CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2025,
Vol. 19, No. 1, pp. 141–156

Chemical Technology

A REVIEW OF ROAD BITUMEN MODIFICATION METHODS. PART 2 - CHEMICAL MODIFICATION

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https://doi.org/10.23939/chcht19.01.141

Abstract. A literature review of modern chemical methods for modifying road bitumen has been conducted, focusing on their popularity and the nature of their impact on binder properties. Sulfur, polyphosphoric acid, maleic anhydride, thermosetting resins (such as phenol-formaldehyde, epoxy, polyester, *etc.*), and polymers are the most commonly used chemical modifiers in road construction practices. The method of producing bituminous materials with varying penetration levels through the chemical modification of oil residues with formaldehyde has been considered. All bituminous materials produced *via* chemical modification demonstrate better homogeneity during high-temperature storage compared to those modified through physical methods due to the chemical interaction between a reactive modifier and bitumen. It has also been shown that chemical modifiers are often used in combination with physical modifiers to enhance their effectiveness.

Keywords: bitumen, chemical modification, sulfur, polyphosphoric acid, maleic anhydride, thermosets, formaldehyde.

1. Introduction

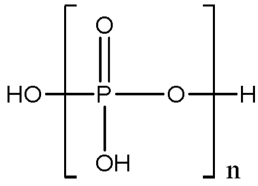
Numerous studies have demonstrated both the advantages and disadvantages of modifying bitumen with polymers.[1] The benefits include improved elastic recovery, enhanced resistance to cracking at low temperatures, and better resistance to rutting at high temperatures. However, drawbacks include thermal instability and issues with the homogeneity of the resulting polymer-modified bitumen (PMB). In addition to physical mixtures of bitumen and polymers, another approach to enhancing the properties of bituminous materials is chemical modification, which involves using a chemical agent to alter the properties of the pure binder through its interaction with the components of the bitumen.[2-4]

Currently, there is no universally accepted classification for the processes of chemical modification of binders, tar, or fuel oils, nor for the types of chemical modifiers. Additionally, there is no clear differentiation of these processes based on the types of catalysts used or the way the modifier affects the oil residue (*i.e.*, how the chemical structure of the residue is altered). In industrial practice, chemical modification processes are less common than physical ones. However, chemical modification often achieves results that are not only comparable to but sometimes even superior to those of physical modification, particularly in terms of the operational characteristics of the modified products.[5-9]

2. Chemical Modification

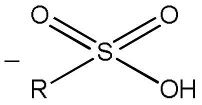
To date, a variety of chemicals have been used to modify bitumen, including:

1) sulfur (S);[10-14]
2) polyphosphoric acid (PPA) –



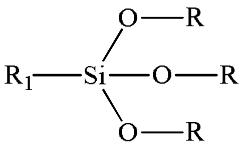
$HO{-}[P(=O)(OH){-}O]_n{-}H$;[15-18]

3) sulfonic acids –



; [19-20]

4) organosilicon compounds –



;[21-24]

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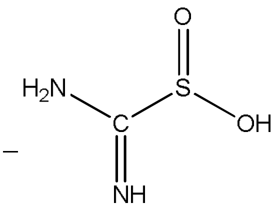
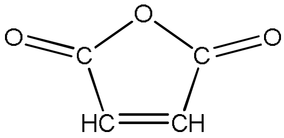
5) thiourea dioxide –



;[25]

6) nanocomposites – polymer/clay, TiO_2, Al_2O_3, and others;[26-34]

7) maleic anhydride (MA) –



;[35-36]

8) thermosets, namely:

- reactive polymers – RET;[37-39]
- epoxy resins;[40-45]
- phenol formaldehyde resins (PhFR);[46-47]
- polyester resins.[48-50]

However, only some of the listed above chemical modifiers are practically applied, namely S, PPA, MA, and thermosets, which are the most common ones.

2.1. Chemical Modification of Bitumens with Sulfur

Some commercial products known as sulfur asphalt (*e.g.*, Shell Thiopave®)[51] are produced using this technology. In this process, many parameters must be considered, with temperature playing a key role. At temperatures below 413 K, sulfur can react with bitumen or form hydrogen sulfide through a dehydrogenation reaction. Higher temperatures enable the formation of C–S bonds, which facilitate the dynamic vulcanization (currying) of bitumen. This process leads to the formation of crosslinks in arenes and naphthenes, altering the chemical composition and colloidal structure of the bitumen. Sulfur is known to dissolve in bitumen at concentrations up to 10-15 wt. %, while at higher concentrations, it recrystallizes and behaves as a filler.[52-53] Some researchers have also suggested that sulfur can self-polymerize when added to the binder.[51]

Nowadays, sulfur is mostly added in small amounts to PMB. Studies have shown that with simultaneous modification of bitumen with 4.0 wt. % of SBS and 0.15 wt. % of sulfur (at 453 K for 3 hours), PMB can achieve superior properties compared to modification with SBS alone.[54-55]

Martínez-Estrada *et al.*[56] conducted a more detailed study of the vulcanization processes in the Bitumen / SBS / S system. In their research, two copolymers, SB and SBS, have been used as polymer modifiers (Table 2). The addition of sulfur to SBS-modified bitumens causes the copolymer molecules to crosslink *via* sulfur addition to the double bonds (vulcanization), forming a PMB structure that prevents phase separation during storage at elevated temperatures.

From a rheological perspective, sulfur-added PMB exhibit better elasticity compared to those without sulfur.[55-56]

Table 1. Characteristics of SBS- and SBS / S-modified bitumen[55]

Parameter	Bitumen	Bitumen / SBS	Bitumen / SBS / S
Penetration at 298 K (P298), dmm	63	49	56
Softening point (SP), K	321.8	337.1	355.2
Ductility at 288 K, cm	>150	36	41
Dynamic viscosity at 333 K, Pa·s	273.8	4658	75200

Table 2. Characteristics of SB-, SBS-, SB / S-, and SBS / S-modified bitumens[56]

Sample *	Softening point (SP), K	Penetration at 298 K (P298), dmm	Softening point (SP), K **	
			Top	Bottom
Bitumen	331	44	331	331
Bitumen / 20S	335	34.2	335	335
Bitumen / 5SB	338	42.3	335	345
Bitumen / 5SBS	340	25.8	338	343
Bitumen / 5SB / 3S	340	27.8	351	343
Bitumen / 5SBS / 1.5S	347	25.7	345	346

* The numbers indicate the component content in PMB, wt. %

**SP of top and bottom after storage (homogeneity), K.

However, the use of sulfur as a chemical modifier comes with several drawbacks. First, the chemical interaction between sulfur and polymer modifiers relies on reactions with double bonds, meaning sulfur use is limited to polymers that contain double bonds. There is also a risk of producing non-homogeneous PMB due to the complexity of sulfur distribution within the mixture. Additionally, localized over-vulcanization of the polymer has been observed. The primary disadvantage, however, is the release of hazardous hydrogen sulfide during PMB preparation. Hydrogen sulfide can be formed during vulcanization through the abstraction of hydrogen atoms from both the bitumen and polymer modifiers, especially at high temperatures. Some researchers argue that the gas release is relatively minor, and most manufacturers are equipped to handle the associated risks and hazards. Shell Oil Company, for example, has used disulfides (R−S−S−R), which do not release sulfur at high mixing temperatures.[57] Disulfides have been shown to improve the compatibility between SBS polymer and bitumen. However, these additives are costly and are generally not used in commercial applications. All these limitations restrict the widespread use of sulfur vulcanization in PMB production.[58]

2.2. Chemical Modification of Bitumens with Polyphosphoric Acid

From a chemical perspective, PPA is an oligomer of orthophosphoric acid (H_3PO_4). The modification of bitumen with PPA is a complex physicochemical process that is highly dependent on the nature of the bitumen. Currently, there is no unified understanding of the chemical interaction between PPA and bitumen, primarily due to the diverse range of molecules present in bitumen. Miknis *et al.*,[59] using NMR spectroscopy, demonstrated that polyphosphoric acid tends to revert to orthophosphoric acid after mixing with bitumen. The NMR spectroscopy data have not shown the formation of organic esters of phosphoric acid as a result of the modification. Kabir *et al.*[17] indicated that bitumen with high sulfur content exhibits stronger intermolecular interactions with PPA. Additionally, it has been suggested that PPA neutralizes polar interactions between asphaltene molecules through protonation.[60] Copolymerization, alkyl aromatization of saturated acids, and other reactions are discussed in more detail in relevant studies.[61-62]

Baldino *et al.*[15] studied the effect of PPA on 50/70 and 70/100 bitumen samples (Fig. 1).

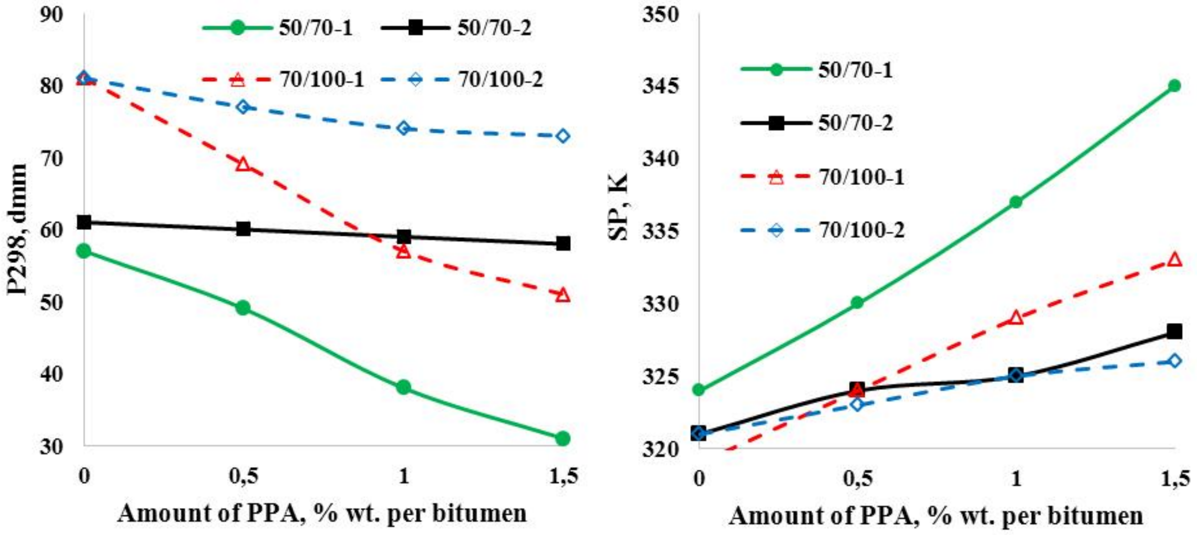


Fig. 1. The effect of the PPA amount on the penetration at 298 K (P298) and the softening temperature (SP) of bitumens[15]

From the results presented in Fig. 1, it can be seen that different bitumens interact variably with PPA. This is attributed to differences in bitumen composition, which is a significant drawback of this technology. PPA can also enhance the homogeneity of polymer-modified bitumens during storage. However, it is important to note that this improvement may depend on various factors, such as the type of polymer and the concentration of PPA.

