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Chemical modification of road oil bitumens by formaldehyde

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Abstract

The chemical modification method of road oil bitumen by formaldehyde (formalin) was proposed to use for improving their physical and mechanical properties. Chemical modification is based on the copolycondensation reactions of bitumen components aromatic fragments and formaldehyde, with the formation of so-called aromatic hydrocarbon formaldehyde resins – formalites. The group hydrocarbon composition and FTIR spectra, the initially distilled oil bitumen of BD 60/90 brand, and formaldehyde modified bitumen were compared. The complex thermogravimetry and differential-thermal analysis were carried out to analyze the initial and modified bitumen. There is shown a considerably increase in the heat capacity (softening point) and adhesion properties (adhesion to glass) in the chemical modification process of distilled bitumen by formaldehyde. There was proved that samples of formaldehyde modified bitumen correspond to polymers modified bitumen (EN 14023) by operating parameters. This will make it possible to use the resulting products as high-quality raw materials for the production of asphalt concrete mixtures and, in the future, reliable and high-quality highways.

***Keywords**: Bitumen; Chemical modification; Copolycondensation; Formaldehyde; Formalin.*

1. Introduction

Oil bitumen is the most large-tonnage organic binder used in construction, primarily in road asphalt concrete, as well as in roofing and waterproofing coatings, in the form of hot and cold mastics, roll materials. Some kinds of problems appear in their production and use. The first is the impossibility to obtain high-quality road distilled bitumen at the refineries, due to the absence of heavy aromatic oil as a raw material. The second is the insufficiently heat-resistant and adhesion properties of commercial distilled and oxidized oil bitumen, that with increasing traffic intensity, heavy haulage volumes, car masses, along with the weather-climatic influencing factors on the road structure, leads to the road surface destruction. The third is the need to add expensive modifiers to bitumen (both distilled and oxidized) to improve their operating properties. It is practically impossible to obtain high-quality road bitumen, which has high operating characteristics, from oil tar at the refineries by known technologies (distillation and oxidation) use. In the world today, these problems are solved by the addition of various polymer modifiers into bitumen. The most popular modifiers are styrene-butadiene-styrene (SBS) thermoplastics: Kraton D (from Kraton Polimers), Calprene (Dynasol Company), and others [1-4]. It is promising to use thermosetting polymer (reactoplast) containing either dual (unsaturated) bonds or chemically active groups. Molecules of which can react with each other or with bitumen molecules under certain conditions (heating, irradiation, or addition of hardener substances). Reactoplastics include epoxy, phenolformaldehyde, carbamide, organosilicon, and other resins [1, 3, 5-7]. The main disadvantage that restrains the increasing pace in output of polymer modified bitumen is their high cost. Adding 2,5 - 3,5% of thermoelastoplast or 1 - 1,5% of terpolymers increases bitumen cost in 1,5 - 2,5 times [2]. Therefore, it is important to search for inexpensive substances or technologies, the implementation of which would improve the working characteristics of oil bitumen. It is known that aromatic hydrocarbons, especially highly condensed, containing heteroatoms, interact with formaldehyde (polycondensation reaction), thus obtaining a large gamma of aromatic hydrocarbon formaldehyde resin, including heavy petroleum residues (tar, distillation and oxidized bitumen) – formalites [8-9]. But in the literature, there is no data on the petroleum residues modification by formaldehyde for the purpose of the road bitumen obtaining from them.

These studies are aimed at solving the expediency of oil bitumen chemical modification by formaldehyde and allowed receiving bitumen without using expensive polymer modifiers with the necessary characteristics.

This technology is a completely new direction in quality binder materials obtaining for the production of asphalt concrete mixtures. And their use will reduce the cost of obtaining road bitumen and significantly improve the bitumen basic physical and mechanical parameters.

2. Experimental

2.1. Initial materials

Withdrawn at Frankivsk Road Construction Department (Lviv, Ukraine) distilled bitumen (BD 60/90) was used for modification. Characteristics of bitumen are given in Table 1. A 37% formaldehyde solution (formalin) was used for chemical modification.

