

The highest reaction rate for the reaction between Ph and PDER is observed in case of 0.8 KOH moles per Ph phenol group. On the other hand, 0.6 moles of the catalyst realizes the mentioned reaction with the effective rate constant $K_{ef} = (4.0\pm0.19)\cdot10^{-4}$ l/(mol·s) (Table 1). Therefore the influence of temperature on the reaction rate we studied with the catalyst amount of 0.6 mol per Ph phenol group (Fig. 2).

As it was expected, the decrease of temperature decreases the effective rate constant (Table 1). The reason of temperature decrease is also the fact that peroxy groups are unstable in the presence of alkali and may decompose already at 323 K [16].

The interpretation of the obtained results in the Arrhenius coordinates (Fig. 3) determines the effective activation energy. For the reaction between Ph and PDER it was found to be 70.30 ± 1.05 kJ/mol.

Table 1

**Effective rate constants
of the reaction between Ph and PDER**

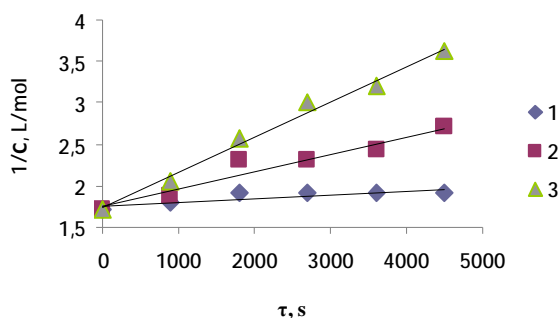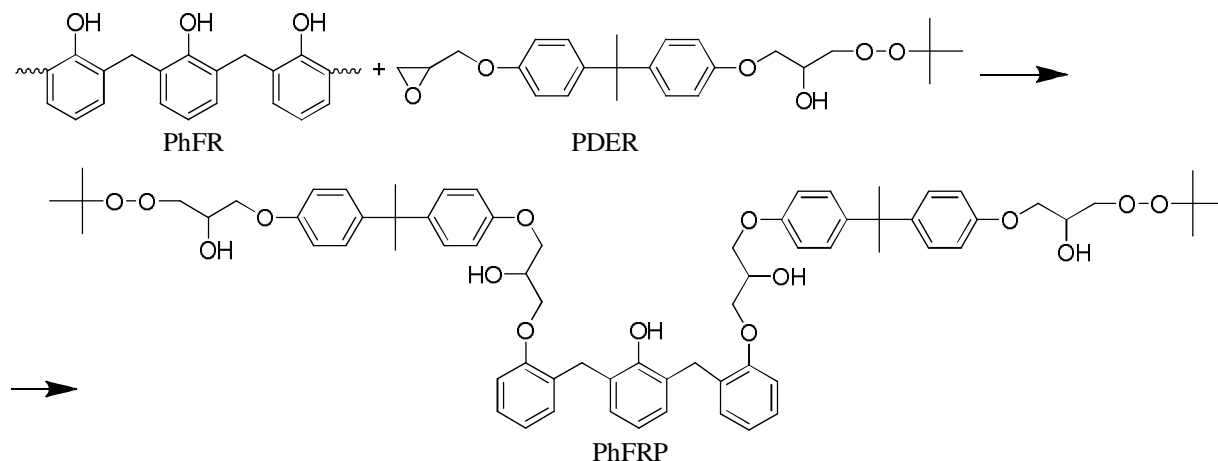| KOH amount per one phenol group, moles	Reaction temperature, K	$K_{ef}\cdot10^4$, l/(mol·s)
0.2	333	2.00±0.04
0.4	333	3.00±0.08
0.6	333	4.00±0.19
0.8	333	8.00±0.16
0.6	313	0.40±0.02
0.6	323	2.00±0.05

Note: isopropyl alcohol is a medium

Fig. 2. Kinetic anamorfozes in the 1/C–τ coordinates for the reaction between Ph and PDER in the isopropanol medium at KOH amount of 0.6 mol/phenol group. PDER:Ph molar ratio is 1.0:1.0. Temperature: 313 (1); 323 (2) and 333 (3)

