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RESEARCH ARTICLE-CIVIL ENGINEERING

Investigation of the Effect of Boron Oxide and Beeswax on Workability and High-Temperature Performance of Bitumen

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Abstract

In recent years, various studies have shown that boron-containing additives improve the rutting performance of the bituminous pavements. However, in these studies, it was stated that these additives would decrease the workability of the bitumen and increase energy required for the construction of the pavement. On the other hand, it has been shown in many studies that waxes increase the workability of the bitumen. In this study, it was aimed to obtain bitumen with high rutting resistance and workability by adding boron oxide (BO) and beeswax (BW) to bitumen. Therefore, modified bitumen was produced by adding BO and BW at different ratios to a 50/70 penetration grade base bitumen. Then, the chemical, physical, and rheological properties of modified bitumen samples were investigated by various experiments. As a result, it has been observed that BO increases the high-temperature performance and viscosity of bitumen; on the other hand, BW decreases rutting resistance and viscosity. When BO and BW were added together to the bitumen, the negative impact of BO on workability and the negative impact of BW on high temperature performance were significantly eliminated. Especially, in 1BO + 1BW and 3BO + 3BW bitumens, the high-temperature performance of the bitumen improved without decreasing the workability.

Keywords Bitumen modification · Boron oxide · Beeswax · Wax · Workability · Rutting

1 Introduction

Bitumen, a by-product of the oil refining process, is the most basic and binding material of asphalt pavements. Increasing the performance of bitumen by modifying it with various additives is a topic of study that is kept up to date worldwide. Considering the traffic and environmental conditions in the area where the pavement will be built, the resistance of bitumen to rutting at high service temperatures, fatigue at medium temperatures, and cracking at low temperatures can be increased by bitumen modification. However, since rutting is one of the most detrimental deformations, bitumen is often modified to increase rutting resistance [1, 2]. Various additives, mainly polymers, are used to improve the high-temperature performance of the bitumen. In the literature, it has been observed that boron-containing additives also improve the rutting resistance of the bitumen by increasing the complex modulus and decreasing the phase angle [3–8].

Boron is a semi-metal and semi-conductor element with the atomic number 5, and it is represented by the symbol B in the periodic table [9]. However, the element boron can never be found in free form in nature. It usually combines with various metal or nonmetal elements to form compounds with different properties [9]. These compounds, which have different properties, make it possible to use boron in various industries [9].

Türkiye has 73.2% of the world's boron reserves with its 952 ton reserves [10]. Therefore, boron minerals and compounds attract the attention of Turkish researchers. However, when the literature is examined, it is seen that there are a limited number of studies in which boron components such

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as boron oxide and boric acid are used in bitumen modification. These studies have shown that boron-containing additives reduce the temperature susceptibility, increase the rutting resistance, and improve the elasticity but decrease the workability of bitumen [3].

When the boron oxide (B_2O_3) obtained from the dehydration of boric acid (H_3BO_3) is added to the bitumen, the workability of the bitumen is adversely affected. Therefore, in this study, the idea of using beeswax was put forward to reduce this disadvantage caused by boron-based additives. In recent years, various waxes with different chemical compositions are often used to reduce the mixing and compaction temperatures of bituminous mixtures by increasing the workability of bitumen. It has been determined that different waxes such as FT paraffin wax (Sasobit) [11–16], montan wax [17, 18], slack wax [19, 20], polypropylene wax [19, 20], carnauba wax [21], sugar cane wax (Deurex) [22–26] etc. effectively improve the workability of bitumen. In addition, in most of these studies and various other studies [27–29], wax additives have been reported to affect the rutting resistance of bitumen positively. However, this effect depends on the chemical composition [29] and melting point [30] of the wax used.

In the light of the above information, in this study, it was aimed to examine the effect of separate and combined use of boron oxide and beeswax on bitumen. Additionally, by using wax and boron oxide together, it is aimed to reduce the negative effect of boron oxide on the workability of bitumen and thus to produce bitumens with high workability and rutting resistance.

While bitumen is a petroleum-based material consisting of long hydrocarbon chains, boron is a salt-like substance in inorganic structure. Due to this structural difference between bitumen and boron, the miscibility of the two additives with each other is poor. When boron is added directly to the bitumen, it is difficult to obtain a homogeneous mixture because it causes lumps in the mixture. Therefore, when the studies with boron compounds in the literature are examined, it is seen that boron oxide or boric acid is not used alone. Generally, when using the boron compound in bitumen modification, the new additive material is synthesized chemically [3, 4, 6, 31]. The bitumen modifier used in these studies is an additive containing boron rather than boron oxide or boric acid alone. Therefore, using boron oxide in the appropriate form as a sole modifier in bitumen is a unique study. Besides, when the previous studies on waxes were examined, the use of beeswax as a bitumen modifier has not been found. For this reason, using both additives separately and together in bitumen constitutes the originality of this study.

