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MODIFICATION OF PETROLEUM BITUMEN WITH RUBBER-POLYMER COMPOSITES

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Annotation. This research paper is devoted to the problem of modification of petroleum bitumen by rubber-polymer composites. The purpose of the study is to improve the rheological and physico-mechanical properties of bitumen of domestic brands PBR 70/100 and PBR 100/130 for the development of new generation road binders adapted to the climatic conditions of Kazakhstan.

The paper considered the effectiveness of composites based on used automobile tires and rubber-polymer composites based on polymer waste such as polyethylene and polypropylene. The literature review analyzes domestic and foreign studies of the composition and properties of bitumen, its improvement by polymers, rubber crumb and composite modifiers.

In the experimental part, the softening temperature, penetration, extensibility, Fraas brittleness temperature, viscosity, and elastic recovery parameters of primary and modified bitumen were determined. The results showed that devulcanized rubber crumb and composite modifiers such as ELTC significantly improve the performance properties of bitumen.

In the conclusion of the study, optimal compositions were proposed to increase the strength of road surfaces in the sharply continental climate of Kazakhstan. In addition, the environmental and economic efficiency of recycling used tires and polymer waste was demonstrated.

Keywords: bitumen, rubber-polymer composite, devulcanized rubber, ELTC modifier, rheological properties, road construction.

Introduction

This research is devoted to the modification of petroleum road bitumen with rubber–polymer composites and is aimed at improving the performance properties of road construction bitumen using modern approaches. Bitumen is a complex mixture of high-molecular-weight hydrocarbons obtained from petroleum refining, and its rheological as well as physicomechanical properties are governed by the SARA fractions (Saturates, Aromatics, Resins, and Asphaltenes) [1–3].

The sharply continental climatic conditions of Kazakhstan—characterized by summer temperatures reaching up to +40 °C and winter temperatures dropping to −30…−40 °C—impose additional stresses on road pavements and require bituminous binders to maintain stable performance over a wide temperature range. Conventional petroleum bitumens are unable to fully meet these requirements; therefore, their effective modification represents an urgent scientific and technological challenge [4–5].

Currently, the main directions in bitumen modification include enhancement with polymer additives, crumb rubber, and rubber–polymer composites. Polymers improve the high-temperature strength of bitumen, while rubber enhances its low-temperature elasticity. The combined use of these components makes it possible to obtain binders with stable performance over a broader temperature range [6–8].

In this study, the effectiveness of rubber–polymer composites based on waste vehicle tires and polymer wastes such as polyethylene and polypropylene was investigated. Devulcanized rubber particles (DRP) and ELTC-type modifiers were employed in comprehensive studies aimed at improving the performance characteristics of domestic road bitumens of grades 70/100 and 100/130 [9–11].

The objective of this research is to enhance the rheological and physicomechanical properties of bitumen through modification with rubber–polymer composites in order to develop a new generation of road binders adapted to the climatic and environmental conditions of Kazakhstan.

Materials and Methods

Waste vehicle tires and household polymer wastes (plastic bottles and other plastic residues based on polyethylene and polypropylene) were used as the research objects. The polymer wastes were prepared using a mechanical recycling method. This method involves mechanical grinding of plastic waste to reduce particle size, enabling subsequent thermal treatment and the production of high-quality modification raw materials.

For bitumen modification, two grades of petroleum road bitumen produced by CASPIBITUM LLP (Kazakhstan) were used in this study:

- 70/100 grade bitumen – a road bitumen with medium viscosity. This grade is adapted to the climatic conditions of Kazakhstan and was selected as a suitable base binder for modification with rubber–polymer composites. It is characterized by high stability at elevated temperatures.
- 100/130 grade bitumen – a relatively soft road bitumen with a high penetration value. Due to this property, it is suitable for investigating elasticity and crack resistance at low temperatures. Devulcanized rubber particles and conventional crumb rubber were incorporated into this grade, and the resulting changes in physicomechanical properties were analyzed.