Table 1. Characteristics of distilled road bitumen

Property	Values	Property	Values
Penetration at 25°C (0.1 mm)	80	Fraas breaking point (°C)	-16
Softening point (ºC)	43	Penetration index	-2.1
Ductility at 25°C (cm)	>100	Plasticity interval (ºC)	59
Adhesion to glass (%)	60		

2.2. Experimental procedure

The bitumen modification was carried out with stirring for 2 hours at 80°C in a three-input reactor. At first, the bitumen was dissolved in benzene; the solvent content was 30% by weight. The solvent was used to reduce the reaction mixture viscosity. After the bitumen-benzene mixture heating to 80°C, the required amount of formalin and concentrated hydrochloric acid (catalyst) was added, and then recorded the beginning of the process, which was carried out for 2 hours. At the end of the modification process, the solvent, water, and unreacted components distillation were performed and then modified bitumen dried in a cabinet for 2 hours at 190°C. The output of modified bitumen was determined by the weighing results of raw materials and modified bitumen.

2.3. Analysis of raw material and products

The group chemical composition was determined according to the Markusson method [10].

FTIR spectra were recorded on a Fourier-transform spectrometer «Thermo scientific Nicolet iS10». The spectrogram obtained in electronic format was processed and identified on the computer by "Thermo scientific Nicolet iS10" spectrometer software.

Thermal analysis was made in the temperature range 20-500°C and atmosphere air on a Q-1500D derivatograph of the Paulik-Paulik-Erdey system connected to a personal computer. The sample heating rate was 5 °C per minute. The sample weight was, on average, 200 mg, and aluminum oxide was as a standard substance.

The softening temperature was determined by [11], penetration by [12] at 25°C, ductility by [13] at 25ºC, brittle temperature by [14].

Adhesion to glass surface was determined by the following method: testing is done on prepared glass plates and bitumen. The surface of rectangular glass plates (made of sheet glass) is wiped by solvent, washed by water with household soap and thereafter – by distilled water. Prepared in this way plates are boiled in distilled water during 30 min, while thereafter they are fixed in the vertical position at room temperature or in drying cabinet at (105±2)°C during (35±5) min. The glass surface is wiped by filter paper before bitumen is applied upon it. After cooling, a thin rectangular contour (70 by 24 mm) is marked by pencil or ball-pen upon one side of the glass plate, within the boundaries of which the glass is covered by bitumen film. The bitumen is applied on the opposite to the contour side of the glass plate. Before testing, the bitumen is dewatered by heating to 105 °C, with gradual mixing by a glass rod. The thickness of the bitumen film on the glass surface shall be (0.2±0.01) mm. For each glass plate (or for each rectangular contour applied upon the glass plate), a portion of bitumen (0.35±0.01 g) is weighed on a scale. Distribution of bitumen over the area of the glass plate, marked by rectangular contour, is done by means of heating under the filament lamp or another heating device at (125±5) ºC during 20 min. In the course of bitumen distribution, they prevent its overflow outside the boundaries of rectangular contour marked on a glass or stone plate.

The glass plates with bitumen films applied upon them are conditioned for 30 min in a horizontal position in the heating cabinet at the temperature (80±3)°C higher than the bitumen softening temperature. After that, the plates are air-cooled for 30 min at room temperature, and the photos are made. On the bottom of a water bath, they put ceramic support (as high as not less than 40 mm) for the plates. Distilled water is filled into the bath, and its temperature is raised till (85±0.5)°C. The end of the thermometer shall be immersed into the water till the level of the surface of the support. The prepared glass plates with bitumen are thoroughly placed horizontally upon the support. The thickness of the water layer upon the bitumen surface shall be 40 mm. The distance between the glass plates shall be 10 mm. The glass plates with bitumen are conditioned in the water at (85±0.5)°C for 25 min. Bitumen separated from the surface of glass or stone plates is removed by filter paper. After conditioning of plates with bitumen – water is gradually filled-up into the water bath in quantity, providing for decreasing the water temperature below the bitumen softening temperature by 10°C. The plates are removed from the water and brought upon a leaf of cardboard, where it shall stay for 15 min, while thereafter, the photo is shot for the second time. After that, on the basis of photos made before and after the testing (and using the applied programs), the area of retained bitumen film on the glass (in percent) is determined.

Penetration index was determined accordingly [15] by the formula:

$$Penetration\ index = \frac{20 \cdot SP + 500 \cdot lgP_{25} - 1952}{SP - 50 \cdot lgP_{25} + 120} \qquad (1)$$

where: SP – softening point (ºC); P_{25} – penetration at 25 °C (0.1 mm).