In this study, modified bitumen was prepared by adding boron oxide and/or beeswax in different ratios to a 50/70 penetration graded bitumen. In order to examine the effect of additives on the chemical, physical, and rheological properties of the base bitumen, Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), conventional bitumen tests, rotational viscosity (RV), rotational thin-film oven (RTFO), pressure aging vessel (PAV) and dynamic shear rheometer (DSR) tests were applied to the prepared samples.

Table 1 Basic properties of boron oxide [8]

Properties	Value
Specific gravity (g/cm^3)	2.17
Moleculer weight (g/mol)	69.62
Melting point (°C)	450
Boiling point (°C)	1860
Particle size (mm)	0.250+
pH	4.64

2 Materials

2.1 Base Bitumen and Additives

The 50/70 penetration graded base bitumen was obtained from the 10th Regional Directorate of Turkish Highways. Base bitumen was chosen from this penetration grade because most of the studies in the literature, both with boron-containing additives and with wax modifiers, were carried out with 50/70 penetration graded base bitumen [3–5, 21, 27, 32, 33]. In addition, this penetration grade is the most widely used penetration grade in the construction of asphalt pavements in Türkiye.

Boron oxide (BO) was obtained from Bandırma Boron and Acid Factories Operations Directorate, affiliated with the General Directorate of Eti Mine Works, one of the most important boron products production centers in Türkiye. Boron oxide is the first additive of this study and was used at the rates of 1%, and 3% by weight of base bitumen. These ratios have been chosen considering the studies conducted with boron-containing additives in the literature [31]. The basic properties of boron oxide are shown in Table 1.

The second additive used in this study is beeswax (BW). (BW) was obtained from local beekeepers in Trabzon/Türkiye and was used at the rates of 1%, 3%, and 5% by weight of the base bitumen. In the selection of these ratios, studies with various wax additives in the literature were taken into account [15, 16, 21, 23, 24, 26, 29, 33–40].

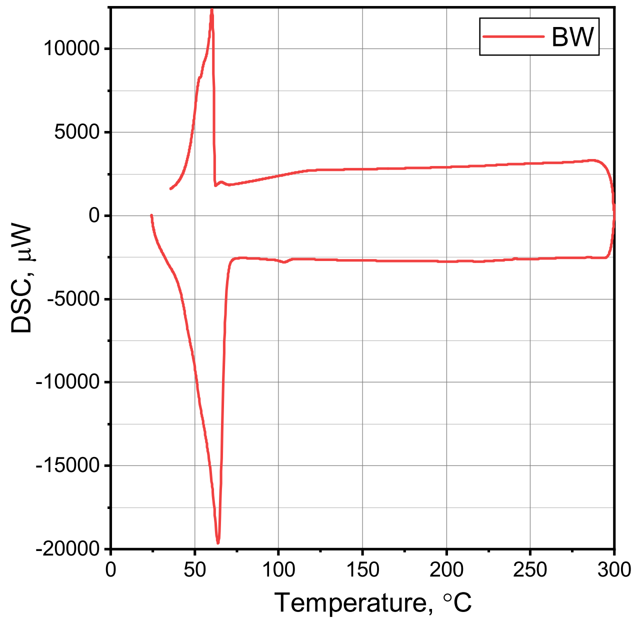

Fig. 1 DSC graphic of BW

2.2 Preparation of Modified Bitumen

In the production phase of modified bitumen, firstly, BO modified bitumen was prepared. Accordingly, 3% BO by weight of bitumen was dissolved in approximately 7 ml, 2–3 ml per gram of BO, of 2-methoxyethanol solvent. Then, this solution and added to the bitumen, which was pre-heated to 150 °C. Thereafter, the bitumen sample was mixed with a four-armed mechanical mixer at 150 °C at 1000 rpm for 1 h. During the mixing of the bitumen and the solution, the solvent, which allows the BO to be dispersed homogeneously in the bitumen, evaporated with the effect of heat and moved away from the mixture. Thus, the production of BO modified bitumen was completed.

On the other hand, DSC analysis was performed as a preliminary test to determine the thermal compatibility of BW with base bitumen and results are given in Fig. 1. As seen in this figure, the melting temperature of BW is 63.3 °C, and its solidification temperature is 60.5 °C. The fact that the melting temperature of BW is lower than the mixing temperatures of bituminous mixtures shows that thermal miscibility of BW and base bitumen is possible.

