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EPOXIDE OF RAPESEED OIL-MODIFIER FOR BITUMEN AND ASPHALT CONCRETE

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Abstract

We managed increasing properties of road bitumen and asphalt concrete based on it with help of modification of road bitumen by epoxy compounds based on renewable raw materials, namely by epoxide of rapeseed oil (ERO). Physical-mechanical properties of initial and ERO modified bitumens and asphalts were researched and analyzed. Also was made a comparison of obtained results with similar indexes for trade additives for road bitumen, namely with wax and polymer modifier of SBS type.

***Keywords**: Bitumen; Epoxide of rapeseed oil; Modification; Asphalt concrete.*

1. Introduction

Oil bitumen have a wide use including applying as binding component in the production of asphalt concrete for building and maintenance of the roads. Unsatisfactory heat resistance, elasticity and adhesion, low temperature behavior of bitumen are among main reasons of early destruction of asphalt concrete coatings on their basis.

As the world practice shows, modifiers of different nature are used to solve this problem and to improve the operational properties of bitumen. Modification reduces the sensitivity of bitumen to changes in temperature and long-term load, increases their cohesive strength, provides elasticity and improves low-temperature properties [1-2]. As a result, the strength, displacement and cracking strength of road surfaces and their resistance to fracture due to fatigue increases.

Epoxy asphalt is also used for road construction, it is a special kind of asphalt concrete as containing epoxy constituents for increasing the strength and deformation properties of asphalt concrete [3-4].

It should be noted that the main reason that hinders the increase in the use of asphalt concrete on the basis of modified bitumen is the high cost of modifiers. Their adding in bitumen raises the cost of binder in 1.5-2.5 times. The use of cheaper additives does not reduce costs due to the required higher content in the mixture (from 5 to 7%). In addition, cheap additives do not provide bitumen with the necessary properties, such as: elasticity, high heat resistance, increased plasticity and deformability at low temperatures, etc. Commodity modifiers are mostly expensive and not manufactured by the Ukrainian industry. Researches that are going in this direction are described in [5-9].

Our research group developed an additive which, at significantly lower cost, would not yield by efficiency to foreign analogues. Conducted search showed that the most suitable basis for modifier is renewable plant raw material, namely rapeseed oil – cheap product that is produced in Ukraine in large quantities. Previously was found that modification of road bitumen by epoxy compounds based on renewable raw material increases properties of bitumen, and due to content of the additive and method of its addition we can receive bitumen with different properties [10]. Based on this previous research we can state that ERO is a perspective and relatively cheap material for modification [11]. In order to simplify process of production and to exclude use of solvent [12] we received ERO by modified method of epoxidation [13]. This allowed us to decrease duration of the process and provided a high quality product without changing such important physical and chemical parameters as epoxy number, iodine and bromine number.

The main goal of this work was to develop a technology for the modification of road oil bitumen by ERO and to obtain improved properties of bitumen and asphalt concrete mixtures on their basis.

2. Experimental

2.1. Initial materials

As initial bitumen for modification we used oxidized bitumen 70/100 (BND 70/100) produced by PJSC "Transnational financial and industrial oil company Ukrtatnafta" (Kremenchuk, Ukraine). Also for comparison experiments we used trade additives for road bitumens: Licomont.BS 100 (Clariant, Switzerland) and SBS type polymer Kraton D1192 (Kraton Polymers, USA). Main physical-mechanical properties of initial bitumen are presented in the Table 1.

Table 1. Main physical and mechanical parameters of bitumen BND 70/100

Index and values	BND 70/100
Penetration at 25°C, м·10^{-4} (0,1 мм)	95
Softening point, °C	45
Ductility at 25°C, м·10^{-2} (см)	>100

Properties of the Licomont.BS 100 and Kraton D1192 are presented in the Table 2 and Table 3. «Licomont BS 100» is a product of reaction of mixtures of the long chain fatty acids with aliphatic diamines. There are two types of this additive –Licomont.BS 100 (used in this work) and Licomont BS 100 MB. Kraton D1192 polymer is a clear linear block copolymer based on styrene and butadiene with bound styrene of 30% mass. There are following types of Kraton D1192: AT - supplied as porous pellets dusted with talc, AS - supplied as porous pellets dusted with amorphous silica, ASM - supplied as powder dusted with amorphous silica, ATM - supplied as powder dusted with talc for the North American market. For this research we used Kraton D1192 AT.

