

Article

Influence of the Chemical Composition of Kulantau Vermiculite on the Structure of Modified Bitumen Compositions

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Abstract: The article presents the chemical composition of vermiculite ores from the Kulantau deposits and the atomic structure of vermiculite during dehydration, in 1-, 2- and 3-layer hydrated states. It has been shown that vermiculites from deposits in the Turkestan region have significant differences in mineralogical composition. Rational ways of using Kulantau vermiculite as an innovative modifying additive in bitumen compositions are considered, which are intended to improve the asphalt concrete mixture during its preparation. A slight increase in structuring resins is a result of the elevated content of high-molecular-weight asphaltenes in the modified bitumen, as indicated by the analysis of the provided spectra. In turn, the systematization or structuring of bitumen leads to an increase in the mixture density, accompanied by a simultaneous rise in internal friction coefficients, and resistance to loads (shear and impact), as well as an enhancement in compressive strength. The influence of the chemical composition of Kulantau vermiculite on the structure of bitumen compositions is characterized by high adsorption capacity and effectively absorbs products resulting from the oxidation of hydrocarbons. Vermiculite is characterized by high efficiency in the activation phase, large pore volume, and selectivity. The alteration of the bitumen's group composition due to the selective diffusion of oils, as well as resins in the material, occurs as a result of the interaction between bitumen and a material characterized by a fine-porous structure and high specific surface area. This process modifies the properties of bituminous layers on the surface of particles and leads to the formation of robust bitumen films appearing on the grain surfaces. Thus, enhancing the longevity of coatings, improving the quality of binding bitumen, and reducing asphalt concrete coverings necessitate the use of vermiculite in creating modified bituminous compositions.

Keywords: vermiculite; expansion; chemical composition; degree of hydration; structure; asphaltenes; modification; bitumen composition



Citation: Syrmanova, K.; Kaldybekova, Z.; Agabekova, A.; Baizhanova, S. Influence of the Chemical Composition of Kulantau Vermiculite on the Structure of Modified Bitumen Compositions. *J. Compos. Sci.* **2024**, *8*, 118. <https://doi.org/10.3390/jcs8040118>

Academic Editors: Francesco Tornabene and Phuong Nguyen-Tri

Received: 13 December 2023

Revised: 16 February 2024

Accepted: 1 March 2024

Published: 22 March 2024



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1. Introduction

High adsorption and ion-exchange properties, ease of obtaining modified form including organomineral forms, and relatively good acid and alkali resistance determine widespread use and sustained interest in studying the structure and properties of vermiculite-based materials.

Vermiculite is a very valuable natural material. Expanded vermiculite, i.e., subjected to heat treatment, is used with great economic effect in various industries. Expanded vermiculite does not burn, does not rot, is chemically inert, durable, bioresistant, completely explosion- and fire-proof, environmentally friendly, has a beautiful golden color, has ion-exchange and sorption properties, and a high ability to absorb and retain liquids and gases [1–7].

According to the US Geological Survey [8], the world's proven reserves of vermiculite are estimated at 50 million tons, and undiscovered reserves—200 million tons (Figure 1).

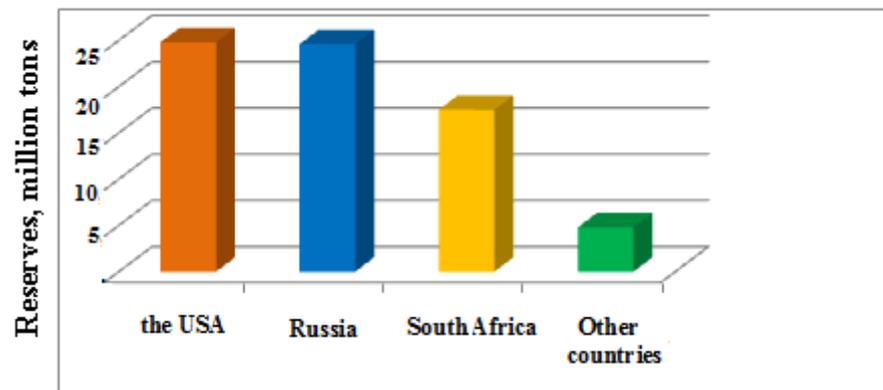


Figure 1. Diagram of distribution of world vermiculite reserves.

The main deposits are located in the USA (South Carolina, Virginia, and Montana), South Africa (90% of the reserves are in the Palabora complex), China (the main deposits of Xinjiang and Hegbei), Great Britain, and Russia (Kovdor deposit). Vermiculite reserves are also available in a number of other countries: Ukraine, Kazakhstan, Uzbekistan, Argentina, Australia, Canada, Brazil, Egypt, India, Japan, Kenya, Zimbabwe, and Uganda. Well-known enterprises for the production and use of vermiculite are Dupre Minerals Ltd. (UK), Caterpillar Inc., Specialty Vermiculite Corp., (USA), Soprema (Belgium), Florareat (Spain), China Hebel Xinha Mineral Industry Co., Ltd. (China), etc. World production of vermiculite exceeds 500,000 tons per year. There are also deposits of vermiculite on the territory of Kazakhstan. In the southeastern part of Karatau Range and Talas Alatau, vermiculite deposits were found, the most promising of which are Kulantau, Iirsu, and Zhylandy [5].

Vermiculite is a clay mineral with a crystalline structure. In nature, vermiculite is formed as a result of the hydration process of magnesium–iron micas–biotite and phlogopite. During the transformation of these micas into vermiculite, almost complete removal of alkalis occurs, protoxidic compounds of iron turn into oxidic compounds, and the amount of water sharply increases. Some rearrangement of atoms (cation exchange) occurs in the layers of the crystal lattice as a result of the introduction of water molecules into the interlayer space [2]. Potassium ions (K^+) located in the interlayer space of the mica of the original composition are replaced by other cations, such as magnesium (Mg^{2+}), or a combination of magnesium and calcium ions (Ca^{2+}).