For the preparation of wax-modified bitumen same mixing procedure was applied for 30 min by adding 1%, 3%, and 5% ratios BW to the base bitumen. Finally, to examine the combined effect of both additives, additives were added to the base bitumen at varying ratios (1% BO + 1% BW, 1% BO + 3% BW, 1% BO + 5% BW, and 3% BO + 3% BW) and mixed at 150 °C at 1000 rpm for 1 h. These mixing parameters were selected by considering the studies on boron-containing additives [7, 8, 41] and the studies on waxes [30, 42, 43].

Table 2 Codes of binders

Sample content	Code
AC 50/70 Bitumen	BASE
AC 50/70 Bitumen + 3% Boron oxide	3BO
AC 50/70 Bitumen + 1% Beeswax	1BW
AC 50/70 Bitumen + 3% Beeswax	3BW
AC 50/70 Bitumen + 5% Beeswax	5BW
AC 50/70 Bitumen + 1% Boron oxide + 1% Beeswax	1BO + 1BW
AC 50/70 Bitumen + 1% Boron oxide + 3% Beeswax	1BO + 3BW
AC 50/70 Bitumen + 1% Boron oxide + 5% Beeswax	1BO + 5BW
AC 50/70 Bitumen + 3% Boron oxide + 3% Beeswax	3BO + 3BW

The codes of binders, including base bitumen, are given in Table 2.

3 Method

3.1 Differential Scanning Calorimetry (DSC) Analysis

One of the analyzes used to examine thermal properties such as melting temperature and glass transition temperature of materials is Differential Scanning Calorimetry (DSC) analysis. In addition, this analysis is frequently used in the characterization of wax additives [30, 34, 39, 44].

In this study, before the modified bitumen samples were prepared, DSC analysis was performed as a preliminary test to determine the thermal compatibility of BW with base bitumen. Approximately 5 mg sample was placed in aluminum crucibles for thermal analysis of BW. The sample was analyzed under nitrogen atmosphere at a heating/cooling rate of 15 °C/min in the temperature range from − 20 to 300 °C using a Hitachi 7020 model DSC device.

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy (FT-IR) is an analytical method used to determine the functional groups, state of bonds, and binding sites in the structure of organic compounds by characterizing the bonds between molecules [45]. In this method, which is based on the interaction between IR radiation and molecules, infrared radiation is absorbed by the material when its frequency coincides with the vibration frequency of a molecule bond [46]. The amount of absorbed radiation is measured as a function of energy that can be expressed with frequency, and the IR spectrum of the material is obtained by reflecting the absorbed radiation as a jump in the spectrogram [46]. Depending on the FT-IR method applied, IR light can pass into the sample or be partially or completely reflected from the sample surface. Recently, the ATR method, which does not require special preparation for viscous or liquid materials such as bituminous binders, and where IR light is completely reflected, has become quite common [46]. In this study, spectral analysis of additives and bitumen samples was performed using Perkin Elmer FT-IR device with ATR module. For measurements, approximately 2–3 mg of sample was taken and placed in the center of the measuring window of the FT-IR device. The sample was then pressed to ensure full contact between the measuring window and the bitumen. The procedure for sample scanning was performed with 4 repetitive measurements within wave number from 700 to 4000 cm^{-1} at a resolution of 1 cm^{-1}.

3.3 Conventional bitumen tests

3.3.1 Penetration and Softening Point Tests

Penetration and softening point tests were performed to determine the physical properties of the bitumen samples. Penetration and softening point tests were carried out according to ASTM D5 and ASTM D36 standards, respectively. The values obtained from these tests give information about the consistency of the bitumen. While the consistency of the sample decreases as the penetration value increases, it increases as the softening point value increases. In other words, an increase in the penetration value indicates that the bitumen softens, and an increase in the softening point indicates that it hardens.

Since bitumen is a thermoplastic material, it is affected by temperature changes. It softens with increasing temperature and hardens with decreasing temperature. This behavior, which significantly affects the character of bitumen, is known as temperature susceptibility. The penetration index (PI) is used to get an idea of the temperature susceptibility of bitumen. An increase in the penetration index indicates a decrease in the temperature susceptibility of the bitumen sample. The PI value of bitumen is usually between − 2 and + 2. The temperature susceptibility of bitumen is considered to be low if this value is close to + 2 and high if it is close to − 2 [28]. PI is often determined by the classical method given in Formula 1 [47].

$$\mathrm{PI} = \frac{1952 - 500 \times \log(Pen25) - 20 \times \mathrm{SP}}{50 \times \log(Pen25) - \mathrm{SP} - 120} \quad (1)$$

where Pen25 is the penetration value of bitumen at 25 °C and SP is the softening point of bitumen.

