

## Modification of Maleinized Bitumen with Polyethylene Glycol

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### Abstract

This paper addresses the limited functionality of existing road bitumen modifiers, which often improve only some of their properties. As an alternative approach, the modification of maleinised bitumen with polyethylene glycol (PEG) is proposed. The aim of this study was to investigate the effect of PEG on the physicochemical properties of bitumen. The paper describes in detail the interaction between modified bitumen and PEG, and presents the results of FTIR spectral and thermogravimetric studies of the modified bituminous product. The influence of PEG molecular weight, modifier concentration, temperature, and duration of the modification process was investigated. RBT analysis of modified bitumen and tar revealed a significant improvement in key bitumen properties, including thermal stability, elasticity, and durability, resulting from the use of PEG. The results indicate the effectiveness of polyethylene glycol as a modifier for asphalt concrete pavements, opening up new prospects for improving the quality and service life of road materials.

**Keywords:** *Bitumen; Modification; Maleic anhydride; Polyethylene glycol.*

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## 1. Introduction

Asphalt concrete pavements are the most common road surface type because they are relatively cheap and easy to lay. However, despite their widespread use, such pavements have significant drawbacks that limit their service life. The main problems are high sensitivity to temperature fluctuations and heavy traffic, which lead to rutting and cracking, and ultimately to the destruction of the road surface [1]. To increase the durability and performance characteristics of road pavements, special attention is paid to modifying petroleum road bitumen - the main component of asphalt concrete mixtures. Existing modification approaches, although effective in improving certain properties, have limited functionality and do not provide a comprehensive solution to all problems. For example, adding polymer additives (SBS, EVA, PE) effectively increases bitumen's elasticity, lowers the brittleness temperature, and increases its resistance to ageing. Chemical modification with maleic anhydride (MA) improves adhesion to mineral aggregate, increases the softening point, reduces the tendency to crack formation, and increases cohesive strength at high temperatures. However, these modifiers do not provide simultaneous and comprehensive improvement of all critical performance characteristics of bitumen, leaving room for the development of new, more universal solutions [2]. At the same time, a promising direction is the chemical modification of bitumen, particularly using maleic anhydride (MA). As shown in studies [3-7], the addition of MA contributes to improved adhesion to mineral aggregate, an increased softening point, and reduced crack susceptibility. Chemical modification with MA

improves bitumen's resistance to low-temperature cracking and increases cohesive strength at high temperatures [8].

To enhance the effectiveness of modification, it is advisable to combine chemical agents with heat-resistant materials. One such material is polyethylene glycol (PEG), an organic phase-change material with high enthalpy, good thermal stability, and the ability to store heat. PEG effectively increases the thermal stability of asphalt concrete pavements and reduces rutting at high temperatures [9]. However, because the melting temperature of PEG is lower than the operational temperature for bitumens, its use requires careful control to ensure the rheological stability of the system [10-11].

Combining maleic anhydride with PEG can provide comprehensive bitumen modification – simultaneously improving adhesion, thermal stability, and durability. This became the aim of our research: to evaluate the effect of PEG on the physicochemical characteristics of MA-modified bitumen and to establish optimal conditions for obtaining an effective binder.

## 2. Material and methodology

### 2.1. Materials

The following materials were used for modification:

- paving bitumen OB2 (oxidized bitumen) produced at JSC Ukrtatnafta (Kremenchuk, Ukraine). Its characteristic is given in Table 1, designated as BND 70/100.
- maleic anhydride MA, white crystalline powder (used as a process modifier/chemical reagent).
- crushed granite from natural stone of igneous rocks (S1), fractions 5-20 mm, fractions 20-40 mm, selected at Mokryansky Stone Quarry No. 3 LLC.

Table 1. Physico-chemical characteristics of raw materials.