The vermiculite formed as a result of this process has a hydrated interlayer space and is bound by weak van der Waals bonds. Weak bonds and the presence of water in the interlayer space of vermiculite are the reasons for its disposition to expansion and delamination.

The general molecular formula of trioctahedral vermiculite is given below [5]:



In Formula (1), the (Mg.Ca) atoms are the exchange interlayer cation, which is surrounded by water molecules, the ($Si_{8-x}Al_x$) atoms are the tetrahedral layer, and the (Mg.Fe) atoms correspond to the cations of the octahedral layer.

Figure 2 shows the structure of vermiculite with octahedral, tetrahedral, and hydrated interlayer cations, which are replaced by magnesium when complete vermiculite formation occurs. The degree of hydration and the type of interlayer cations have a significant impact on its physical and chemical properties and therefore affect its performance and application. The authors [3] conducted studies of vermiculite to determine the dependence of the degree of expansion on the amount of water contained in mica. The Monte Carlo method and molecular dynamics simulations method were used to study the change in the basal space of this clay mineral with increasing water content, as well as the increase in this space at different hydration states when exposed to temperature. It was found that the

effect of temperature is much greater on highly hydrated clay and insignificant for weakly hydrated clay.

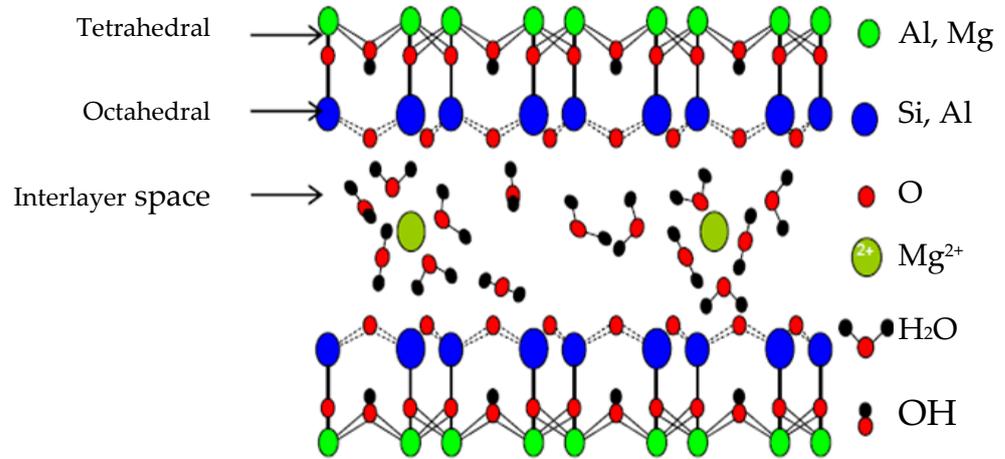


Figure 2. Different types of vermiculite structures.

The diffusion behavior of water and sodium ions (Na^+) in the interlayer space of various hydrated vermiculite was also studied using molecular dynamics. It was established that the diffusion of water is much faster than (Na^+) in the same hydrated state [8]. The atomic structure of vermiculite during expansion is shown in Figure 3.

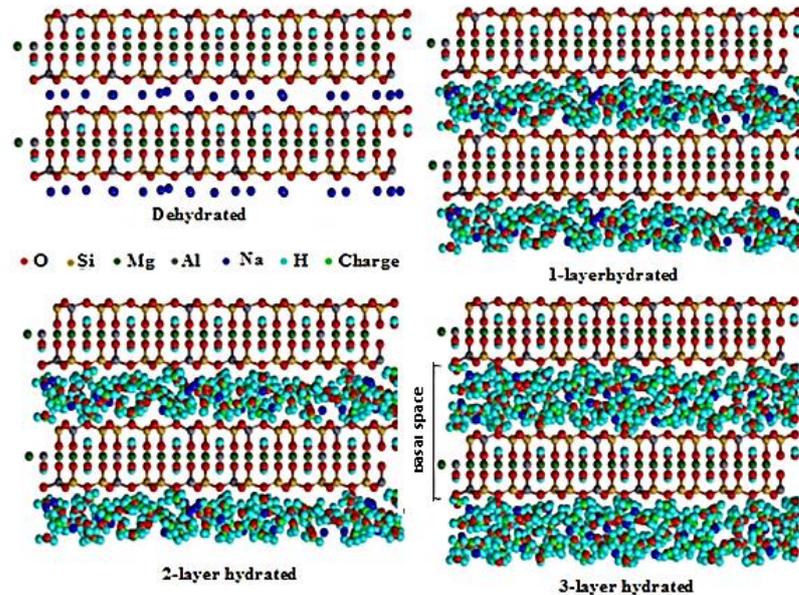


Figure 3. Atomic structure of vermiculite during dehydration, in 1-, 2- and 3-layer hydrated states.

Vermiculite structures contain aqueous interlamellar layers that undergo hydration and dehydration processes. Hydration is controlled by interlayer Mg^{2+} cations and small amounts of Ca^{2+} , Na^+ , and K^+ . The radius and charge of the cation influence the degree of hydration state in the intermediate layer and the sequence of overlay layers. The state of vermiculite hydration was determined by the number of layers of water in the interlayer space. According to Walker G.F., the basal space of Mg-vermiculite is 0.902 nm for a zero-water layer, 1.150 nm for a single layer, and 1.440 nm for a 2-layer hydration state [2,5].

