CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2022,
Vol. 16, No. 3, pp. 475–483

Chemical Technology

PRODUCTION OF BITUMEN MODIFIED WITH LOW-MOLECULAR ORGANIC COMPOUNDS FROM PETROLEUM RESIDUES. 6. TEMPERATURE EFFECT ON THE CHEMICAL MODIFICATION OF BITUMEN WITH MALEIC ANHYDRIDE

Volodymyr Gunka[1], *Yurii Hrynchuk*[1], *Iurii Sidun*[1], *Yuriy Demchuk* [1],
Yuriy Prysiazhnyi[1], *Michael Bratychak*[1,✉]

https://doi.org/10.23939/chcht16.03.475

Abstract. The oxidized bitumen produced at the Ukrainian refinery was modified with maleic anhydride. The process temperature was proved to have the most significant effect on modification. The chemical interaction of maleic anhydride with the components of oxidized bitumen was confirmed. At low temperatures (up to 403 K) the chemistry of the modification process is another than chemistry of the process carried out at high temperatures. The structures of the modified bitumen were established at different process temperatures (403, 423 and 443 K) using FTIR spectroscopy. A thin film heating at 436 K (RTFOT method) was performed for the bitumen under study. It was found that for bitumen modified at 403 K, the formed structure is destroyed after heating by RTFOT, which is confirmed by a decrease in the softening point of the bitumen. The FTIR spectra of the original oxidized bitumen and bitumen modified with maleic anhydride at 403 and 443 K were recorded after the RTFOT heating process. Based on the obtained data, the structural transformations that occurred during heating were established.

Keywords: bitumen, maleic anhydride, chemical modification, temperature effect.

1. Introduction

Bitumen is one of the main components of asphalt concrete mixtures, which plays an important role as a binder in asphalt concrete. The vast majority of asphalt mixtures problems occur due to the low quality of distillation and oxidized paving bitumen. The most promising way to improve the quality of binders, in order to obtain a road surface with high performance, is to modify them. For the modification of bituminous binders, one uses the following types of polymers: elastomers (natural rubber and rubber),[1-3] thermoplastics (polyethylene, polypropylene, polyvinyl chloride, *etc.*),[4-7] thermoelastomers (styrene-butadiene-styrene, ethylene-vinyl acetate, *etc.*)[8-10] and thermosetting polymers (polyurethane resins).[11] It should be outlined that thermoplastics and thermoplastic elastomers are by far the most often used among the above-mentioned polymers.[1] The polymers, such as styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS), are the most common modifiers for bitumens out of thermoplastic elastomers.[1,8-10]

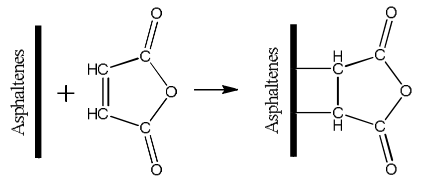
Depending on the polymer effect, SBS- and SIS-modified bitumens fall into bitumen-polymer and poly-mer-bitumen binders. Bitumen-polymer binders with a 3.5 %-composition by mass of SBS and SIS have greater penetration, higher softening temperature, and greater elasticity.[1] High cost is probably the one and only drawback of such modifiers.

As alternative additives to bitumens, resins have been studied actively to be used with various functional groups, produced from non-target products or by-products of the coal conversion (phenol-cresol-formaldehyde resins and phenol-formaldehyde resins with labile peroxy bonds or methacrylic components),[12-19] petroleum resins with epoxy, hydroxyl or carboxy groups,[20] low-molecular organic compounds (formaldehyde and maleic anhydride)[21-26] and sulfur/organic copolymers.[27]

Maleic anhydride (MA) was studied in the previous work[28,29] as a low molecular weight modifier that chemically interacts with bitumen. Asphaltenes, which are a part of bitumen, can react with maleic anhydride according to the following schemes:[29]

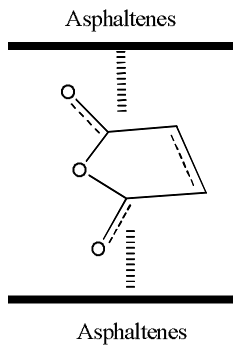
• *via* the Diels-Alder reaction

[1] Lviv Polytechnic National University
12, S. Bandery St., Lviv, 79013, Ukraine
✉ *mbratychak@gmail.com*



(1)

• with the formation of π-π complexes



(2)

In our previous work,[23] we studied the effect of different factors on the bitumen modification with MA, namely temperature, duration and MA amount. The temperature was found to have the greatest influence on the process. We observed an anomaly that at low modification temperatures (383–403 K) the bitumen modified with maleic anhydride (OBMA) has a higher heat resistance to compare with that obtained at the temperatures above 423 K. Therefore, in this work the effect of temperature on the process of oxidized bitumen modification with MA was studied in more detail.

2. Experimental

2.1. Materials

The following materials were used for modification:

• paving bitumen OB1 (oxidized bitumen) produced at JSC Ukrtatnafta (Kremenchuk, Ukraine). Its characteristic is given in Table 1, designated as BND 60/90;

• MA, white crystalline powder (used as a process modifier / chemical reagent).

