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Araştırma Makalesi / Research Article

Investigation of the Effect of Lignin on Aged Bitumen

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Abstract

Globally, sustainability is an important issue. Bitumen is obtained from crude oil, is solid at ambient temperature, almost completely soluble in toluene, is in a non-volatile, sticky form, and is defined as a waterproofing material. In terms of low carbon dioxide emissions, the asphalt industry is looking for more sustainable options. Lignin is one of the most common natural polymers on earth. Its role is to hold the chemical components, which is the wall material, together in the matrix structure in plant cells and to provide resistance. Millions of tons of lignin are released after pulp production which is considered waste material. Depolymerized fractions cause significant environmental problems due to toxic chemical structures. In this study, short-term aged bitumen was modified by lignin at the rates of 15% and 20% to bitumen weight, and conventional Penetration Test, Ductility Test, and Scanning Electron Microscope (SEM) analysis were carried out to determine the rheological effect. In addition, it was aimed at determining the effective rate of lignin usage. In conclusion, the current research aimed to demonstrate that lignin, as a value-added modifier, is a promising solution with both environmental and engineering values. Also, as the lignin rate increased, the hardening rate of short-term aged bitumen increased in both penetration and ductility tests. Furthermore, SEM data revealed that particles with irregular surfaces are homogeneously distributed in aged bitumen. However, with the increase in usage rate, the distribution of lignin particles in bitumen became irregular.

Keywords: Sustainability, Lignin modified bitumen, Bitumen microstructure.

Ligninin Yaşlandırılmış Bitüm Üzerindeki Etkisinin İncelenmesi

Öz

Sürdürülebilirlik dünya genelinde önemsenen bir konudur. Bitüm, ham petrolden elde edilerek, ortam sıcaklığında katı olan, tolüen içerisinde tamamına yakını çözünen, uçucu olmayan, yapışkan formda olup, su yalıtım malzemesi olarak tanımlanır. Asfalt piyasası düşük karbondioksit emisyonu açısından sürdürülebilirliği daha yüksek alternatifler aramaktadır. Bitümün kısmen yerini alabilen alternatif sürdürülebilir bağlayıcıların kullanımı karbondioksit emisyonlarının azaltılmasına katkıda bulunur. Lignin, yeryüzünde en fazla bulunan doğal polimerlerden birisidir. Rolü, bitki hücrelerinde, çeper maddesi olan kimyasal bileşenleri matris yapı içinde bir arada tutmak ve direnç sağlamaktır Kâğıt hamuru üretimi sonrası milyonlarca ton lignin açığa çıkmakta, bunlar atık olarak görülmektedir. Depolimerize olan fraksiyonlar, yapılarındaki toksik kimyasal yapılardan dolayı önemli çevre sorunlarına sebep olmaktadır. Çalışma kapsamında laboratuvar ortamında kısa dönem yaşlandırılmış bitüm, ağırlığınca %15 ve %20 oranlarında lignin eklenmesiyle modifiye edilmiş, reolojik etkisinin belirlenmesi için geleneksel Penetrasyon ve Süneklik Deneyleri yapılarak ve Taramalı Elektron Mikroskobu (SEM) görüntüleri analiz edilmiştir. Bununla beraber lignin kullanımının etkin oranının belirlenmesi hedeflenmiştir. Elde edilen bulgular, lignin kullanımının artmasıyla, gerek penetrasyon gerekse de süneklik testlerinde, bitümde sertleşme oranını arttırdığını göstermiştir. Ayrıca, SEM verilerine dayanarak, lignin parçacıklarının yüzeyi düzensiz moleküller olduğu ve bitüm içerisinde homojen dağıldığı gözlenmiştir. Fakat, kullanım oranının artması ile lignin parçacıkları bitüm içerisindeki dağılımı düzensizleşmiştir.

Anahtar Kelimeler: Sürdürülebilirlik, Lignin modifiyeli bitüm, Bitüm mikroyapısı.