Vermiculite is characterized by the following isomorphous substitutions:





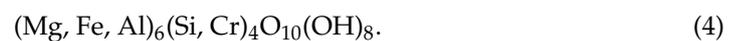
The chemical composition of vermiculite may vary due to its structural features such as possible isomorphic substitutions: SiO_2 —34–42%; Al_2O_3 —10–17%; Fe_2O_3 —3–17%; Mg —14–25%; and $\text{H}_2\text{O} < 20\%$.

Deposits in the Turkestan region have significant differences in mineralogical composition. Thus, vermiculite from the Kulantau deposit (Figure 4) contains mainly minerals of the phlogonite series, and vermiculite from Irsu and Zhylandy deposits consists mainly of biotite and hydrobiotite.



Figure 4. Vermiculite from Kulantau deposit.

The main component of vermiculite from the Kulantau deposit, according to microscopic and X-ray diffraction studies, is kochubeite with the formula:



In Kochubeyite, which exhibits a scaly appearance of brown mica, and is a product of biotite alteration with increased content of K_2O and decreased content of K_2O , impurities of chlorite, calcite, and quartz crystals are encountered [7].

Vermiculite is characterized by high adsorption capacity and effectively absorbs products resulting from the oxidation of hydrocarbons, for example, resins, oxygen-containing compounds, and other heteroorganic products [5]. The expansion coefficient of vermiculite is in the range of 4.8–11, the average value is 6. After the expansion process, it can be concluded that vermiculite is a hydromica with an average degree of hydration.

The degree of expansion of vermiculite is largely determined by the size of the particles and the rate at which heating occurs. Small vermiculite particles measuring about 0.01 mm expand slightly or do not expand at all. Slow heating is also not accompanied by a sharp increase in volume. Vermiculite delaminates at a temperature of about 300 °C, and at a lower temperature, even with rapid heating, expansion cannot occur. Maximum expansion is observed when hydromica plates are rapidly heated to a high temperature.

Expanded vermiculite is a lightweight porous material that is widely used in construction for thermal insulation and waterproofing. Delamination of vermiculite occurs in a direction perpendicular to the cleavage plane. This is explained by the rapid removal of water (more precisely, its vapors) from the interlayer space. Introducing vermiculite very quickly into a hot oven promotes instantaneous vaporization. The vapors, not having time to escape, produce strong pressure on the layers of vermiculite between which there was water, resulting in expansion.

Analysis of literature data [9–13] indicates that it is recommended to activate vermiculite before use. In this case, activation allows dissolution to remove a significant part of the oxides of magnesium, iron, and aluminum. Against the background of the removal of other oxides, the percentage of silicon oxide SiO_2 in the sample increases, which makes it possible to increase the adsorption capacity.

Kulantau deposit in the Turkestan region is of greatest practical interest [5]. It is located in the dividing part of the Kulantau Mountains, 8 km northwest from of Vysokoyevillage. The deposit is located in very favorable economic conditions: it is located 5–6 km from Alma-Ata—Tashkent asphalt road, and 12–15 km from the railway. Operating conditions and hydrogeological conditions are also very favorable. The content of vermiculite in ore varies widely—from the first units to 25–35%. The volumetric weight of expanded vermiculite ranges from 75 to 200 kg/m^3 . The average volumetric weight for the deposit is 135 kg/m^3 . The size of expanded vermiculite corresponds to fractions of +0.15–5.0 mm. At that, up to 80% of vermiculite has a particle size of +0.5–5 mm. The grain fragility index is from 2 to 30–40%. The expansion coefficient of vermiculite ranges from 4.8–11, the average coefficient is 6. According to the expansion coefficient, vermiculite belongs to hydromicas with an average degree of hydration. Vermiculite reserves, calculated according to categories C, with a volumetric weight of 200 kg/m^3 are 0.5 million tons, which is equivalent to 3.0–3.5 million m^3 of expanded vermiculite. In addition, by analyzing samples of vermiculite ore, it was established that the ore also contains hydrobiotite, the volumetric weight of which ranges from 200 to 460 kg/m^3 . After roasting the ore, hydrobiotite is well extracted using air separation and, undoubtedly, can find application both in construction and in agriculture. Its amount is 12–13% of the deposit. Taking into account hydrobiotite, hydromica reserves amount to 1.0 million tons.

Zhylandy deposit is located 12–15 km west of the Kulantau deposit, at the foot of the southern slope of Boraldai-Tau Range, in the Satur Mountains, as well as 10 km north from of Vannovka village and 8 km from Tulkubas railway station. Vermiculite-bearing rocks are developed over an area of 400 × 40 m. The average thickness of the ore zone is 15 m.

The average vermiculite content is 8%. Vermiculite reserves at the deposit are 100 thousand tons.

On the territory of the northwestern spurs of TalasAlatau, four areas of vermiculite occurrence were identified. The Irisu site is in the area of the Irisu iron-copper deposit, located in the interfluvium of the Irisu and the Aksu rivers and located 20 km to the southeast from Tulkubas station. In the area of Irisu massif, four vermiculite-bearing zones were identified: Aksu, Karatau, Fourth, and First—in areas of the iron-ore zones of the same name.

Only the Fourth and partial Karatau zones received a preliminary assessment as the most accessible areas for small-scale mining. In the area of the Fourth ore zone, vermiculite content can be traced in an area up to 1200 m long with a width of 200 to 400 m. The vermiculite content ranges from 10 to 15%. The thickness of the vermiculite zone is at least 20 m. Approximate vermiculite reserves of 1.2–1.5 million tons are somewhat less in the Karatau zone, where vermiculite is more fine-grain and its content is within 5–10%. When carrying out targeted work in areas covered by conglomerates, it is possible to identify vermiculite in a volume of 5–6 million tons. Total reserves will amount to the first tens of millions of tons.

Two occurrences of vermiculite were identified in the Daubaba River basin.