Plasticity interval was determined as the algebraic sum of softening temperature and bitumen breaking point:

$$Plasticity\ interval\ = SP + F \qquad (2)$$

where: SP – softening point (ºC); F – Fraas's breaking point (ºC).

3. Results and discussion

3.1. FMB obtaining

The BND 70/100 modification process was carried out under the conditions given in Table 2. The conditions were chosen according to [8]. They were selected to establish the petroleum bitumen by formaldehyde modifying feasibility. The influence of these conditions on the modification process will be considered more in further studies.

Table 2. Chemical modification conditions of distilled bitumen by formaldehyde

Parameter	Value
Temperature, °C	80
Modification time, hour	2
Reaction mixture composition, % wt. on the bitumen:	
distilled bitumen	100
benzene (bitumen/benzene = 70/30)	44.4
formalin	10 / 20
including formaldehyde	3.7 / 7.4
concentrated HCl	2.5 / 5.0

Benzene was used as a solvent to reduce the viscosity of the reaction mixture. Concentrated hydrochloric acid was used as a catalyst for the copolycondensation process of bitumen aromatic fragments and formaldehyde.

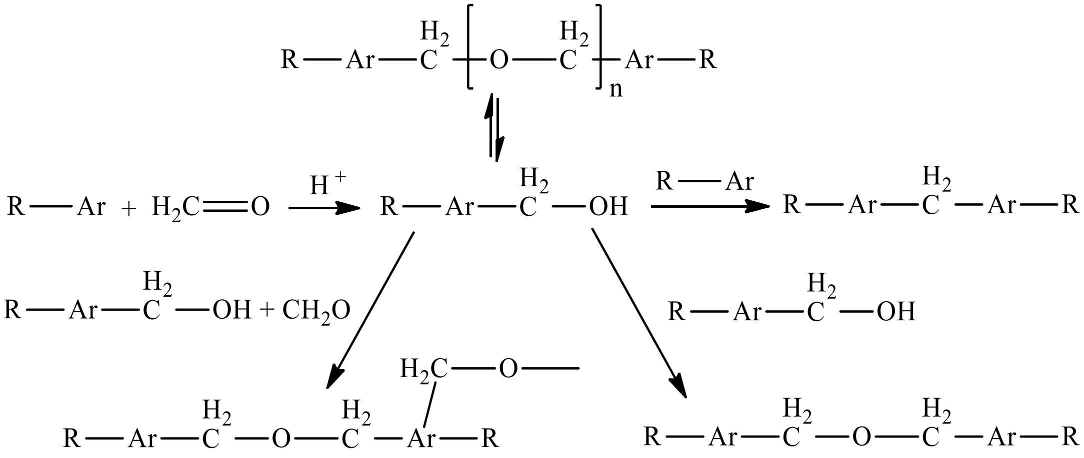
Table 3 presents the main technical characteristics of the distilled oil bitumen modification process by formaldehyde.

Table 3. The main technical characteristics of the distilled oil bitumen modification process by formaldehyde

Bitumen	Content of formalin during modification (including formaldehyde), % wt. on bitumen	Output of modified bitumen, % wt. on bitumen	Softening point (°C)	Penetration at 25°C (0.1 mm)
BD 60/90	0	–	43	80
FMBD1	10 (3.7)	112.7	55	54
FMBD2	20 (7.4)	114.4	60	46

Table 3 shows the increasing of bitumen output in the modification process. It is explained by two reasons. The first is the addition of the formaldehyde molecule to the aromatic fragment of the bitumen molecule; the second is the able of solvent molecule benzene also enters the copolycondensation process that confirms by the data in [8].

According to the literature [8-9], the copolycondensation process of aromatic fragments is a complex set of reactions that results in the formation of methylol, ether, acetal, and methylene groups:



The polycondensation degree of such copolymers is not high due to the rapid onset of the gel-effect. The pretty big size of the resinous-asphaltene molecule also contributes to this [8].

In the investigated reaction, it is necessary to consider separately the chain growth stopping processes and chain breakage. Due to the rapid onset of the gel-effect and the stop of chain growth, i. e., the preservation of functional groups which in the conditions of this reaction no longer react will have a predominant value (especially after distillation of the solvent). It can be assumed that chain growth stopping will cause its breakage, and the reason for this will be physical factors. True chain breakage is possible in the case of carbocation and counterion interaction, which are present in the system, for example, Cl^-, that will cause a change in the functional groups.