Table 2. Properties of the Licomont BS 100

Characteristics	Unit	Target value	Test method
Acid value	mg KOH/g	max. 8	ISO 2114
Drop point	°C	139 - 144	ISO 2176
Density (23°C)	g/cm³	~ 1,00	ISO 1183
Bulk density	g/l	450 - 700	ISO 60

Table 3. Properties of the Kraton D1192

Characteristics	Unit	Typical Value	Test Method
Hardness, Shore A (15 sec)	-	70	ASTM D 2240
Bulk Density	kg/dm^3	0,4	ASTM D 1895 method B
Specific gravity	-	0,94	ISO 2781
Melt flow rate, 200C/5kg	g/10min.	<1	ISO 1133
300% modulus	MPa	4,8	ISO 37
Elongation at break	%	1000	ISO 37
Tensile strength	MPa	33	ISO 37

2.2. Experimental procedure

2.2.1. Obtaining of ERO

Epoxidation of rapeseed oil (RO) was conducted by method created for epoxidation of soy oil [13]. For synthesis we used trade samples of RO without additional purification. Influence of solvent and time of reaction on conversion of C=C – bonds during epoxidation of RO T=70ºC is shown in the Table 4.

Table 4. Influence of solvent at time of reaction on conversion of the C=C – bonds during epoxidation of RO at T=70°C

№	Solvent	Reactants			General time of re-action, hr	Conversion C=C -bonds, %	EN ERO, %	Mass ERO, g
		RO, g/mol C=C	H_2O_2, g/mol	HCOOH, g/mol				
1	Toluene	372/1.82	225/3.97	46/1	3.5	59.3	5.10	408
2	Toluene	372/1.82	225/3.97	46/1	4.5	76.0	5.63	405
3	Cyclohexane	372/1.82	225/3.97	46/1	4.5	75.0	5.58	406
4	No solvent	372/1.82	225/3.97	46/1	4.0	90.5	6.12	461
5	No solvent	372/1.82	225/3.97	46/1	4.0	92.0	6.72	401

The relatively low epoxy number of the obtained product and the high residual value of the bromine number indicate incomplete conversion of double bonds (~ 60%). With an increase in the time of adhering the mixture to 2 hours and the time to withstand of the reaction mass to 2.5 hours, the conversion of C = C-bonds increases to almost 76% (Table 1). The epoxy number of the resulting epoxy increases to 5.63%. The use of cyclohexane as a solvent practically does not affect the performance of the process.

The value of the epoxy number was determined according to the standard methodology described in the work [13]. It was established that the use a of RO with an epoxy number of ~ 0,3% as raw material allows its epoxidation without solvent and without the additional addition of epoxidized oil into the system. In this case, the conversion of C = C-bonds over 90%is achieved, and the obtained epoxidized oil has an epoxy number equal to 6.7%, with a theoretically possible 7.2- 7.4%, depending on the content of C = C-bonds in raw materials.

Thus, the proposed improvement makes it possible to abandon the preliminary treatment of RO and the use of solvent, and hence the additional energy costs associated with solvent distillation and to improve the environmental aspects of production.

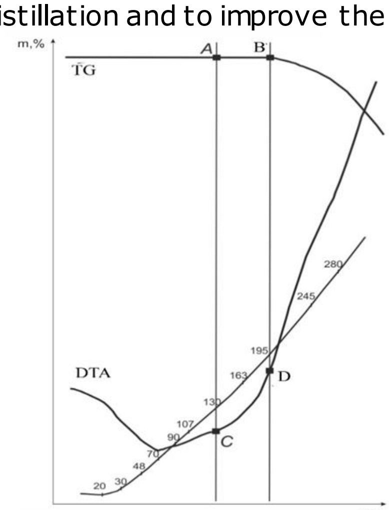

Figure 1. Curves of thermogravimetric and differential thermal analysis to epoxide of rapeseed oil

In order to determine the temperature range in which ERO can be used to modify road bitumen, its thermal stability was studied by the method of complex thermogravimetric and differential-thermal analysis (Figure. 1).

The nature of the curves of thermogravimetric and differential-thermal analysis shows that before temperature is 130°C (point C) the epoxide is stable, on the DTA curve there is an endeavor associated with the heating of the ERO sample. In the region of temperatures 130-195°C (points C and D), according to the differential thermal analysis, there are processes that are accompanied by the release of heat, which may be due to the disclosure of the epoxy cycle and the partial crosslinking of the chains to the oligomers, which corresponds to the appearance on the DTA curve of the exothermic effect. This process is not accompanied by the release of volatile scheduled products and the loss of mass on the TG curve (points A and B). At a temperature above 195°C on the curve of TG (point B) there is an intense mass loss that corresponds to the process of thermal destruction of the sample and is accompanied by the appearance of a pronounced exothermic effect on the DTA curve.

In order to confirm the obtained results an IR spectral analysis of samples of RO and its epoxy at different temperatures was made.

The data of the IR spectral analysis of samples confirm the fact of the disclosure of the epoxy cycle at temperatures above 130°C, since the intensity of the band corresponding to the fluctuation of epoxy groups decreases. According to the results of complex thermo-gravimetric and differential-term analysis and infrared spectra, it can be argued that the rapeseed oil epoxy is thermally stable in the temperature range up to 130°C.