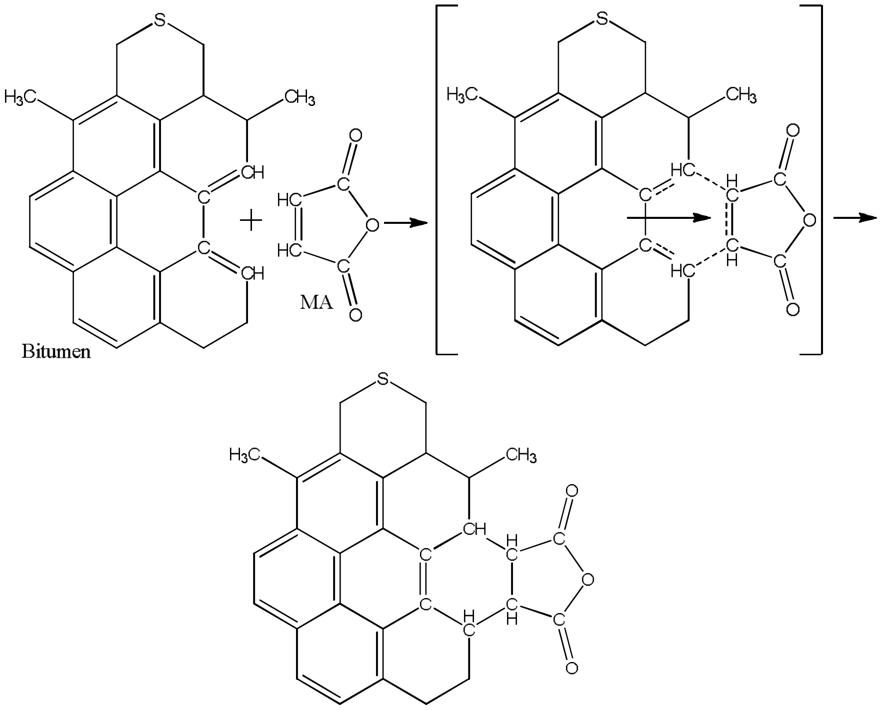
2.3. Chemical Modification of Bitumens with Maleic Anhydride

The chemistry of the interaction between MA and bitumen is complex and largely depends on the varying composition of bituminous materials. To date, there is no consensus among researchers on this matter. Chemical reactions between MA and bitumen have been studied by comparing modifications under a nitrogen blanket using MA, succinic anhydride (similar to MA but without the double bond), and the corresponding diacids. Results from FTIR analysis, gas chromatography, and mass spectrometry have revealed the presence of two acidic groups (−COOH) both in the case of using MA and succinic anhydride. This suggests that both anhydride rings open to form the corresponding diacids. Additionally, in the case of MA, the disappearance of the double bond absorption band has been observed in the FTIR spectra of MA-modified bitumen.[35]

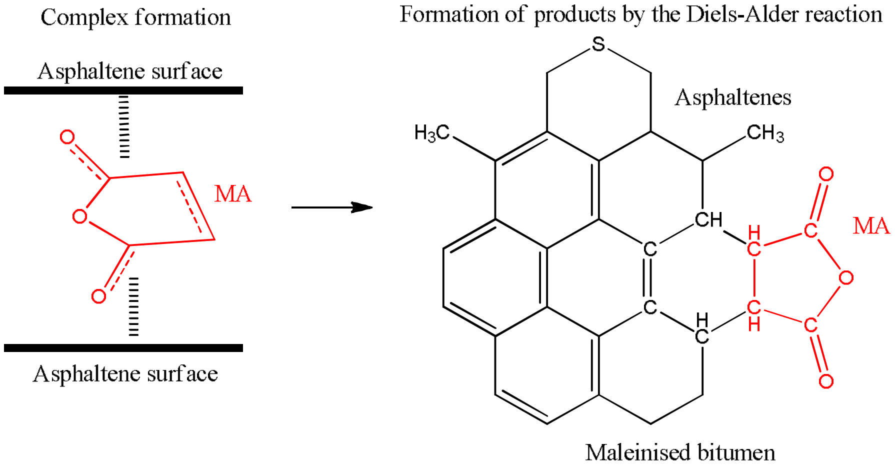
Several studies have demonstrated that the rheological properties of bituminous mixtures, formed by adding MA, succinic anhydride, and various organic diacids to bitumen, follow the next order:

MA > succinic anhydride ≈ dicarboxylic acids >
> monocarboxylic acids

These results suggest that the two carboxyl groups are capable of binding two bitumen molecules. The superior performance observed when MA is added to bitumen is attributed to the presence of an MA double bond, which reacts with bitumen molecules. However, recent studies present conflicting results regarding the MA-bitumen reaction. FTIR analysis has indicated that the MA rings remained intact during the MA-bitumen reaction.[65] This observation has led to the hypothesis that, instead of ring-opening, Diels-Alder reactions and π–π complex formation between MA and asphaltenes might be involved.



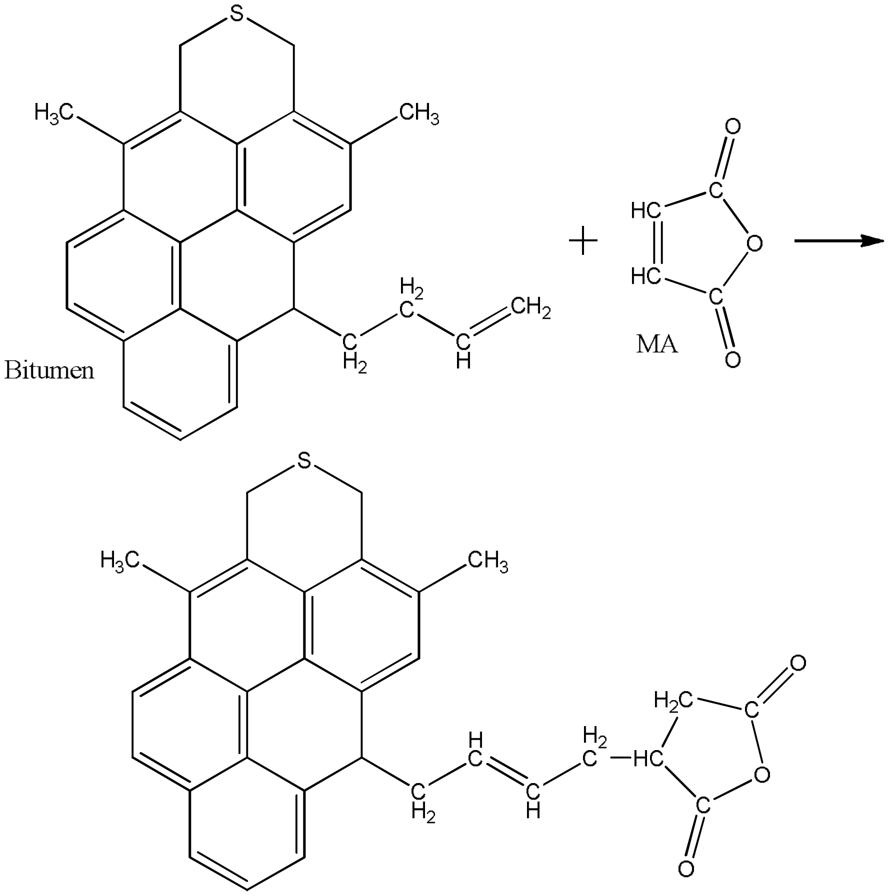
(1)



(2)

The π–π charge transfer process is likely due to the polycyclic aromatic structure of asphaltenes, which act as donors in such processes.

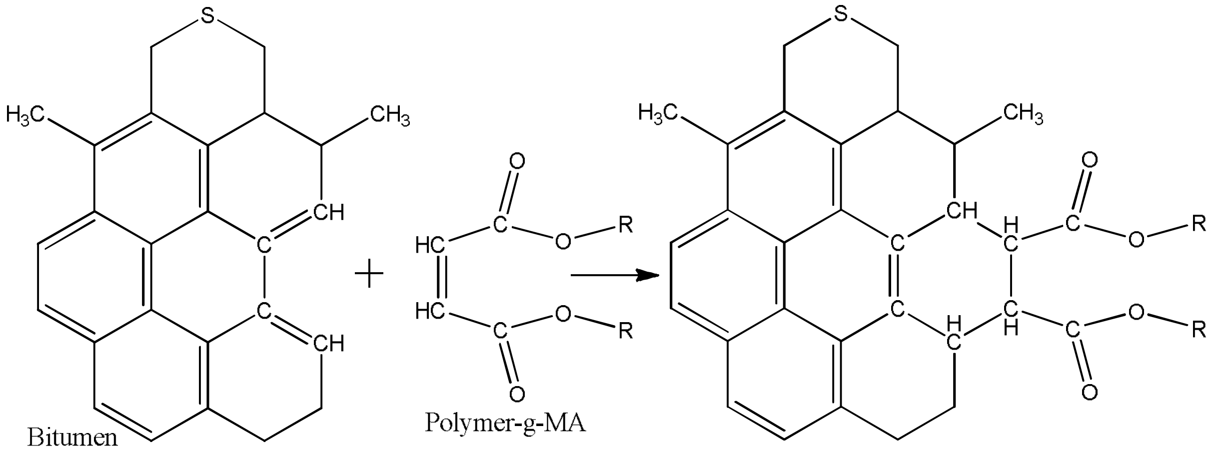
It is also possible for MA to react not only with the diene fragments in bitumen (the Diels-Alder reaction) but also with alkenes:



(3)

These reactions occur at higher temperatures than Diels-Alder reactions.