(a) The western site is located in the middle part of the Daubaba River, at a distance of 20 km from Sas-Tobe station, in a southeast direction. Visually, the content of vermiculite and hydrobiotite is 10–15%. The site belongs to small-type deposits with reserves of up to 100 thousand tons.

(b) The eastern site is located in the upper reaches of the Daubaba River and is located 10 km east southeast of the western site. Visually, the content of vermiculite and hydrobiotite is at least 20–25%. The area of vermiculite occurrence deserves assessment work.

Promising areas for vermiculite on the territory of TalasAlatau are the area of development of alkaline rocks Kaindy and Jetysay, where the presence of vermiculite was

established; the southeastern end of Chu-Bulkhash watershed in the area of Dalan-Karin and Anarkhay diorite and granodiorite massifs; and Trans-Ili Alatau, where rocks of medium and basic composition are developed.

Chemical analysis of varieties of vermiculite ore from deposits in the Turkestan region is presented in Table 1 from which it follows that even for the most hydrated last variety, the process of transformation into vermiculite is not fully completed: the transition of iron from the 2-valent form to the 3-valent form is also not completed, i.e., mica minerals of the deposits do not contain vermiculite in the mineralogical meaning of the word, and the term “vermiculite” should be understood as the most highly hydrated micas of the transition series (vermiculites of Iirsu and Zhylandy deposits).

Table 1. Chemical composition of vermiculite ores from Iirsu, Zhylandy, and Kulantau deposits.

Components, %	Vermiculites		
	Iirsu	Zhylandy	Kulantau
K ₂ O	7.5–10.4	5.8–11.5	-
MgO	6.8–11.6	0.4–27.4	15.5–22.8
Al ₂ O ₃	10.2–16.3	9.5–30.6	10.2–12.8
SiO ₂	38.5–44.4	32.7–44.1	37.1–41.5
Fe ₂ O ₃	0.01–0.03	0.14–21.2	6.4–17.2
H ₂ O	0.6–5.5	0.85–4.4	8.3–17.5
FeO	-	2.4–30.0	1.4–2.8

Differences in the mineralogical composition of the ores (Kulantau vermiculite)—the main component is minerals of the phlogonite series, and Iirsu and Zhylandy vermiculite—the main phase is biotite and hydrobiotite (Table 2) also determined a different approach to solving the problem of ore enrichment. For Kulantau ores, the wet enrichment method using depositing machines was chosen. For Iirsu and Zhylandy vermiculites, it is possible to enrich the ore using the dry method using electromagnetic separation. Heat treatment affects vermiculite in two ways: firstly, an increase in the treatment temperature leads to the removal of residual tightly bound water molecules and, consequently, to an increase in the number of high-energy adsorption centers, and secondly, to the compaction of the secondary porous structure of minerals [5,7].

Table 2. Qualitative characteristics of Kulantau vermiculite.

№	Humidity, %	Degree of Hydration, %	Volumetric Weight, kg/m ³	Vermiculite Content, %
1	6.2	65	178	30
2	9.0	70	200	35
3	3.7	60	130	28
4	3.1	75	140	26

The obtained results of the qualitative characteristics of Kulantau vermiculite are shown in Table 2.

The chemical composition of expanded vermiculites from Iirsu, Zhylandy, and Kulantau deposits is given in Table 3.

X-ray structural analysis and microscopic studies of vermiculite samples from Kulantau revealed that the main component is kochubeite (Mg, Fe, Al)₆(Si, Cr)₄O₁₀(OH)₈, a product of biotite alteration in the form of brown mica flakes. It has an increased content of H₂O and a decreased content of K₂O [7]. Such impurities as calcite, chlorite crystals, and

quartz are observed. The results obtained (Table 3) basically do not contradict the literature data [5–9]; expanded Kulantau vermiculite was chosen as the research object in this work.

Table 3. Chemical composition of expanded vermiculites from Iirsu (1), (2), and Kulantau deposits (3).

№	Vermiculite	Content of Components, %							
		SiO ₂	CaO	MgO	K ₂ O + Na ₂ O	Fe ₂ O ₃	Al ₂ O ₃	H ₂ O	Other
1	Iirsu	38.96	1.81	8.41	7.3	0.21	10.88	4.31	28.13
2	Zhylandy	33.82	1.96	21.45	1.15	7.85	14.99	4.75	14.03
3	Kulantau	37.44	2.10	23.88	1.18	6.01	11.23	10.98	17.18

A photograph of expanded vermiculite is shown in the Figure 5.



Figure 5. Kulantau vermiculite sample.

2. Research Methods

The research objects were Kulantau vermiculite and bitumen compositions using polymer wastes—low-density polyethylene (LDPE) and Kulantau vermiculite.

To prepare bitumen compositions, a laboratory experimental mixing installation was assembled (Figure 6).

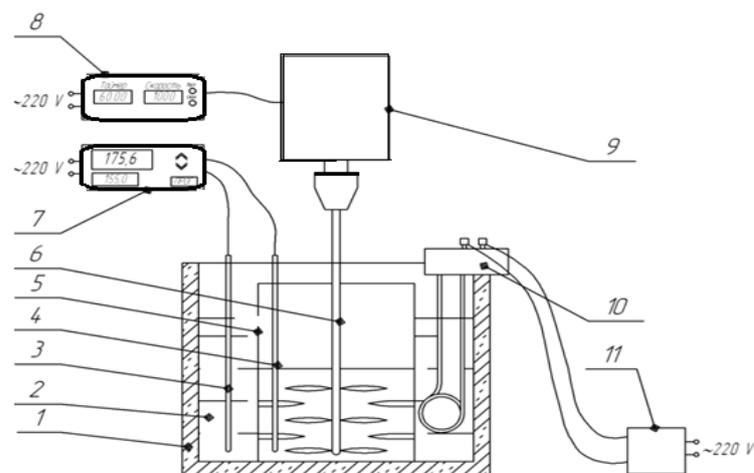


Figure 6. Illustration of an experimental mixing plant in a laboratory for the production of polymer bitumen binders. 1—isolated bath; 2—silicone oil PMS; 3—pocket for thermocouple, temperature measurement in oil; 4—pocket for thermocouple, temperature measurement in bitumen; 5—container with bitumen, 6—paddle mixer; 7—temperature meter; 8—engine control unit; 9—electric motor; 10—electric heater, heating element; and 11—laboratory autotransformer.

