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# Modification of Bitumen with Mechanochemically Devulcanized Crumb Rubber

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## Abstract

This study investigates the modification of bitumen using mechanochemically devulcanized crumb rubber. The objective of this research is to enhance the performance characteristics of bituminous binders while addressing the inherent limitations associated with conventional crumb rubber (CCR), such as insufficient dispersion, elevated viscosity, and phase instability. Preliminary chemical activation of the crumb rubber was performed using a planetary ball mill, followed by thermomechanical devulcanization on a two-roll open mixing mill. Structural features of the devulcanized crumb rubber were analyzed using infrared spectroscopy, which confirmed the breakdown of S–S bonds. This study presents a comparative analysis of the performance characteristics of rubber–bitumen binders produced using both conventional rubber crumb (CRC) and devulcanized rubber crumb (DRC). The use of DCR, obtained mechanochemically from rubber waste, improved penetration, Fraass breaking point and the ring and ball softening point on average at high concentrations (20; 25% crumb rubber) compared to conventional crumb rubber by 33%, 66% and 2.4%, respectively. Optical microscopy revealed the formation of a uniform mesh-like rubber structure within the bitumen matrix, which contributes to enhanced performance characteristics of the modified binder and improved mechanical strength of the material. The key contribution of this work lies in the development and experimental validation of an efficient approach to deep devulcanization of crumb rubber via mechanochemical activation using readily available nitrogen-containing reagents. Furthermore, the study establishes a direct correlation between the degree of devulcanization, the dispersion quality of rubber particles within the bitumen matrix, and the resultant performance characteristics of the modified binder.

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**Keywords:** petroleum bitumen; modification; mechanochemically devulcanized crumb rubber; infrared spectroscopy; optical microscopy

## 1. Introduction

The use of rubber waste in the production of modified asphalt plays a critical role in conserving natural resources and protecting the environment [1,2]. However, the increasing number of vehicles demands roads with higher quality and advanced engineering design. Despite the advantages of modern technologies for producing modified binders, such materials can increase the total cost of asphalt concrete mixtures by up to 40% [3,4].

Rubber waste can serve as a partial replacement for traditional materials, enhancing the mechanical properties of road surfaces. Its active use as a bitumen modifier is aimed at improving performance characteristics and reducing road construction costs. Crumb rubber has long been utilized in the production of modified asphalt.

Numerous studies have shown that adding crumb rubber to petroleum asphalt improves its performance at both high and low temperatures, enhances aging resistance, and increases the service life of pavement compared to conventional asphalt mixtures. Rubber–bitumen mixtures help reduce noise, slow the formation of reflective cracks, improve binder–filler adhesion, and increase skid and wear resistance [5–7].

Research on the modification of bitumen with crumb rubber has explored the addition of crumb rubber enhances rutting and fatigue resistance [8–17]. However, rubber–bitumen binders are associated with several challenges, such as the need for higher production and installation temperatures, increased energy consumption, and continuous mixing to prevent phase separation [2,18,19].

To address these issues, various approaches have been investigated, including the addition of modifiers and the devulcanization of rubber [10,11,20–25]. Devulcanized crumb rubber is of particular interest due to its altered structure, which helps overcome problems such as high viscosity and phase separation [26–31].

Devulcanization enables the restoration of waste tire rubber to a state closer to the original raw material by breaking cross-linked sulfur bonds while preserving the polymer backbone [29–32]. Vulcanized rubber contains disulfide and polysulfide bonds, which can be converted to monosulfide bonds and broken under heat and shear stress. Several devulcanization methods exist, including thermal, mechanical, thermomechanical, chemical, mechanochemical, biological, microwave, ultrasonic, and hybrid methods such as thermochemical and thermosonic [31–33].

Thermal devulcanization involves the breakdown of S–S, C–S, and carbon–carbon double bonds, which requires a significant amount of energy. The process is often accompanied by the unintentional breaking of crosslinks between sulfur and the main polymer chain, reducing overall efficiency. Thermal processing is typically conducted in autoclaves at temperatures ranging from 180 to 260 °C and pressures up to 15 bar. While this method can be enhanced by integrating other technologies to improve performance, it remains energy-intensive and can lead to thermal degradation of the material [29–35].

Mechanical and thermomechanical devulcanization utilize shear stresses generated in equipment such as two-roll mills or twin-screw extruders, combined with heat. The combined action of mechanical and thermal forces leads to the breaking of chemical bonds. For instance, the use of a twin-screw extruder can enable the replacement of up to 65% of virgin natural rubber with recycled material. Selective destruction of crosslinks is achieved by controlling factors such as temperature, screw rotation speed, and the degree of localized heating [35–40].

Microwave devulcanization uses uniform volumetric heating, enabled by the ability of carbon black in the rubber to absorb microwave energy and convert it into heat. This method does not require the use of chemical additives but demands precise control of radiation time and power. While longer processing times can enhance devulcanization, they may also cause degradation of the polymer's main chain. The process allows for selective breaking of cross-links at relatively low temperatures, whereas higher temperatures contribute to the breakdown of the rubber's primary structure [41–48].