Kang *et al.* have studied the preliminary synthesis of polymer-MA (creating a reactive polymer) and its subsequent use to modify bitumen.[65] The chemical interaction between such a polymer and bitumen components ensures better homogeneity and stability during the PMB storage. Moreover, this type of chemical modification allows the incorporation of various polymers and by-products of polymer production into bitumen, providing tailored PMB properties.[67-69] However, an additional purification step is needed to remove an unreacted MA monomer, which increases production costs.



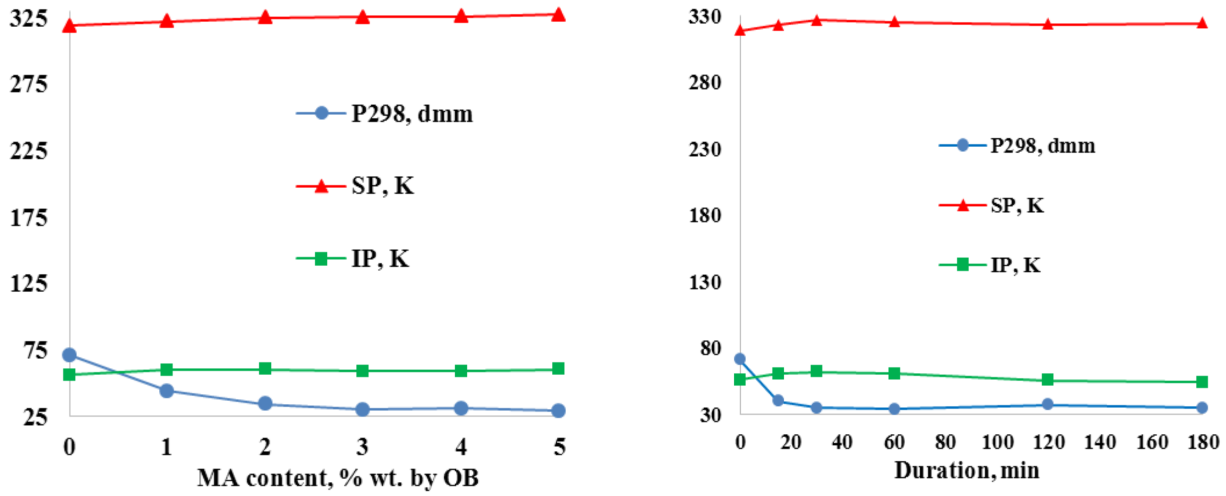
(4)

Becker *et al.*[66] have compared the storage stability of PMB produced using SBS, SEBS, and two commercial SEBS variants with different maleic anhydride contents (under conditions of 443 K, 6000 rpm, and 4 hours). SEBS with grafted maleic anhydride (SEBS-*g*-MA) has exhibited better storage stability, although it has not significantly enhanced the rheological behavior of the binder.

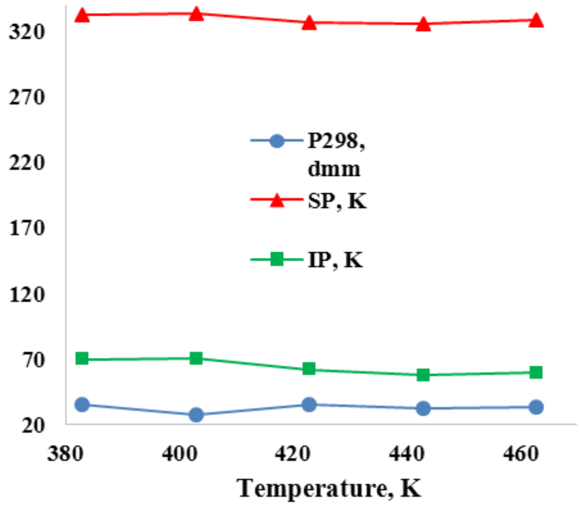
Fig. 2 presents the influence of key technological parameters on the physical and mechanical properties of the resulting maleinized bitumens (OBMA). It has been determined that the optimal modification involves adding 2.0% of maleic anhydride by weight to the bitumen, with a reaction time of no more than 30 minutes. Further increases in these parameters have not led to significant improvements in the physical and mechanical properties of the final products.

The modification temperature has the greatest impact on the physical and mechanical properties of OBMA (Fig. 2). This is due to changes in the modification chemistry. At temperatures below 403 K, π-π complexes form between large polycyclic aromatic components of the raw materials (asphaltenes) and MA. At temperatures above 423 K, bitumen reacts with MA *via* the Diels-Alder reaction.

The presence of absorption bands in the 1880-1680 cm^{-1} region of the FTIR spectra for products prepared at temperatures above 423 K (Fig. 3) supports the occurrence of the Diels-Alder reaction. These absorption bands are characteristic of maleic anhydride copolymers, indicating that temperature selection is a critical factor in the modification process.



423 K; 60 min. **MA - 2 % wt. by OB; 423 K**



MA - 2 % wt. by OB; 30 min.

Fig. 2. The effect of technological parameter on the modification of oxidized bitumen with maleic anhydride

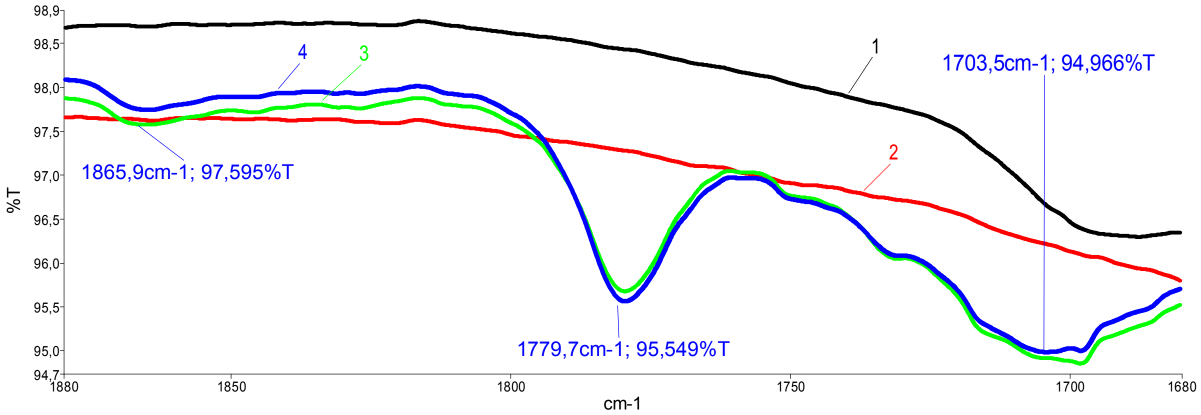


Fig. 3. FTIR-spectra of: 1 – OB; 2 – OBMA prepared at 403 K; 3 – OBMA prepared at 423 K ; 4 – OBMA prepared at 443 K

To produce OBMA and TMA as a separate binder with a higher SP, modification temperatures below 403 K are required. However, further asphalt concrete production will also demand adjustments in temperature regimes.

At modification temperatures below 403 K, OBMA with an SP of 333.2 K is formed. Increasing the modification temperature significantly reduces an SP, indicating a transition from π-π complexes to chemical interaction between MA and bitumen as the process temperature rises above 403 K. This finding has been confirmed by heating OBMA samples (obtained at 403 K and 443 K) to 436 K using the RTFOT method. When the OBMA prepared at 403 K was heated, an anomalous and unexpected decrease in an SP by 8.8 K was observed, while the OBMA prepared at 443 K showed an increase in SP by 2.8 K. This characteristic of maleic anhydride suggests its potential use as an inhibitor of bitumen aging.[67-69]

2.4. Chemical Modification of Bitumens with Thermosets

Thermosets include reactive ethylene terpolymers (RET), which are based on terpolymers containing reactive groups such as glycidyl methacrylate, acrylic acid, and others. Compared to non-reactive polymers like PE, PP, *etc.*, PMB made with RET exhibits better homogeneity due to the formation of a strong covalent bond between RET and bitumen. However, one potential drawback is the risk of uncontrolled and undesirable crosslinking of unsaturated polymers through a radical mechanism. As a result, saturated polymers such as SEBS, PE, PP, *etc.*, are often more suitable for this process.

The use of RET with acrylic functional groups increases the polarity and reactivity of the resulting PMB. Despite these advantages, RET is more expensive than other polymers and can cause issues with gelation due to the high number of reactive groups in each macromolecule. To avoid these problems, the amount of RET used is typically limited to 2-2.5 wt. %, and in many cases, it is kept below 1.0 wt. %.[70] Thus, RET is primarily employed to improve the compatibility between bitumen and other polyolefins, as demonstrated by Yeh *et al.*[71]

Poly(ethylene butyl acrylate/glycidyl methacrylates), marketed as Elvaloy® AM and Elvaloy® 4170 (DuPont, Wilmington, DE, USA), have been blended with bitumen to test the storage stability of the mixture.[37] After storing at high temperatures, all samples remained fully homogeneous, showing that RET helps ensure storage stability.

