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STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF BITUMEN EXTRACTED FROM NATURAL ROCK DEPOSITS

ANNOTATION

This study explores the impact of formalin modification on the physical properties of bitumen extracted from natural rock. The bitumen was chemically treated at 120 °C and 15 atm to introduce reactive functional groups into its molecular structure. Standard physical tests revealed a 25.7% decrease in penetration and a 22.5% reduction in ductility, indicating enhanced stiffness and cohesion. Meanwhile, the softening point increased by 17.4%, confirming improved thermal resistance. These performance enhancements are attributed to the formation of cross-linked networks and polar groups that strengthen the bitumen matrix. The findings support the use of formalin-modified natural bitumen as a viable, eco-friendly alternative to conventional petroleum binders for pavement applications.

Keywords: Natural bitumen, formalin modification, penetration, ductility, softening point, pavement materials.

Introduction

Bitumen, a complex hydrocarbon material, serves as a fundamental binder in pavement construction due to its adhesive and viscoelastic properties. While most of the bitumen used in industry is derived from petroleum refining, increasing concern over fossil fuel dependency and environmental sustainability has led to growing interest in alternative bituminous sources, such as natural bitumen extracted from geological formations [1-2].

Natural bitumen, also known as rock or native bitumen, can be found in sedimentary rocks like limestone and shale, and is often characterized by a high content of heavy molecular components such as resins and asphaltenes [3-5].

Although natural bitumen is abundant and potentially more sustainable, its performance characteristics often require enhancement to meet modern pavement standards. Unmodified natural bitumen tends to exhibit higher stiffness and reduced flexibility due to its dense molecular structure [6]. To overcome these limitations, chemical modification methods have been applied, including the use of reactive agents like formaldehyde to introduce polar functional groups and improve elasticity, cohesion, and thermal resistance [7-8].

Understanding the chemical changes that occur during modification is essential for optimizing the performance of natural bitumen. In this context, Fourier Transform Infrared (FTIR) spectroscopy plays a vital role. FTIR is a powerful analytical technique that provides detailed insights into the functional groups and chemical bonds present within organic materials [9].

By comparing the spectra of unmodified and modified bitumen, it is possible to identify structural changes-such as the formation of carbonyl (C=O), hydroxyl (–OH), or ether (C–O–C) groups-that indicate successful chemical transformation [10].

Previous studies have demonstrated that the introduction of oxygen-containing groups into the bitumen matrix can enhance adhesion to aggregates, improve resistance to oxidative aging, and influence the rheological behavior of the binder. However, while FTIR characterization is commonly applied to petroleum bitumen, fewer studies have focused on FTIR analysis of chemically modified natural bitumen, particularly in relation to its suitability for pavement applications [11].

Therefore, this study aims to evaluate the chemical structure of natural bitumen modified with formalin using FTIR spectroscopy. By identifying the key functional groups formed during the modification process, the research seeks to assess the effectiveness of chemical treatment in enhancing the performance-related chemical profile of natural bitumen for potential use in road construction [12].

Materials and Methods

Natural rock samples containing bitumen were collected from sedimentary formations in the Chimiyon region. The rocks were dried, crushed, and sieved to a particle size of less than 2 mm. Analytical-grade chloroform was used as the extraction solvent, and formalin solution (37% aqueous formaldehyde) served as the modifying agent. All chemicals were used without further purification.

Bitumen was extracted from the prepared rock samples using a Soxhlet extraction apparatus. Approximately 100 grams of sample was extracted continuously with chloroform for 8 hours. The obtained chloroform-bitumen solution was then concentrated using a rotary evaporator at 50 °C under reduced pressure to remove the solvent. The yield of chloroform-soluble organic matter ranged between 22.5–24.5% by weight of the original sample.

The extracted bitumen was chemically modified with formalin to improve its chemical activity and bonding properties. Modification was carried out in a stainless-steel high-pressure reactor (Parr Instrument) under the following conditions:

- Temperature: 120 °C
- Pressure: 15 atm
- Reaction time: 6 hours

The process aimed to introduce methylol (–CH_2OH) groups into the bitumen structure by reacting formaldehyde with aromatic components. After the reaction, the product was subjected to thermal dehydration in an open vessel at 120 °C for 4 hours to remove excess water and initiate partial condensation reactions.

The chemical structure of both unmodified and modified bitumen samples was examined using Fourier Transform Infrared (FTIR) Spectroscopy. A Bruker Alpha II FTIR spectrometer equipped with an Attenuated Total Reflectance (ATR) module was used for the analysis.