The mechanochemical method is widely applied, utilizing chemical adjuvants in combination with mechanical forces to accelerate devulcanization reactions [28,29,49].

The authors of [28] proposed a low-temperature desulfurization technology aimed at maximizing the desulfurization potential of crumb rubber for the production of modified asphalt. The resulting material exhibited enhanced low-temperature performance, improved storage stability, and reduced susceptibility to segregation. However, its resistance to rutting and deformation under high-temperature conditions was adversely affected.

Thermal devulcanization requires high energy input and may degrade the material, as it involves the random scission of sulfur bonds. In contrast, mechanochemical devulcanization—where mechanical forces are combined with chemical agents—offers advantages such as low cost, simple equipment, high efficiency, and low odor, making it suitable for large-scale production. In mechanochemical devulcanization, diphenyl disulfide is one of the most commonly used devulcanizing agents. However, it is not environmentally friendly and has been associated with rubber degradation due to its tendency to break not only sulfur crosslinks but also some of the main chains [50]. The incorporation of devulcanized rubber into asphalt binders continues to yield inconsistent results with respect to physical and mechanical performance, and this area remains the subject of ongoing investigation [51–54].

In this study, bitumen was modified using devulcanized rubber crumb obtained through mechanochemical activation with acetamide, glycine, and ammonium bicarbonate under planetary milling conditions. This approach significantly increased the rheological compatibility of the rubber with bitumen. Amino group-containing and weakly alkaline reagents were employed for the preliminary chemical activation of the rubber prior to thermomechanical devulcanization.

The aim of the study is to improve the performance of bitumen binders through modification of bitumen using mechanochemically devulcanized rubber crumb (DRC).

## 2. Materials and Methods

Unmodified bitumen grade 100/130 was used as the base material for modification. The characteristics of this petroleum bitumen are presented in Table 1.

In this study, fine crumb rubber (particle size < 0.5 mm) (EcoShina, Shymkent, Kazakhstan) obtained from end-of-life car tires by mechanical grinding was used. The devulcanized crumb rubber is produced by a mechanochemical method using a high-precision two-roll open mixing mill manufactured by Qingdao Ouli Machine CO., LTD. (Qingdao, China). Before mechano-chemical devulcanization acetamide, glycine and ammonium bicarbonate were mixed with crumb rubber in a vertical planetary ball mill MF-BM0.4A. at $23 \pm 2$ °C.

Process conditions for two-roll mill mechanochemical devulcanization: maintained at 110 °C to minimize carbon–carbon chain degradation; duration was 10 min to selectively cleave sulfur bonds without excessive polymer breakdown; shear/friction: minimal nip (~0 mm) with friction ratio of ~1.1–1.8 to ensure effective shear while limiting heat buildup.

**Table 1.** Characteristics of road bitumen grade 100/130.

| Bitumen Properties | Normative Indicators of the Road Bitumen | Actual Value | Test Method |
|---|---|---|---|
| Penetration at 25 °C, not lower | 101–130 | 113 | Kazakhstani standards 1226/EN 1426:2024 [55] |
| Softening point °C, not below | 43 | 44 | Kazakhstani standards 1227/EN 1427:2015 [56] |
| Ductility at 25 °C, not less than, cm | 90 | >150 | Kazakhstani standards 1374/EN 13589:2018 [57] |
| Dynamic viscosity at 135 °C, $mm^2/s$, not less | 180 | 352 | Kazakhstani standards 1210/EN 12596:2023 [58] |
| Flash point °C, not below | 230 | 282 | Kazakhstani standards 1804/EN ISO 2592:2017 [59] |
| Fraass breaking point, °C, not higher | −22 | −24 | Kazakhstani standards 1229/EN 12593:2015 [60] |
| Solubility %, not less | 99.0 | 99.9 | Kazakhstani standards 1228/EN 12592:2015 [61] |

Ammonium bicarbonate was chosen because it easily decomposes at modified bitumen processing temperatures foaming the materials and increasing its specific surface area. The crystalline structure of $NH_4HCO_3$ enhances friction during rubber shear processing. This allows to expand the contact surface area, contributing to a higher degree of devulcanization. This is attributed to the synergistic effect between tribological forces and reagent diffusion [62].

Glycine, in its turn, is known as rubber vulcanization additive to increase mechanical and anti-aging properties [63]. In addition, glycine can be used also in rubber devulcanization process as low-molecular reagent, capable easily penetrate in the rubber structure and due to its amine and carbonyl functionalities participate in free radical induced cross-link rearrangement process, including scission of S–S and C–S bonds [62].

To prepare samples modified bitumen, an installation was assembled—the scheme of the installation is shown in Figure 1.