Index	OB2	Method
Penetration at 25 °C (dmm)	82	EN 1426
Softening point (°C)	47.2	EN 1427
Ductility at 25 °C (cm)	>150	EN 13398
Fraass breaking point (°C)	-12	EN 12593
Penetration index	-0.70	EN 12591
Resistance to hardening at 163°C (RTFOT method):		EN 12607-1
mass change (%)	0.13	
softening point after RTFOT (°C)	53.0	
penetration at 25 °C after RTFOT (dmm)	48	
softening point change (°C)	5.8	
residual penetration (%)	58.0	
Adhesion to gravel (mark)	3.0	DSTU 8787:2018

### 2.2. Methodology - preparation of modified binders

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, heated to a temperature ensuring its mobile state. Stirring was switched on, and the raw material was heated to the process operating temperature. Next, the modifier (MA) was added via a separating funnel/dosing device. The modification was carried out under stirring (1000 rpm) in an inert gas (N<sub>2</sub>) atmosphere. The modified bitumen was analysed according to the main performance characteristics: penetration at 25°C (P<sub>25</sub>), softening point (SP), ductility (D), Fraas breaking point (FBP), plasticity interval (PI), and adhesion to gravel (AG).

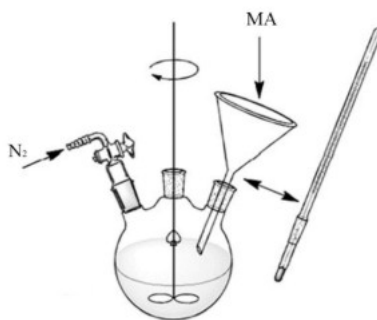


Figure 1. Scheme of the laboratory setup for the modification of bitumen with MA.

## 2.3 Test methods

### 2.3.1. Physical properties

Parameters were determined according to the standards: penetration at 25 °C EN 1426, softening point EN 1427, ductility at 25°C EN 13398, Fraass breaking point EN 12593, penetration index EN 12591, and RTFOT method EN 12607-1.

### 2.3.2. FTIR analysis

The FTIR spectra were recorded on a Spectrum Two spectrometer (PerkinElmer, USA) using a 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  $\text{cm}^{-1}$ , with a spectral resolution of 4  $\text{cm}^{-1}$ .

### 2.3.3. TGA analysis

Thermogravimetric analysis of the studied samples was carried out on a thermal analyser Linseis STA 1600 (Linseis Messgeräte GmbH, Selb, Germany) in the air in the temperature range of 20-220°C. Pre-weighed samples with a mass of 50-70 mg were placed in corundum crucibles and heated together with an empty same etalon corundum crucible at a rate of 2°C/min.

### 2.3.4. Adhesive properties

Bitumen adhesion to stone material was determined according to [25,28]; rolling bottle tests were conducted according to EN 12697-11. We used crushed stone of 8/11 and 20/40 mm fractions obtained from natural stone (S1) and selected at the LLC Novograd-Volyn Stone Crushing Plant (Ukraine)

## 3. Results

### 3.1. Influence of modification parameters on bitumen properties

The study of the influence of various factors on the bitumen modification process enables the optimisation of its properties and the expansion of its areas of application. Special attention is paid to three key parameters: the molecular weight of PEG, its concentration, and the temperature-time conditions of the modification process. Establishing optimal conditions makes it possible to obtain a material with improved physicochemical characteristics.

#### 3.1.1. Influence of PEG molecular weight

In Table 2, the values for modification time and temperature are given, separated by a slash, for the first and second modifiers, respectively. Table 2 shows the influence of the molecular weight of the PEG modifier on the quality indicators of the modified bitumens.

Table 2. Influence of the molecular weight of the PEG modifier on the quality indicators of the modified bitumens.

Modifier №1	Modifier №2	Time, min	Temperature, °C	The operational indicators of the obtained modified bitumens			
				SP	P <sub>25</sub>	D <sub>25</sub>	E <sub>25</sub>
MB	PEG-200	60/120	130/130	53.8	52	8.4	58.8
MB	PEG-400	60/120	130/130	53.5	43	41.6	32.2
MB	PEG-2000	60/120	130/130	55.1	38	40.2	25.1
MB	PEG-200	60/120	130/180	52.2	45	52.5	28.6
MB	PEG-400	60/120	130/180	53.3	51	35	37.7
MB	PEG-2000	60/120	130/180	53.5	43	82.9	32.8
MB	PEG-200	60/240	130/180	55.2	30	36.1	22.7
MB	PEG-2000	60/240	130/180	54.4	36	25.6	35.5
MB	PEG-2000	60/240	180/180	55.6	32	27.9	-