Diffraction patterns of Kulantau vermiculite before and after expansion are shown in Figures 7 and 8.

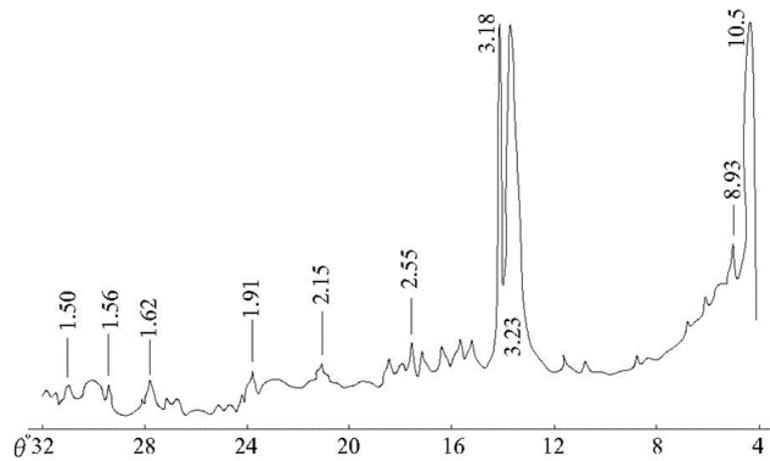


Figure 7. Diffraction pattern of unexpanded vermiculite.

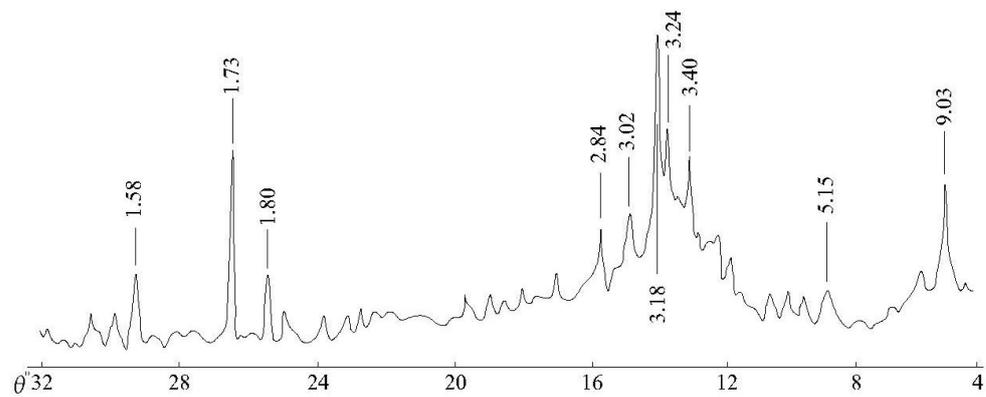


Figure 8. Diffraction pattern of expanded vermiculite.

The initial bitumen, weighing 500 g, is loaded into a preheated metallic container, and heated to 100–120 °C. The bitumen is first warmed and then melted at the same temperature.

Next, polymer waste and expanded Kulantau vermiculite are added. Next, the temperature is increased to 150–180 °C at a rate of 5–10 °C/min. Mixing takes place within 2–2.5 h. Then the physical and mechanical properties of the resulting bitumen composition (BC) are determined depending on various factors under study [7,14,15].

IR spectra of the structures of the original bitumen and the studied bitumen compositions and BC with different contents of vermiculite (from 2% to 25%) were recorded on a Shimadzu IR Prestige-21 Fourier transform spectrometer with a Miracle attenuated total internal reflection (ATR) attachment from PikeTechnologies [16–19].

3. Discussion of Methods

It is known that the manufacture of asphalt concrete mixtures for paving roads with heavy traffic is impossible without using modifiers. At the same time, world practice shows that along with the “primary” modifiers (such as SBS), effective “secondary” modifiers are widely used, in particular, those obtained from polymer waste. However, the use of polymer bitumen is limited by technological factors of working with this material: the impossibility of its long-term storage; special requirements for bitumen storage; transport difficulties; and other problems. These disadvantages are eliminated by an innovative modifying additive—expanded Kulantau vermiculite, which is a complex modifier designed to improve the asphalt concrete mixture during its preparation. Several studies have evaluated the possibility of using residues to make asphalt mixtures [20–27].

The characteristic peaks of the study of the structure of organic binders by Fourier transform infrared spectroscopy of the compositions BND 70/100 + LDPE and BND 70/100 + LDPE + expanded Kulantau vermiculite are shown in Figures 9–13.