The use of these two bitumen grades made it possible to compare their properties in the base and modified states, to evaluate the effects of various rubber–polymer additives, and to determine optimal compositions adapted to the climatic conditions of Kazakhstan. The characteristics of the 70/100 and 100/130 grade petroleum road bitumens are presented in Tables 1 and 2.

Table 1 – Characteristics of viscous bitumen for oil roads of the B 70/100 brand

№	Name of the indicator	Road bitumen 70/100	Actual value	Test method
1	25 °C penetration, not less, mm	87±5	87.2	ST RK 1226
2	Softening temperature for the ring and ball, °C, not less	45.8±1.6	45.85	ST RK 1227
3	Fraas brittleness temperature, °C, not more	– 21±3	– 21	ST RK 1229
4	Solubility %, not less	99.75 ±0.1	99.75	ST RK 1228
5	Ignition temperature °C, not less	334 ±4	335	ST RK 1804

Table 2-characteristics of viscous bitumen of oil track grade 100/130 of the state enterprise

№	Name of the indicator	Road bitumen 70/100	Actual value	Test method
1	25 °C penetration, not less, mm	101-130	113	ST RK 1226
2	0 °C penetration, not less, mm	30	32	
3	Softening temperature for the ring and ball, °C, not less	43	44	ST RK 1227
4	Elongation at 25 °C, cm, not less	90	>150	ST RK 1374
5	Elongation at 0 °C, cm, not less	4.0	6.9	
6	Dynamic viscosity at 60 °C, Pa*s, not less	120	138	ST RK 1211
7	Kinematic viscosity at 135 °C, mm2/s, not less	180	352	ST RK 1210
8	Ignition temperature °C, not less	230	282	ST RK 1804
9	Fraas brittleness temperature, °C, not more	–22	–24	ST RK 1229
10	Penetration index	from –0.1 to +1.0	–0.7	

11	Solubility %, not less	99.0	99.9	ST RK 1228
12	Paraffin content %, not more	2.5	0.4	ST RK 1230

The research results confirmed that the actual properties of the viscous petroleum road bitumens of grades 70/100 and 100/130 comply with the requirements of ST RK 1373-2013**.**

Bitumen modification was carried out using a laboratory bitumen modification unit. The setup consisted of a cylindrical reactor with a length of 20 cm and an inner diameter of 15 cm. The reactor was heated by an electric furnace. Temperature measurement and control inside the reactor were ensured by a thermometer connected to a temperature controller. The mixing rate of bitumen with polymer additives was regulated using a mixer, with a rotational speed of 6000 rpm. Heating was controlled by increasing the furnace voltage via a temperature controller.

The average mass of the modified bitumen sample was approximately 200 g. Prior to the modification process, the bitumen sample was heated to a fluid state (at a temperature not exceeding 105 °C), after which plastic waste was gradually added. The polymer was then incorporated into the mixture of molten bitumen and waste materials, and the mixture was continuously stirred and heated until a homogeneous composition was obtained. The temperature was maintained in the range of 175–180 °C, and depending on the type of modifier, the mixing duration was up to 180 minutes.

To assess the conformity of the prepared polymer–bitumen binders, the following key physicomechanical properties were determined: softening point, needle penetration depth (penetration), ductility (elasticity), and Fraass breaking point temperature. The softening point was determined by the ring-and-ball method in accordance with ST RK 1227**.** Penetration was measured using a penetrometer in accordance with ST RK 1226**.** Ductility, which indirectly characterizes bitumen adhesion and is related to the nature of its components, was determined using a CKB-974N ductilometer in accordance with ST RK 1374**.** The Fraass breaking point temperature was determined using an ATX-04 apparatus designed to evaluate the low-temperature brittleness of bitumen.

Results and Discussion

Conventional crumb rubber (CCR) and mechanochemically devulcanized rubber particles (DRP) were introduced into BND 100/130 grade bitumen in the range of 5–25 wt.%. The results are presented in Table 3.