2.2.2. Obtaining of modified binders

The bitumen modification process was performed by adding an additive when stirred in a thermostatically controlled reactor with a shaker blender. The temperature of the process of modification of the ERO was 190°C, the content of the additive-2, 3, 5, 7% by weight, the agitation time with stirring was 1-5 hr. [14]. Technological parameters of modification by commodity additives were following: modification of BND 70/100 by synthetic wax Licomont BS 100, modification temperature 160°C, time 3 hr, modification by polymer Kraton D1192 made at temperature 180°C during 5 hr.

2.3. Analysis of raw material and products

Temperature of softening was defined by [15], penetration at temperature 25 °C [16], ductility at temperature 25°C [17], elasticity at 25 °C [18].

The strength limit at compression at 20°C and 50°C of asphalt concrete was determined on mechanical presses at the speed of the press plate (3.0± 0.1) mm/min. Before testing, the specimens are thermostated in a container with water for (60±5) min at the temperature: (50±1)°C, (2± 1)°C. For tests of a compression strength of 50°C before being thermostated at a given temperature, samples are placed in dense polyethylene bags to prevent their contact with water. The average density of asphalt concrete was determined by hydrostatic weighing. Water saturation was determined by the amount of water absorbed by the sample at a given saturation regime in a vacuum installation. The coefficient of long-term water resistance was established by reducing the strength of compression at a temperature of (20 ± 1)°, samples of asphalt concrete under the action of water for 15 days in comparison with the samples sustained in the air at a temperature (20±1)°C.

3. Results and discussion

3.1. Modification of bitumen by ERO

As it was determined [14] the optimum temperature of the modification of bitumen by ERO is 190°C, the addition of the additive and bitumen was carried out exactly at that temperature. Changing the penetration and softening temperature depending on the content of the additive (over the bitumen mass) and the modification time at a given temperature is given in Fig. 2 and 3 respectively.

Analyzing the Fig. 2-3 with an increase in the concentration of ERO in bitumen, initially the softening temperature decreases at the initial stages of modification, but when stirred for 3 hours, the content of the additive 2 and 3% by weight softening temperature begins to grow. A similar effect of the modifier is observed on penetration of bitumen. That is so, because the ERO first provides bitumen plasticity, and then certain transformations in the structure of the binder (which need to be further investigated) occur, which leads to an increase in its hardness. We establish that variants of the content of the modifier 2 and 3% by weight and the modification time of 5 hours at 190°C may be modifications in the effective variants. Bitumen modification was also made by Licomont BS 100-3% by weight, and Kraton D1192 AT-3% by weight over a mass of bitumen.