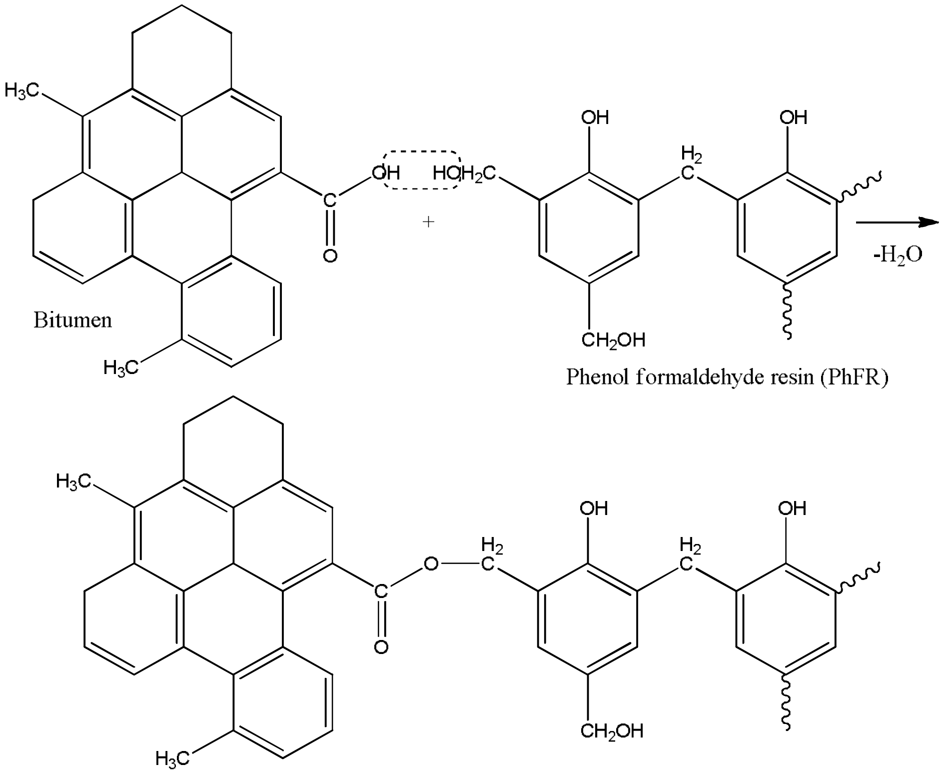
Cubuk *et al.*[41] have investigated the effect of bisphenol-A-based epoxy resin on the properties of bitumen 50/70. Adding 2-3 wt. % of the epoxy increased the viscosity, reduced P298 from 62 to 54 dmm, and raised SP from 322.2 to 325.2 K. This type of PMB is recommended for use in regions with hot climates, as it maintains high FBP.

FTIR spectroscopy has confirmed that bisphenol-A-based epoxy resin (in amounts of 2, 5, 10, and 15 wt. %) interacts with oxidized bitumen at 473 K (for 30 minutes at 1000 rpm).[44] The greatest increase in SP, to 284 K, has occurred with 5 wt. % of the epoxy resin.

Ivashkiv *et al.*[43] have also found that using epoxy resins increases the SP of the final PMB while significantly improving their adhesive properties.

The main disadvantage of using epoxy resins as bitumen modifiers is their poor elastic-deformation behavior, particularly at low temperatures, as well as their higher cost compared to other modifiers.

In some studies,[72-74] PhFR (Bakelite) is considered a physical modifier of bitumen. Other research,[47] using FTIR spectroscopy, has proven a chemical interaction between PhFR and bitumen:



(5)

The modification of bitumen with PhFR results in an increase in the amount of asphaltenes. This indicates that, during the interaction between bitumen and PhFR, the resulting product becomes part of the asphaltene fraction, contributing to the transformation of bitumen into a gel-like structure. This change significantly impacts the rheological properties of PMB.

Cubuk *et al.*[41] have studied the modification of bitumen 50/70 with PhFR (Bakelite with SP > 403 K). This modification enhances the bitumen's strength due to the crystallization and cross-linking effects of the additive, which results from chemical interactions. Such properties are desirable for flexible road pavements. Additionally, the modification improves the resistance of the bitumen mixture to deformation and increases adhesion at the bitumen/aggregate interface. This leads to more durable pavements, particularly under heavy traffic, and is especially beneficial in regions with hot climates.

PhFR as a bitumen modifier are still not extensively studied, likely due to the high cost of these resins.[75-78]

2.5. Polycondensation of Arenes with Formaldehyde

Special attention should be given to the reaction of arenes with formaldehyde to form AFR, which presents a promising method for developing new bituminous materials.[79-81] The formation of AFR occurs through the interaction of arenes – ranging from simple ones like benzene to more complex structures such as asphaltenes – with formaldehyde *via* two typical polycondensation reactions:

$$(n+1)HArH + nCH_2O \rightarrow$$
$$\rightarrow H(ArCH_2)_nArH + nH_2O \quad (6)$$

$$(n+1)HArH + (n+m)CH_2O \rightarrow$$
$$\rightarrow HAr[CH_2Ar]_n(CH_2O)_mH + nH_2O \quad (7)$$

The primary condensation products are arylmethanols:[80-82]

$$ArH + CH_2O \rightarrow ArCH_2OH \quad (8)$$

However, synthesizing arylmethanols are challenging because they are highly reactive in acidic environments and undergo further transformations at a rapid rate.

In the presence of HCl and CH_3COOH, chloromethylation and acetoxymethylation reactions can occur, respectively:[80,82]

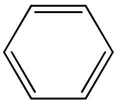
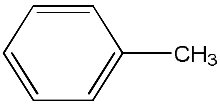
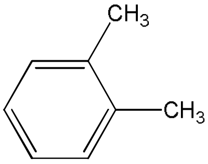
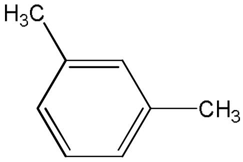
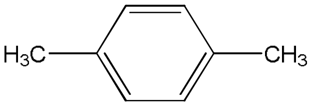
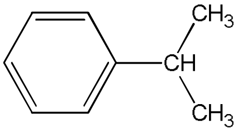
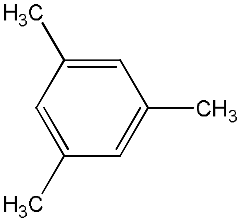
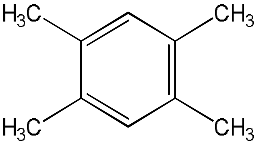
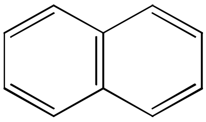
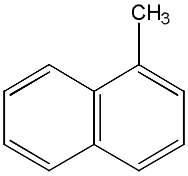
$$ArH + CH_2O + HCl \rightarrow ArCH_2Cl + H_2O \quad (9)$$

$$ArH + CH_2O + CH_3COOH \rightarrow$$
$$\rightarrow ArCH_2OCOCH_3 + H_2O \quad (10)$$

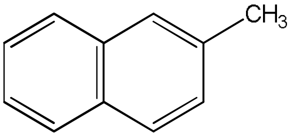
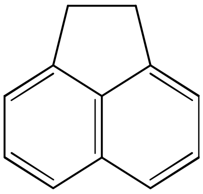
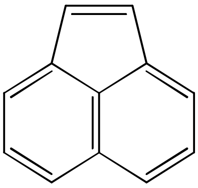
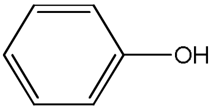
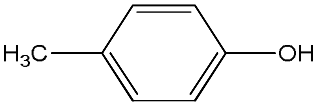
To prevent these side reactions, alternative acids like sulfuric acid should be used.[81-83]

The reactivity of arenes in condensation with formaldehyde depends on their structure. Table 3 illustrates the relative rates of condensation reactions between various arenes and formaldehyde to form AFR.

Table 3. Relative reaction rates of the condensation of aromatic hydrocarbons and formaldehyde

Aromatic hydrocarbons	Structural formula	Relative reaction rate
1	2	3
Benzene		1
Toluene		10-15
o-Xylene		21.2
m-Xylene		430
p-Xylene		72
Cumene		8.9
Mesitylene		400-500
Durene		322
Naphthalene		50
α-Methylnaphthalene		660

Continuation of **Table 3**

1	2	3
β-Methylnaphthalene		512
Acenaphthene		13,300
Acenaphthylene		23,000
Phenol		56,400
p-Cresol		55,100

Conventionally, the relative rate of benzene's condensation with formaldehyde is taken as 1, representing the slowest rate of interaction. From Table 3, it can be concluded that the rate of condensation between arenes and formaldehyde is strongly influenced by the arene structure and increases with:

- increasing molecular weight of the raw materials (aromatic hydrocarbons);
- increasing the number of aromatic rings;
- increasing the number of methyl substituents and their location;
- the presence of heteroatoms (functional groups); for instance, phenols react with formaldehyde at a much higher rate than arenes.[84-86]

All these criteria are met by petroleum residues after vacuum distillation of crude oil (tars) and bitumen. Therefore, it is particularly interesting to explore the process of tar condensation with formaldehyde to produce products with higher viscosity compared to the raw material (tar), which could meet the specifications for various grades of viscous petroleum bitumen used in road construction (depending on process conditions). The novelty of this method lies in the fact that the required oligomer for modification (to improve properties) is formed directly during the process from the raw material (*i.e.*, tar) components. Additionally, a significant advantage of this process is that the resulting oligomer does not need to be isolated from the mixture (bitumen).[87-88]

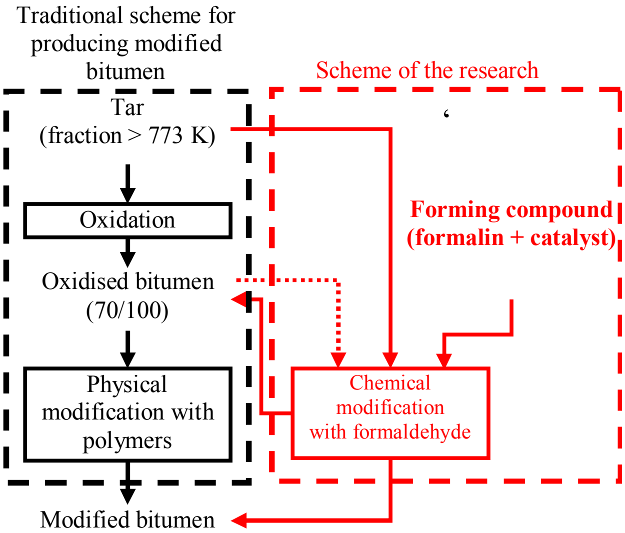


Fig. 4. Scheme of the reasearch

Fig. 4 illustrates the scheme of tar modification with formaldehyde to produce road bitumen. The required oligomer – arene-formaldehyde resin (AFR) – is formed directly in the tar or bitumen through the polycondensation of aromatic structures (primarily those containing functional groups, such as hydroxyl) with formaldehyde.