The effect of introducing PEG with molecular weights of 200, 400, and 2000 into maleinised bitumen (MB) containing 2 wt.% MA was investigated. The PEG concentration in all cases was 4 wt.%. The results showed that as the PEG molecular weight increases, the softening point (SP) increases moderately; penetration (P<sub>25</sub>) decreases, indicating increased hardness; and ductility (D<sub>25</sub>) and elasticity (E<sub>25</sub>) exhibit unstable behaviour, depending on both molecular weight and process temperature. Thus, the selection of PEG molecular weight allows for targeted control of the final product's properties.

### 3.1.2. Influence of PEG concentration

To evaluate the effect of PEG-2000 content, its concentration was varied from 0 to 8 wt.% at a constant temperature (180°C) and duration (120 min). It was found that SP decreases with increasing PEG content, indicating reduced thermal stability; D<sub>25</sub> increases significantly at 4%, reaches a maximum, and then decreases; E<sub>25</sub> has a maximum at 2% PEG content. The optimal PEG-2000 concentration is 2–4%, depending on the required flexibility and hardness (Table 3).

Table 3. Influence of PEG-2000 modifier concentration on the quality indicators of modified bitumens.

PEG-2000 content, wt.%	Operational indicators of the obtained modified bitumens			
	SP	P <sub>25</sub>	D <sub>25</sub>	E <sub>25</sub>
0	56,2	42	19	37,3
<b>2</b>	<b>55,8</b>	<b>33</b>	<b>19,6</b>	<b>41,3</b>
4	53,5	43	82,9	32,8
6	52,6	45	22,8	29,6
8	52,4	46	26,8	20,4

### 3.1.3. Influence of modification temperature

The modification process was carried out at temperatures of 140–200°C. It was found that SP increases from 54°C to 55.8°C; P<sub>25</sub> and D<sub>25</sub> reach their maxima at 160°C; and elasticity (E<sub>25</sub>) is also highest at 160°C. Therefore, a temperature of 160°C is optimal for balancing hardness and elasticity (Table 4).

Table 4. Dependence of quality indicators of obtained modified bitumens on modification temperature.

Temperature of maleinized bitumen modification, °C	Operational indicators of the obtained modified bitumens			
	SP	P <sub>25</sub>	D <sub>25</sub>	E <sub>25</sub>
140	54	39	45.8	36.5
160	53.4	44	38.7	44
180	55.8	33	19.6	41.3

### 3.1.4. The influence of modification duration the modification time was varied from 60 to 480 minutes under fixed temperature conditions

SP steadily increases up to 360 minutes, after which it changes insignificantly. D25 has a sharp peak at 120 minutes (82.9 cm), indicating the formation of a branched structure. Further increases in time lead to decreased flexibility. Thus, the optimal modification duration is about 120–240 minutes, which ensures high elasticity and stability.

Table 5. Dependence of quality indicators of modified bitumen on the time of modification

Time of maleinized bitumen modification. min	Operational indicators of the obtained modified bitumens			
	SP	P <sub>25</sub>	D <sub>25</sub>	E <sub>25</sub>
60	52.4	45	83.1	33.5
120	53.5	43	82.9	32.8
240	54.4	36	25.6	35.5
360	56.8	35	40	26.9
480	56.2	32	12	36.5

### 3.2. FTIR spectroscopic study

FTIR analysis confirmed the chemical interaction between MA and PEG with the formation of new functional groups. Specifically, characteristic bands at  $1733\text{ cm}^{-1}$  (carbonyl groups) and  $1145\text{--}1111\text{ cm}^{-1}$  (ether linkages  $\text{--C--O--C--}$ ) indicate the effective attachment of PEG to maleinized bitumen. The intensity of the peaks depends on the molecular weight of PEG, which correlates with the physico-mechanical data.