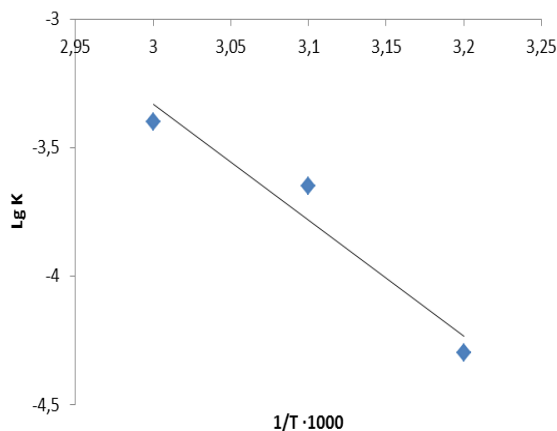**Fig. 3.** Dependence of lg$K$ on 1/T for the reaction between Ph and PDER in the isopropanol medium. KOH amount is 0.6 mol/phenol group and PDER amount is 1.0 mol

The obtained results were used for the investigations of the reaction proceeding between PhFR and PDER.

3.2. Regularities of the Reaction between PhFR and PDER

The reaction proceeds in accordance with the following equation:

Synthesis conditions and characteristics of the reaction products

KOH moles per PhFR phenol group	PhFR:PDER ratio, moles	Reaction temperature, K	Reaction time, h	Characteristics of the obtained products		
				e.n., %	[O]$_{act}$, %	Yield, %
0.6	1.0 : 0.5	323	0.5	2.2	1.8	90
0.6	1.0 : 0.5	323	1.0	1.4	1.6	90
0.6	1.0 : 0.5	323	2.0	1.2	2.0	64
0.6	1.0 : 1.0	333	2.0	–	1.8	50
0.4	1.0 : 0.5	323	0.5	3.4	1.2	98
0.4	1.0 : 0.5	323	3.0	2.3	1.1	98
0.4	1.0 : 0.5	323	5.0	0.2	1.6	87
0.4	1.0 : 0.5	323	6.0	–	1.2	85
0.2	1.0 : 0.5	323	5.0	1.4	1.3	100

Note: isopropyl alcohol is a medium
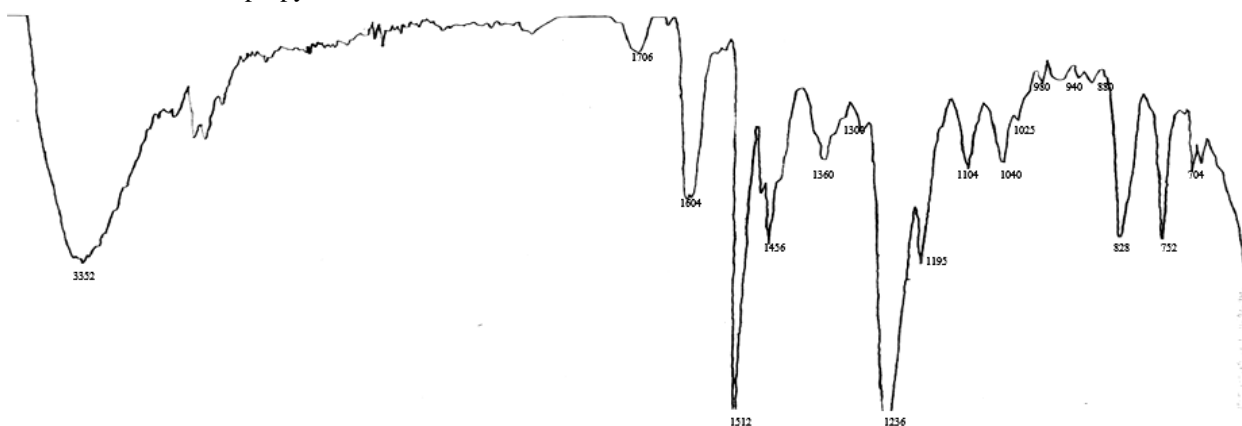
Fig. 4. IR-spectrum of PhFRP
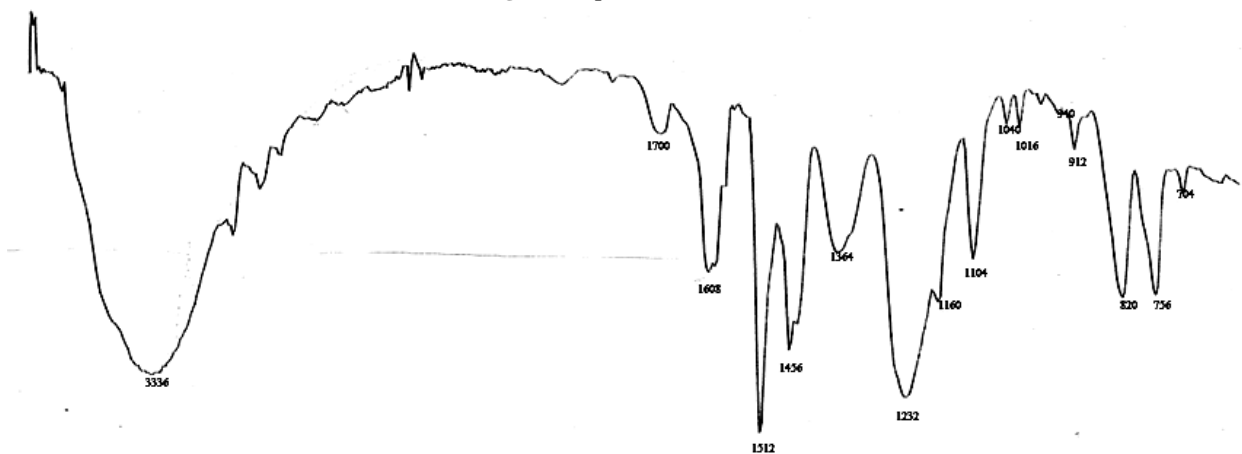
Fig. 5. IR-spectrum of PhFR