Table 1. Characteristics of OB1 bitumen

Index	Unit of measurement	Value
Penetration at 298 K (P298)	dmm	71
Softening point (SP)	K	319
Ductility at 298 K	cm	>100
Adhesion to gravel	point	2.5
Fraas breaking point (FBP)	K	263
Plasticity interval (PI)	K	56
Resistance to hardening at 436 K (RTFOT method):		
mass change	wt %	0.03
softening point after RTFOT	K	325.2
penetration at 298 K after RTFOT	dmm	55
softening point change	K	6.2
residual penetration	%	77.5

2.2. Experimental Procedure

Chemical modification of bitumen with MA was carried out using a laboratory setup, the scheme of which is shown in Fig. 1.

The flask was loaded with raw material (OB1) heated to a temperature that ensures its mobile state. The stirring was switched on and the raw material was heated to the process operating temperature. Next, a modifier (MA) was added using a separating funnel/dosing device. The modification was carried out under stirring (1000 rpm) in an inert gas (N_2) medium. The obtained modified bitumen was analyzed according to the main performance characteristics: penetration at 298 K (P298), softening point (SP), Fraas breaking point (FBP), plasticity interval (PI), and adhesion to gravel (AG).

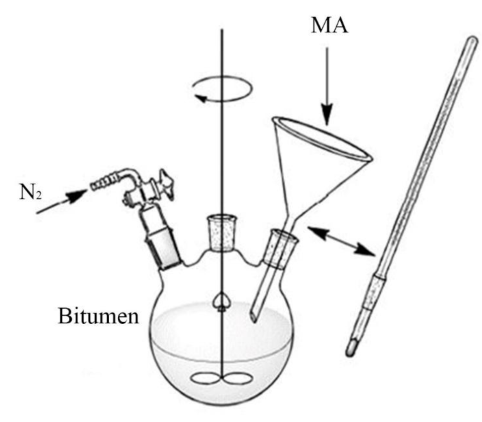


Fig. 1. Scheme of the laboratory setup for modification of bitumen with MA

2.3. Analysis Methods

The following physico-technological characteristics of the original (OB1) and modified bitumen (OBMA) were determined according to the standard procedures: softening temperature;[30] penetration;[31] Fraas breaking point;[32] ductility;[33] adhesion to gravel;[34] plasticity interval,[13,16] and resistance to hardening at 436 K (RTFOT method).[35]

To determine the adhesion to gravel (AG) the fraction of 20–40 mm was used. The fraction was obtained from natural stone supplied by JSC "Mokriansky Stone Quarry No.3" (Ukraine).

The FTIR spectra were recorded on a Spectrum Two spectrometer (PerkinElmer, USA) by using with diamond U-ATR single reflection accessory. PerkinElmer Spectrum software was used to draw the spectra. The spectra (16 scans per spectrum) of the samples were collected in the mid-infrared wavenumber range from 1800 to 500 cm^{-1}, with a spectral resolution of 4 cm^{-1}.

3. Results and Discussion

To study the effect of temperature on the properties of OBMA all other options were fixed (Table 2).

Table 2. Experimental conditions

Option	Unit of measurement	Value
Raw	–	OB1
Duration	hours	0.5
Modifier (MA) amount	kg/100 raw	2.0

The effect of temperature on the main performance characteristics (P298, SP, FBP, PI and AG) is shown in Figs. 2-6.

Fig. 2 shows that P298 of the modified bitumen is reduced almost twice, from 71 to 27–35 dmm.