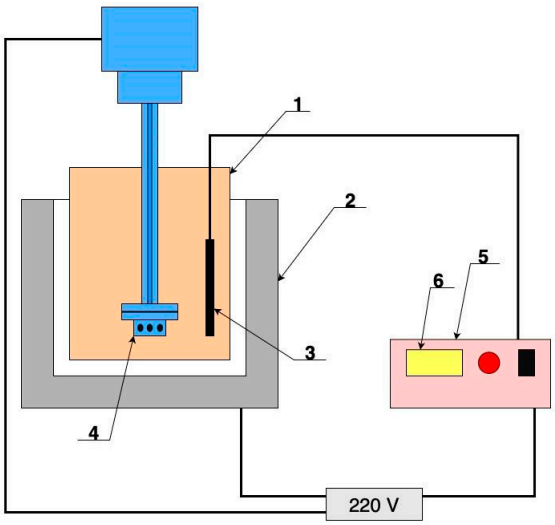



**Figure 1.** Scheme of the installation for the preparation of modified bitumen binders: 1–reactor; 2—electric furnace; 3—thermometer; 4—high-shear mixer; 5—high-shear mixer speed controller; 6—automatic temperature controller.

A high-shear mixer FLC-IV manufactured by Shanghai Farfly Energy Technology Co., Ltd., (Shanghai, China) was employed in the laboratory for bitumen modification.

Bitumen and crumb rubber were mixed in the following percentage ratios: 95:5; 90:10; 85:15; 80:20; 75:25.

The procedure included the following steps:

1. Heating the road bitumen in an oven to 140 °C.
2. Gradual addition of devulcanized crumb rubber to the bitumen, followed by mixing at 6000 rpm at 190 °C.
3. Continuous mixing of the components was carried out for 3 h for more complete interaction of bitumen with crumb rubber and obtaining a homogeneous mass. Continuous mixing for 3 h [21,29,64].

The structural properties of the devulcanized crumb rubber were analyzed using Fourier-transform infrared spectroscopy (FTIR). The IR spectra were obtained using a Vertex 70v FTIR spectrometer (Bruker, 76275 Ettlingen, Germany) at a resolution of 4 $cm^{-1}$. Spectra were recorded and processed within the wavenumber range of 4000–500 $cm^{-1}$ using a PIKE MIRacle single-bounce attenuated total reflection (ATR) accessory equipped with a germanium crystal. Data analysis was performed with OPUS software, version 7.2.139.1294.

The morphology of rubber–bitumen binders, prepared using conventional and devulcanized crumb rubber with various formulations, was studied using an optical microscope (Leica DM 6000 M, Leica Microsystems, Wetzlar, Germany).

The physical properties of the rubber–bitumen binders were evaluated using standard testing methods. The softening point was determined using the IKSh-MG-4 apparatus (Stroipribor, Chelyabinsk, Russia), with two parallel measurements performed in accordance with [56]. The penetration test was conducted using the PNB-05 device (LLC "Grant", Ufa, Russia), also with two parallel measurements according to [55]. The ductility of the binders was measured using the DMF-1480 apparatus (LLC "PTF InterStroyPribor-SPb", Saint Petersburg, Russia), following [57], with two parallel extensibility measurements. The Fraass breaking point was determined using the ATX-04 device (LLC "Grant", Ufa, Russia), based on [60], with two parallel measurements performed.

The errors and statistical deviations of the experiment were on average 5%.

## 3. Results

The structural features of devulcanized crumb rubber, studied using FTIR, are demonstrated in Figure 2.

The absorption bands observed at 2918 $cm^{-1}$, 1018 $cm^{-1}$, and within the range of 810 $cm^{-1}$ to 667 $cm^{-1}$ suggest that the crumb rubber contains unsaturated bis-olefins and benzene ring-conjugated olefins connected through sulfide bonds [65]. The absorption bands within the range 1450 $cm^{-1}$–1670 $cm^{-1}$ as well as 697–749 $cm^{-1}$ have been assigned to SBR, whereas the absorption bands at 2962 $cm^{-1}$ and 2840 $cm^{-1}$ have been assigned to natural rubber, both intensively used in manufacturing of tires [66].

More intense absorption bands at 3000–3500 $cm^{-1}$ of the devulcanized rubber denote to larger contribution of polar moieties, e.g., hydroxyl groups formation, because of cleavage of S–S bonds and increased number of chains ends capable to H-bonding. Integrated area under the peak of DCR is almost 3 times larger than in the case of CCR. The absorption bands at 2925 and 2852 $cm^{-1}$ are characteristic of methylene groups, which indicate the degree of branching in aliphatic paraffin chains and are typical for alkyl substituents of the R–$CH_3$ and R–$CH_2$ types [67]. The band at 1599 $cm^{-1}$ reflects the presence of oxygen-containing compounds, suggesting that oxidation occurs alongside devulcanization, resulting in the formation of carboxylic acids. The absorption band at 1443–1396 $cm^{-1}$ corresponds to aliphatic chains or saturated ring structures. The peak situated between 1000 $cm^{-1}$ and 1300 $cm^{-1}$