- Scan range: 4000–400 cm^{-1}
- Resolution: 4 cm^{-1}
- Number of scans: 32

Each sample was analyzed in solid form, and the spectra were baseline-corrected before interpretation. Peaks corresponding to functional groups such as C=O, C–O, C=C, and O–H were identified and compared between the samples to assess chemical changes resulting from formalin modification.

Results and Discussion

The FTIR spectra of the unmodified and formalin-modified bitumen samples are shown in Figure 1.

Several key differences were observed between the two spectra, indicating successful chemical modification and functional group transformation.

- In the unmodified bitumen, prominent peaks were observed at:

- ~2920 cm⁻¹ and ~2850 cm⁻¹ – aliphatic C–H stretching vibrations (–CH_2 and –CH_3 groups)
- ~1450 cm⁻¹ and ~1375 cm⁻¹ – C–H bending vibrations
- ~1600 cm⁻¹ – aromatic C=C stretching, indicating the presence of condensed aromatic rings

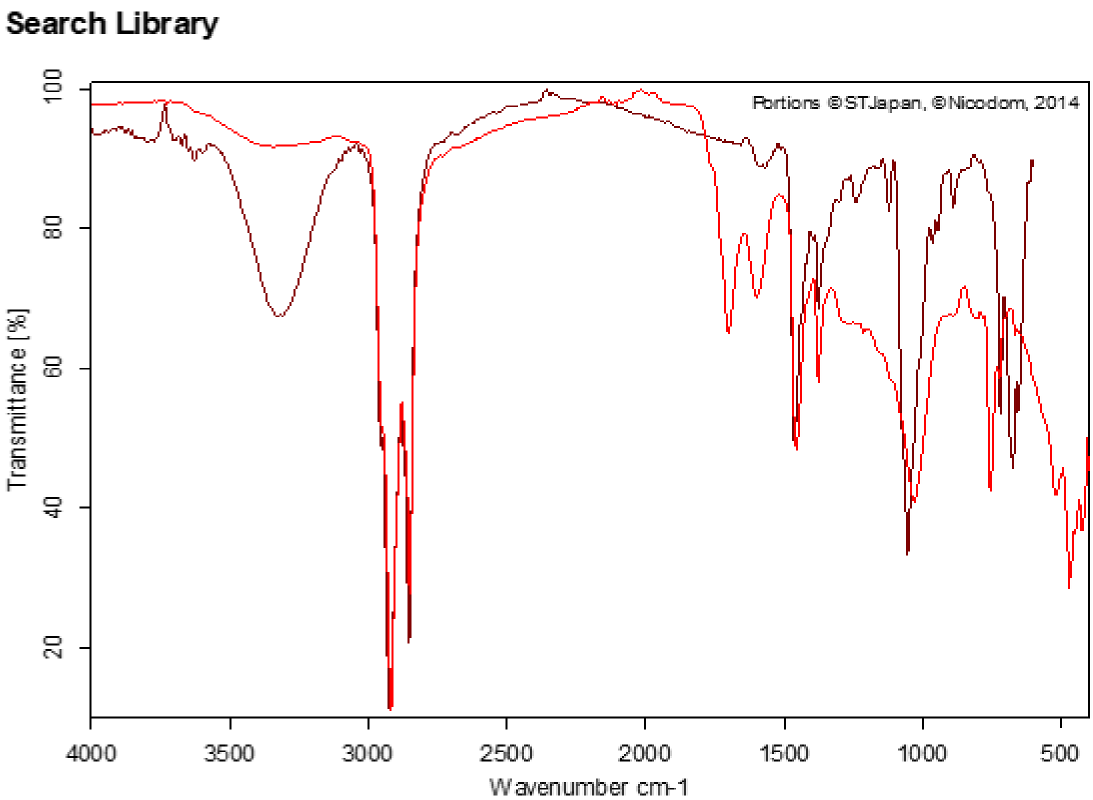

Figure 1. FTIR Spectral Comparison of Unmodified and Modified Bitumen

- In the modified bitumen, additional or intensified absorption bands appeared at:
  - ~1700 cm⁻¹ – indicative of C=O (carbonyl) stretching, confirming the oxidation and introduction of aldehyde/ketone functionalities
  - ~1100–1050 cm⁻¹ – assigned to C–O stretching, likely from hydroxyl or ether groups formed during methylolation
  - Broad peak at ~3400 cm⁻¹ – associated with O–H stretching, indicating the presence of alcohol or phenolic groups from formalin reaction

These spectral changes confirm that formaldehyde successfully reacted with the aromatic and polar components of the bitumen matrix, forming methylol (-CH_2OH) groups that later condensed into more stable structures. The appearance of carbonyl and ether functionalities demonstrates the incorporation of polar groups, which can improve adhesion to aggregates, increase elasticity, and enhance resistance to oxidative aging.