FMT has been compared with traditional binders used in Ukraine, namely oxidized bitumen (OB-1 and OB-2), which are produced at the tar oxidation plant of PJSC "UKRTATNAFTA." Two samples of oxidized bitumen, OB-1, and OB-2, have been prepared from two selected tar samples (T-1 and T-2) at different time intervals during the industrial oxidation process. The technological parameters for modification, as well as the physical and mechanical properties of the tars (T-1 and T-2) and the oxidized bitumens produced from them (OB-1 and OB-2), are presented in Table 4.[89-91]

Table 4. Technological parameters for modification and the physical and mechanical properties of the resulting FMT

Parameter for modification / Properties of a product	T-1	T-2	OB-1	OB-2	FMT-1	FMT-2	FMT-3	FMT-4	FMT-5	FMT-6	FMT-7	FMT-8	FMT-9	FMT-10	FMT-11
Parameters for modification															
Raw material	–	–	T-1	T-2	T-1							T-2			
Formaline content, wt. % to tar	–	–	–	–	**1.0**	**1.9**	**3.0**	3.2	1.0	2.0	3.0	1.0	2.0	3.0	3.0
Catalyst	–	–	–	–	**H_2SO_4**			HCl	H_3PO_4			H_2SO_4		HCl	H_3PO_4
Catalyst content, wt. % to tar	–	–	–	–	**1.1**	**1.7**	**3.2**	3.1	1.0	2.0	3.0	1.0	2.0	3.0	3.0
Temperature, K	–	–	–	–	**383**	**378**	**383**	373	403	403	403	403	403	403	403
Time, min	–	–	–	–	**0.6**	**0.6**	**0.8**	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Properties of a product															
Penetration at 298 K (P298), dmm	247	208	82	75	144	89	47	131	139	95	83	58	43	78	99
Softening point (SP), K	312	314.2	320.2	321.8	321	332	356.4	320.4	319.4	324.6	331.8	325.4	345	321.8	324.2
Ductility at 298 K (D298), cm	58.1	>100	>150	>150	42	16	4	59	79	111	134	15	12	>100	86
Fraas breaking point (FBP), K	255	244	261	249	256	258	264	259	253	256	259	253	256	259	260
Plasticity interval (IP), K	330	343.2	332.2	345.8	338	347	365.4	334.4	339.4	341.6	345.8	345.4	362	345.8	347.2
Adhesion to glass, %	42	36	29	31	65	81	94	83	89	97	94	78	96	92	83
Adhesion to gravel, mark	2.5	2.5	3.0	2.5	3.5	4.5	5.0	4.5	4.5	5.0	5.0	4.5	5.0	5.0	4.5

A notable advantage of FMT is its significantly higher SP at the same P298, as shown in Table 4, indicating superior heat resistance of FMT in comparison to oxidized bitumens.[92-95]

Based on current regulatory standards, the resulting FMT samples meet the main physical and mechanical property requirements for the following binder materials (Table 4):

- **petroleum road viscous bitumen according to DSTU 4044:2019:**[96] BND 150/220 − FMT-12; BND 100/150 − FMT-1, FMT-4, and FMT-5; BND 70/100 – FMT-2, FMT-6, FMT-7, FMT-10, FMT-11; BND 50/70 – FMT-8;
- **polymer-modified bitumen (except for elasticity) according to DSTU 9116:2021:**[97] PMB 70/100-55 − FMT-2, FMT-7; PMB 35/50-70 − FMT-3, FMT-9;
- **bitumen modified with synthetic waxes according to SOU 42.1-37641918-068:2017:**[98] WMB-S 60/90 – FMT-2, FMT-7; WMB-S 40/60 – FMT-3, FMT-9;
- **bitumen modified with adhesive additives according to SOU 45.2-00018112-067:2011:**[99] BND-A 70/100 – FMT-6, FMT-7, FMT-10; BND-A 35/50 – FMT-3, FMT-9.

Hence, this method is flexible, and by adjusting the amount of the modifier (formylating mixture), it allows for the production of binders with different P298 and SR values.

Another advantage of FMT over oxidized bitumens is their high adhesive properties. FMT produced using HCl and H_3PO_4 exhibits the best adhesion to acidic mineral fillers (Table 4).

Upon the chemical modification of tar with formaldehyde, the group composition changes. To confirm this, the group composition of the raw materials (T-1) and the products (FMT-1, FMT-2, and FMT-3) has been determined using the Markusson method (Fig. 5).

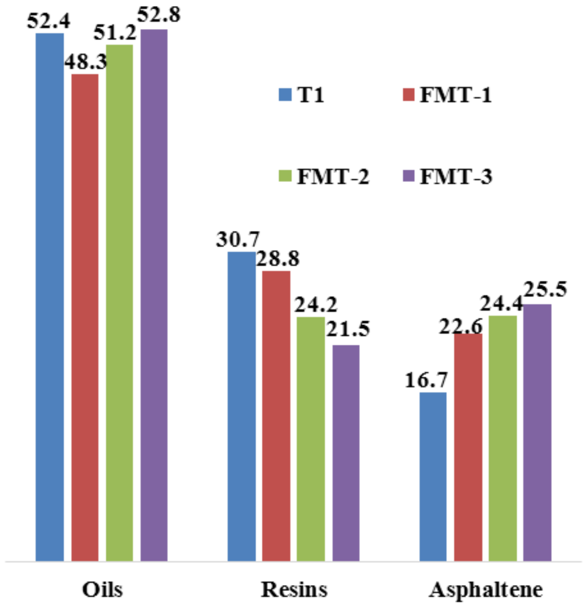


Fig. 5. Group composition of the raw materials and the products of chemical modification of tar with formaldehyde

FMT samples differ in terms of P298 and SP: FMT-1 – 144 dmm and 321.0 K, respectively; FMT-2 – 89 dmm and 332.0 K; and FMT-3 – 47 dmm and 356.4 K (Table 4). The content of carbenes and carboids remains unchanged with an increase in the modifier amount. The primary transformations during the modification occur with resins, which are converted into asphaltenes. This is evidenced by a decrease in resin content and an increase in asphaltene content (Fig. 5). This outcome is logical, as resins and asphaltenes contain heteroatomic compounds that are more prone to condensation with formaldehyde.

3. Conclusions

The primary disadvantages of using distillation and oxidized bitumens are their low heat resistance and poor adhesion to traditional acidic mineral fillers. These issues contribute to the formation of ruts and cracks in asphalt concrete pavements that use such binders, ultimately shortening the service life of the pavements. To address these problems, distillation and oxidized bitumens are often modified with polymers, typically plastics processing waste (such as PE, PP, PET, *etc.*) and specially synthesized block copolymers like styrene-butadiene-styrene (SBS). Road pavements made with polymer-modified bitumen (PMB) are far more resistant to deformation and cracking caused by road traffic than those made with unmodified bitumen. However, most polymers used in bitumen modification have poor compatibility with bitumen, leading to the delamination of PMB during long-term storage at high temperatures. A partial solution to this issue is the use of chemicals in the modification process.

It has been demonstrated that chemical modification of petroleum residues (tars) and bitumens to produce high-quality binders for road construction has been less explored compared to physical modification with polymers. The advantage of chemical modification is that it enables chemical interactions within the bitumen (or tar) and modifier system, resulting in binders with enhanced properties such as heat resistance, improved adhesion to mineral fillers in asphalt concrete, and resistance to delamination during storage. An overview of the effects of various modifiers has been conducted.

The potential of modifying petroleum residues and bitumens using an inexpensive and readily available modifier – a 37% aqueous formaldehyde solution (formalin) – was also explored. Formaldehyde can undergo copolycondensation reactions with aromatic compounds, especially heteroatomic ones, under certain conditions. Petroleum residues (tars) as well as distillation and oxidized bitumens contain significant quantities of such large heteroatomic polycyclic arenes (resins and asphaltenes). Modifying these materials with formaldehyde, depending on the amount used, allows for the production of bituminous materials with the desired penetration and softening point.

Acknowledgments

This work was supported by the National Research Foundation of Ukraine (Grant No. 2023.05/0026).

Abbreviations

AFR	Arene-formaldehyde resins
BND	Road oil bitumen
BND-A	Road oil bitumen modified with adhesive additives
D298	Ductility at 298 K
FBP	Fraas breaking point
FMT	Formaldehyde modified tar
FTIR	Fourier transform infrared spectroscopy;

IP	Plasticity interval
MA	Maleic anhydride
NMR	Nuclear magnetic resonance
OB	Oxidized bitumen
OBMA	Oxidized bitumen modified with maleic anhydride
P298	Penetration at 298 K
PE	Polyethylene
PhFR	Phenol formaldehyde resin
PMB	Polymer-modified bitumen
PP	Polypropylene
PPA	Polyphosphoric acid
RET	Reactive ethylene terpolymer
S	Sulfur
SB	Block copolymer styrene-butadiene
SBS	Block copolymer styrene-butadiene-styrene
SEBS	Block copolymer styrene-ethylene/butylene-styrene
SP	Softening point
T	Tar
TMA	Tar modified with maleic anhydride
WMB-S	Bitumen modified with synthetic waxes

References

[1] Porto, M.; Caputo, P.; Loise, V.; Eskandarsefat, S.; Teltayev, B.; Oliviero Rossi, C. Bitumen and Bitumen Modification: A Review on Latest Advances. *Appl. Sci.* **2019**, *9*, 742. https://doi.org/10.3390/app9040742

[2] Pyshyev, S.; Gunka, V.; Grytsenko, Y.; Bratychak, M. Polymer Modified Bitumen. *Chem. Chem. Technol.* **2016**, *10*, 631–636. https://doi.org/10.23939/chcht10.04si.631

[3] Cuadri, A. A.; Partal, P.; Navarro, F. J.; García-Morales, M.; Gallegos, C. Bitumen Chemical Modification by Thiourea Dioxide. *Fuel* **2011**, *90*, 2294–2300. https://doi.org/10.1016/j.fuel.2011.02.035

[4] Onyshchenko, A.; Lisnevskyi, R.; Poliak, O.; Rybchynskyi, S.; Shyshkin, E. Study on the Effect of Butonal NX4190 Polymer Latex on the Properties of Bitumen Binder and Asphalt Concrete. *Chem. Chem. Technol.* **2023**, *17*, 688–700. https://doi.org/10.23939/chcht17.03.688