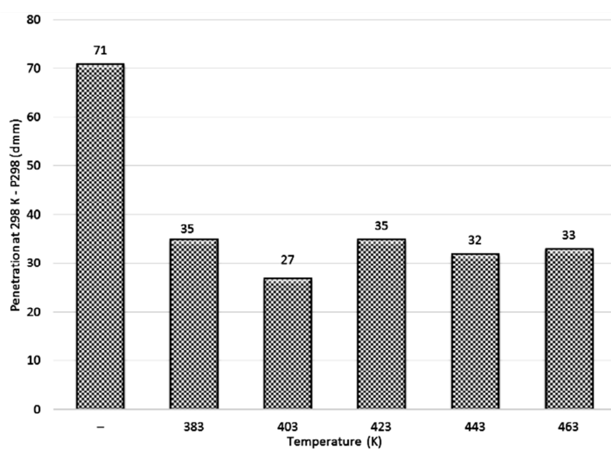


Fig. 2. Temperature effect on P298

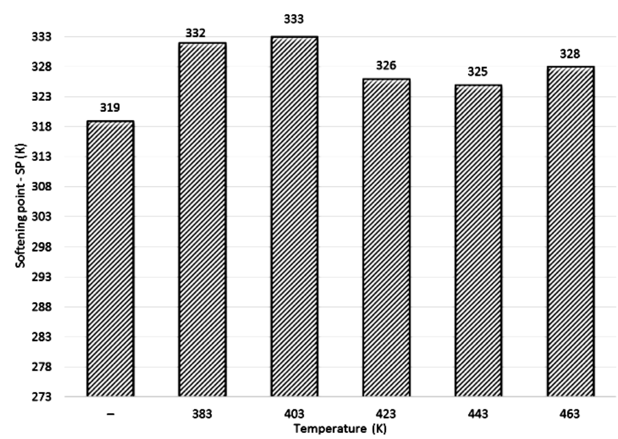


Fig. 3. Temperature effect on SP

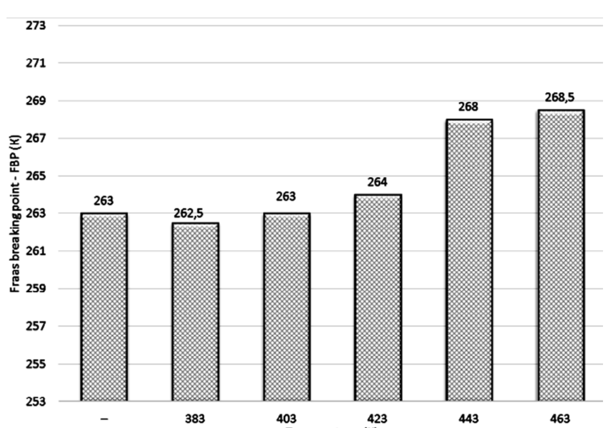


Fig. 4. Temperature effect on FBP

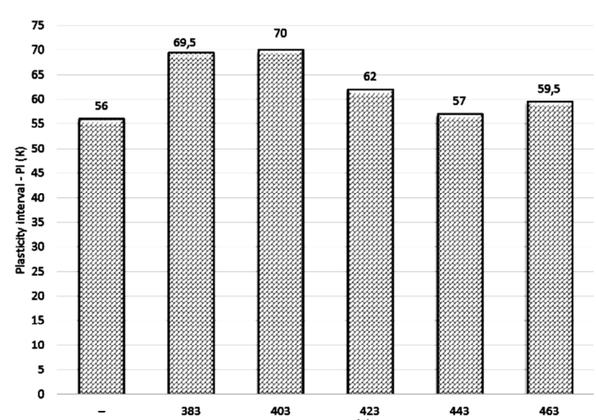


Fig. 5. Temperature effect on PI

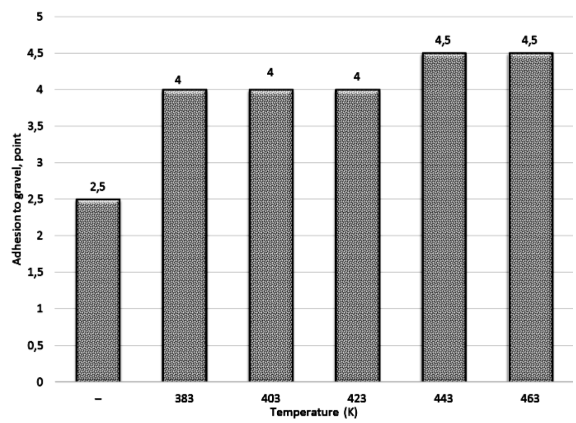


Fig. 6. Temperature effect on AG

At low modification temperatures (383–403 K), a significant increase in the softening point is observed – up to 333 K (Fig. 3). At higher modification temperatures (423–463 K) bitumen with much lower heat resistance is obtained (softening point is 325–328 K; Fig. 3). This indicates that the reaction chemistry of maleic anhydride with the components of oxidized bitumen at lower modification temperatures (383–403 K) differs from the chemistry at higher temperatures (423–463 K).

At modification temperatures of 383–423 K, the low-temperature behavior of the obtained samples practically does not change, as evidenced by almost identical values of FBP (263–264 K, Fig. 4); a further increase in process temperature leads to an increase in FBP.

At modification temperatures of 383–403 K, bitumen with a high PI value (70 K) are obtained (Fig. 5).

Also, bitumen modified with maleic anhydride is characterized by high adhesion to gravel, compared with the original oxidized bitumen. The AG index is 4–4.5 points (Fig. 6).

To establish the chemistry of the MA bitumen modification process, FTIR spectral studies were performed for the original oxidized bitumen (OB1) and three bitumen samples (OBMA1, OBMA2 and OBMA3), which were obtained at different modification temperatures. The conditions for obtaining and the main performance characteristics of these samples are given in Table 3. The FTIR spectra of samples OB1, OBMA1, OBMA2, and OBMA3 are given in Fig. 7.

Table 3. Performance characteristics of the samples for which FTIR spectra were recorded

Sample	Modification temperature (K)	Characteristics			
		SP (K)	P298 (dmm)	FBP (K)	PI
OB1	–	319	71	263	56
OBMA1	403	333	27	263	70
OBMA2	423	326	35	264	62
OBMA3	443	325	32	268	57

Note: process conditions: duration – 0.5 hours, MA amount – 2.0 kg/100 raw (OB1)