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1. Introduction

Lignin is a complex organic polymer found in the cell walls of many plants, providing structural support and rigidity (Sun et al., 2017). It is the second most abundant organic substance on Earth after cellulose. While cellulose consists of long-chain glucose molecules, lignin consists of phenolic compounds and is highly resistant to degradation. Chemically, lignin is a complex molecule composed mainly of phenolic compounds such as coniferyl, sinapyl, and p-coumaryl alcohols. Its exact composition may vary between plant species.

Lignification is the process by which lignin is deposited in the cell walls of certain specialized cells, such as xylem cells in vascular plants. It is formed through the polymerization of phenolic compounds.

Lignin is a binding substance in cell walls, providing strength and rigidity to plant structures and allowing them to stand upright. It also acts as a barrier against pathogens and helps move water throughout the plant (Mastrolitti et al., 2021). Due to its complex structure, lignin is highly resistant to degradation, making it difficult for many organisms to break down. However, some fungi, bacteria, and special enzymes produced by some organisms have evolved to break down lignin, which is necessary for the breakdown of plant material in nature.

Lignin has various industrial applications. It is a byproduct of papermaking and is often used as a fuel in biomass energy production (Watkins et al., 2015). Additionally, research is ongoing to find ways to extract lignin and use it as a component in various products, such as adhesives, carbon fibers, and even some bioplastics. Understanding degradation is crucial for processes such as the carbon cycle in ecosystems. As plants decompose, the breakdown of lignin causes carbon to be released back into the environment. Finding effective ways to break down lignin, particularly for biofuel production or other industrial purposes, remains an active area of research. Scientists are investigating various methods, including biological, chemical, and thermal approaches, to unlock lignin's potential for sustainable use (European Commission, 2015).

The potential use of lignin in bitumen-based materials represents an area of interest in sustainable infrastructure development combining renewable and bio-based resources, researchers aim to improve the performance of construction materials while reducing environmental impact (Razza et al., 2020).

The most used type of transportation in the world is the road. Bitumen is used as the superstructure material of highway formation. It is a mixture of mineral, coarse and fine aggregate, and adhesive bituminous binder. Bitumen chemical is used in asphalting and insulation materials to prevent water penetration. It exists as a solid at room temperature. It has a dark-colored mixture. It is mainly used as a binder to ensure that the aggregates in the asphalt mixture hold each other better. It consists of aggregate within the coating layers of flexible superstructures and bitumen-containing materials used as binders to each other. When looking at the total weight of the mixture in bituminous hot mixtures, the aggregate weight is around 93-95% by weight, while the remaining 5-7% consists of bitumen. It is the heavy oil component that remains after volatile and light fuels are refined from crude oil (Rasman et al., 2018).

Lignin has been investigated as a potential additive or modifier in bitumen-based materials such as asphalt used in road construction. Bitumen, a sticky, black, highly viscous liquid or semi-solid petroleum, is an essential ingredient in asphalt for road surfaces, roofing, and waterproofing (Abraham and Herbert, 1938).

The use of lignin together with bitumen is evaluated as a bio-based additive that improves the performance of bitumen, due to its natural adhesive properties and ability to bind materials together has been examined. It also has the potential to improve the properties of asphalt mixtures. Adding to bitumen, can potentially increase the stability, durability, and resistance to aging of asphalt pavements. It can also contribute to better rutting, cracking, and fatigue resistance.

Using lignin as an additive in bitumen can provide environmental benefits by reducing dependence on petroleum-derived additives and incorporating renewable, bio-based materials into infrastructure construction (Patel, 2022). However, incorporating lignin into bitumen mixtures comes with challenges. Ensuring optimum compatibility between lignin and bitumen to ensure homogeneous mixing, preservation of desired properties, and scalability for large-scale applications are areas of ongoing research.

Oil resources have now shown a trend towards scarcity. Biomaterials have become one of the main areas of interest due to their renewable, low energy consumption, and environmental friendliness. Bio-bitumen is a cementitious material obtained by adding a certain bio-oil fraction to a conventional petroleum pitch. Biomass, the fourth largest energy source, is abundant and the most important feedstock for bio-oil production (Wang et al., 2020). Lignin is currently considered the primary aromatic renewable resource and is mainly found in the waste solution produced in the papermaking process (Gonçalves and Benar, 2001). The annual waste solution amount of the Chinese paper industry is approximately 4 billion tons, accounting for more than 15% of the total industrial wastewater (Wang et al., 2020). As a result of recent studies, lignin, which is a hydrocarbon, is partially substituted with bitumen, creating a change in the performance of bitumen.