During solidification, functional groups that have not reacted during the reaction begin to react with the formation of additional cross-links. Reactions occur primarily through a sol-fraction since the fixed molecules are not mobile.

The group composition comparison of the initial (BD 60/90) and modified (FMBD1) distilled bitumen is given in Fig. 1.

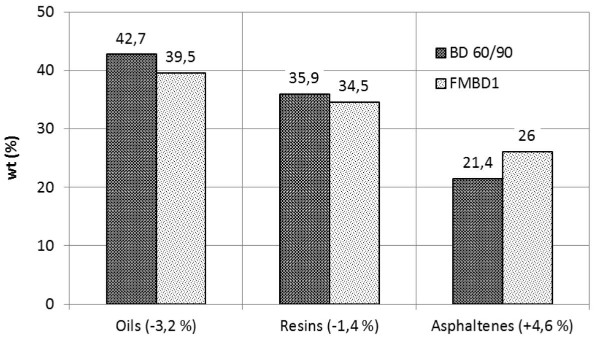


Figure 1. Group chemical composition

Figure 1 shows content decreasing of oils to 3.2, resins – to 1.4 and their total content to 4.6% by weight. At that, asphaltene content increases to 4.6% by weight. Carbenes and carbides were not detected at the determining group composition of BD 60/90 and FMBD1. From the results presented in Fig. 1 it can be concluded that copolycondensation reaction with formaldehyde is best achieved by aromatic fragments of resin molecules (4.6%) that converted into asphaltenes.

Asphaltenes practically do not take part in the copolycondensation reaction because the size of their molecules is bigger than oils and resins, but they can attach methylol cation ($^+CH_2$–OH). The scheme sequence conversion group of hydrocarbon in the modification process is as follow:

	-3.2%		- 4.6%	
Oils	→	**Resins**	→	**Asphaltenes**

3.2. FTIR spectra analysis

Figure 2 shows the FTIR spectra comparison of initially distilled bitumen (BD 60/90) and two formaldehyde modified bitumen (FMBD1 and FMBD2). Characteristics of the main absorption bands the FTIR spectra of bitumen (Fig. 2) are given in Table 4.

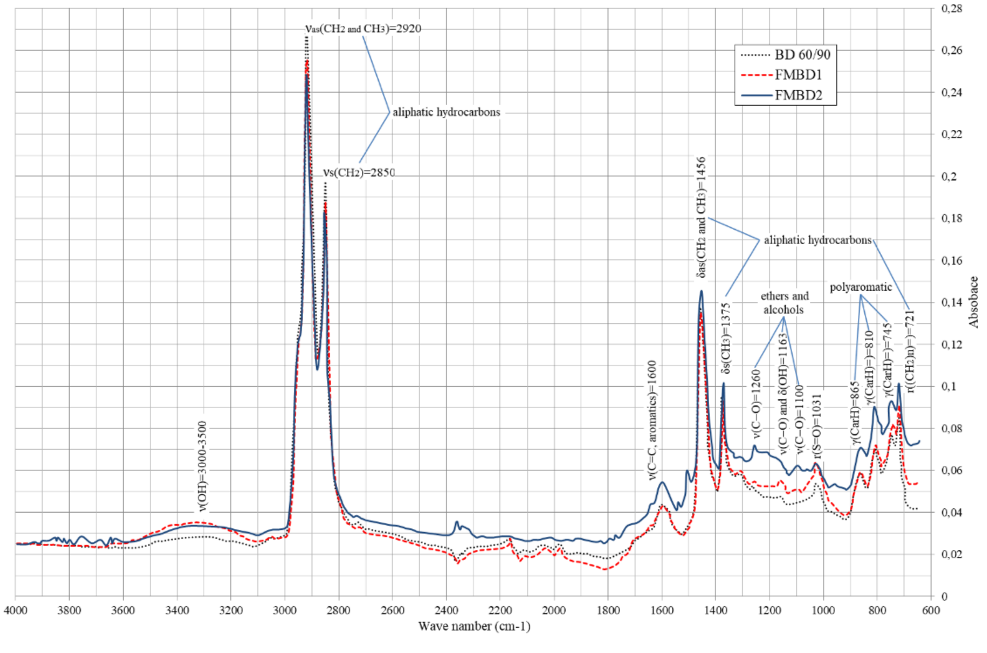


Figure 2. FTIR spectra of the bitumen in the wave number range from 4000 to 600 cm^{-1}