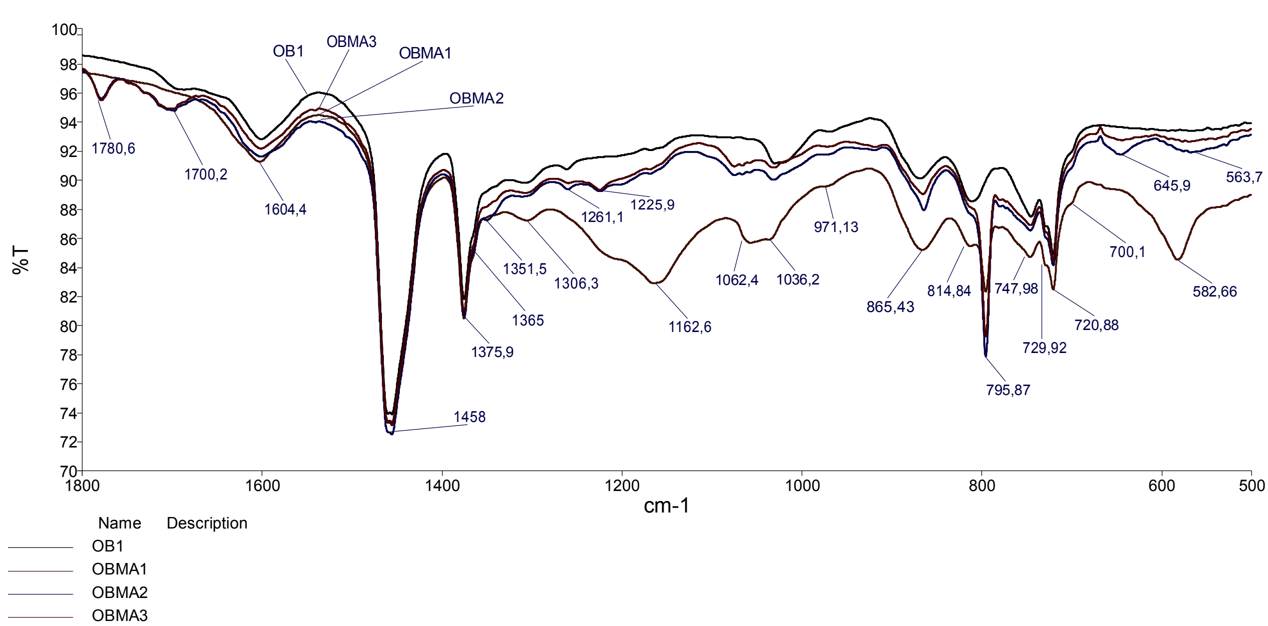


Fig. 7. FTIR spectra of OB1, OBMA1, OBMA2, and OBMA3

The spectrum of the original bitumen (Fig. 7) shows an absorption band at 1700 cm^{-1}, which corresponds to the stretching vibrations of the carbonyl group that is part of the acid structure and is formed due to the oxidation of tar. Along with this, the absorption band at 1604 cm^{-1} is observed, which indicate the presence of benzene rings. Benzene rings are not in the free state, but are replaced by various methylene groups ($–CH_2–$), as evidenced by the stretching vibrations at 1458, 1306, 1036, 865, 815, 796, 748 and 721 cm^{-1}. Free $–CH_3$ groups at 1376 cm^{-1} were also found in the structure of bitumen.

In the FTIR spectrum of bitumen modified at 403 K (OBMA1) we observed an absorption band at 1604 cm^{-1}, which corresponds to the stretching vibrations of the benzene ring and substituted benzene rings at 1036, 865, 814, 796, 748 and 721 cm^{-1}. Methylene groups (ν $–CH_2–$) were confirmed by the presence of absorption bands at 1458 and 1306 cm^{-1}. The free CH_3 group, which is bound to benzene rings, had a band at 1376 cm^{-1}. In contrast to the FTIR spectrum of OB1, absorption bands at 1163, 1062 and 583 cm^{-1} were found in the OBMA1 spectrum. Such absorption bands can be attributed to maleic anhydride (1163 cm^{-1}), stretching vibrations of the carbonyl group in maleic anhydride (1062 cm^{-1}) and the double bond in such anhydride (583 cm^{-1}). This indicates that at the modification temperature of 403 K MA molecules do not attach to oxidized bitumen molecules by the Diels-Alder reaction (Eq. 1). MA in this mixture is in the free state. Therefore, in our opinion, at lower modification temperatures (383–403 K), an increase in the softening point to 333 K is caused by the formation of π-π complexes (Eq. 2).

The spectrum of bitumen modified at the temperature of 423 (OBMA2) or 443 K (OBMA3), shows the above-mentioned absorption bands, which belong to the benzene ring, substituted benzene rings, methylene and methyl groups; the absorption band at 583 cm^{-1} is not observed. This indicates the attachment of MA molecules to bitumen at the mentioned temperatures and the destruction of formed π-π complexes. The presence of maleic anhydride fragments in the structure of bitumen is confirmed by the absorption band at 1062 cm^{-1}, which can be attributed to the stretching vibrations of the carbonyl group in the bitumen-attached fragment of MA. This once again confirms that the chemical interaction of MA molecules occurs at the temperatures of 423 K and above.

To compare the heat resistance of the modified samples, which were obtained *via* modification at 403 K (OBMA1) and 443 K (OBMA3), they were heated by the RTFOT method. The heating temperature according to RTFOT is 436 K. The study of technological aging processes for MA modified bitumen is presented in Table 4.

OBMA1, which was obtained at a lower temperature (403 K), shows an abnormal behavior during heating by the RTFOT method – there is a decrease in heat resistance (softening point decreases by 7.6 K). For comparison, the softening point of OB1 and OBMA1 increases by 6.2 and 3.2 K, respectively. Since the heating temperature by the RTFOT method (436 K) is much higher than the modification temperature of OBMA1 (403 K), in the process of heating the structure (π-π complexes) is destroyed with a significant decrease in the heat resistance of this sample.

Therefore, in order to obtain a binder material with great heat resistance, the process of bitumen modification with MA should be carried out at relatively low temperatures – up to 403 K, an increase in this temperature leads to the irreversible destruction of the formed structure.