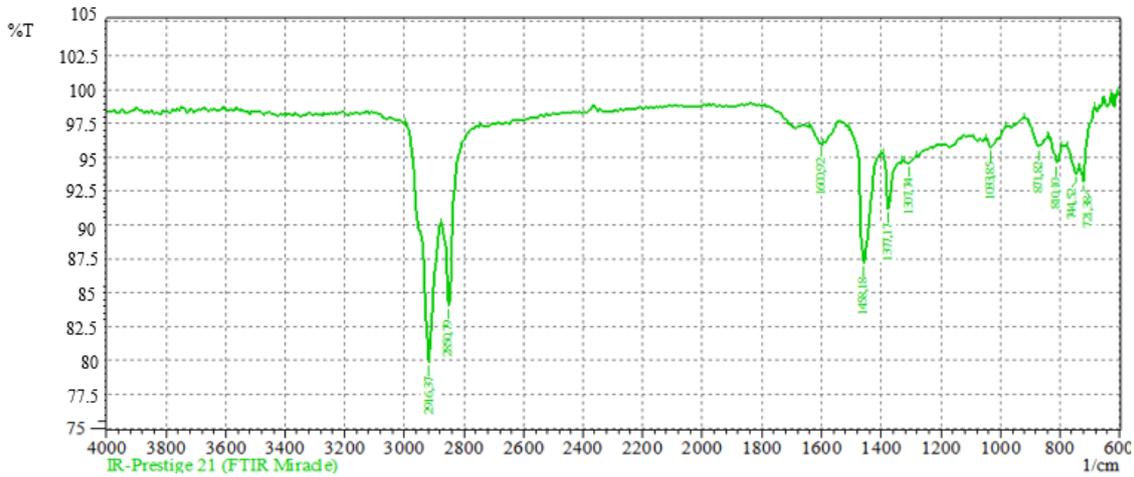


Figure 9. IR spectrum of the structure of bitumen BND 70/100.

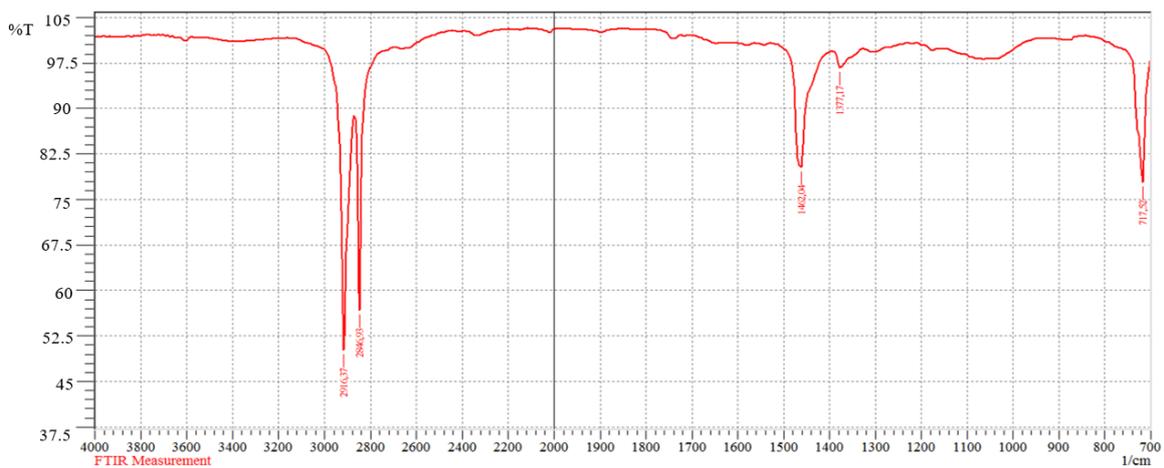
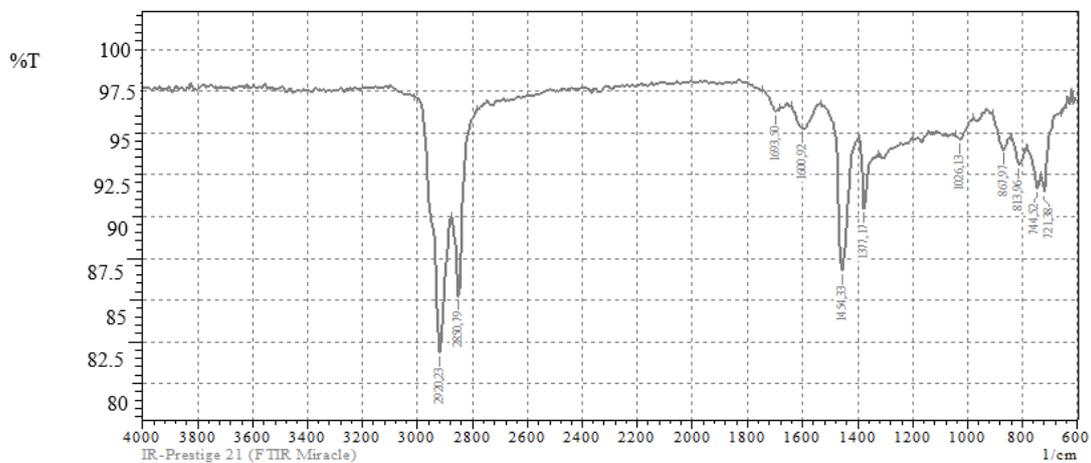


Figure 10. IR spectrum of bitumen composition with recycled LDPE. (bitumen + LDPE).



Sample—2 (5%)

Figure 11. IR spectrum of bitumen composition with the addition of 5% vermiculite.



Sample—2a (10%)

Figure 12. IR spectrum of bitumen composition with the addition of 10% vermiculite.