It is seen that in the region 1260-1100 cm^{-1} FTIR spectra (Fig. 2) corresponding to the absorption bands of C-O and OH (Table 4), observed increase in the intensity of these peaks in series BD 60/90 - FMBD1 - FMBD2. This confirms the formation of a large number of new hydroxyl and etheric groups, while the content of these groups increases with the formaldehyde amount increasing at the distilled bitumen modification (Table 3).

The more hydroxyl group's presence in FMBD1 and FMBD1, as compared with BD 60/90, also confirms by the wide absorption band in the range 3500-3000 cm^{-1} FTIR spectra (Fig. 2 and Table 4).

Table 4. The frequencies (cm^{-1}) of the bands observed in the FTIR spectra of the studied bitumens

Absorption band, cm^{-1}	Groups, compound	Characteristic of the peak
3500-3000	OH (alcohols and water)	Bending vibration OH [16-18]
2920	CH_3 and CH_2 (aliphatic hydrocarbons)	Asymmetric stretching vibrations CH in CH_3 and CH_2 groups of hydrocarbon chain segments [16, 18-20]
2850	CH2 (aliphatic hydrocarbons)	Symmetric stretching vibrations CH in CH_2 group of hydrocarbon chain segments [16, 18-20]
1600	aromatic rings	Stretching Stretching vibrations C=C in aromatic rings of bitumen compounds [16- 19, 21]
1456	CH_2 and CH_3 (aliphatic hydrocarbons)	Asymmetric bending vibration CH in CH2 and CH_3 groups [18-22]
1375	CH_3 (aliphatic hydrocarbons)	Symmetric bending vibration CH in CH3 group [18-19, 21-22]
1260	C–O (ethers and alcohols)	Stretching vibrations C–O [17-18]
1163	C–O and OH (ethers and alcohols)	Stretching vibrations C–O and bending vibration OH [16-18]
1100	C–O (ethers and alcohols)	Stretching vibrations C–O [17-18]
1031	S=O (sulfoxides)	Rocking vibrations (bending with torsion) S=O [18-22]
865	Polyaromatic	Deformation vibrations of the CH groups in the aromatic ring [18-19, 21]
810	Polyaromatic	Deformation vibrations of the CH groups in the aromatic ring [18-19, 21]
745	Polyaromatic	Deformation vibrations of the CH groups in the aromatic ring [18-19, 21]
721	(CH2)n (aliphatic hydrocarbons)	Rocking vibrations (bending with torsion) CH in $(CH_2)n$ segments [18- 21]

Also, during the bitumen modification, the characteristic absorption bands intensity for the arene structures is increased, namely 1600, 865, 810 and 745 cm^{-1} (Fig. 2 and Table 4), that explains the increase of asphaltenes in the modified bitumen samples (Fig. 1), which are characterized by a higher degree of aromatics, in comparison with other constituent parts of bitumen (oils and resins).

Consequently, FTIR spectra analysis confirms that distilled oil bitumen interacts with formaldehyde during the modification process with the formation of new OH (peaks at 3500-3000 and 1163 cm^{-1}) and C–O (peaks at 1260, 1163 and 1100 cm^{-1}) bonds. An increase in softening temperature of modified bitumen (Table 3) is mainly occurred by the number of asphaltenes increasing (peaks at 1600, 865, 810 and 745 cm^{-1}), that is, due to the polycondensation reactions of oils and resins aromatic structures (Fig. 1) with formaldehyde, to form formalites (asphaltenes).

3.3. Thermal analysis

The results of the complex thermal analysis of the initial (BD 60/90) and modified (FMBD1) distillated bitumen, which includes thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA), are presented at the thermograms (Figure 3-5) and Table 5.

At the first stage of thermolysis and 44-239 °C temperature range, there is a clear endothermic effect on the curves of DTA samples that corresponds to the melting process of bitumen samples. It should be noted that the melting point temperature of FMBD1 (55°C) is shifted to a higher temperature region than the melting point temperature of the initially distilled bitumen (44°C) and indicating an increased FMBD1 heat resistance. The depth of the endothermic melting effect of FMBD1 (Fig. 5) in comparison with the initial bitumen is greater.