On the other hand, most preparation technologies take place at temperatures much higher than 403 K. This must be taken into account for the future preparation of asphalt mixtures. Therefore, the choice of the temperature of bitumen modification with maleic anhydride is quite complex and requires a thorough approach.

To confirm the structure of OBMA at different modification temperatures, the OB1, OBMA1 and OBMA3 spectra were taken before and after the bitumen heating process by the RTFOT method.

Fig. 8 shows that heating the oxidized bitumen OB1 at 436 K has virtually no effect on the bitumen structure. Stretching vibrations at 1600 and 1455 cm^{-1} indicate the presence of aromatic rings in the bitumen. These rings are 1,2,4-substituted (868 cm^{-1}), 1,3-substituted (812 cm^{-1}) and monosubstituted (745 and 720 cm^{-1}). The absorption band observed at 1375 cm^{-1} indicates an interconnection of aromatic rings by $–CH_2–$ groups.

Table 4. Investigations of technological aging processes by RTFOT method

Index	Unit of measurement	Before RTFOT			After RTFOT		
		OB1	OBMA1	OBMA3	OB1-RTFOT	OBMA1-RTFOT	OBMA3-RTFOT
Change in weight	wt %	–	–	–	0.03	0.23	0.55
Softening point (SP) after RTFOT	K	319.0	333.0	325.0	325.2	324.4	328.2
Penetration at 298 K after RTFOT	dmm	71	27	32	55	38	35
ΔSP	K	–	–	–	6.2	-7.6	3.2
Residual penetration	%	–	–	–	77.5	140.7	109.4

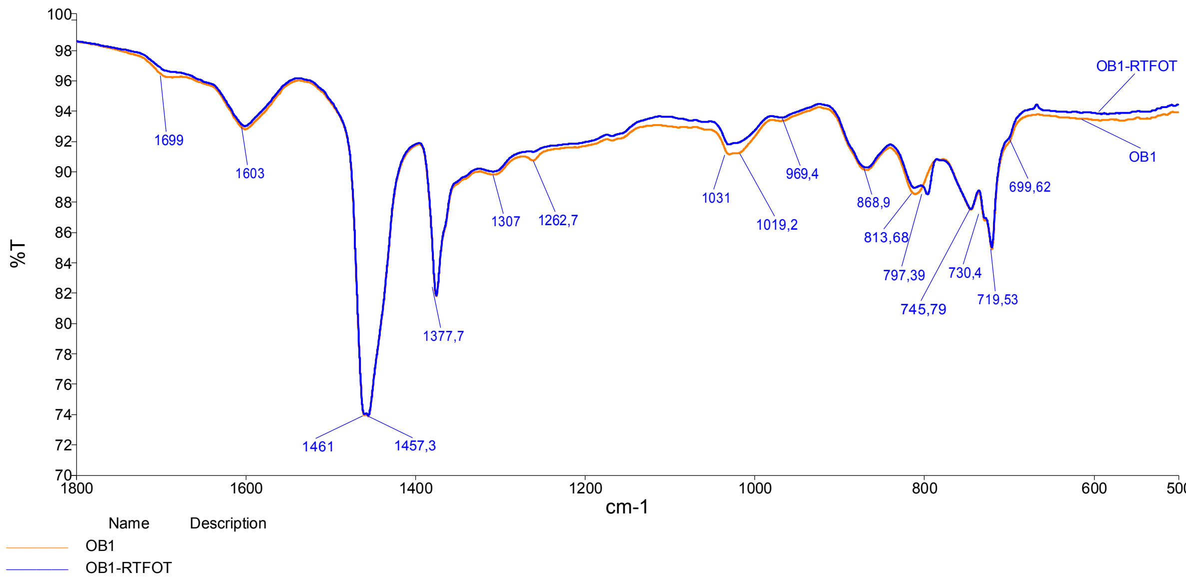


Fig. 8. FTIR spectra before (OB1) and after RTFOT (OB1-RTFOT)