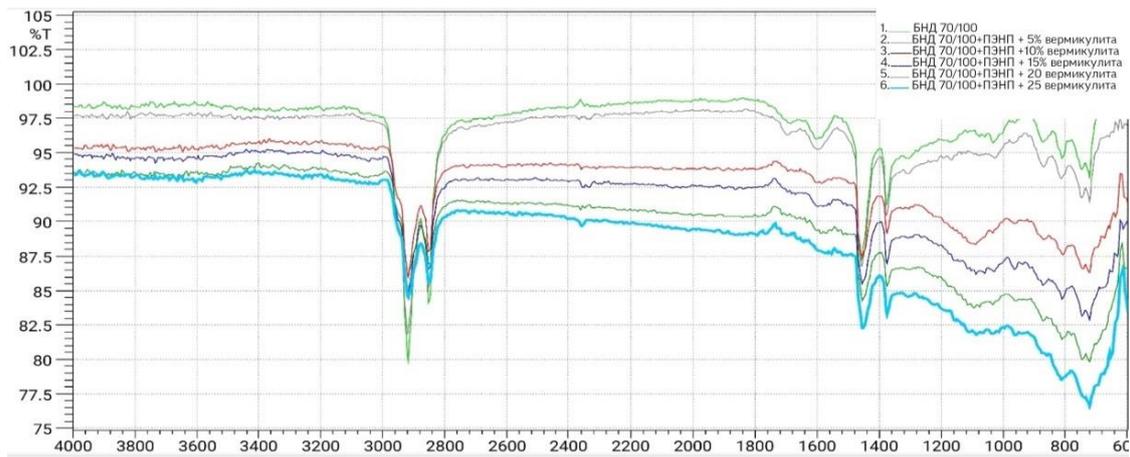


Figure 13. Combined infrared spectra of bitumen compositions with different concentrations of vermiculite (from 5% to 25%). 1. BND 70/100; 2. IR spectrum of BND 70/100+LDPE+5% vermiculite; 3. IR spectrum of BND 70/100+LDPE+10% vermiculite; 4. IR spectrum of BND 70/100+LDPE+15% vermiculite; 5. IR spectrum of BND 70/100+LDPE+20% vermiculite; 6. IR spectrum of BND 70/100+LDPE+25% vermiculite.

The spectra obtained through IR spectroscopy, following the methodology for conducting a comparative analysis of the chemical composition of compounds, were overlaid with scaling based on CH_2 groups, with content independent of experimental conditions.

The presence of intense bands characteristic of bitumen within the range of $3000\text{--}2800\text{ cm}^{-1}$ (deformation vibrations of $n(\text{CH})$ and CH_2 groups), 1470 cm^{-1} (deformation vibrations of $5(\text{CH}_2)$), and 1377 cm^{-1} (deformation vibrations of $55(\text{CH}_3)$) was revealed by the analysis of experimental data extracted from the study of bitumen BND 70/100. The presence of these bands is consistently observed in the spectra of paraffins, hydrocarbons, and oils [16,18,19]. The transmission band is clearly depicted in the spectra of components at 722 cm^{-1} , corresponding to the deformation vibrations of $5(\text{CH}_2)$ groups in free paraffin chains. Additionally, the characteristic triplet at $722, 740,$ and 820 cm^{-1} is distinctly traced, serving as an indicator of the presence of aromatic structures.

The presence of oxygen-containing compounds is indicative of the fact that the transmission bands within the range of $1380\text{--}1480\text{ cm}^{-1}$ exhibit significantly higher intensity.

For instance, the band at 1600 cm^{-1} describes the valence changes of unsaturated C=C bonds, predominantly in cyclic structures, particularly benzene rings [7].

According to [20], substances from asphaltene gather free radicals, which, in turn, determine the predisposition of asphaltenes to association. The presence of free radicals is attributed to the fact that asphaltenes predominantly have aromatic structures, leading to the phenomenon of paramagnetism. Consequently, intermolecular interactions arise, contributing to the formation of supramolecular structures.

Therefore, it is evident that hydrogen bonds of carboxyl groups can be characterized by changes in the region of n(OH) stretching vibrations, as well as partially in the bands of (C=O), leading us to hypothesize the possible formation of intermolecular hydrogen bonds [27].

The increase in the absorption band of the carbonyl group at 1458 cm^{-1} (shift in modified bitumen from 1458 to 1600 cm^{-1} and aromatic rings at 1602 cm^{-1}) occurs with a slight increase in structuring-type resins, indicating the presence of an elevated content of high-molecular-weight asphaltenes in the modified bitumen. There is also a decrease in the content of the oil fraction in bitumen when interacting with expanded vermiculite, specifically in paraffin-naphthenic hydrocarbons characterized by paraffinic chains, exhibiting spectral bands at 718 cm^{-1} . These changes are inferred from the analysis of the spectra provided above.

Conversely, the reduction in paraffin-naphthenic hydrocarbons in bitumen prompts an increase in the lyophilicity of asphaltenes, characterized by solvation and expansion in aromatic hydrocarbons, as well as insolubility in paraffin-naphthenic hydrocarbons. This type of bitumen has the peculiarity that asphaltenes interact with their own polar (lyophobic) surface areas, leading to the formation of aggregates and nuclei of coagulation structures. Here, asphaltenes on the lyophilic outer side have adsorbed and oriented resins.

The alteration of the group composition of bitumen results from the contact of bitumen with a material characterized by a fine-porous structure and high specific surface area, due to the selective diffusion of resins and oils into the material. This process leads to the modification of the properties of bitumen layers and the formation of robust bitumen films on particle and grain surfaces. The impact of Kulantau vermiculite on the composition of bitumen compositions can be characterized by its high adsorption capacity and efficient absorption of products formed as a result of hydrocarbon oxidation: oxygen-containing compounds, resins, and other heteroorganic products. Porous vermiculite, passing hydrocarbons with straight chains through its pores and retaining cyclic hydrocarbons and hydrocarbons with a branched molecular structure, thereby combines the bitumen film with oil components and enriches it with asphaltenes and resins, which is accompanied by a hardening of the bitumen film. The choice of vermiculite is also explained by its low price [7].