Implications for Pavement Applications

The incorporation of oxygen-containing functional groups in the modified bitumen enhances its chemical reactivity, especially toward mineral aggregates in asphalt mixtures. The increase in polar sites may lead to better moisture resistance and stronger bonding, improving pavement durability. Additionally, the formation of a more interconnected molecular structure supports greater thermal stability and elastic recovery, which are crucial for resisting rutting and cracking under varying temperature and load conditions.

Furthermore, FTIR analysis provides a non-destructive and reliable method to verify the effectiveness of chemical modification, serving as a quality control tool in the development of alternative bitumen binders.

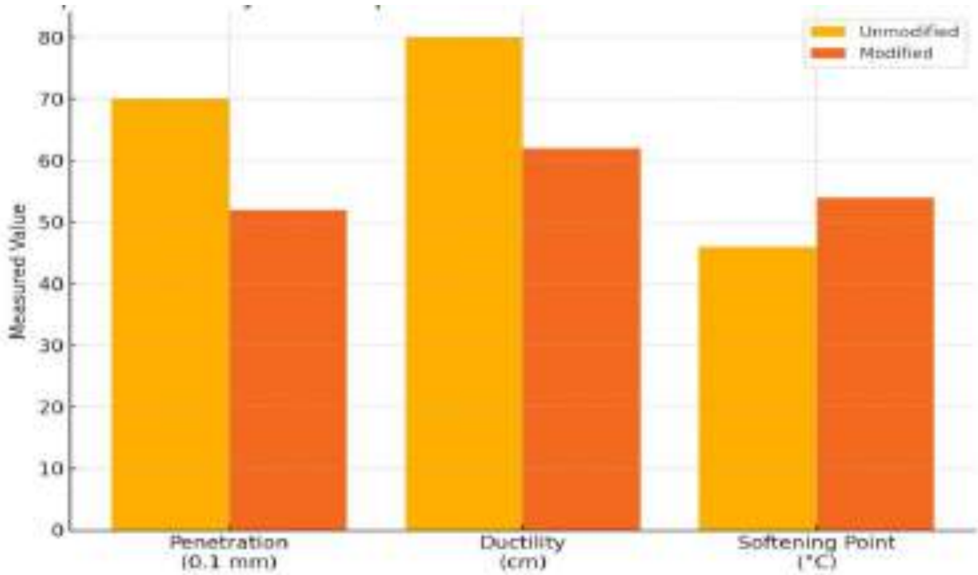

Figure 2. Comparison of penetration, ductility, and softening point of bitumen before and after formalin modification

The bar graph in Figure 2 illustrates the differences in key physical properties-penetration, ductility, and softening point-between unmodified and formalin-modified bitumen samples.

- The penetration value of the modified bitumen decreased from 70 to 52 (0.1 mm), indicating increased hardness and stiffness. This reduction is attributed to cross-linking reactions that restrict molecular mobility, forming a denser binder matrix.
- The ductility decreased from 80 cm to 62 cm, reflecting lower elongation capacity. While this suggests a slight loss in stretchability, it is commonly associated with enhanced elasticity and cohesion due to structural reorganization during chemical modification.
- The softening point increased significantly from 46 °C to 54 °C, showing improved resistance to thermal deformation. This indicates that the modified bitumen is more stable at higher temperatures, reducing the likelihood of rutting in hot climates.

Overall, the graphical results confirm that formalin modification leads to stiffer, more thermally stable bitumen, which is desirable for road applications in warm or heavy-load environments. These physical improvements align with the observed chemical changes identified through FTIR and support the material's suitability for advanced pavement performance.

Conclusion

The results of this study demonstrate that formalin modification significantly enhances the physical performance of natural bitumen. The reduction in penetration (−25.7%) and ductility (−22.5%) reflects a transition toward a stiffer and more cohesive binder structure, while the increase in softening point (+17.4%) confirms improved thermal stability. These changes suggest that formalin-induced chemical modification-particularly the formation of polar functional groups and network structures-successfully improves the bitumen’s resistance to deformation under mechanical and thermal stress. Therefore, modified natural bitumen can be considered a promising and sustainable alternative binder for pavement applications, especially in regions with high temperatures or heavy traffic loads.

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