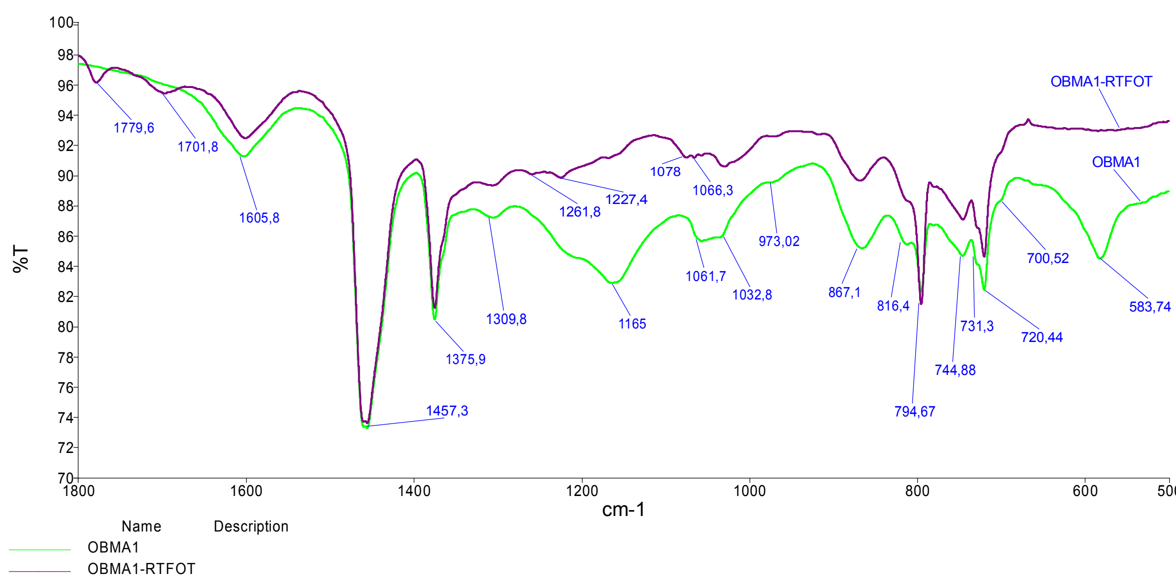


Fig. 9. FTIR spectra before (OBMA1) and after RTFOT (OBMA1-RTFOT)

One can see in Fig. 9 that when OBMA1 is heated to 436 K, the MA contained in the mixture in the free state interacts with the molecules of oxidized bitumen. This is evidenced by the absence of an absorption band at 1165 cm^{-1}, which can be attributed to free MA, and the absorption band at 584 cm^{-1}, which characterizes the double bond in MA. At the same time, an absorption band at 1780 cm^{-1} was found, which corresponds to the stretching vibrations of the carbonyl group in the bitumen-attached MA. In addition, under the experimental conditions, partial oxidation of bitumen molecules to acid groups is possible, as indicated by the presence in the OBMA1-RTFOT spectrum of the absorption band at 1702 cm^{-1}, which can be attributed to stretching vibrations in acids.

Analysis of the spectra represented in Fig. 10 shows that for the sample, in which the MA molecules were completely attached to the bitumen (Fig. 7), no changes are observed after heating at 436 K. This means the aging resistance of the product under mentioned conditions.

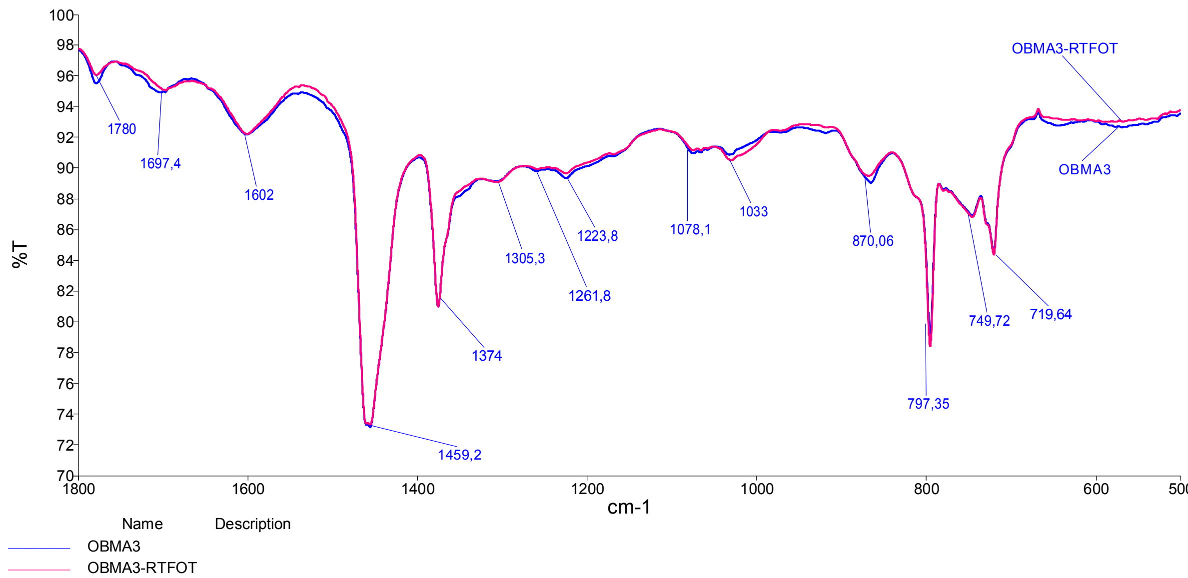


Fig. 10. FTIR spectra before (OBMA3) and after RTFOT (OBMA3-RTFOT)

4. Conclusions

We examined the effect of the process temperature on the modification of oxidized bitumen BND 60/90 (Ukraine) with maleic anhydride. The temperature has an impact on the main operational properties of the modified bitumen, namely penetration at 298 K, softening point, Fraas breaking point, plasticity interval and adhesion to gravel. In the process of oxidized bitumen chemical modification with maleic anhydride, the penetration at 298 K is reduced twice, from 71 to 27–35 dmm. At the modification temperatures of 383–403 K, the softening point increases significantly to 333 K, and at higher modification temperatures (423–463 K), bitumen with lower softening points of 325–328 K were obtained, which indicates that at 383–403 K the chemistry of maleic anhydride interaction with the oxidized bitumen components differs from the chemistry of process taking place at higher temperatures (423–463 K). The temperature has practically no effect on the low-temperature properties of the obtained bitumen (Fraas breaking point), especially at the modification temperatures of 383–423 K. At the temperatures of 383–403 K we obtained bitumen with a high value of the plasticity interval – 70 K. Bitumen modified with maleic anhydride is characterized by high adhesion to the gravel – 4–4.5 points.