The quality of the asphalt concrete structure depends on many factors, but, obviously, it is largely determined by the quality of the binder in thin films formed under the influence of the surface of the mineral component grains. It is known that the potential resistance of the material structure to operational influences depends on the activity of interaction at the bitumen-polymer interface, since bitumen structuring occurs on the surface of the polymer, the intensity of which is determined by the contact surface area and the adsorption capacity of the mineral component. The surface area of the mineral powder makes up more than 90% of the total surface area of the particles of the mineral components of asphalt concrete, so the nature of the interaction of this surface with bitumen is of particular importance. As the amount of vermiculite increases, the thickness of the bitumen films on the surface of the particles decreases, which at a certain concentration leads to a sharp strengthening of the contacts between the grains. Structuring of bitumen ensures an increase in the density of the mixture, an increase in the coefficient of internal friction, an increase in resistance to shear and impact loads, compressive strength, and a decrease in fragility. The characteristics of expanded vermiculite are also of great importance, affecting the intensity

and nature of the interaction at the bitumen-polymer interface—particle size and shape, surface texture and porosity.

It is known that bitumen, in accordance with the micellar theory, is a colloidal system in an oil medium in which asphaltenes are surrounded by a shell of resins. Thus, the most chemically active functional groups included in the resin- asphaltene complexes are blocked by a chemically inert oil shell. As a result of the interaction of bitumen with a material having a high specific surface area and a fine-porous structure, a change in the group composition of bitumen occurs due to the selective diffusion of oils and resins into the material, which leads to a change in the properties of the bitumen layers on the surface of the particles and the formation of durable bitumen films on the surface of the grains.

A comprehensive approach, taking into account both chemical and physics-mechanical processes, was employed in the development of a technology for producing asphalt compositions. This approach considers the presence of such processes in the initial bitumen and mixtures with expanded Kulantau vermiculite, as well as in the final products—road and asphalt concrete coatings.

This technology is based on mixing expanded Kulantau vermiculite with a bitumen mixture and LDPE. The molecular polar groups of vermiculite contribute to the stability of the overall dispersed heterogeneous mixture and ensure high and long-lasting binder adhesion. Thanks to this type of structure, the binder possesses the necessary elasticity, making it suitable for practical applications. The physical and mechanical characteristics of the bitumen composition are given in Table 4.

Table 4. Physical and mechanical properties of asphalt concrete based on the bitumen composition modified with expanded Kulantau vermiculite.

№	Indicators	Petroleum Bitumen BND 70/100	Composition of a Bitumen Composition Containing Varying Amounts of Expanded Kulantaus Vermiculite		
			№1	№2	№3
1	Needle penetration depth, 0.1 mm, at temperature:				
	25 °C	100	111	106	117
	0 °C	30	41	59	46
2	Extensibility, cm, at temperature:				
	25 °C	70	>70	>70	>70
	0 °C	55	>70	>70	>70
3	Softening temperature, °C	45	45.5	45	45.5
4	Fragility temperature, °C	−18	−25	−27	−27
5	Elasticity, %, at temperature:				
	25 °C	-	59	67	72
	0 °C	-	31	38	34
6	Change in softening temperature after heating, °C	3.0	4.0	4.5	6.0
7	Change in mass after heating, %	0.30	0.23	0.45	0.61
8	Tensile strength, MPa	5.97	7.6	6.55	6.88
9	Plasticity range, °C	63	70.5	72	72.5
10	True viscosity at 50 °C, Pa·s	85	-	250	-
11	Number of alternating load cycles before destruction of the bitumen film	800	-	2500	-

Analysis of the obtained indicators of bitumen compositions modified with expanded Kulantau vermiculite and quality indicators to the technical conditions of ST RK 1373-2013 [28,29] shows that it is possible to obtain bitumen compositions with improved quality indicators, which in terms of physical and chemical characteristics fully satisfy ST RK 1373-2013.

4. Conclusions

From the analysis of relevant studies, it can be observed that natural vermiculite is quite common and can be considered a promising material. The potential of this material can be defined by its absorbent capacity and developed surface properties. The distinctive features of the layered structure of vermiculites account for their specific properties, thereby expanding the range of applications in technological processes.

The results, as well as their reliability and validation, were confirmed using modern research methods employed in the study of asphalt compositions' structures, particularly the Fourier-transform infrared (FTIR) spectroscopy method with a Shimadzu IR Prestige-21 instrument. Additionally, the research explored structural changes occurring during the production of asphalt compositions with expanded vermiculite. The spectrum of modified bitumen, featuring a characteristic absorption band of carbonyl groups that determines the concentration of free radicals, is one of the factors indicating the predisposition of asphaltenes to association and molecular interactions, thereby contributing to the formation of supramolecular structures.

The stable adhesion of the asphalt composition across a broad temperature range, along with an increased specific surface area that imparts additional energy capacity to enhance bonding with asphalt, is achieved through the utilization of Kulantau vermiculite. Therefore, the heightened strength of the asphalt composition is a characteristic feature throughout the studied temperature range when using expanded vermiculite, which further justifies its selection due to its relative cost-effectiveness and availability.

Thus, in order to obtain modified bitumen compositions with a given set of properties in each specific case, it is necessary to make the correct choice of bitumen raw materials and carry out a set of works to optimize the formulation of the composite material.

These studies were carried out with the support of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (grant AP19679034 "Development of technology for producing bitumen materials for the road industry with the disposal of polymer wastes in the technological process").

Author Contributions: Conceptualization, K.S., A.A. and Z.K.; methodology, K.S., A.A. and S.B.; investigation, K.S.; data curation, K.S. and A.A.; writing—original draft preparation K.S. and Z.K.; writing—review and editing, K.S. and A.A.; supervision, K.S., Z.K. and S.B.; project administration; K.S., Z.K. and A.A.; funding acquisition, K.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19679034).

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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