3.3.2 Rotational Viscosity (RV) Test

Bitumen must be sufficiently fluid at high temperatures to be mixed with the aggregate homogeneously, laid on the road surface, and compacted. One of the most important tests used to determine the workability of bitumen is the rotational viscosity (RV) test. In this study, the viscosity of the bitumen samples was measured with Brookfield DV2T rotational viscometer using spindle no#21. The temperature-viscosity line was drawn with the results of the RV test carried out at different temperatures, and the mixing and compaction intervals that corresponding to 170 ± 20 cP and 280 ± 30 cP, respectively on this line of the bitumen samples were determined [48, 49].

3.4 Aging of Bitumen Samples

Bitumen is exposed to short-term aging with the effect of air and temperature during the mixing and compaction processes until the construction of the pavement layer is completed. During the service life bitumen ages in long term due to traffic loads and environmental conditions such as climate. These two types of aging are commonly simulated in the laboratory by RTFO and PAV tests [50, 51]. In this study, these methods were used for the aging of bitumen.

In the RTFO test carried out according to ASTM D2872 [52] standard, the tubes in which 35 ± 0.5 g of bitumen were poured into each are placed in the RTFO device set at 163 ± 0.5 °C. Airflow is provided into the test device at a speed of 4000 ± 200 ml/min, and the samples are rotated at 15 ± 0.2 rpm for 85 min. In addition to determining the post-aging properties of the RTFO-aged samples with other tests, mass loss can be calculated using Formula 2. As the percentage of mass loss increases, the amount of bitumen affected by short-term aging increases. In the Superpave specification, the percentage of mass loss is limited to a maximum limit of 1% [53].

$$\%\ mass\ loss = \frac{original\ mass - aged\ mass}{original\ mass} \times 100 \quad (2)$$

In the PAV test carried out according to ASTM D6521 [54] standard, 50 ± 0.5 g RTFO-aged bitumen samples are placed in the test device. The samples are aged for 20 h under 2.10 MPa pressure at 90 °C, 100 °C, or 110 °C according to their high-temperature performance grade. In this study, the PAV test was carried out at 100 °C.

3.5 Dynamic Shear Rheometer (DSR) Test

The most common test used to determine the rheological properties of bitumen is the DSR test. With this test conducted based on ASTM D7175 [55], the resistance of unaged or

RTFO-aged bitumen to rutting at high temperatures and PAV-aged bitumen to fatigue at intermediate temperatures can be determined. For unaged and RTFO-aged samples, a 1 mm thick bitumen sample is placed between two parallel plates, one fixed, and one moving, with a diameter of 25 mm, and the sample is exposed to the oscillating movement of the moving plate. For PAV-aged bitumen, the same process is applied to samples prepared with 2 mm thickness using 8 mm diameter plates.

As a result of the test, the complex shear modulus (G*), which is a measure of the resistance of the bitumen sample against deformations, and the phase angle parameter (δ), which indicate the phase delay between stress and strain, are obtained. G*/sinδ is taken as the indicator of the resistance of the specimen against rutting, and the G*·sinδ value is taken as the symbol for its fatigue resistance. In the Superpave specification, the rutting parameter, G*/sinδ, is limited to a minimum value of 1.0 kPa and 2.2 kPa for unaged and RTFO-aged samples, respectively ASTM D6373 [53]. In addition, it is stated that the fatigue parameter, G*·sinδ, should not exceed 5000 kPa at the temperature corresponding to the high temperature performance grade [53]. In this study, the rheological properties of bitumen samples were determined at a frequency of 1.59 Hz under controlled stress conditions using the Bohlin DSR II rheometer. The tests were conducted at temperature varying from 64 to 76 °C with 6 °C increments. When the G*/sinδ parameter of bitumen samples at 64 °C provided 1.0 kPa for unaged samples and 2.2 kPa for RTFO-aged samples, an upper temperature was tested, and when these values were not met, experiments were performed at a lower temperature.

3.6 Statistical Analysis

In addition to the direct interpretation of the experimental results obtained in the study, statistical analyses were carried out and further evaluations were made. Accordingly, the data obtained from the experiments were analyzed using IBM SPSS Statistic V25 application. Firstly, