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Investigation of flow properties and activation energy of magnesium lignosulfonate modified bitumen

Magnezyum lignosülfonat modifiyeli bitümün akış özelliklerinin ve aktivasyon enerjisinin araştırılması

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Research Article

Abstract

Recently, many studies have been carried out on the use of waste materials in bitumen modification. In this way, environmental and economic benefits are obtained and a field of use is created for waste materials. In this study, magnesium lignosulfonate (MLS), which is an organic waste material released during paper production from wood, was added to B50/70 bitumen. Penetration, softening point, rolling thin film oven test (RTFOT) and rotational viscometer (RV) tests were performed on modified binders. As a result of the experiments, it was determined that MLS increased the consistency, softening point and short-term aging resistance of the asphalt and decreased the temperature sensitivity. In addition, the activation energy values were determined using the Arrhenius equation and the flow properties were evaluated.

Keywords: Bitumen, Recycling, Organic additive, Lignin, Magnesium lignosulfonate

Özet

Son zamanlarda atık malzemelerin bitüm modifikasyonunda kullanımı konusunda çok sayıda çalışma yapılmıştır. Bu sayede çevresel ve ekonomik faydalar elde edilmekte, atık malzemeler için bir kullanım alanı oluşturulmaktadır. Bu çalışmada, odundan kağıt üretimi sırasında açığa çıkan ve organik bir atık madde olan magnezyum lignosülfonat B50/70 bitüme ilave edilmiştir. Magnezyum lignosülfonat (MLS) ilave edilmiş bağlayıcılar üzerinde penetrasyon, yumuşama noktası, dönel ince film halinde yaşlandırma (RTFOT) ve dönel viskozimetre (RV) deneyleri uygulanmıştır. Yapılan deneyler sonucunda MLS ilavesinin bitümün kıvamını, yumuşama noktasını ve kısa süreli yaşlanma direncini arttırdığı, sıcaklık hassasiyetini düşürdüğü tespit edilmiştir. Ayrıca Arrhenius denklemi kullanılarak aktivasyon enerjisi değerleri belirlenmiş, akış özellikleri değerlendirilmiştir.

Anahtar kelimeler: Bitüm, Geri dönüşüm, Organik katkı, Lignin, Magnezyum lignosülfonat

1. Introduction

Highways constitute the majority of the world's transportation network, and highways are generally built as flexible pavements. As it is known, flexible pavements generally consist of bituminous binder which obtained by refining petroleum and aggregate. Since these two materials are non-renewable, their overuse creates both economic and environmental consequences. Therefore, it is important to improve the properties of the materials used in the mixture and to reuse them with recycling approaches [1–6]. The most common method used to improve the properties of bituminous binders is the modification. With this method, various additives are added to the binder to improve its properties. The high quality bitumen obtained will make the pavement stronger against heavy and repetitive traffic loads, environmental effects, temperature differences [7–10]. A wide variety of additives can be used to modify the bitumen. The most commonly used additives are polymers such as Styrene butadiene styrene (SBS), Styrene isoprene SIS, Ethylene vinyl acetate (EVA) etc [11]. Studies have shown that these polymers, which are grouped as thermoplastic elastomer and plastomer, give very good results on bitumen performance [12–17]. However, the researchers focused on using waste materials in bitumen modification due to the difficulty of obtaining and expensive additive materials.