Table 3 - Results of modification of B100/130 grade with the addition of CCR and DRP

Composition	**Softening temperature for the ring and ball, not lower, °C 25 °C**	**Needle penetration depth at 25 °C, not lower, mm**	**Elongation at 25 °C, not lower, cm**	**Brittleness temperature on Fraas, not higher, °C**
BND 100/130	44	113	150	-24
BND 100/130 - 95% CCR - 5%	45,8	69	139,7	-17,7
BND 100/130 - 95% DRP - 5%	55,7	117	63,2	-18,8
BND 100/130 - 90% CCR - 10%	54,5	65	115,8	-18,6
BND 100/130 - 90% DRP - 10%	64,5	105	48,4	-19,5

BND 100/130 - 85% CCR - 15%	56,8	63	53	-19,1
BND 100/130 - 85% DRP - 15%	61	94	37	-26,5
BND 100/130 - 80% CCR - 20%	61,9	60	21,9	-20,3
BND 100/130 - 80% DRP - 20%	63,5	83	33	-34
BND 100/130 - 75% CCR - 25%	65,6	56,3	15,6	-30,6
BND 100/130 - 75% DRP - 25%	67,1	72	25	-27,7

Compositions containing 5–25 wt.% of both CCR and mechanochemically devulcanized rubber particles (DRP) demonstrated a significant increase in high-temperature strength, with the softening point rising from the initial 44 °C to 60–67 °C.

As the content of CCR increased, the bitumen became progressively stiffer and the penetration value decreased rapidly. In contrast, although the softening point increased markedly in the presence of DRP, penetration values remained relatively higher. This indicates that the use of DRP provides a more effective balance between workability and mechanical strength. The Fraass breaking point temperature was observed to improve with increasing rubber content. In particular, compositions containing 15–20 wt.% DRP exhibited a significant reduction in brittleness temperature to the range of −26.5 to −34 °C, indicating enhanced resistance to low-temperature cracking under cold climatic conditions. Compared with compositions containing conventional crumb rubber, DRP-modified samples retained superior low-temperature flexibility.

For the modification of BND 70/100 grade bitumen, a hybrid ELTC modifier containing devulcanized rubber, polyethylene (PE), polypropylene (PP), and additives was employed. The modified compositions were compared with bitumen modified with styrene–butadiene–styrene (SBS). The results are presented in Table 4.

Table 4 - Results of modification of B70/100 grade with SBS and ELTC+PE systems

Composition	**Softening temperature for the ring and ball, not lower, °C 25 °C**	**Needle penetration depth at 25 °C, not lower, mm**	**Elastic recovery, %**
B 70/100	48,3	90,8	0
4% SBS t = 160ºC, 60 min	76,4	67,3	60
ELTC 20%+PE 10% t = 180ºC, 30-90 min	65,9-67,7	56,2-57,0	37-39
ELTC 20%+PE 20% t = 180ºC, 30-90 min	>80	35,6	33
ELTC 20%+PE 40% t = 180ºC, 30-90 min	>80	26,6	30

The incorporation of an ELTC-type modifier based on waste tire rubber and polyethylene (PE) and polypropylene (PP) significantly improved the high-temperature properties of bitumen. In ELTC+PE systems, the softening point increased to 65–80 °C and higher; however, when the PE content reached 20–40 wt.%, excessive stiffening of the binder was observed, accompanied by a reduction in elastic recovery.

In ELTC+PP systems, both the softening point and penetration values were maintained at relatively high levels, while elastic recovery reached approximately 50–55%, indicating enhanced resistance to long-term fatigue cracking. For comparison, BND 70/100 bitumen modified with 4 wt.% SBS polymer exhibited an increase in softening point to 76.4 °C and an elastic recovery of about 60%. Certain ELTC+PP-based compositions (e.g., with 10–20 wt.% PP) achieved softening point, penetration, and elasticity values comparable to or approaching those of SBS-modified bitumen. This demonstrates the potential of rubber–polymer composite modifiers to partially or fully replace expensive SBS polymers.