[5] Gunka, V., Astakhova, O., Hrynchuk, Y., Sidun, I., Reutskyy, V., Mirchuk, I., Poliak, O. A Review of Road Bitumen Modification Methods. Part 1 - Physical Modification. *Chem. Chem. Technol.* **2024**, *18*, 295–304. https://doi.org/10.23939/chcht18.02.295

[6] Grynyshyn, O.; Donchenko, M.; Khlibyshyn, Yu.; Poliak, O. Investigation of Petroleum Bitumen Resistance to Aging. *Chem. Chem. Technol.* **2021**, *15*, 438–442. https://doi.org/10.23939/chcht15.03.438

[7] Zhu, J.; Birgisson, B.; Kringos, N. Polymer Modification of Bitumen: Advances and Challenges. *Eur. Polym. J.* **2014**, *54*, 18–38. https://doi.org/10.1016/j.eurpolymj.2014.02.005

[8] Grynyshyn, O.; Donchenko, M; Kochubei, V.; Khlibyshyn, Y. Main Features of the Technological Process of Aging of Bitumen Obtained from the Residues from Ukrainian Crude Oil Processing. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2023**, *3*, 54–62. https://doi.org/10.32434/0321-4095-2023-148-3-54-62

[9] Pstrowska, K.; Gunka, V.; Sidun, I.; Demchuk, Y.; Vytrykush, N.; Kułażyński, M .; Bratychak, M. Adhesion in Bitumen/Aggregate System: Adhesion Mechanism and Test Methods. *Coatings* **2022**, *12*, 1934. https://doi.org/10.3390/coatings12121934

[10] Mousavi, M.; Kabir, S. F.; Fini, E. H. Effects of Sulfur Phase Transition on Moisture-Induced Damages in Bitumen Colloidal Structure. *J. Environ. Chem. Eng.* **2022**, *107*, 109–117. https://doi.org/10.1016/j.jiec.2021.11.040

[11] Nguyen, T. T.; Tran, N. H.; Kien Bui, N.; Vu, T. T., Pham, H. K.; Bui, X. C. The Investigation on the Effects of Sulphur on the Performance of Sulphur-Bitumen Binder. *Road Mater. Pavement Des.* **2022**, *24*, 795–818. https://doi.org/10.1080/14680629.2022.2049351

[12] Sakib, N.; Bhasin, A.; Islam, M. K.; Khan, K.; Khan, M. I. A Review of the Evolution of Technologies to Use Sulphur as a Pavement Construction Material. *Int. J. Pavement Eng.* **2021**, *22*, 392-403. https://doi.org/10.1080/10298436.2019.1612064

[13] Singh, M.; Jain, K.; Kahlon, S. S. Use of Sulphur as an Additive in Bitumen: A Review. *Int. Res. J. Eng. Technol,* **2020**, *7*, 36–43.

[14] Xie, S.; Yi, J.; Zhou, T.; Fini, E. H.; Feng, D. Phase Transition Process of Sulfur in Bitumen and its Effect on Rheological Properties of Bitumen. *Constr. Build. Mater.* **2023**, *364*, 129914. https://doi.org/10.1016/j.conbuildmat.2022.129914

[15] Baldino, N.; Gabriele, D.; Lupi, F. R.; Rossi, C. O.; Caputo, P.; Falvo, T. Rheological Effects on Bitumen of Polyphosphoric Acid (PPA) Addition. *Constr. Build. Mater.* **2013,** *40*, 397–404. https://doi.org/10.1016/j.conbuildmat.2012.11.001

[16] Liu, S.; Zhou, S.; Peng, A. Evaluation of Polyphosphoric Acid on the Performance of Polymer Modified Asphalt Binders. *J. Appl. Polym. Sci.* **2020,** *137*, 48984. https://doi.org/10.1002/app.48984

[17] Kabir, S. F.; Mousavi, M.; Hung, A. M.; Fini, E. H. High-Sulfur Bitumen Amplifies the Effect of Polyphosphoric Acid. *Fuel* **2022**, *314*, 123128. https://doi.org/10.1016/j.fuel.2021.123128

[18] Masson, J. F. Brief Review of the Chemistry of Polyphosphoric Acid (PPA) and Bitumen. *Energy Fuels* **2008**, *22*, 2637–2640. https://doi.org/10.1021/ef800120x

[19] Özdemir, D. K. High and Low Temperature Rheological Characteristics of Linear Alkyl Benzene Sulfonic Acid Modified Bitumen. *Constr. Build. Mater.* **2021,** *301*, 124041. https://doi.org/10.1016/j.conbuildmat.2021.124041

[20] Ortega, F. J.; Navarro, F. J.; García-Morales, M. Dodecylbenzenesulfonic Acid as a Bitumen Modifier: A Novel Approach to Enhance Rheological Properties of Bitumen. *Energy Fuels* **2017**, *1*, 5003–5010. https://doi.org/10.1021/acs.energyfuels.7b00419

[21] Aldagari, S.; Hung, A. M.; Shariati, S.; Kabir, S. F.; Ranka, M.; Bird, R. C.; Fini, E. H. Enhanced Sustainability at the Bitumen-Aggregate Interface Using Organosilane Coating Technology. *Constr. Build. Mater.* **2022,** *359*, 129500. https://doi.org/10.1016/j.conbuildmat.2022.129500

[22] Mirzababaei, P.; Moghadas Nejad, F.; Naderi, K. Effect of Liquid Silane-Based Anti-Stripping Additives on Rheological Properties of Asphalt Binder and Hot Mix Asphalt Moisture Sensitivity. *Road Mater. Pavement Des.* **2020,** *21*, 570–585. https://doi.org/10.1080/14680629.2018.1507920

[23] Peng, C.; Chen, P.; You, Z.; Lv, S.; Zhang, R.; Xu, F.; Chen, H. Effect of Silane Coupling Agent on Improving the Adhesive Properties between Asphalt Binder and Aggregates. *Constr Build Mater.* **2018,** *169*, 591–600. https://doi.org/10.1016/j.conbuildmat.2018.02.186

[24] Rossi, C. O.; Caputo, P.; Baldino, N.; Szerb, E. I.; Teltayev, B. Quantitative Evaluation of Organosilane-Based Adhesion Promoter Effect on Bitumen-Aggregate Bond by Contact Angle Test. *Int. J. Adhes. Adhes.* **2017**, *72*, 117–122. https://doi.org/10.1016/j.ijadhadh.2016.10.015

[25] Cuadri, A. A.; Partal, P.; Navarro, F. J.; García-Morales, M.; Gallegos, C. Influence of Processing Temperature on the Modification Route and Rheological Properties of Thiourea Dioxide-Modified Bitumen. *Energy Fuels* 2011, *25*, 4055–4062. https://doi.org/10.1021/ef200801h

[26] Bagshaw, S. A.; Kemmitt, T.; Waterland, M.; Brooke, S. Effect of Blending Conditions on Nano-Clay Bitumen Nanocomposite Properties. *Road Mater. Pavement Des.* **2019**, *20*, 1735–1756. https://doi.org/10.1080/14680629.2018.1468802

[27] Bala, N.; Kamaruddin, I.; Napiah, M.; Sutanto, M. H. Polymer Nanocomposite-Modified Asphalt: Characterisation and Optimisation Using Response Surface Methodology. *Arab. J. Sci. Eng.* **2019**, *44*, 4233–4243. https://doi.org/10.1007/s13369-018-3377-x

[28] Dehouche, N.; Kaci, M.; Mouillet, V. The Effects of Mixing Rate on Morphology and Physical Properties of Bitumen/Organo-Modified Montmorillonite Nanocomposites. *Constr. Build. Mater.* **2016,** *114*, 76–86. https://doi.org/10.1016/j.conbuildmat.2016.03.151

[29] Günay, T.; Ahmedzade, P. Physical and Rheological Properties of nano-TiO_2 and Nanocomposite Modified Bitumens. *Constr. Build. Mater.* **2020,** *243*, 118208. https://doi.org/10.1016/j.conbuildmat.2020.118208

[30] Gulzar, S.; Underwood, S. Use of Polymer Nanocomposites in Asphalt Binder Modification. In *Advanced Functional Textiles and Polymers: Fabrication, Processing and Applications*; Ul Islam, Sh.; Butola, B. S., Eds.; Scrivener publishing, 2019; pp 405–431. https://doi.org/10.1002/9781119605843.ch14

[31] Kosma, V.; Hayrapetyan, S.; Diamanti, E.; Dhawale, A.; Giannelis, E. P. Bitumen Nanocomposites with Improved Performance. *Constr. Build. Mater.* **2018,** *160*, 30–38. https://doi.org/10.1016/j.conbuildmat.2017.11.024

[32] Mahali, I.; Sahoo, U. C. Rheological Characterization of Nanocomposite Modified Asphalt Binder. *Int. J. Pavement Res. Technol.* **2019**, *12*, 589–594. https://doi.org/10.1007/s42947-019-0070-8

[33] Mamuye, Y.; Liao, M. C.; Do, N. D. Nano-Al_2O_3 Composite on Intermediate and High Temperature Properties of Neat and Modified Asphalt Binders and their Effect on Hot Mix Asphalt Mixtures. *Constr. Build. Mater.* **2022**, *331*, 127304. https://doi.org/10.1016/j.conbuildmat.2022.127304

[34] Merusi, F.; Giuliani, F.; Polacco, G. Linear Viscoelastic Behaviour of Asphalt Binders Modified with Polymer/Clay Nanocomposites. *Procedia Soc. Behav. Sci.* **2012**, *53*, 335–345. https://doi.org/10.1016/j.sbspro.2012.09.885

[35] Herrington, P. R.; Wu, Y.; Forbes, M. C. Rheological Modification of Bitumen with Maleic Anhydride and Dicarboxylic Acids. *Fuel* **1999**, *78,* 101–110. https://doi.org/10.1016/S0016-2361(98)00120-3

[36] Singh, B.; Kumar, L.; Gupta, M.; Chauhan, G. S. Polymer□Modified Bitumen of Recycled LDPE and Maleated Bitumen. *J. Appl. Polym. Sci.* **2013**, *127*, 67–78. https://doi.org/10.1002/app.36810

[37] Bulatović, V. O.; Rek, V.; Marković, J. Rheological Properties of Bitumen Modified with Ethylene Butylacrylate Glycidylmethacrylate. *Polym. Eng. Sci.* **2014**, *54*, 1056–1065. https://doi.org/10.1002/pen.23649