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Industrial by-products emerge as a result of various productions, and these waste materials have negative effects on our environment. These materials, which cause a wide variety of pollution such as soil, water and air pollution, need to be used in various processes or recycled [18–20]. Recently, there have been many studies on the use of waste materials as a modifier for bitumen or hot mix asphalt (HMA) [4, 21–24]. In the study carried out by Shafabakhsh et al. for the use of waste rubber powders in HMA, the resistance to rutting was measured with a dynamic shear rheometer (DSR). In the results obtained, it was determined that the rubber powders added at the rate of 10% of the bitumen weight increase the resistance against rutting on the bitumen and increase the service life of the pavement [25]. Yan et al. inspected the rheological features of asphalt using waste tire rubber and ethylene vinyl acetate, one of the most widely used waste modifiers, and concluded that its high temperature performance was improved [26]. In addition, organic wastes are also used in bitumen modification and very successful results are obtained. Bostancıoğlu investigated the usability of activated carbon obtained from hazelnut shell wastes and furan resin obtained from vegetable wastes in bitumen modification. Both modified mixtures were noted to provide resistance to rutting and fatigue strength. It has also been stated that furan resin is a more resistant additive to moisture resistance compared to activated carbon [27, 28]. In another study, Yu et al. used waste packaging polyethylene (WPE) and organic montmorillonite (OMT) in asphalt modification and investigated the storage stability and rheological properties. WPE increased the rheological properties and permanent deformation resistance of the binder at high temperatures, while the combined use of WPE and OMT formed an exfoliated structure and increased the storage stability due to the high activity and adsorption properties of this structure [29].

Lignin is an organic molecule found in the structure of the cell wall together with cellulose and gives the plant its woody structure. Lignin, which is found in many trees and plants, enables the plant to stand upright and to transmit water to the higher leaves and branches by repelling water molecules. However, lignin is mostly encountered as a waste material in papermaking and is thrown into the environment as magnesium lignosulfonate as a result of the kraft method. Magnesium lignosulfonate (MLS) is an organic waste that is a dark liquid. However, lignin can provide various benefits when utilised in various applications. A major benefit is that it can absorb UV rays due to the benzene ring it contains. In addition, it can be used as a dispersion element for rubber materials due to its hydrophobic structure (benzene ring and carbon chain) [30–32].

In this study, magnesium lignosulfonate (MLS) obtained from lignin, which is a paper production waste, was used as a bitumen additive. In this context, it has been modified by adding 2, 4, 6 and 8% MLS to the bitumen. Then, conventional binder tests were applied and flow properties were determined by rotational viscometer test (RV). Flow characterization was supported by the activation energy value obtained by the Arrhenius equation.

2. Materials and Method

In the study, bitumen with a penetration grade of B50/70 supplied from Tüpraş Izmit Refinery and magnesium lignosulphate, a waste material from paper production, were used as additives. The physical properties of the bitumen used are given in Table 1.

Table 1. Properties of bitumen

Test	Standard	Value
Penetration (100g, 25°C, 5sn), dmm	ASTM D5	57
Softening point, °C	ASTM D36	50
Ductility (25°C, 5cm/min),cm	ASTM D113	100+
Flash point, °C	ASTM 92	248
Specific Gravity, (25°C), g/cm^3	ASTM D70	1,022
Fraass Breaking Point, °C	IP80	-10

Modified binders were obtained by adding 2%, 4%, 6% and 8% MLS to the pure binder, mixing at a mixing temperature of 155 °C and a speed of 1000 rpm. Penetration, softening point and rotational viscometer (RV) tests were carried out to determine the physical and rheological properties of modified asphalt binders. The viscosity values of the samples were obtained at 105°C, 135°C, 165°C, and 180°C using a Brookfield DV2T rotary viscometer device. RV test device was shown in Figure 1. Subsequently, to simulate short-term aging of pure and modified bitumens, Rolling Thin Film Oven Test (RTFOT) was performed. RV test was applied to RTFOT aged samples to determine flow characteristics of aged bitumens.

Figure 1. Rotational Viscometer (RV) test device

The resistance of the binder's molecules towards flow decreases with temperature increase, and molecules begin to move. In flowing liquids, the molecules that slide on each other must defeat the intermolecular forces that resist movement. This resistance power is called activation energy (E_a), and this value must be exceeded for the flow to begin [33, 34]. A large Ea value indicates that the viscosity of the bitumen is more sensitive to temperature [11]. This relationship is explained by the Arrhenius equation, and many successful studies have been carried out so far [35–37]. The Arrhenius equation was given in Equation 1.

$$\eta = A \times e^{\frac{Ea}{RT}} \quad (1)$$

Here, η is the viscosity of the binder (Pa.s), A is the regression coefficient, E_a is the activation energy (kJ/mol), T is the temperature of the test, and R is the universal constant of gas (8.314 J. mol.$^{-1}$.K^{-1}).

3. Results

3.1. Penetration test results

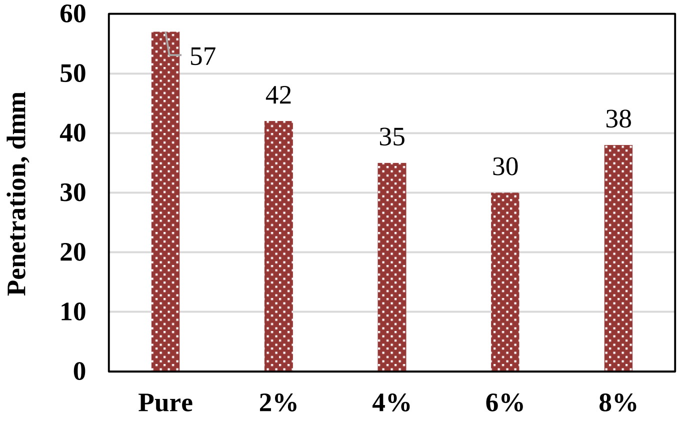

Figure 2. Penetration test results

Penetration test results of pure and 2, 4, 6 and 8% MLS modified bitumen was given in Figure 2. A regular decrease was observed in the penetration values up to the 6% additive addition, and the penetration value increased at the 8% additive addition. In general, it is seen that the penetration values of all samples increased compared to the pure binder. According to these results, it can be said that the additive hardens the bitumen. Using this bitumen will perform better at high temperatures and will provide higher strength than pure bitumen.

3.2. Softening point test results

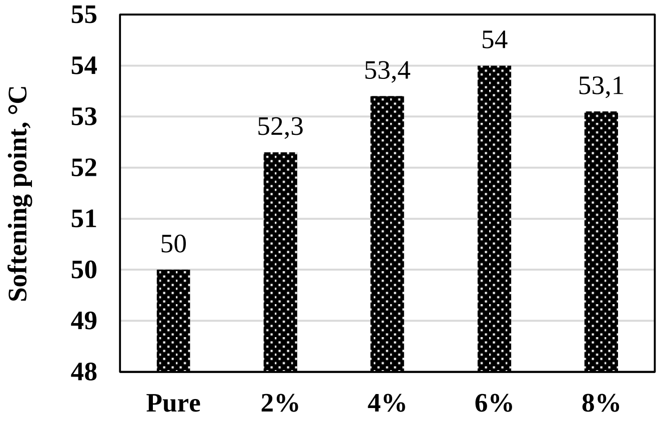

Figure 3. Softening point test results

The results of the softening point test applied to pure and modified binders are given in Figure 3. When Figure 3 is examined, a regular increase was observed until the addition of 6% additive, then this value decreased in the binder with 8% additive added. The results confirm the penetration test results. According to these results, it can be said that the additive material hardens the bitumen and starts to melt at higher temperatures.

3.3. Rotational Viscometer (RV) Test results

RV test results which performed on non-aged and RTFOT-aged samples was given in Figures 4 and 5. According to Figure 4 and Figure 5, the viscosity values of the binders decreased with the increase in temperature. As the temperature increased, the molecular mobility increased, the resistance to flow decreased. However, this decrease was limited by the increase in the contribution rate. In other words, the addition of MLS provided higher viscosity values than the pure binder at the same temperature. Viscosity values after RTFOT were higher than non-aged samples. With the volatilization of the light components in the bitumen, the heavy components increased proportionally, which increased the viscosity. At the same time, it is pleasing that the viscosity values are higher than the pure binder with the increase in the additive ratio. The higher the viscosity value, the higher the rutting resistance.