It comprises benzene rings with randomly attached methoxyl and hydroxyl, carbonyl, and aliphatic double bonds. Lignin, which is chemically aromatic, contains a highly unsaturated aromatic ring (Brauns and Brauns, 1960). It has been found that modified bitumen obtained by adding lignin has a high viscosity. The increase in viscosity is directly related to the lignin content (Sundstrom et al., 1983). Dynamic shear rheometer (DSR) experiments based on Superpave specifications indicate that the high-temperature resistance observed in lignin-modified bitumen mixtures increases. This directly affects the rutting performance at high temperatures positively (McCready and Williams, 2008). In general, lignin addition has been shown to develop the range of bitumen's performance grades. Based on literature studies, the effect of lignin modification on fatigue cracking occurring in bituminous hot mixtures has not been adequately examined. The coating becomes brittle due to volatile substances evaporating from the surface due to environmental factors, causing cracks in areas close to the surface. Due to lignin's polyphenolic structure and free radical activity, lignin shows high anti-oxidation potential (Queen and Tollefsbol, 2010). There are very few studies on the use of lignin in antioxidant form in bituminous binders. (Robertson et al., 2006). Eight types of asphalt binders and two types of lignin commonly used in Kansas were selected and mixed at various concentrations. As a result of investigating the effect of lignin addition on the aging performance of bituminous mixtures, it was observed that the performance varies according to the binder type, depending on the aging index. Accordingly, the performance change that may occur in the case of aging should be examined by considering the chemical change of bitumen (Liu et al., 2017).

Bio-bitumen refers to bitumen that has been modified, partially substituted, or replaced with renewable energy sources generated from or based on plants (Kumar et al., 2020). There have been notable increases in the use of lignin forms as bituminous mixture additives due to growing awareness of the advantages of sustainability and the use of eco-friendly materials (Yatish et al., 2024). Viscosity, softening point, penetration, and DSR tests were used to assess bitumen's rheological and physical properties treated with 4% lignin. Consequently, the increase in modified bitumen's viscosity and softening point values were between 10-30%. Furthermore, it was shown that the penetration values improved with increased lignin use (Terrel and Rimsritong, 1979). In addition to these tests, the Linear Amplitude Sweep (LAS) results indicated that bitumen containing lignin showed less fatigue resistance. Noted otherwise, the tolerance level against possible deformations is reduced (Ren et al., 2021).

This study's primary goal is to use several laboratory tests to determine the characteristics and performance of an unaged and aged asphalt binder treated with lignin. With proof of its benefits in use, lignin—a potential alternative for sustainable road design—will be used more frequently. Utilizing it frequently will reduce pollution and minimize the need for bitumen.

To the authors' knowledge, the number of studies about the rheological behavior of lignin-modified bitumen is limited in the literature. When the literature is analyzed from a national perspective, this study can be considered pioneering. This study is original with its contributions to the literature.

2. Materials

A typical 50/70 bitumen was designated as the reference bitumen in this study. Blends containing 15% and 20% lignin powder were also created. Characteristics like penetration, softening point, and force ductility were measured for reference and all developed blended materials. The bitumen was aged for a short-term period at the laboratory. Next, lignin and short-term aged bitumen were uniformly combined. A high-speed mixer was used to make sure the mixture was homogeneous. Wood lignin (the brown powder) used in this study was taken from waste products of the paper industry. According to chemical analysis of five chemical components, which were Klason lignin (91.5%), Acid-soluble lignin (4.9%), Carbon-hydrate (1.9%), Ash (1.2%) and other (0.5%), respectively (Wu et al., 2021).

Short-term aged bitumen (with a penetration value of 50/70) was obtained by keeping it at 163°C for 5 hours. The mixture was applied to a heating table at high speed so that lignin and bitumen could be homogeneously mixed. A short-term aged bitumen mixture was prepared at 15% and 20% lignin addition rates specified in the test program. The homogeneous mixtures were poured into molds while they were hot for penetration testing, ductility testing, and scanning electron microscopy (SEM).