One can see that complex systems are used for this reaction. They contain different by nature functional groups that create difficulties during kinetic investigations. Therefore, taking into account the results represented in the Subsection 3.1, we carried out our experiments in accordance with the procedure described in Subsection 2.4. It was necessary to establish the effect of potassium hydroxide amount, the initial reagents ratio, process temperature and time on the characteristics of the obtained mixture. The experimental results are represented in Table 2.

One can see that at 323 K, KOH amount of 0.4 mol, PhFR:PDER ratio of 1.0:0.5 or 1.0:1.0 and process time of 5-6 h the obtained product does not contain epoxy groups. It indicates the complete joining of PDER molecules to the PhFR molecules. The same result we obtained in case of 333 K, KOH amount of 0.6 mol, PhFR:PDER ratio of 1.0:1.0 and process time of 2.0 h. But in that case the product yield is only 50 % (Table 2).

Taking into account all mentioned above, the following conditions of PhFRP synthesis were proposed: temperature 323 K, KOH amount 0.4 mol, PhFR:PDER ratio 1.0:0.5 and process time 6 h.

3.3. PhFRP Synthesis and Characteristics

PhFRP structure was confirmed by IR-spectroscopy. IR-investigations of the initial PhFR were carried out for the comparison.

In the IR-spectrum (Fig. 4) the absorption band at 910 cm^{-1} is not observed indicating the absence of epoxy groups in PhFRP. At the same time, the absorption band at 880 cm^{-1} is observed in IR-spectrum of PhFRP compared with that of PhFR (Fig. 5). This band is typical of stretching vibrations of –O–O– bond and confirms the presence of peroxy groups in the synthesized product. The shift of the decreased absorption band to 3352 cm^{-1} reveals about incomplete substitution of phenol OH-groups for PDER fragments and appearance of the secondary hydroxyl groups due to joining PDER molecules with PhFR ones. The appearance of absorption band at 1025 cm^{-1} also confirms the above-mentioned fact. This band corresponds to the stretching vibrations ν_{c-o} typical of =C–O–C= group. The presence of secondary hydroxyl groups formed due to joining PDER molecules with PhFR is confirmed by absorption band at 1300 cm^{-1} (Fig. 4).

3.4. Bitumen-Polymeric Mixtures

Bitumen-polymeric mixtures were studied in accordance with the procedure described in Subsection 2.4. The described above PhFRU and PhFRP were used as polymeric components. The conditions of mixtures preparation and their characteristics are given in Table 3.

The introduction of PhFRU into the mixture decreases ductility and penetration but increases the mixture adherence. The increase of PhFRU amount leads to the further decrease of ductility and penetration, and to the increase of adherence. At the same time the softening temperature remains constant. Therefore, taking into account the operational characteristics of bitumen-polymeric mixtures, the amount of PhFRU equals to 3 mass parts per 100g of the initial bitumen was found to be the optimum one.

The decrease of preparation time to 0.5 h slightly increases ductility and remains penetration at the constant level but considerably decreases adherence to glass. On the contrary, the increase of preparation time to 2 h decreases ductility by 5 times and penetration – by 1.5 times, the maximum value of the adhesion to glass being achieved.