Using FTIR spectroscopy, the structural transformations that occur in the process of chemical modification of oxidized bitumen with maleic anhydride depending on the process temperature were studied. It was found that at the temperatures up to 403 K the chemical interaction of maleic anhydride with bitumen does not occur, in the FTIR spectrum of modified 403 K bitumen there is an absorption band of 583 cm^{-1}, which belongs to the double bond of maleic anhydride. The increase in the softening point to 333 K is due to the formation of π-π complexes of maleic anhydride with bitumen components. At the modification temperatures above 423 K, maleic anhydride interacts with bitumen by the Diels-Alder reaction, there is no absorption band at 583 cm^{-1} in the FTIR spectra of such bitumen.

The process of heating in a thin film at 436 K (RTFOT method) of the original oxidized bitumen and bitumen modified with maleic anhydride was carried out at the temperatures of 403 and 443 K. It was found that during the heating process for the original oxidized bitumen and bitumen modified at 443 K, the softening point increases by 6.2 and 3.2 K, respectively. For bitumen modified at 403 K after heating by RTFOT, the softening point decreases by 7.6 K, which indicates the destruction of the formed π-π complexes and the interaction of maleic anhydride with bitumen by the Diels-Alder reaction. This is also confirmed by FTIR spectroscopic studies.

Acknowledgements

This work was supported by the National Research Foundation of Ukraine (Grant No. 2020.02/0038).

The research was performed on the equipment of the Scientific Equipment Collective Use Center: “Laboratory of Advanced Technologies, Creation and Physico-Chemical Analysis of a New Substances and Functional Materials” Lviv Polytechnic National University (https://lpnu.ua/ckkno).

Abbreviations

AG	Adhesion to gravel
FBP	Fraas breaking point (K)
MA	maleic anhydride
OB1	oxidized bitumen
OBMA	oxidized bitumen modified with maleic anhydride
P298	penetration at 298 K (dmm)
PI	plasticity interval (K)
RTFOT	rolling thin film oven test
SP	softening point (K)

References

[1] 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

[2] Koval, I.; Starchevskyy, V. Gas Nature Effect on the Destruction of Various Microorganisms under Cavitation Action. *Chem. Chem. Technol.* **2020**, *14 (2)*, 264-270. https://doi.org/10.23939/chcht14.02.264

[3] Shevchuk, L.; Strogan, O.; Koval, I. Equipment for Magnetic-Cavity Water Disinfection. *Chem. Chem. Technol.* **2012**, *2 (6)*, 219-223. https://doi.org/10.23939/chcht06.02.219

[4] Polacco, G.; Berlincioni, S.; Biondi, D.; Stastna, J.; Zanzotto, L. Asphalt Modification with Different Polyethylene-Based Polymers. *Eur. Polym. J.* **2005**, *41*, 2831-2844. https://doi.org/10.1016/j.eurpolymj.2005.05.034

[5] Giavarini, C.; De Filippis, P.; Santarelli, M.L.; Scarsella, M. Production of Stable Polypropylene-Modified Bitumens. *Fuel* **1996**, *75*, 681-686. https://doi.org/10.1016/0016-2361(95)00312-6

[6] Abdel-Goad, M.A.H. Waste Polyvinyl Chloride-Modified Bitumen. *J. Appl. Polym. Sci.* **2006**, *101(3)*, 1501-1505. https://doi.org/10.1002/app.22623

[7] Padhan, R.K.; Sreeram, A.; Mohanta, C.S. Chemically Recycled Polyvinyl Chloride as a Bitumen Modifier: Synthesis, Characterisation and Performance evaluation. *Road Mater. Pavement Des.* **2021**, *22(3)*, 639-652. https://doi.org/10.1080/14680629.2019.1614968

[8] Lu, X.; Isacsson, U. Modification of Road Bitumens with Thermoplastic Polymers. *Polym. Test.* **2000**, *20(1)*, 77-86. https://doi.org/10.1016/S0142-9418(00)00004-0

[9] 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

[10] Jasso, M.; Hampl, R.; Vacin, O.; Bakos, D.; Stastna, J.; Zanzotto, L. Rheology of Conventional Asphalt Modified with SBS, Elvaloy and Polyphosphoric acid. *Fuel Process. Technol.* **2015**, *140*, 172-179. https://doi.org/10.1016/j.fuproc.2015.09.002

[11] 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

[12] Gunka, V.; Demchuk, Yu.; Pyshyev, S.; Starovoit, A.; Lypko, Y. The Selection of Raw Materials for the Production of Road Bitumen Modified by Phenol-Cresol-Formaldehyde Resins. *Pet. Coal* **2018**, *60 (6)*, 1199-1206.