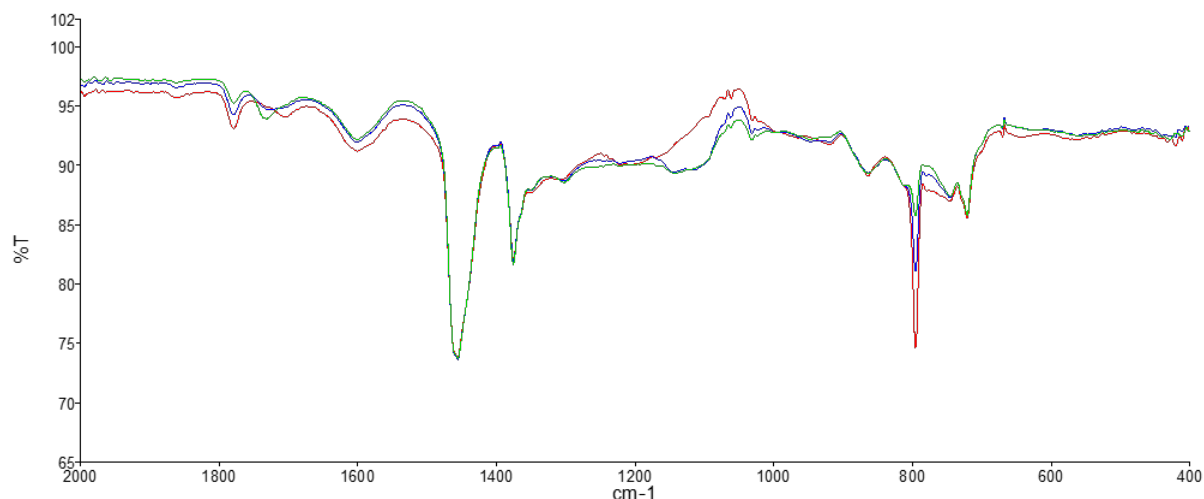


Figure 2. FTIR spectrum for maleinized bitumen (a) with the addition of PEG-400 (b) and PEG-2000 (c).

In the spectra of MB and MBP samples, characteristic bands were observed, confirming the chemical interaction between maleic anhydride (MA) and polyethylene glycol (PEG). The band at  $1781\text{ cm}^{-1}$  is present in all samples and corresponds to the stretching vibration of the carbonyl group ( $\text{C=O}$ ) in MA. The band at  $1733\text{ cm}^{-1}$  is present only in MBP and indicates the formation of carbonyl groups due to the opening of the anhydride ring upon interaction of MA with PEG. Its intensity is higher when using PEG-200 (lower molecular weight). The band at  $1703\text{ cm}^{-1}$ , characteristic of MA fragments, is present only in the initial MB and disappears after PEG modification, indicating complete or partial interaction. Bands at  $1145$  and  $1111\text{ cm}^{-1}$ , which correspond to the stretching vibrations of  $\text{--C--O--C--}$  groups, are clearly visible in MBP samples but absent in the initial MB — this is additional confirmation of the formation of ether linkages.

### 3.3. Thermogravimetric analysis (TGA)

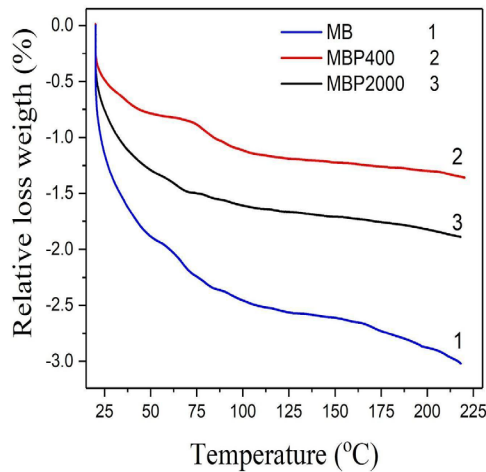


Figure 3 shows that modified samples have higher thermal stability than unmodified bitumen. This is particularly evident in samples containing PEG-2000, confirming the effectiveness of this polymer as a heat-resistant modifier.

Figure 3. Thermogravimetric analysis (TGA) for maleinized bitumen with the addition of polyethylene glycol.