3. Methods

Laboratory tests performed to determine the effect on bitumen behavior as a result of the modification of aged and unaged bitumen with lignin can be seen below:

3.1. Penetration Test

The penetration test is a standard laboratory test to determine the consistency of bitumen. In this test, a needle is inserted into a test sample at a certain weight, described in the specifications, and its depth and release are measured in millimeters, taking temperature, load, and time into account. Moreover, penetration values can indicate bitumen's behavior under different environmental conditions, such as temperature changes. The lower the penetration value, the better the bitumen's performance at higher temperatures, whereas the higher the penetration value, the better the bitumen's performance at lower temperatures. The test was conducted according to ASTM D5 (Standard Test Method for Penetration of Bituminous Materials).

3.2. Ductility Test

A ductility test is a standard laboratory test designed to measure the ductility of bitumen. Ductility refers to bitumen flexing at low temperatures without breaking or cracking. This test aims to evaluate the elongation properties of bitumen under certain conditions. Ductility testing helps understand how bitumen behaves in low-temperature conditions. It provides information about the performance of bitumen in cold climates where flexibility and resistance to cracking are required for road durability.

Ductility testing also forms the basis for research and development efforts to improve the properties of bitumen by adding additives or modifiers aimed at improving its flexibility and elongation properties.

Various organizations standardize bitumen ductility testing to ensure consistency, accuracy, and reliability of test results across different laboratories. The experiment followed the ASTM D113 (Standard Test Method for Ductility of Asphalt Materials) procedure.

3.3. Scanning Electron Microscope (SEM) Analyses

Scanning Electron Microscopy (SEM) testing for bitumen is a method used to analyze the microstructure and morphology of bitumen at the microscopic level. SEM is a powerful tool that provides high-resolution images and detailed information about bitumen samples' surface properties, particle distribution, and internal structure. The main purpose of the bitumen SEM Test is to determine the microstructure of bitumen. SEM allows researchers to visualize the surface morphology of bitumen samples, providing information about texture, roughness, and surface properties. This information is valuable in understanding the properties that affect the adhesion, cohesion, and durability of bitumen in construction applications.

Additionally, SEM analysis for modified bitumen helps evaluate the distribution and interaction of additives or modifiers within the bitumen matrix. It helps to understand how these additives affect modified bitumen's overall structure and performance.

In this context, the bitumen samples poured into silicone molds were kept in the refrigerator at a temperature that would not melt them until the experiment started.

4. Findings and Discussion

The first penetration test was performed to define the effect of Lignin in aged bitumen with an addition of 15% and 20% by the weight of bitumen. Figure 1 shows the results of specimens that are prepared as the specified contents. The results compared with the neat aged bitumen. Accordingly, it was observed that the increase in lignin addition increased the hardness of short-term aged bitumen.

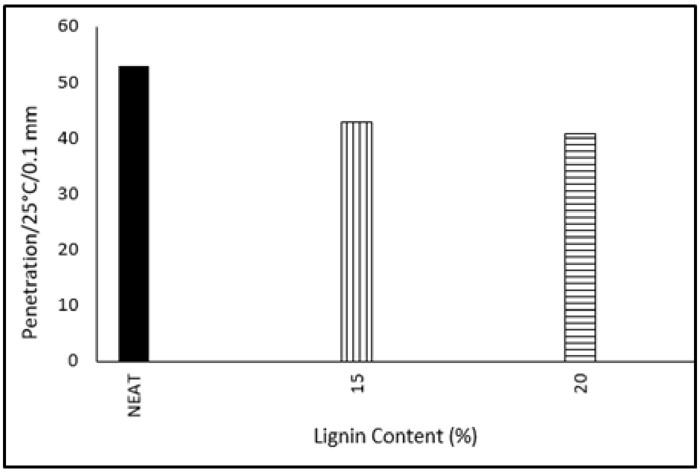

Figure 1. Penetration test results.

Figure 2 shows the ductility test results for adding 15% and 20% lignin to short-term aged bitumen specimens. Accordingly, the increase in lignin content reduced the elongation of these specimens. This situation seems compatible with the penetration test results and reveals that the bitumen becomes harder with the addition of lignin.