[38] Geckil, T.; Seloglu, M. Performance Properties of Asphalt Modified with Reactive Terpolymer. *Constr. Build. Mater.* **2018**, *173*, 262–271. https://doi.org/10.1016/j.conbuildmat.2018.04.036

[39] Kumandaş, A.; Çavdar, E.; Oruç, Ş.; Pancar, E. B.; Kök, B. V. Effect of WCO Addition on High and Low-temperature Performance of RET Modified Bitumen. *Constr. Build. Mater.* **2022**, *323*, 126561. https://doi.org/10.1016/j.conbuildmat.2022.126561

[40] Apostolidis, P.; Liu, X.; Erkens, S. M. J. G.; Scarpas, A. Evaluation of Epoxy Modification in Bitumen. *Constr. Build. Mater.* **2019**, *208*, 361–368. https://doi.org/10.1016/j.conbuildmat.2019.03.013

[41] Çubuk, M.; Gürü, M.; Çubuk, M. K.; Arslan, D. Rheological Properties and Performance Evaluation of Phenol Formaldehyde Modified Bitumen. *J. Mater. Civ. Eng.* **2014**, *26*, 04014015. https://doi.org/10.1061/(ASCE)MT.1943-5533.0000889

[42] Chopra, A.; Singh, S. Performance Evaluation on Epoxy Modified Bituminous Mix. *Mater. Today: Proc.* **2022**, *51*, 1197–1200. https://doi.org/10.1016/j.matpr.2021.07.206

[43] Ivashkiv, O.; Astakhova, O.; Shyshchak, O.; Plonska-Brzezinska, M.; Bratychak, M. Structure and Application of ED-20 Epoxy Resin Hydroxy-Containing Derivatives in Bitumen-Polymeric Blends. *Chem. Chem. Technol.* **2015**, *9*, 69–76. https://doi.org/10.23939/chcht09.01.069

[44] Motamedi, M.; Attar, M. M.; Rostami, M. Performance Enhancement of the Oxidized Bitumen Binder Using Epoxy Resin. *Prog. Org. Coat.* **2017**, *102*, 178–185. https://doi.org/10.1016/j.porgcoat.2016.10.011

[45] Starchevskyy, V.; Hrynchuk, Y.; Matcipura, P.; Reutskyy, V. Influence of Initiators on the Adhesion Properties of Bitumen Modified by Natural Origin Epoxide. *Chem. Chem. Technol.* **2021**, *15*, 142–147. https://doi.org/10.23939/chcht15.01.142

[46] Cubuk, M.; Gürü, M.; Çubuk, M. K. Improvement of Bitumen Performance with Epoxy Resin. *Fuel* **2009**, *88*, 1324–1328. https://doi.org/10.1016/j.fuel.2008.12.024

[47] Xia, Q.; Li, Y.; Xu, H.; Luo, H.; Zheng, Y.; Zhao, R.; Xu, H. Using Phenol Formaldehyde Resin, Hexamethylenetetramine and Matrix Asphalt to Synthesize Hard-Grade Asphalts for High-Modulus Asphalt Concrete. *Sustainability* **2022**, *14*, 15689. https://doi.org/10.3390/su142315689

[48] Ahmedzade, P.; Yilmaz, M. Effect of Polyester Resin Additive on the Properties of Asphalt Binders and Mixtures. *Constr. Build. Mater.* **2008**, *22*, 481–486. https://doi.org/10.1016/j.conbuildmat.2006.11.015

[49] Shi, X.; Zhang, H.;Bu, X.; Zhang, G.; Zhang, H.; Kang, H. Performance Evaluation of BDM/Unsaturated Polyester Resin-Modified Asphalt Mixture for Application in Bridge Deck Pavement. *Road Mater. Pavement Des.* **2022**, *23*, 684–700. https://doi.org/10.1080/14680629.2020.1828154

[50] Zhang, H.; Su, C.; Bu, X.; Zhang, Y.; Gao, Y.; Huang, M. Laboratory Investigation on the Properties of Polyurethane/Unsaturated Polyester Resin Modified Bituminous Mixture. *Constr. Build. Mater.* **2020**, *260*, 119865. https://doi.org/10.1016/j.conbuildmat.2020.119865

[51] Hunter, R. N.; Self, A.; Read, J. *The shell bitumen handbook*; Shell Bitumen: London, UK, 2015.

[52] Das, A. K.; Panda, M. Investigation on Rheological Performance of Sulphur Modified Bitumen (SMB) Binders. *Constr. Build. Mater.* **2017**, *149*, 724–732. https://doi.org/10.1016/j.conbuildmat.2017.05.198

[53] Fritschy, G.; Papirer, E.; Chambu, C. Sulfur Modified Bitumen: A New Binder. *Rheol Acta* **1981**, *20*, 78–84. https://doi.org/10.1007/BF01517475

[54] De Carcer, Í. A.; Masegosa, R. M.; Viñas, M. T.; Sanchez-Cabezudo, M.; Salom, C.; Prolongo, M. G.; Páez, A. Storage Stability of SBS/Sulfur Modified Bitumens at High Temperature: Influence of Bitumen Composition and Structure. *Constr. Build. Mater.* **2014**, *52*, 245–252. https://doi.org/10.1016/j.conbuildmat.2013.10.069

[55] Zeng, J.; Zhao, J. Mechanism and Performance Investigation of SBS/Sulfur Composite Modified Asphalt. *Pet. Sci.* **2022**, *62*, 732–739. https://doi.org/10.1134/S0965544122050140

[56] Martínez□Estrada, A.; Chávez□Castellanos, A. E.; Herrera□Alonso, M.; Herrera□Nájera, R. Comparative Study of the Effect of Sulfur on the Morphology and Rheological Properties of SB□and SBS□Modified Asphalt. *J. Appl. Polym. Sci.* **2010**, *115*, 3409–3422. https://doi.org/10.1002/app.31407

[57] Schermer, W. E. M.; Steernberg, K. Preparation process for polymer-modified bitumen. US 5719216 A, February 17, 1998.

[58] Wręczycki, J.; Demchuk, Y.; Bieliński, D.M.; Bratychak, M.; Gunka, V.; Anyszka, R.; Gozdek, T. Bitumen Binders Modified with Sulfur/Organic Copolymers. *Materials* **2022**, *15,* 1774. https://doi.org/10.3390/ma15051774

[59] Miknis, F. P.; Thomas, K. P. NMR Analysis of Polyphosphoric Acid-Modified Bitumens. *Road Mater. Pavement Des.* **2008**, *9*, 59–72. https://doi.org/10.1080/14680629.2008.9690107

[60] Baumgardner, G. L.; Masson, J. F.; Hardee, J. R.; Menapace, A. M.; Williams, A. G. Polyphosphoric Acid Modified Asphalt: Proposed Mechanisms. *J. Assoc. Asphalt Paving Technol.* **2005**, *74*, 283–305.

[61] Lesueur, D. The Colloidal Structure of Bitumen: Consequences on the Rheology and on the Mechanisms of Bitumen Modification. *Adv. Colloid Interface Sci.* **2009**, *145*, 42–82. https://doi.org/10.1016/j.cis.2008.08.011

[62] Masson, J. F.; Gagné, M. Polyphosphoric Acid (PPA)-Modified Bitumen: Disruption of the Asphaltenes Network Based on the Reaction of Nonbasic Nitrogen with PPA. *Energy Fuels* **2008**, *22*, 3402–3406. https://doi.org/10.1021/ef8002944

[63] Han, Y.; Tian, J.; Ding, J.; Shu, L.; Ni, F. Evaluating the Storage Stability of SBR-Modified Asphalt Binder Containing Polyphosphoric Acid (PPA). *Case Stud. Constr. Mater.* **2022**, *17*, e01214. https://doi.org/10.1016/j.cscm.2022.e01214

[64] Singh, S. K.; Pandey, A.; Ravindranath, S. S. Effect of Additives on the Thermal Stability of SBS Modified Binders during Storage at Elevated Temperatures. *Constr Build Mater.* **2022**, *314*, 125609. https://doi.org/10.1016/j.conbuildmat.2021.125609

[65] Kang, Y.; Wang, F.; Chen, Z. Reaction of Asphalt and Maleic Anhydride: Kinetics and Mechanism. *Chem. Eng. J.* **2010**, *164*, 230–237. https://doi.org/10.1016/j.cej.2010.08.020

[66] Becker, M. Y.; Muller, A. J.; Rodriguez, Y. Use of Rheological Compatibility Criteria to Study SBS Modified Asphalts. *J. Appl. Polym. Sci.* **2003**, *90*, 1772–1782. https://doi.org/10.1002/app.12764

[67] Gunka, V.; Prysiazhnyi, Y.; Hrynchuk, Y.; Sidun, I.; Demchuk, Y.; Shyshchak, O.; Bratychak, M. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 2. Bitumen Modified with Maleic Anhydride. *Chem. Chem. Technol.* **2021**, *15*, 443–449. https://doi.org/10.23939/chcht15.03.443

[68] Gunka, V.; Prysiazhnyi, Yu.; Demchuk, Yu.; Hrynchuk, Yu.; Sidun, I.; Reutskyy, V.; Bratychak, M. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 5. Use of Maleic Anhydride for Foaming Bitumens. *Chem. Chem. Technol.* **2022**, *16*, 295–302. https://doi.org/10.23939/chcht16.02.295

[69] Gunka, V.; Hrynchuk, Yu.; Sidun, I.; Demchuk, Yu.; Prysiazhnyi, Yu.; Bratychak, M. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 6. Temperature Effect on the Chemical Modification of Bitumen with Maleic Anhydride. *Chem. Chem. Technol.* **2022**, *16*, 475–483. https://doi.org/10.23939/chcht16.03.475

[70] Polacco, G.; Stastna, J.; Biondi, D.; Antonelli, F.; Vlachovicova, Z.; Zanzotto, L. Rheology of Asphalts Modified with Glycidylmethacrylate Functionalized Polymers. *J. Colloid Interface Sci.* **2004**, *280*, 366–373. https://doi.org/10.1016/j.jcis.2004.08.043

[71] Yeh, P. H.; Nien, Y. H.; Chen, J. H.; Chen, W. C.; Chen, J. S. Thermal and Rheological Properties of Maleated Polypropylene Modified Asphalt. *Polym. Eng. Sci.* **2005**, *45*, 1152–1158. https://doi.org/10.1002/pen.20386

[72] Ahmad, M.; Beddu, S.;Hussain, S.; Manan, A.; Itam, Z. B. Mechanical Properties of Hot-Mix Asphalt Using Waste Crumber Rubber and Phenol Formaldehyde Polymer. *AIMS Mater. Sci.* **2019**, *6*, 1164–1175. https://doi.org/10.3934/matersci.2019.6.1164

[73] Gupta, A.; Chopra, E. Comparative Study of Conventional and Bakelite Modified Bituminious Mix. *Int. J. Civ. Eng.* **2019**, *10*, 1386–1392. https://ssrn.com/abstract=3457096

[74] Saha, S. K.; Suman, S. K. Characterization of Bakelite-Modified Bitumen. *Innov. Infrastruct. Solut.* **2017**, *2*, 3. https://doi.org/10.1007/s41062-017-0052-0

[75] Gunka, V.; Demchuk, Y.; Sidun, I.; Kochubei, V.; Shved, M.; Romanchuk, V.; Korchak, B. Chemical Modification of Road Oil Bitumens by Formaldehyde. *Pet. Coal* **2020**, *62*, 420–429.