### 3.4. Application

#### 3.4.1. Adhesion test (RBT)

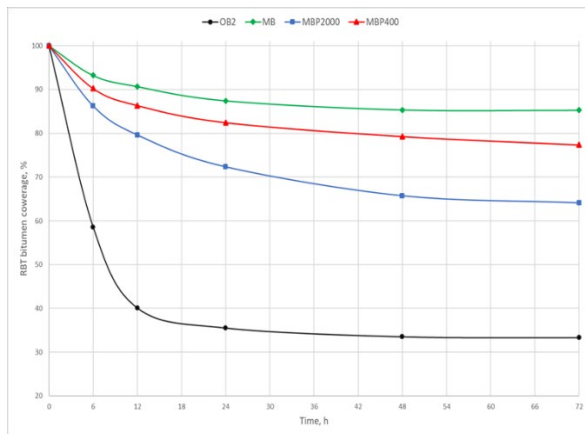


Figure 4. Results of RBT analysis for modified bitumen compared to the original.

Modified MBP samples adhere significantly more strongly to crushed stone than OB2. The best results are observed with PEG-2000, with up to 70% of the coating retained after 48 hours. The test results were processed using Photoshop CS6 and ImageJ. Photos of the samples were taken with a Nikon D3100 camera and an AF-P DX NIKKOR 18-55mm lens.

The change in the degree of bitumen coating on stone over time is shown for four samples: OB2, MB, MBP2000, and MBP400. Sample OB2 shows an intensive decrease in coating during the first 12 hours, followed by stabilisation at approximately 30%. Sample MB demonstrates the highest stability - the

coating remains above 80% throughout the entire period. Samples MBP2000 and MBP400 show a gradual decrease in coating, stabilising at approximately 60% and 70%, respectively. The results indicate increased adhesion for the modified samples, especially with PEG-400.

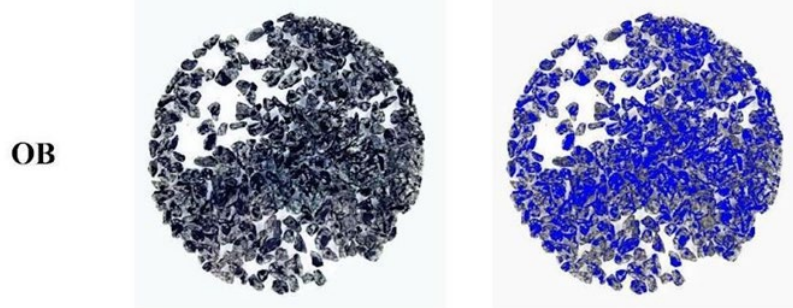


Figure 5. Photo of RBT analysis results for modified bitumen compared to the original (48 hours) (OB sample).

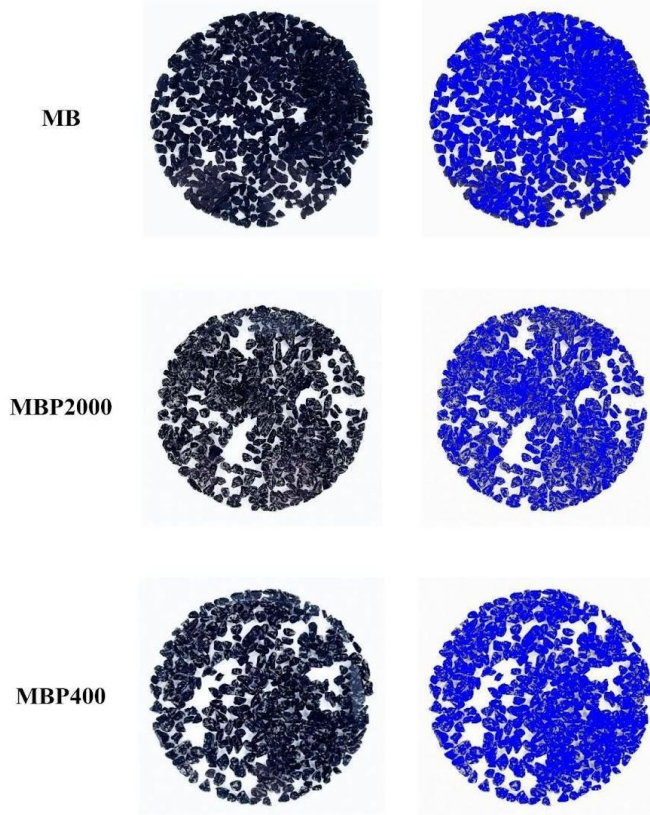


Figure 5. Photo of RBT analysis results for modified bitumen compared to the original (48 hours)

**3.4.2. Asphalt concrete mixtures (SMA-20)**

Samples with MBP have the lowest water saturation and the highest density among all variants. This indicates high compaction and durability of the mixtures.