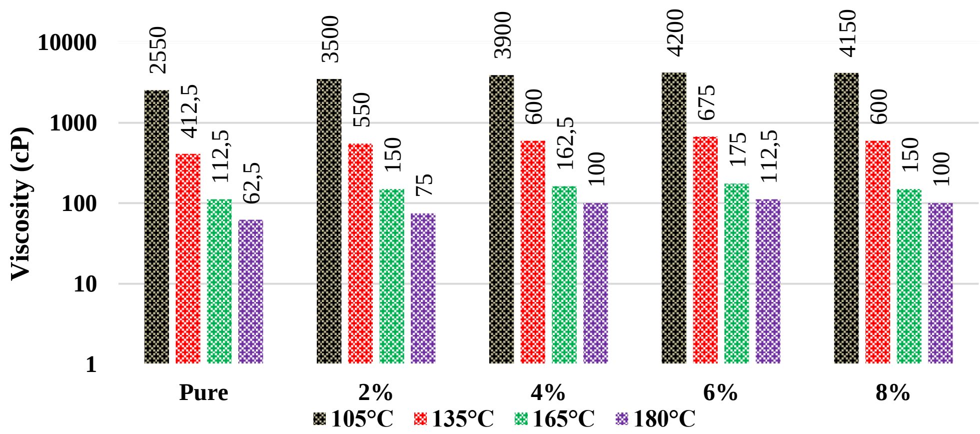

Figure 4. Rotational viscometer test results of non-aged pure and MLS modified binders

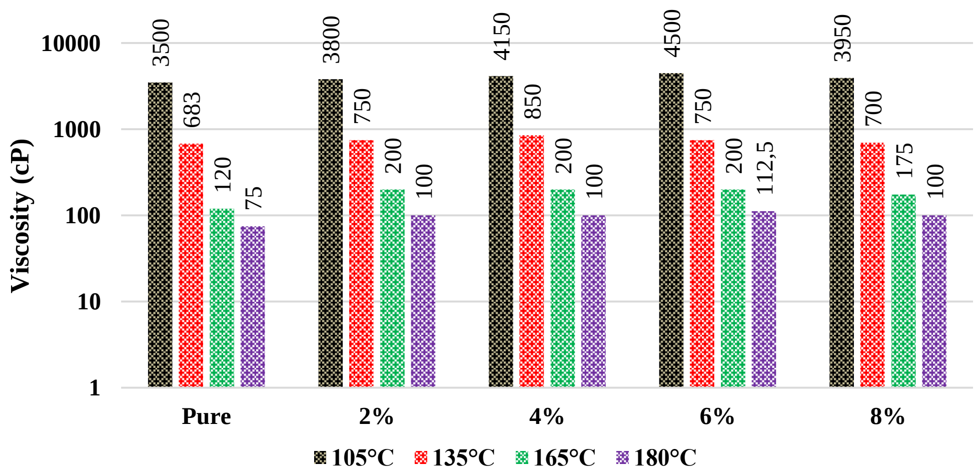

Figure 5. Rotational viscometer test results of RTFOT-aged pure and MLS modified binders

The activation energy (Ea) results which obtained by applying the Arrhenius equation to the viscosity values was given in Table 2. To see more clearly the effect of the additive ratio and the aging process Figure 6 was plotted.