has been ascribed to C-$S_x$-C bridged groups of crosslinked rubber, with x indicating different sulfur linkage lengths [66]. The reduced intensity of the absorption bands of devulcanized rubber in the 1098–1020 $cm^{-1}$ range indicates the breakdown of S=O bonds, represented by $RSO_3H$ and $RSO_3$ groups, which signifies the cleavage of S–S bonds. A distinct signal around 600 $cm^{-1}$ confirms the rupture of S–S bonds [66]. Additionally, the weakening of the band at 640 $cm^{-1}$ may indicate to polycondensation reactions and partial degradation of aliphatic chains under thermal influence [7].

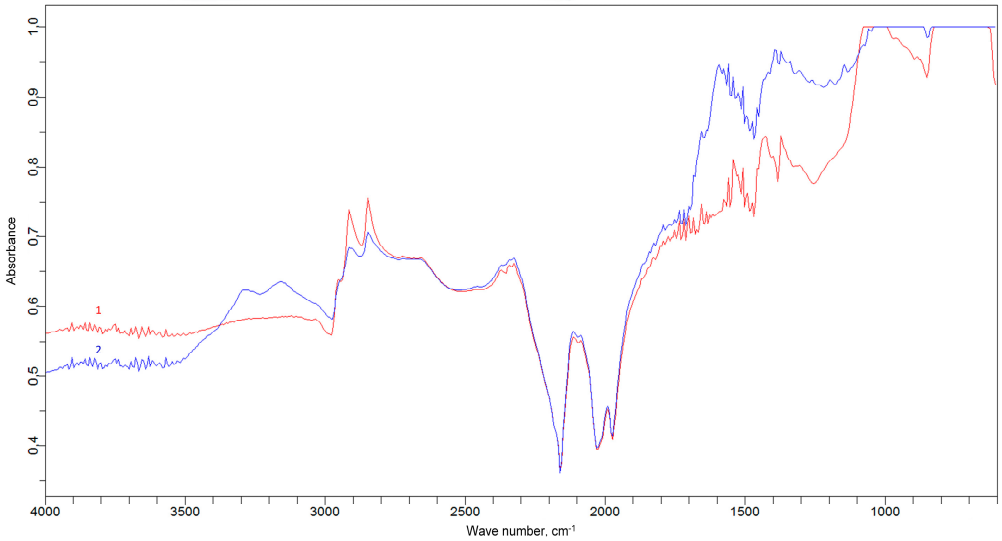



**Figure 2.** The IR spectrum of the crumb rubber before (red curve 1) and after (blue curve 2) the devulcanization process.

The modification of 100/130 grade road bitumen with both conventional and devulcanized crumb rubber was analyzed. As shown in Figure 3, increasing the proportion of crumb rubber—either conventional or devulcanized—leads to a higher softening point, indicating increased material hardness. During the interaction between rubber crumb and bitumen, the rubber particles selectively absorb the aromatic fraction of the bitumen, resulting in an increased relative concentration of resins and asphaltenes in the binder matrix. This compositional shift enhances the high-temperature performance characteristics of the rubber-modified bitumen [67]. This suggests progressive densification of the bitumen matrix due to the formation of strong network structures. These structures are more robust in the presence of devulcanized rubber due to its greater reactivity, which results in a more homogeneous blend and increased softening temperature.

Figure 4 presents the penetration values of modified bitumen as a function of rubber content. As rubber is added, penetration decreases due to increased system viscosity and stiffness. The use of devulcanized rubber results in reduced penetration, remaining consistently higher than in samples with conventional rubber. This behavior is likely due to faster swelling and better interaction of the desulfurized rubber with the bitumen matrix. The difference in penetration values between conventional and devulcanized crumb rubber is attributed to variations in dispersibility, interaction with bitumen, and their respective effects on mixture viscosity. Devulcanized crumb rubber, particularly at low concentrations, tends to increase the viscosity of the asphalt mixture to a lesser extent. Acting partially as a plasticizer, it contributes to relatively higher penetration values compared to conventional crumb rubber.