Conclusions

The present study focused on improving the rheological and physicomechanical properties of BND 70/100 and BND 100/130 grade bitumens through modification with rubber–polymer composites derived from waste tire rubber and polymer wastes.

- The initial properties of the base bitumens were found to comply with national standards, confirming their suitability as reliable base binders.
- The incorporation of conventional and devulcanized rubber particles into BND 100/130 bitumen increased the softening point to 60–67 °C and improved low-temperature flexibility. In particular, the use of devulcanized rubber provided a more effective balance between strength and workability.
- Modification of BND 70/100 bitumen with the ELTC modifier significantly enhanced high-temperature performance. ELTC+PP systems were distinguished by higher elastic recovery, contributing to improved long-term durability.
- Certain ELTC+PP compositions demonstrated performance comparable to SBS-modified bitumen, indicating the feasibility of partially replacing costly SBS polymers.
- From an environmental perspective, rubber–polymer modifiers enable the recycling of waste tires and plastic wastes, thereby reducing environmental burden.
- The optimal compositions were identified as 15–20 wt.% devulcanized rubber particles for BND 100/130 and 10–20 wt.% ELTC+PP-based modifier for BND 70/100.

Overall, the results indicate that the use of rubber–polymer composites, particularly ELTC+PP systems, represents a promising approach for producing high-temperature-resistant and elastic road bitumens adapted to the sharply continental climatic conditions of Kazakhstan.

REFERENCES

1. Porto, M., Caputo, P., Loise, V., Eskandarsefat, S., Teltayev, B., & Oliviero Rossi, C. (2019). Bitumen and bitumen modification: A review on latest advances. Applied sciences, 9(4), 742.

2. Shivokhin, M.; Garcia-Morales, M.; Partal, P.; Cuadri, A.A. Rheological behaviour of polymer-modified bituminous mastics: A comparative analysis between physical and chemical modification. Constr. Build. Mater. 2012, 27, 234–240

3. Ashoori, S.; Sharifi, M.; Masoumi, M.; Salehi, M.M. The Relationship between SARA Fractions and Crude Oil Stability. Egypt. J. Pet. 2017, 26, 209–213.

4. Sheremata, J.M.; Gray, M.R.; Dettman, H.D.; McCaffrey, W.C. Quantitative molecular representation and sequential optimization of Athabasca asphaltenes. Energy Fuels 2004, 18, 1377–1384.

5. Yarranton, H.W.; Fox, W.A.; Svrcek, W.Y. Effect of Resins on Asphaltene Self-Association and Solubility. Can. J. Chem. Eng. 2007, 85, 635–642.

6. Polacco, G.; Filippi, S.; Merusi, F.; Stastna, G. A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility. Adv. Colloid Interface Sci. 2015, 224, 72–112.

7. The World of Bitumen from Ancient Uses to Modern Applications https://highways.today/2024/07/10/world-of-bitumen/

8. Li, J.; Xing, X.; Hou, X.; Wang, T.; Wang, J.; Xiao, F. Determination of SARA fractions in asphalts by mid-infrared spectroscopy and multivariate calibration. Measurement 2022, 198, 111361.

9. Zhang, J.; Yao, Z.; Yu, T.; Liu, S.; Jiang, H. Experimental evaluation of crumb rubber and polyethylene integrated modified asphalt mixture upon related properties. Road Mater. Pavement Des. 2019, 20, 1413–1428.

10. Wang, T.; Xiao, F.; Amirkhanian, S.; Huang, W.; Zheng, M. A review on low temperature performances of rubberized asphalt materials. Constr. Build. Mater. 2017, 145, 483–505.