Table 2. Activation energy values of non-aged and RTFOT aged bitumens

		Pure	2%	4%	6%	8%
Non-aged	***Ea (kJ/mol)***	68.681	68.224	67.738	67.699	69.399
	R^2	0.9414	0.9452	0.904	0.9272	0.8914
RTFOT-aged	***Ea (kJ/mol)***	76.203	72.24	71.21	70.451	70.388
	R^2	0.9609	0.9989	0.9894	0.9721	0.9829

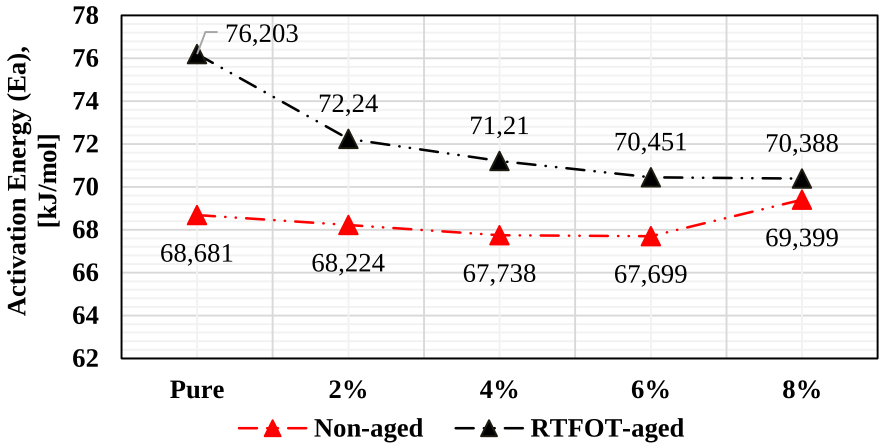

Figure 6. Activation energy (Ea) values of pure and modified binders

Activation energy is a threshold value that bitumen molecules must exceed in order to start moving [11]. Activation energy is an important parameter since the material needs to be liquefied for flexible pavement construction. An increase in this value means an increase in energy consumption. When Table 2 and Figure 6 are examined, the activation energy (Ea) value decreased with the increase in the additive ratio. It can be said that the decrease in Ea facilitated the occurrence of viscous flow. According to the traditional test results, it is seen that the material has hardened, but it has become easier for the material to take action for the flow phenomenon. Thanks to the activation energy analysis, in-depth evaluations can be made. It is seen that the Ea values after the RTFOT test increased compared to the unaged samples. The aging of the material adversely affected the flow character and increased the amount of energy required for flowing. However, it is pleasing that the Ea value decreases regularly with the use of additive. In general, it can be said that the material has become resistant to aging, in other words, it has not lost its flow properties despite aging.

4. Conclusion

In this study, the usability of magnesium lignosulfonate (MLS), a waste material released during paper production, in bitumen modification was investigated. For this purpose, 2%, 4%, 6% and 8% MLS were added to the pure bitumen and the effects were investigated. The results are given below in items:

- When the penetration test results were examined, it was observed that the penetration values of bitumen decreased with the increase in the additive ratio. This shows that the addition of MLS increases the consistency of the bitumen and increases its strength.
- According to the result of the softening point test, with the addition of MLS, the temperature value at which the bitumen starts to lose its properties, in other words, at which it starts to melt, has increased.
- RV results showed that the viscosity values of bitumen decreased with the increase in temperature values, but higher viscosity values were obtained compared to pure bitumen at the same temperature values with the use of MLS.

- According to the RV test performed on RTFOT-aged samples, the addition of MLS made the bitumen resistant to aging.
- Viscosity results are analyzed in depth with the Arrhenius equation. Activation energy values were obtained with the Arrhenius equation, and it was observed that the use of MLS caused a decrease in the activation energy values. A decrease in the activation energy means a decrease in the energy required for the bitumen to start flow.
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In general, a usage area has been obtained for this waste material, which is released as a result of paper production. In this way, not only economic and environmental benefits are provided, but also the properties of the bituminous binder are improved.

5. Author Contribution Statement

Author 1 contributed to making the design, and the literature review contributed to forming the idea, and the analysis of the results. Author 2 contributed to conducting experimental studies, writing the article checking the spelling, and checking in terms of content.

6. Ethics Committee Approval and Conflict of Interest

There is no need for an ethics committee approval in the prepared article. There is no conflict of interest with any person/institution in the prepared article.

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