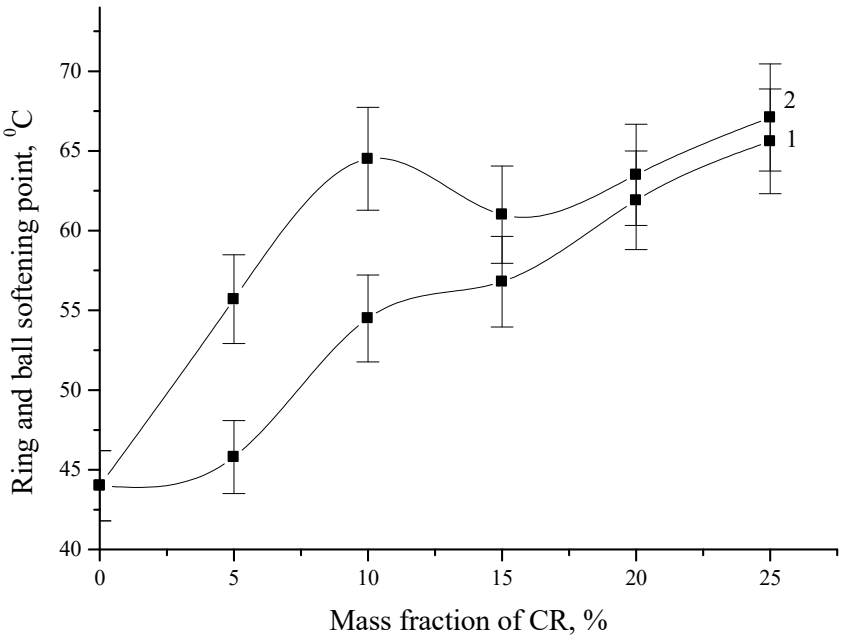



**Figure 3.** Dependence of the softening temperature of rubber–bitumen binders on the amount of added crumb rubber: 1—with conventional crumb rubber; 2—with devulcanized crumb rubber.

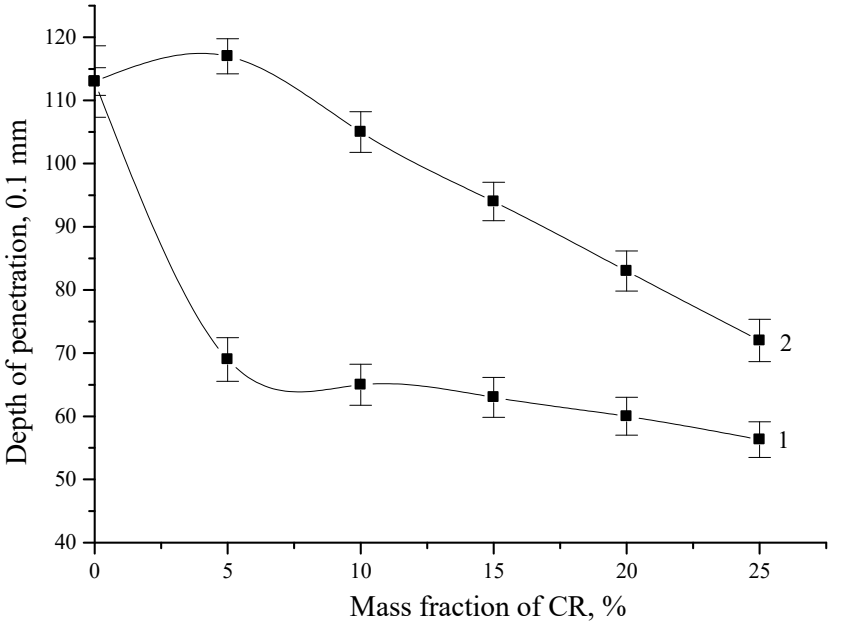



**Figure 4.** Dependence of penetration of rubber–bitumen binders on the amount of added crumb rubber: 1—with conventional crumb rubber; 2—with devulcanized crumb rubber.

As shown in Figure 5, the extensibility of rubber–bitumen binders decreases steadily with increasing crumb rubber content, reaching a minimum at 25 wt%. This is attributed to the influence of resins and polyaromatic compounds within the swollen rubber particles. In samples with devulcanized rubber, the extensibility decreases more sharply, likely due to better dispersion and a more uniform composition. Devulcanized rubber may also act as a filler, lowering the surface energy of the bitumen and further reducing extensibility [68].

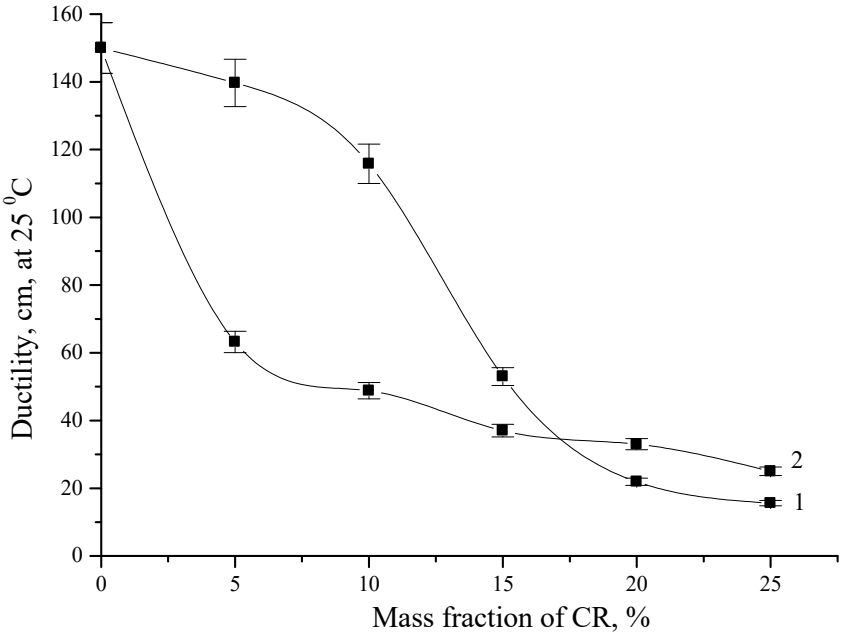



**Figure 5.** Dependence of the ductility of rubber–bitumen binders on the amount of added crumb rubber: 1—with conventional crumb rubber; 2—with devulcanized crumb rubber.

Figure 6 illustrates the effect of rubber content on the Fraass breaking point of the modified bitumen.

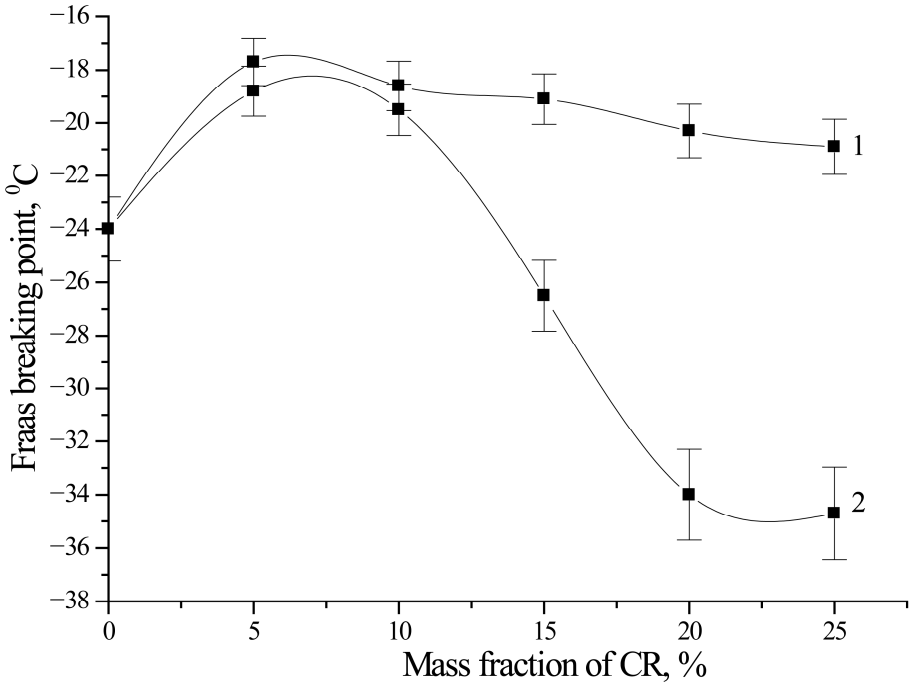



**Figure 6.** Dependence of the Fraass breaking point of rubber–bitumen binders on the amount of added rubber crumb rubber: 1—with conventional crumb rubber; 2—with devulcanized crumb rubber.

The graph demonstrates that modification of bitumen with devulcanized crumb rubber results in a non-linear change in Fraass breaking point: the value initially increases, then decreases. This behavior can be attributed to two competing mechanisms. At low dosages, Fraass breaking point rises due to inadequate elasticity introduced by the additive. As the dosage increases, low-temperature crack resistance increases as a more elastic structure develops. Devulcanized crumb rubber contains finely dispersed fractions with residual

plasticity, which begins to offset the inherent brittleness of bitumen only after a threshold concentration is reached [69].

In contrast, when conventional crumb rubber is used, Fraass breaking point also initially increases, followed by a slight decrease; however, it remains consistently higher than that observed with devulcanized crumb. This is primarily due to the limited interaction between conventional rubber crumb and bitumen, which fails to enhance flexibility. As a result, the modified binder remains more brittle at low temperatures. The minor reduction in Fraass breaking point at higher dosages is attributed to improve physical dispersion rather than any substantive enhancement in low-temperature crack resistance. Within error bars the relationship between 1 and 2 curves could be as follows, i.e., devulcanized rubber is effective in decreasing Fraass, while conventional is practically not effective.

Among the tested samples:

- Binders with 15–25 wt% conventional crumb rubber (CCR) meet the RBB 50/70 specifications: softening point (ring and ball) $\geq$ 56 °C, penetration at 25 °C of 50–70, extensibility $\geq$ 10 cm, and brittleness temperature $\leq -15$ °C.
- Binders with 5–25 wt% devulcanized crumb rubber (DCR) meet the Kazakhstani RBB 70/100 standard: softening point $\geq$ 52 °C, penetration at 25 °C of 71–100, extensibility $\geq$ 12 cm, and brittleness temperature $\leq -18$ °C.

Morphology study of the rubber–bitumen binder samples by optical microscope demonstrate, that rubber crumb partially dissolves in bitumen forming network like rubbery structures at higher dosages (Figure 6).

Such morphology testifies that polymer-bitumen binders behave as composite materials, where the bitumen serves as the matrix and the rubber acts as the dispersed reinforcing phase—enhancing performance beyond that of the individual components [2,70].

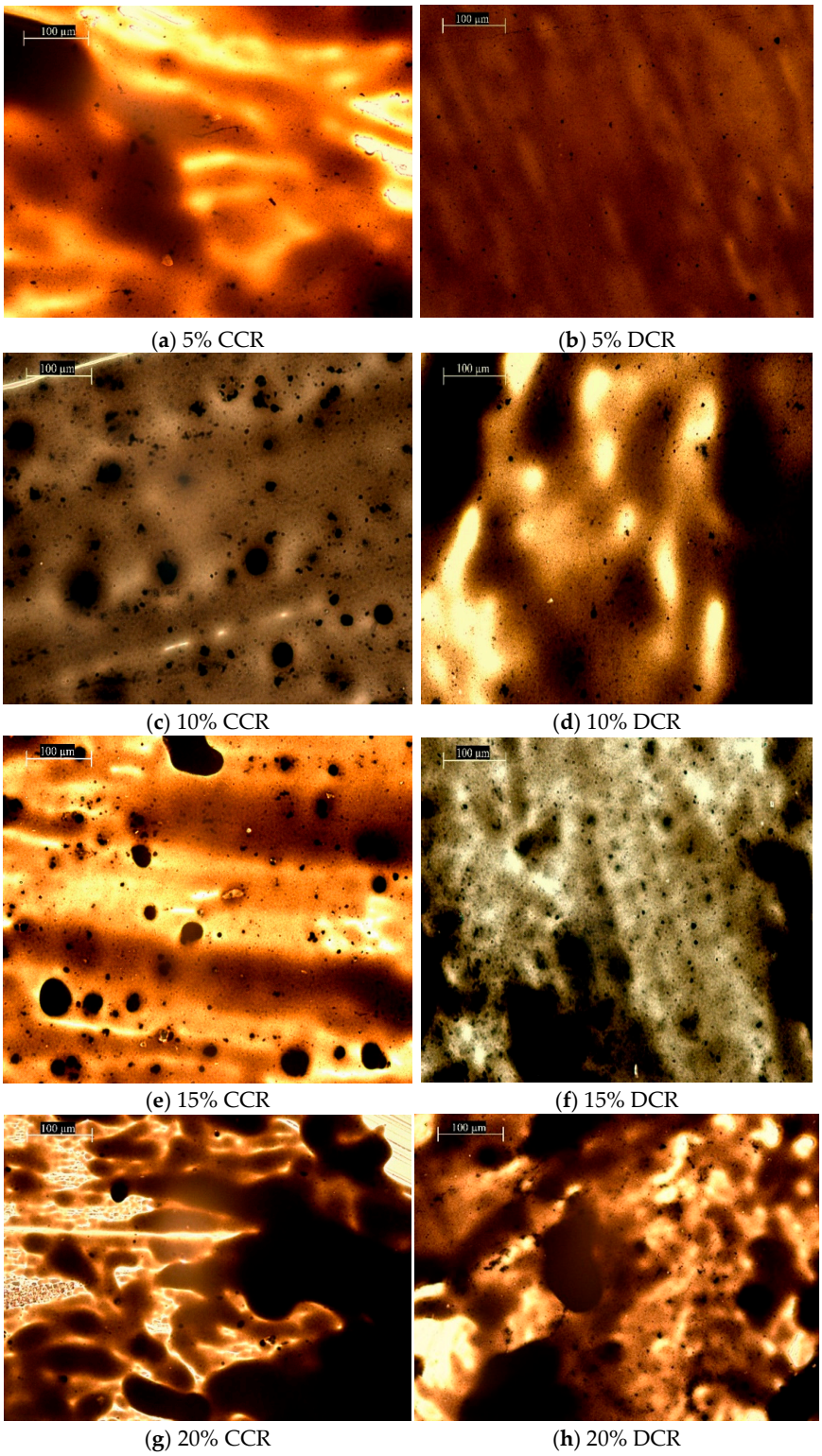
As demonstrated in Figure 7, in general DCR modified bitumen demonstrate smoother morphology with blurry contoured bitumen particles, which may testify on better swelling and dissolving of rubbery particles within bitumen matrix. The improved morphology of DCR modified bitumen is likely due to the increased reactivity of the devulcanized material, which facilitates interaction with the maltene fraction of bitumen. In contrast, conventional rubber crumb exhibits limited chemical compatibility and poor interaction with bituminous components. The maltene fraction, rich in aromatic compounds, promotes swelling, dispersion, and partial dissolution of devulcanized crumb rubber, enhancing its integration into the binder matrix.

In study [29], Fourier-transform infrared spectroscopy (FTIR) analysis of bitumen modified with desulfurized rubber powder revealed that no new chemical bonds were formed, indicating that the modification process is predominantly physical in nature.

- At 5% rubber content (Figure 7a,b), particle fusion with bitumen occur. DCR modified bitumen composition demonstrates much better dispersion of rubber particles within bitumen matrix.
- At 10% (Figure 7c,d), fibrous structure form. The addition of 10% devulcanized crumb rubber resulted in significantly improved dispersion within the bitumen matrix (Figure 7d) compared to the same concentration of conventional crumb rubber (Figure 7c). Moreover, the incorporation of devulcanized rubber at this concentration led to the formation of fibrous structure, which is associated with enhanced mechanical strength and elasticity (Figure 7d).
- At 15% dosage (Figure 7e), the morphology of the CCR modified binder shows poorer dispersion with the formation of large agglomerates [71]. At 15% dosage (Figure 7f), dispersion of DCR particles in the bitumen matrix occurs and the formation of network structures [72] begins, which are observed in Figure 7h. This observation explains why the previously measured performance of DCR modified bitumen is superior to that

of CCR modified bitumen. Moreover, the formation of a network structure seems to start at lower dosages in DCR modified systems, indicating a more efficient interaction and compatibility with the bitumen matrix. This supports previous findings that mechanochemical treatment enhances surface roughness and reactivity [29].

- Increasing the concentration of devulcanized rubber crumb to 20% resulted in further improvement of dispersion in the bitumen matrix (Figure 7h) and development of a network structure.




(**a**) 5% CCR (**b**) 5% DCR

(**c**) 10% CCR (**d**) 10% DCR

(**e**) 15% CCR (**f**) 15% DCR

(**g**) 20% CCR (**h**) 20% DCR

**Figure 7.** Morphology of modified bitumen binder with conventional and devulcanized crumb rubber.

## 4. Conclusions

Based on the results of the conducted research, the following conclusions were drawn:

1. Devulcanized rubber crumb readily interacts with bitumen, partially dissolving into its components and promoting closer physical compatibility. This leads to the formation of a more homogeneous modified system. Consequently, the microstructure of the modified binder differs fundamentally from that of unmodified bitumen, as elastic network structures are formed throughout the binder matrix.
2. Devulcanized rubber derived from waste materials enhances the binder performance, notably improving penetration values, brittleness temperature, and the ring-and-ball softening point compared to the conventional crumb rubber.
3. The mechanochemical method offers more selective cleavage of sulfur (sulfide) bonds compared to thermal or microwave alternatives, causing minimal damage to the main polymer chain. This selectivity, achieved through the synergy of mechanical grinding and mild chemical action, helps preserve the rubber's elasticity and structural integrity. Using environmentally friendly reagents such as glycine, the process is safe, scalable, and energy-efficient, with no need for complex by-product disposal.
4. Devulcanized rubber, as a result of the cleavage of sulfur (sulfide) crosslinks, is more effectively dispersed within the bitumen matrix, forming a homogeneous, mesh-like structure. This microstructure facilitates uniform stress distribution and enhances the compatibility between the rubber and bitumen phases, thereby improving the elasticity and thermal stability of the binder. Consequently, the modified bitumen exhibits increased resistance to high-temperature deformation while maintaining flexibility at low temperatures—attributes that significantly enhance the mechanical performance of asphalt concrete pavements.

Future work will include a comprehensive investigation of the rheological behavior of the modified binders and an in-depth analysis of their aging characteristics to evaluate long-term durability and functional reliability under varying climatic conditions.

**Author Contributions:** Conceptualization, A.A., A.B., U.Y. and V.H.; formal analysis, R.M.M., Y.I. and Y.A.; methodology, A.A., U.Y., S.S. and V.H.; software, Y.I. and A.M.; validation, A.A., U.Y., V.H. and A.B.; investigation, A.B., U.Y., Y.A., Y.I. and S.S.; resources, S.S. and U.Y.; data curation, A.B. and R.M.M.; writing—original draft preparation, A.A., A.B. and U.Y.; writing—review and editing, A.A., A.B., V.H. and R.M.M.; visualization, R.M.M., Y.I. and A.M.; supervision, A.A.; project administration, A.A.; funding acquisition, A.A. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

**Conflicts of Interest:** Author Serik Sydykov is affiliated with LLP "JV" CASPI BITUM Aktau Bitumen Plant. Author Yerbolat Ayapbergenov is affiliated with Branch of LLP "KMG Engineering" "KazNIPImunaigas". The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The LLP "JV" CASPI BITUM Aktau Bitumen Plant and Branch of LLP "KMG Engineering" "KazNIPImunaigas" companies in affiliation had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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