Table 6. Selected SMA-20 composition

Material dosage	%. over 100%	%. in 100%	per 1000kg
Crushed stone fr. 10-20	57	54.1	541
Crushed stone fr.5-10	21	19.9	199
Granite smalls	11	10.4	104
Mineral powder	11	10.4	104
Bitumen. incl. ad. additive 0.33%	5.3	5.0	50
Cellulose 0.3% of stone materials	0.03	0.03	3
Total	105.33	100.0	1000

Compaction was carried out using a B041M gyratory compactor (Matest). The manufacturing temperature for all studied mixtures was held constant at 160°C, and compaction proceeded for 200 gyrations per sample.

Analysis of the compaction results for SMA-20 mixtures manufactured at 160°C and compacted with 200 gyrations showed that the sample based on OB2+PEG-2000 (2%) had the best characteristics. This sample had the highest average density and the lowest water saturation level, indicating effective compaction of the structure. High compaction rates were also recorded for mixtures modified with OB2+MA (2%)+PEG-2000 (2%) and OB2+MA (2%)+SBS (2%)+PEG-2000 (2%).

Table 7. Physical and mechanical properties of SMA-20 samples.

Nº	SMA-20 Sample No.	Average density. g/cm <sup>3</sup>	Water saturation. % by volume	Compressive strength at 20°C	Compressive strength at 50°C	Binder
1	Nº1	2.388	3.3	4.44	0.79	Bitumen BND 70/100 OB2
2	Nº2	2.394	3.9	3.96	1.04	OB2+MA 2%
3	Nº3	2.431	2.3	4.32	0.87	OB2+MA 2%+SBS 2%
4	Nº4	2.413	2.8	3.71	0.64	OB2+SBS 2%
5	Nº5	2.447	1.7	3.46	0.79	OB2+MA 2%+PEG2000 2%
6	Nº6	2.451	0.6	4.58	0.93	OB2+PEG2000 2%
7	Nº7	2.476	0.7	3.92	0.95	OB2+MA 2%+ SBS 2%+PEG2000 2%

#### 4. Conclusions

Effective modification of maleinized bitumen (MB) with polyethylene glycol (PEG) significantly improves its physicochemical and operational properties, confirming its suitability for asphalt concrete pavements. Optimal modification conditions, which include the use of PEG with a specific molecular weight (2000), a concentration of 2–4 wt.%, a temperature of 160°C, and a duration of 120–240 minutes, yield the best results, balancing hardness and elasticity. FTIR spectroscopy confirmed the successful chemical interaction between MA and PEG, and thermogravimetric analysis showed increased thermal stability of the modified samples, especially with PEG-2000. Adhesion tests (RBT) demonstrated a significant improvement in adhesion to crushed stone, particularly for samples with PEG-2000 and PEG-400. Asphalt concrete mixtures with MBP had the highest density and lowest water saturation, indicating high compaction and durability. Thus, PEG is a promising modifier for improving the quality and service life of road materials.

#### Abbreviations

OB2	<i>oxidized bitumen</i>
MA	<i>maleic anhydride</i>
PEG	<i>polyethylene glycol</i>
MB	<i>maleinized bitumen</i>
MAPEG	<i>maleic anhydride + polyethylene glycol</i>
MBP	<i>maleinized bitumen with polyethylene glycol</i>
RBT	<i>rolling bottle test</i>
SP	<i>softening point</i>
P25	<i>penetration</i>
D25	<i>ductility</i>
E25	<i>elasticity</i>
AG	<i>adhesion to gravel</i>
S1	<i>natural stone selected at the LLC Novograd-Volyn Stone Crushing Plant (Ukraine)</i>

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