11. Akkenzheyeva, A., Haritonovs, V., Bussurmanova, A., Merijs-Meri, R., Imanbayev, Y., Serikbayeva, A., ... & Turkmenbayeva, M. (2024). The use of rubber-polymer composites in bitumen modification for the disposal of rubber and polymer waste. Polymers, 16(22), 3177.

МҰНАЙ БИТУМЫН РЕЗЕҢКЕ-ПОЛИМЕРЛІ КОМПОЗИТТЕРМЕН МОДИФИКАЦИЯЛАУ

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Аңдатпа. Бұл ғылыми-зерттеу жұмысы мұнай жол битумын резеңке-полимерлі композиттермен модификациялау мәселесіне арналған. Зерттеудің мақсаты – Қазақстанның климаттық жағдайларына бейімделген жаңа буынды жол байланыстырғыштарын әзірлеу үшін отандық МЖБ 70/100 және МЖБ 100/130 маркалы битумдардың реологиялық және физика-механикалық қасиеттерін жақсарту.

Жұмыста пайдаланылған автокөлік шиналары негізгізделген және полиэтилен, полипропилен сияқты полимер қалдықтарына негізделген резеңке-полимерлі композиттердің тиімділігі қарастырылды. Әдеби шолуда битумның құрамы мен қасиеттері, оны полимерлермен, резеңке үгіндісі және композиттік модификаторлармен жетілдіру жөніндегі отандық және шетелдік зерттеулер талданды.

Эксперименттік бөлімде бастапқы және модификацияланған битумдардың жұмсару температурасы, пенетрациясы, созылғыштығы, Фраас сынғыштық температурасы, тұтқырлығы және серпімді қалпына келу көрсеткіштері анықталды. Нәтижелер бойынша девулканизацияланған резеңке үгіндісі мен ELTC типті композиттік модификаторлардың битумның эксплуатациялық қасиеттерін айтарлықтай жақсартатыны дәлелденді.

Зерттеу қорытындысында Қазақстанның күрт континенттік климатында жол жабындарының беріктігін арттыруға мүмкіндік беретін оңтайлы құрамдар ұсынылды. Сонымен қатар, пайдаланылған шиналар мен полимер қалдықтарын қайта өңдеудің экологиялық және экономикалық тиімділігі көрсетілді.

Түйін сөздер: битум, резеңке-полимерлі композит, девулканизацияланған резеңке, ELTC модификаторы, реологиялық қасиеттер, жол құрылысы.

МОДИФИКАЦИЯ НЕФТЯНОГО БИТУМА РЕЗИНОВО-ПОЛИМЕРНЫМИ КОМПОЗИТАМИ

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Аннотация. Данная научно-исследовательская работа посвящена проблеме модификации нефтяного дорожного битума резино-полимерными композитами. Цель исследования – улучшение реологических и физико-механических свойств битумов отечественных марок БНД 70/100 и БНД 100/130 для разработки дорожных связующих нового поколения, адаптированных к климатическим условиям Казахстана.

В работе рассматривалась эффективность композитов на основе использованных автомобильных шин и резино-полимерных композитов на основе полимерных отходов, таких как полиэтилен и полипропилен. В литературном обзоре проанализированы отечественные и зарубежные исследования состава и свойств битума, его совершенствования полимерами, резиновыми крошками и композитными модификаторами.

В экспериментальной части определены температура размягчения, пенетрация, растяжимость, температура хрупкости Фраас, вязкость и показатели упругого восстановления первичных и модифицированных битумов. Результаты показали, что девулканизированная резиновая крошка и композитные модификаторы типа ELTC значительно улучшают эксплуатационные свойства битума.

В заключении исследования были предложены оптимальные составы, позволяющие повысить прочность дорожных покрытий в резко континентальном климате Казахстана. Кроме того, была продемонстрирована экологическая и экономическая эффективность переработки использованных шин и полимерных отходов.

Ключевые слова: битум, резино-полимерный композит, девулканизированная резина, модификатор ELTC, реологические свойства, дорожное строительство