This is due to the fact that FMBD1 has more crosslinked (condensed) structure, compared to the initial bitumen.

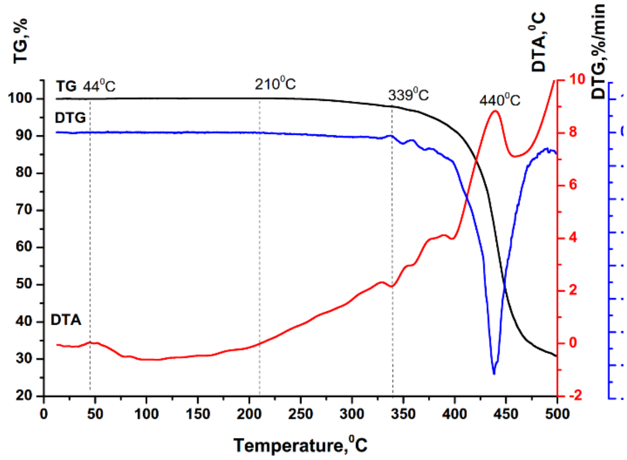


Figure 3. BD 60/90 thermograms

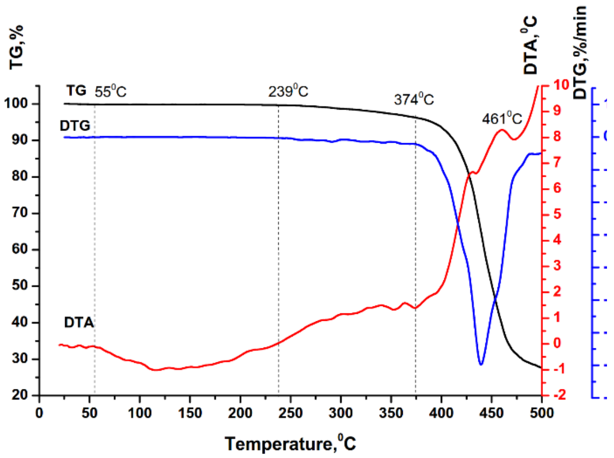


Figure 4. FMBD1 thermograms

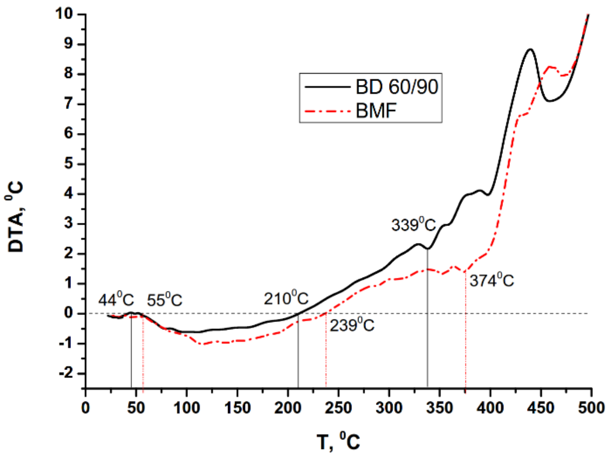


Figure 5. BD 60/90 and FMBD1 DTA curves

At the second stage of thermolysis and 210-374 °C temperature range, there is thermooxidative destruction of samples [23-24].

This process is accompanied by a slight mass loss of samples and the exothermic effect appearance on the DTA curves. It should be noted that the beginning of thermooxidative and destructive processes in FMBD1 (239°C) in comparison with the initially distilled bitumen (210°C) is shifted to a higher temperature region and indicating a higher FMBD1 thermal stability. The appearance in the second thermolysis stage, a less rapid exothermic effect of this sample, confirms that (Fig. 5).