[76] Demchuk, Y.; Gunka, V.; Sidun, I.; Solodkyy, S. Comparison of Bitumen Modified by Phenol Formaldehyde Resins Synthesized from Different Raw Materials. *Proc. of EcoComfort*. **2020**, *100*, 95–102. https://doi.org/10.1007/978-3-030-57340-9_12

[77] Gunka, V.; Demchuk, Y.; Pyshyev, S.; Anatolii, S.; Lypko, Y. The Selection of Raw Materials for the Production of Road Bitumen Modified by Phenol-Cresol-Formaldehyde Resins. *Pet. Coal* **2018**, *60*, 1199–1206.

[78] Pyshyev, S.; Demchuk, Y.; Gunka, V.; Sidun, I.; Shved, M.; Bilushchak, H.; Obshta, A. Development of Mathematical Model and Identification of Optimal Conditions to Obtain Phenol-Cresol-Formaldehyde Resin. *Chem. Chem. Technol*. **2019**, *13*, 212–217. https://doi.org/10.23939/chcht13.02.212

[79] Demchuk, Y.; Gunka, V.; Pyshyev, S.; Sidun, I.; Hrynchuk, Y.; Kucińska-Lipka, J.; Bratychak, M. Slurry Surfacing Mixes on the Basis of Bitumen Modified with Phenol-Cresol-Formaldehyde Resin. *Chem. Chem. Technol.* **2020**, *14*, 251–256. https://doi.org/10.23939/chcht14.02.251

[80] Demchuk, Y.; Sidun, I.; Gunka, V.; Pyshyev, S.; Solodkyy, S. Effect of Phenol-Cresol-Formaldehyde Resin on Adhesive and Physico-Mechanical Properties of Road Bitumen. *Chem. Chem. Technol.* **2018**, *12*, 456–461 https://doi.org/10.23939/chcht12.04.456

[81] Gunka, V.; Demchuk, Y.; Sidun, I.; Miroshnichenko, D.; Nyakuma, B. B.; Pyshyev, S. Application of Phenol-Cresol-Formaldehyde Resin as an Adhesion Promoter for Bitumen and Asphalt Concrete. *Road Mater. Pavement Des.* **2021**, *22*, 2906–2918. https://doi.org/10.1080/14680629.2020.1808518

[82] Strap, G.; Astakhova, O.; Lazorko, O.; Shyshchak, O.; Bratychak, M. Modified Phenol-Formaldehyde Resins and their Application in Bitumen-Polymeric Mixtures. *Chem. Chem. Technol.* **2013**, *7*, 279–287. https://doi.org/10.23939/chcht07.03.279

[83] Imoto, M.; Huang, C. Y.; Iguchi, T.; Sakurai, F.; Kuraya, T.; Yoshioka, S.; Itakura, J. Preparation of Thermosetting Hydrocarbon Resin. Resins from Formaldehyde, LXIII. *Die Makromolekulare Chemie: Macromol. Chem. Phys.* **1961**, *43*, 189–219. https://doi.org/10.1002/macp.1961.020430121

[84] Higashihara, G.; Okoshi, A. Aromatic hydrocarbon formaldehyde resin, modified aromatic hydrocarbon formaldehyde resin and epoxy resin, and method for producing these. US 9725551 B2, August 08, 2017.

[85] Moshchynska, N. K. *Polimerni materialy na osnovi aromatychnykh vuhlevodniv i formaldehidu*; Technika: Kyiv, 1970.

[86] Gunka, V.; Prysiazhnyi, Y.; Hrynchuk, Y.; Sidun, I.; Demchuk, Y.; Shyshchak, O.; Poliak, O.; Bratychak, M. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 3. Tar Modified with Formaldehyde. *Chem. Chem. Technol.* **2021**, *15*, 608–620. https://doi.org/10.23939/chcht15.04.608

[87] Gunka, V.; Bilushchak, H.; Prysiazhnyi, Y.; Demchuk, Y.; Hrynchuk, Y.; Sidun, I.; Bratychak, M. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 4. Determining the Optimal Conditions for Tar Modification with Formaldehyde and Properties of the Modified Products. *Chem. Chem. Technol.* **2022**, *16*, 142–149. https://doi.org/10.23939/chcht16.01.142

[88] Gunka, V.; Hrynchuk, Y.; Demchuk, Yu.; Donchenko, M.; Prysiazhnyi, Y.; Reutskyy, V.; Astakhova, O. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 7. Study of the Structure of Formaldehyde Modified Tars. *Chem. Chem. Technol.* **2023**, *17*, 211–220. https://doi.org/10.23939/chcht17.01.211

[89] Gunka, V.; Donchenko, M.; Demchuk, Yu.; Drapak, I.; Bratychak, M. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 8. Prospects of Using Formaldehyde Modified Tars in Road Construction. *Chem. Chem. Technol.* **2023**, *17*, 701–710. https://doi.org/10.23939/chcht17.03.701

[90] Gunka, V.; Sidun, I.; Poliak, O.; Demchuk, Y.; Prysiazhnyi, Y.; Hrynchuk, Y.; Drapak, I.; Astakhova, O. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 9. Stone Mastic Asphalt Using Formaldehyde Modified Tars. *Chem. Chem. Technol.* **2023**, *17*, 916–922. https://doi.org/10.23939/chcht17.04.916

[91] Pstrowska, K.; Gunka, V.; Prysiazhnyi, Yu.; Demchuk, Yu.; Hrynchuk, Yu.; Sidun, Iu.; Kułażyński, M.; Bratychak, M. Obtaining of Formaldehyde Modified Tars and Road Materials on Their Basis. *Materials* **2022**, *15*, 5693. https://doi.org/10.3390/ma15165693

[92] Bratychak, M.; Gunka, V.; Prysiazhnyi, Y.; Hrynchuk, Y.; Sidun, I.; Demchuk, Y.; Shyshchak, O. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 1. Effect of Solvent Nature on the Properties of Petroleum Residues Modified with Folmaldehyde. *Chem. Chem. Technol.* **2021**, *15*, 274–283. https://doi.org/10.23939/chcht15.02.274

[93] Gunka, V.; Sidun, I.; Solodkyy, S.; Vytrykush, N. Hot Asphalt Concrete with Application of Formaldehyde Modified Bitumen. *Lect. Notes Civ. Eng.* **2019**, *47*, 111–118. https://doi.org/10.1007/978-3-030-27011-7_14

[94] Gunka, V.; Hidei, V.; Sidun, I.; Demchuk, Y.; Stadnik, V.; Shapoval, P.; Sobol, Kh.; Vytrykush, N.; Bratychak, M. Wastepaper Sludge Ash and Acid Tar as Activated Filler Aggregates for Stone Mastic Asphalt. *Coatings* **2023**, *13*, 1183. https://doi.org/10.3390/coatings13071183

[95] Gunka, V.; Demchuk, Y.; Drapak, I.; Korchak, B.; Bratychak, M. Kinetic Model of the Process of Polycondensation of Concentrated Phenols of Coal Tar with Formaldehyde. *Chem. Chem. Technol.* **2023,** *17*, 339–346. https://doi.org/10.23939/chcht17.02.339

[96] DSTU 4044:2019 Petroleum road viscous bitumen. Technical conditions.

[97] DSTU 9116:2021 Bitumen and bitumen binders. Road bitumen modified with polymers. Technical conditions.

[98] SOU 42.1-37641918-068:2017 Viscous road bitumen modified with wax-based additives. Technical conditions.

[99] SOU 45.2-00018112-067:2011 Construction materials. Viscous road bitumen modified with adhesive additives. Technical conditions. Amendment No. 1.

Received: October 04, 2024 / Revised: October 25, 2024 /
Accepted: November 11, 2024

ОГЛЯД МЕТОДІВ МОДИФІКУВАННЯ ДОРОЖНІХ БІТУМІВ. ЧАСТИНА 2 – ХІМІЧНЕ МОДИФІКУВАННЯ

Анотація. *Проведено літературний огляд сучасних хімічних методів модифікування дорожніх бітумів за популярністю та характером впливу на властивості в'яжучих. Найуживанішим модифікатором хімічної дії в дорожній практиці є сірка, поліфосфорна кислота, малеїновий ангідрид, термореактивні смоли (фенолоформальдегідні, епоксидні, поліефірні тощо) та полімери. Розглянуто спосіб одержання різних за пенетрацією бітумних матеріалів методом хімічного модифікування нафтових залишків формальдегідом. Усі бітумні матеріали, які одержано способом хімічного модифікування, характеризуються кращою однорідністю при зберіганні за високих температур порівняно з в'яжучими, одержаними методами фізичного модифікуванням, що зумовлено хімічною взаємодією між реагентом-модифікатором і бітумом. Показано, що часто хімічні модифікатори застосовують у комплексі з фізичними для підсилення їхньої дії.*

Ключові слова: *бітум, хімічне модифікування, сірка, поліфосфорна кислота, малеїновий ангідрид, термореактивні смоли, формальдегід.*