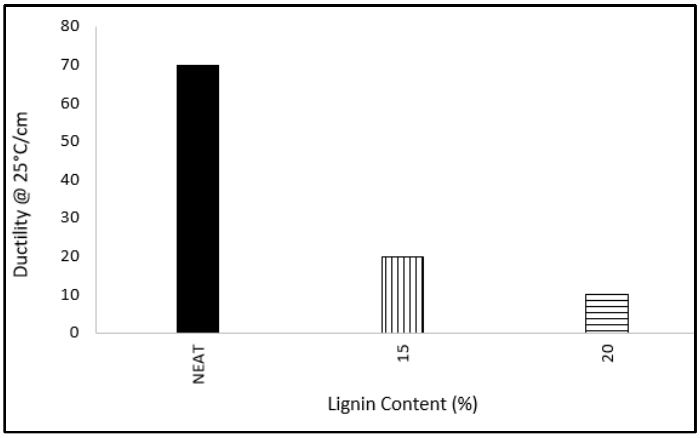

Figure 1. Ductility test results.

Figures 3a and 3b shows the SEM analyses of two different amounts of lignin-added specimens. Both images were taken at the same sensitivity level. The effect of adding 15% (Figure 3a) and 20% (Figure 3b) lignin to short-term aged bitumen samples, images show homogeneous distribution. Accordingly, it was observed that the increase in lignin addition caused agglomeration in short-term aged bitumen. The lack of homogeneous spread indicates that there are lumps in places.

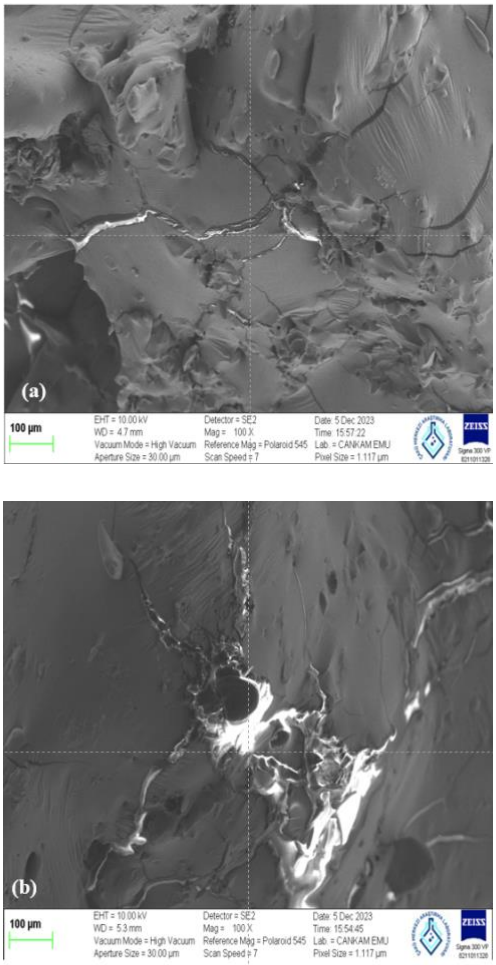

Figure 3. SEM analysis results for (a) 15% lignin addition, (b) 20% lignin addition.

5. Conclusions and Recommendations

Based on the laboratory study, the following results can be drawn:

- In conclusion, based on the penetration test results, it has been observed that the amount of lignin added to the bitumen over a short time significantly increased its hardness value.
- The results of the ductility test show a significant reduction in the elongation amount of short-term aged bitumen after adding lignin, as observed from the results of the ductility test. There is no doubt that this situation is comparable with the penetration test results and indicates that bitumen becomes increasingly harder when the amount of lignin in it is increased.
- It was found that the addition of lignin significantly reduced the amount of elongation observed in short-term aged bitumen after the addition of lignin, according to the SEM analysis. In this case, it seems that the penetration test results are consistent with the facts that the bitumen becomes harder when there is more lignin added to it.

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Authors’ Contributions

Genç Ömer: Research, Formal Analysis, Methodology, Writing

Varli Bingöl Başak: Research, Formal Analysis, Methodology, Writing, Review and Editing

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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