The same results are observed at the increase and decrease of the process temperature. The increase of temperature to 443 K leads to the formation of mixtures with the adherence 73.2; temperature increase to 483 K – 99.9 %. The other values, such as ductility and penetration in any case (decrease or increase of temperature) are considerably less compared with those for bitumen without PhFRU. Using non-modified initial PhFR in the mixtures (sample 10) does not improve any operational characteristics of the polymeric mixtures (Table 3).

The preparation conditions and characteristics of bitumen-polymeric mixtures based on PhFRP are given in Table 4. The mixtures with the initial PhFR were investigated for the comparison.

One can see from Table 4 that the increase of PhFRP amount increases adherence to glass but decreases penetration (the same as in a previous case). The peculiarity of PhFRP use in the mixtures is that at PhFRP amount of 1 mass part per 100 g of bitumen not only adherence is doubly increased but ductility is increased as well. This regularity is preserved at heating during 0.5 h but adherence is insignificantly decreased. At heating to 443 K the ductility increases but adherence remains at the level of pure bitumen (48.8 %). The increase of temperature to 483 K decreases mixture ductility almost twice at the high level of adherence (99.9 %).

The initial PhFR without PDER fragments used as a polymeric component for the production of bitumen-polymeric mixtures does not significantly increase adhesion but considerably decreases their ductility. The obtained results allow to suggest the following conditions for PhFRP using in the bitumen-polymeric mixtures: PhFRP amount – 1 mass part per 100 g of bitumen; temperature – 463 K; process time – 1 h. The obtained mixtures have better adherence and ductility compared with those of the initial bitumen.

To establish the reason of some operational characteristics improvement or worsening the group structure of bitumen-polymeric mixtures with modified PhFR was studied. The investigations were carried out in accordance with the procedure described in [14, 15]. The results are represented in Tables 5 and 6.

The introduction of PhFRU into the bitumen increases the content of carbenes and carboides and decreases the asphaltenes content in the mixtures. The content of resins and oils in such mixtures depends on the preparation conditions. While using the initial non-

modified PhFR as a polymeric component in the mixtures the content of carbenes and carboides is practically not changed. The rest indexes remain at the level of pure bitumen. Moreover, the operational characteristics of the obtained mixtures are considerably worsened (Table 3).

Thus, the presence of unsaturated fragments in the modified PhFRU favors the transfer of asphaltenes and resins into carbenes and carboides (Table 5) and the presence of side chains increases the adherence of bitumen-polymeric mixtures to glass.

Table 3

The preparation conditions and characteristics of bitumen-polymeric mixtures based on PhFRU

Sample number	PhFRU amount per 100 g of bitumen	Process temperature, K	Process time, h	Characteristics of bitumen-polymeric mixtures			
				Softening temperature, K	Ductility at 298 K, cm	Penetration at 298 K, 0.1 mm	Adherence, %
1	0	463	1.0	321	75	46	41.2
2	1	463	1.0	321	66	43	67.8
3	3	463	1.0	321	58	42	96.2
4	5	463	1.0	321	48	37	98.1
5	7	463	1.0	321	33	30	99.8
6	3	463	0.5	320	61	42	69.6
7	3	463	2.0	321	15	30	99.9
8	3	443	1.0	321	60	40	73.2
9	3	483	1.0	319	48	31	99.9
10	3	463	1.0	324	37	37	58.4

Note: the sample 10 contains the initial PhFR in the amount 3 mass parts per 100 g of bitumen

Table 4

The preparation conditions and characteristics of bitumen-polymeric mixtures based on PhFRP

Sample number	PhFRU amount per 100 g of bitumen	Process temperature, K	Process time, h	Characteristics of bitumen-polymeric mixtures			
				Softening temperature, K	Ductility at 298 K, cm	Penetration at 298 K, 0.1 mm	Adherence, %
1	0	463	1.0	321	75	46	41.2
2	1	463	1.0	322	88	41	97.8
3	3	463	1.0	323	53	38	99.0
4	5	463	1.0	323	42	37	99.9
5	1	463	0.5	321	87	41	95.3
6	1	463	2.0	323	48	38	99.9
7	1	443	1.0	322	88	42	48.8
8	1	483	1.0	322	46	37	99.9
9	1	463	1.0	323	42	37	88.1
10	3	463	1.0	324	37	37	68.4
11	5	463	1.0	326	15	35	50.5

Note: samples 9, 10 and 11 are bitumen-polymeric mixtures with the initial PhFR in the amount of 1, 3 or 5 mass parts per 100 g of bitumen, respectively.