[13] 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 (4)*, 456-461. https://doi.org/10.23939/chcht12.04.456

[14] 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 (2)*, 212-217. https://doi.org/10.23939/chcht13.02.212

[15] Demchuk, Y.; Gunka, V.; Pyshyev, S.; Sidun, I.; Hrynchuk, Y.; Kucinska-Lipka, J.; Bratychak, M. Slurry Surfacing Mixes on the Basis of Bitumen Modified with Phenol-Cresol-Formaldehyde Resin. *Chem. Chem. Technol.* **2020**, *14 (2)*, 251-256. https://doi.org/10.23939/chcht14.02.251

[16] 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 (12)*, 2906-2918. https://doi.org/10.1080/14680629.2020.1808518

[17] 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_1

[18] Pyshyev, S.; Demchuk, Y.; Poliuzhyn, I.; Kochubei, V. Obtaining and Use Adhesive Promoters to Bitumen from the Phenolic Fraction of Coal Tar. *Int. J. Adhes. Adhes.* **2022**, *118*, 103191. https://doi.org/10.1016/j.ijadhadh.2022.103191

[19] 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

[20] Bratychak, M.; Grynyshyn, O.; Astakhova, O.; Shyshchak, O.; Wacławek, W. Functional Petroleum Resins Based on Pyrolysis By-Products and Their Application for Bitumen Modification. *Ecol. Chem. Eng.* **2010**, *17*, 309-315.

[21] 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 (1)*, 420-429.

[22] Bratychak, M.; Gunka, V.; Prysiazhnyi, Yu.; Hrynchuk, Yu.; Sidun, I.; Demchuk, Yu.; 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 (2)*, 274-283. https://doi.org/10.23939/chcht15.02.274

[23] Gunka, V.; Prysiazhnyi, Yu.; Hrynchuk, Yu.; Sidun, I.; Demchuk, Yu.; 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 (3)*, 443-449. https://doi.org/10.23939/chcht15.03.443

[24] Gunka, V.; Prysiazhnyi, Yu.; Hrynchuk, Yu.; Sidun, I.; Demchuk, Yu.; 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 (4)*, 608-620. https://doi.org/10.23939/chcht15.04.608

[25] Gunka, V.; Bilushchak, H.; Prysiazhnyi, Yu.; Demchuk, Yu.; Hrynchuk, Yu.; Sidun, I.; Shyshchak, O.; 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 (1)*, 142-149. https://doi.org/10.23939/chcht16.01.142
[26] 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 (2)*, 295-302. https://doi.org/10.23939/chcht16.02.295
[27] 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(5)*, 1774. https://doi.org/10.3390/ma15051774
[28] Herrington, P.R.; Wu, Y.; Forbes, M.C. Rheological Modification of Bitumen with Maleic Anhydride and Dicarboxylic Acids. *Fuel* **1999**, *78 (1)*, 101-110. https://doi.org/10.1016/S0016-2361(98)00120-3
[29] Kang, Y.; Wang, F.; Chen, Z. Reaction of Asphalt and Maleic Anhydride: Kinetics and Mechanism. *Chem. Eng. J.* **2010**, *164 (1)*, 230-237. https://doi.org/10.1016/j.cej.2010.08.020
[30] BS EN 1427:2015, Bitumen and bituminous binders. Determination of the softening point. Ring and Ball method, 2015.
[31] BS EN 1426:2015, Bitumen and bituminous binders. Determination of needle penetration, 2015.
[32] BS EN 12593:2015, Bitumen and bituminous binders. Determination of the Fraass breaking point, 2015
[33] BS EN 13587:2016, Bitumen and bituminous binders. Determination of the tensile properties of bituminous binders by the tensile test method, 2016.
[34] DSTU 8787:2018 (National Standard of Ukraine), Bitumen and bituminous binders. Determination of adhesion with crushed stone, 2018.
[35] BS EN 12607-1:2014, Bitumen and bituminous binders. Determination of the resistance to hardening under influence of heat and air RTFOT method, 2014.

Received: January 10, 2022 / Revised: January 24, 2022 / Accepted: February 09, 2022

ОДЕРЖАННЯ БІТУМУ, МОДИФІКОВАНОГО НИЗЬКОМОЛЕКУЛЯРНИМИ ОРГАНІЧНИМИ СПОЛУКАМИ ІЗ НАФТОВИХ ЗАЛИШКІВ. 6. ВПЛИВ ТЕМПЕРАТУРИ НА ПРОЦЕС ХІМІЧНОГО МОДИФІКУВАННЯ БІТУМІВ МАЛЕЇНОВИМ АНГІДРИДОМ

Анотація. *Проведено процес хімічного модифікування окисненого бітуму виробленого на українському нафтопереробному заводі малеїновим ангідридом. Доведено, що найбільш суттєво впливає на модифікування - температура процесу. Підтверджено, що в процесі модифікування малеїновий ангідрид хімічно взаємодіє із складовими частинами окисненого бітуму. Показано, що за нижчих температур (до 403 К) процес модифікування відбувається за іншим хімізмом ніж за вищих температур. Проведено FTIR спектральні дослідження для бітумів модифікованих малеїновим ангідридом за різних температур процесу (403, 423 та 443 К) та встановлено структури цих модифікованих бітумів. Також проведено процес прогріття в тонкій плівці за 436 К (методом RTFOT) для бітумів модифікованих малеїновим ангідридом при різних температурах. Встановлено, що для бітуму модифікованого малеїновим ангідридом за 403 К після прогріття за методом RTFOT відбувається руйнування утвореної структури, що підтверджується зменшенням температури розм'якшення модифікованого бітуму. Також знято FTIR спектри вихідного окисненого бітуму та бітумів модифікованих малеїновим ангідридом за 403 і 443 К після процесу прогріття за методом RTFOT. На основі одержаних FTIR спектрів встановлено структурні перетворення, що відбуваються в процесі прогріття з цими бітумами.*

Ключові слова: *бітум, малеїновий ангідрид, хімічне модифікування, вплив температури.*