Table 5. Summary table the main thermolysis stages of the initial (BD 60/90) and modified (FMBD1) distilled bitumen

Bitumen	Stage	Temperature range, °C	Mass loss, % wt	Effect	Processes
BD 60/90	I	44-210	0	endothermic	melting
	II	210-339	2.08	exothermic	thermooxidative destruction
	III	339-500	67.02	exothermic	combustion
FBMD1	I	55-239	0.19	endothermic	melting
	II	239-374	3.40	exothermic	thermooxidative destruction
	III	374-500	68.47	exothermic	combustion

At the third stage of thermolysis and 339-500°C temperature range, there is the combustion of destructive product samples. This process is accompanied by intense mass loss of samples (Fig. 3 and 4) and the rapid appearance of extremums on DTA curves (Fig. 5). The maximum of the main extremum FMBD1 (461°C) in comparison with the maximum (440°C) of the initial bitumen is shifted to the higher temperatures region (Fig. 5). This indicates that the combustion process of the FMBD1 sample occurs at higher temperatures.

Consequently, the thermal analysis results confirm that formaldehyde modified bitumen has a higher heat resistance and thermal stability than unmodified, due to the more condensed (crosslinked) structure.

3.4. Applying

The basic physical and mechanical parameters (Table 6), the initial distilled bitumen BND 70/100 brand, and formalin modified bitumen (FMBD1 and FMBD2) were compared to confirm the positive effect of bitumen modifying by formaldehyde.

Table 6. Physical and mechanical parameters of bitumen

Property	Values		
	BD 60/90	FMBD1	FMBD2
Penetration at 25 °C (0.1 mm)	80	54	46
Softening point (ºC)	43	55	60
Ductility at 25 °C (cm)	>100	>100	92
Adhesion to glass (%)	60	97	98
Fraas breaking point (°C)	-16	-11	-8
Penetration index	-2.1	0.2	0.8
Plasticity interval (ºC)	59	66	68

Presented in Table 6, results show that during the bitumen modification by formalin, the bitumen softening temperature significantly increases from 43 to 55 and 60 °C, while the plastic performance of modified bitumen decreases (penetration decreases from 80 to 45 and 46 mm^{-1}). FMBO1, according to EN 14023 [25], corresponds to the polymer modified bitumen of PMB 45/80-50 and FMBO2 – PMB 25/55-60 brands.

During the modification, the road bitumen adhesive properties are also significantly improved, adhesion to the glass surface increases from 60 to 98% (Table 6). In our opinion, adhesion increase is as result of oxygen-containing groups (C–O and O–H) entering into the bitumen structure and this confirms by FTIR spectra analysis (Fig. 2 and Table 4).

4. Conclusions

The chemical modification of distilled road oil bitumen was carried out, and respectively FMBD1 with output 112.7 and FMBD2 with 114.6% by weight were obtained at 80°C for 2 hours with formalin content 10 and 20% by weight on bitumen and benzene addition as the solvent.

The group hydrocarbon composition of the initially distilled bitumen and modified FMBD1 were determined. There was established the content decrease of oils by 3.2, resins – 1.4, and their total content by 4.6% in the process of chemical modification. At that, asphaltene content was increased by 4.6%. Carbenes and carbides were not detected at the determining group composition of BD 60/90 and FMBD1. There was established the best achieved copolycondensation reaction with formaldehyde aromatic fragments of resin molecules (4.6%), resins less (3.2) that converted into formalities (asphaltenes). The asphaltene aromatic fragments practically do not take part in the copolycondensation reaction.

FTIR spectra analysis confirms that distilled oil bitumen BD 60/90 interacts with formaldehyde during the modification process with the formation of new OH (peaks at 3500-3000 and 1163 cm^{-1}) and C–O (peaks at 1260, 1163 and 1100 cm^{-1}) bonds. An increase in softening temperature of modified bitumen is mainly occurred by the number of asphaltenes increasing (peaks at 1600, 865, 810 and 745 cm^{-1}), that is, due to the polycondensation reactions of oils and resins aromatic structures with formaldehyde, to form formalites (asphaltenes).

The higher heat resistance and thermal stability of formaldehyde modified bitumen than at unmodified bitumen due to the more condensed (crosslinked) structure were confirmed by thermal analysis of BD 60/90 and FMBD1.

During the bitumen modification by formalin, the bitumen softening temperature significantly increases from 43 to 55 and 60 °C, while the plastic performance of modified bitumen decreases (penetration decreases from 80 to 45 and 46 mm^{-1}). FMBD1, according to EN 14023 corresponds to the polymer modified bitumen of PMB 45/80-50, and FMBD2 – PMB 25/55-60 brands.

During the modification, the road bitumen adhesive properties are also significantly improved, adhesion to the glass surface is increased from 60 to 97 and 98%.

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