Table 5

Group structure of bitumen-polymeric mixtures with PhFRU

Sample number in accordance with Table 3	Content of carbenes, carboides and mechanical impurities, %	Asphaltenes content, %	Resins content, %	Oils content, %
1	0.12	21.30	25.47	53.11
8	0.18	18.24	21.22	60.36
3	0.40	19.69	24.71	55.20
9	1.23	20.12	28.42	50.23
10	0.16	21.12	21.93	56.78

**Hydrocarbon-group structure
of bitumen-polymeric mixtures with PhFRP**

Sample number in accordance with Table 3	Content of carbenes, carboides and mechanical impurities, %	Asphaltenes content, %	Resins content, %	Oils content, %
1	0.12	21.30	25.47	53.11
2	0.12	22.65	23.70	53.53
9	0.13	21.77	25.54	52.56

The results of group analysis of the bitumen-polymeric mixtures containing PhFRP as a polymeric component are represented in Table 6.

The introduction of only 1 mass part PhFRP into the mixture decreases the amount of resins and increases the amount of asphaltenes.

In case of PhFRU the structural changes in the bitumen-polymeric mixtures take place due to the participation of unsaturated groups while forming products with three-dimensional structure, which in their turn, form more complicated structures (carbenes and carboides). In case of PhFRP the peroxy groups take part in the structures formation. Under the preparation conditions (443 K and higher temperatures) peroxy groups of PhFRP decompose and form free radicals with further transfer of resins into asphaltenes (Table 6). The sample 9 (Tables 4 and 6) contain the initial PhFR without peroxy groups. Hence, the transfer resins → asphaltenes is not observed. The latter fact affects the operational properties of the mixtures (Table 4), *i.e.* we observe low ductility, adherence and penetration of bitumen-polymeric mixtures with non-modified initial PhFR.

4. Conclusions

New PhFR with labile peroxy groups in the side chains (PhFRP) were synthesized *via* chemical modification of novolac phenol-formaldehyde resins by peroxy derivative of epoxy resin. The effective rate constants for the reaction between PDER and Ph were calculated in the presence of potassium hydroxide as a catalyst. The effective activation energy for this reaction was found to be 70.30 ± 1.05 kJ/mol.

The synthesis procedure was developed and new PhFRP was synthesized. The presence of labile peroxy groups in the synthesized product was confirmed by chemical analysis and IR-investigations. The absorption band at 880 cm^{-1} corresponds to the stretching vibrations of –O–O– bond.

It was shown that 1 mass part of PhFRP per 100 g of bitumen in the mixtures increases ductility and adherence to glass by more than 2 times at 463 K and heating for 1 h. Using phenol-formaldehyde resin with methacrylate fragments in the side chains (PhFRU) as a polymeric component (3 mass parts) of bitumen-polymeric mixtures improves adherence to glass. The group analysis confirmed that the presence of PhFRU in bitumen-polymeric mixtures favors the transfer of resins into asphaltenes. Moreover, PhFRU decreases the amount of resins and asphaltenes and favors their transfer into carbenes and carboides.

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МОДИФІКОВАНІ ФЕНОЛ-ФОРМАЛЬДЕГІДНІ СМОЛИ ТА ЇХ ЗАСТОСУВАННЯ У БІТУМ-ПОЛІМЕРНИХ СУМІШАХ

Анотація. *Вивчена можливість використання як полімерного компоненту бітум-полімерних сумішей фенол-формальдегідних смол (ФФС), які містять у бічних відгалуженнях реакційноздатні метакрилатні фрагменти або лабільні пероксидні зв'язки. Враховуючи те, що ФФС з пероксидними фрагментами на основі епоксидної смоли в літературі не описана, розроблена методика її синтезу. Кінетичні закономірності реакції між пероксидною похідною епоксидної смоли (ППЕС) і фенольною групою ФФС вивчені на прикладі ППЕС з фенолом. Структура ФФС з пероксидними групами (ФФСП) підтверджена ІЧ-спектроскопічними дослідженнями. Бітум-полімерні суміші, що містили ФФСП або фенол-формальдегідну смолу з ненасиченими фрагментами (ФФСН) в кількості 1, 3, 5 чи 7 мас.част. на 100 г нафтового бітуму вивчені за температур 443, 463 або 483 К впродовж 0,5, 1,0 чи 2,0 год. З використанням структурно-групового методу аналізу встановлено склад бітум-полімерних сумішей.*

__Ключові слова__: фенол-формальдегідна смола, модифікація, пероксид, ненасичені зв'язки, кінетика, ІЧ-спектроскопія, бітум-полімерні суміші, структурно-груповий аналіз.