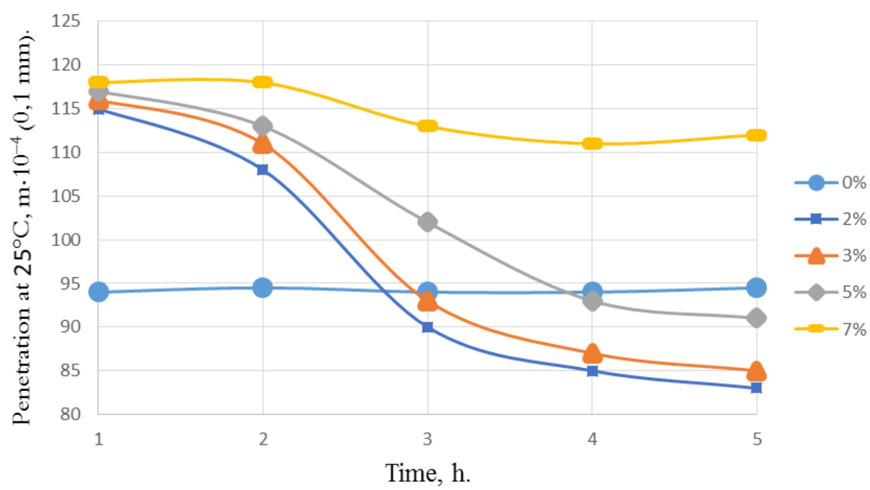

Figure 2. Dependence of penetration from ERO content and time of modification

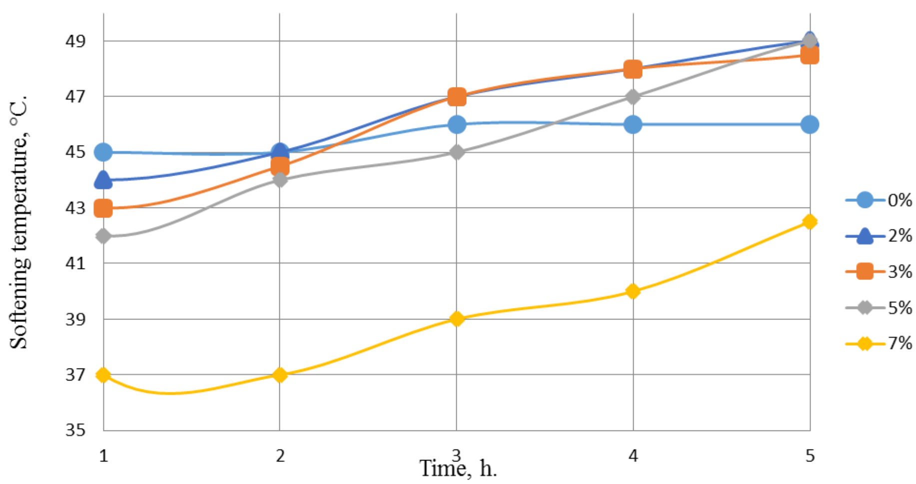

Figure 3. Dependence of softening temperature from ERO content and time of modification

A comparison of the properties of modified bitumen for the same dosage (3% by weight over the weight of bitumen) is shown in Table. 5. BND 70/100+ERO did not significantly change the properties of bitumen, but created the hypothesis that asphalt concrete using such a binder would be characterized by increased physical and mechanical performance.

Table 5. Physical-mechanical properties of initial and modified bitumen

Index	BND 70/100	BND 70/100 + ERO	BND 70/100 + Licomont.BS 100	BND 70/100 + Kraton D1192
Homogeneity		homogeneous		
Penetration at 25°C, м·10^{-4} (0,1 мм)	95	85	62	51
Softening point, °C	45	49	77	57
Ductility at 25°C, м·10^{-2} (см)	>100	>100	59	38
Elasticity за 25 °C, %	-	-	-	84

3.2. Influence of ERO on quality of asphalt concrete

To study the effectiveness of the modifiers, the granulometric composition of the mineral part of the asphalt concrete mixture (hot fine-grained dense with residual porosity from 2% to 5%, with a grain size of more than 5 mm-45-55% and a maximum grain size of up to 20 mm) was selected on the basis of granite gravel and non-activated limestone mineral powder

(Table 6) respectively. Bituminous content in asphalt concrete mixtures on unmodified and modified astringents was 6.2 wt. % over the weight of mineral constituents. Physical and mechanical properties of preformed models of asphalt concrete are given in Table. 7

Table 6. Composition of asphalt concrete

Material	Content of material in asphalt concrete, %	Material	Content of material in asphalt concrete, %
Rubble fr. 20-15 mm	5.0	Rubble waste fr. 0,63-0,071 mm	18.0
Rubble fr. 15-10 mm	15.0	Mineral powder	10.0
Rubble fr. 10-5 mm	20.0	**Total, %**	100.0
Rubble waste fr. 5-0,63 mm	32.0	Bitumen	6.2

Table 7. Physical and mechanical characteristics of fine-grained asphalt concrete

Index	Asphalt concrete with bitumen:			
	BND 70/100	BND 70/100+ERO	BND 70/100+ Licomont BS 100	BND 70/100 + Kraton D1192
Average density, g/sm^3	2.40	2.40	2.40	2.40
Water saturation, % for volume	0.50	0.45	0.49	0.40
Compressive strength. MPa, at a temperature:				
20°C	4,1	6,7	4,9	6,5
50°C	1,4	2,6	1,6	2,5
Coefficient of long-term water resistance	0.92	0.98	0.95	0.97

Analyzing Table 6, we note that the strength of asphalt concrete with BND 70/100+ERO at a temperature of 20°C increases 1.6 times, and 1.8 times at 50°C, compared with asphalt concrete on unmodified bitumen. That may indicate that this asphalt concrete is characterized by a higher heat resistance, and the coating, arranged with its use, will have greater resistance to corrosion under operating conditions. The obtained water saturation and the coefficient of long-term water resistance of asphalt concrete on BND 70/100+ERO indicate a better water resistance of this material. In general, the impact of ERO on asphalt concrete is similar to the effect of polymer modification.

4. Conclusion

1. The basis of the technology of high-quality road bitumens modified by rapeseed oil epoxy was developed.
2. We improved the method of obtaining rapeseed oil epoxide, which was first used as a modifier of road bitumen, improves the properties of modified bitumen and road pavements on their basis.
3. The thermal stability of rapeseed oil epoxide was studied, the temperature limits of its stability were established and it was shown that the ERO is thermally stable in the temperature range up to 130°C.
4. It is shown how the properties of modified by ERO road bitumen depend on its content, temperature and time of modification.
5. There are no special changes in the physico-mechanical parameters of bitumen for the modification of its ERO, but it is unambiguous to increase the quality characteristics of the made samples of asphalt concrete. Additional research is needed to understand this interesting fact.

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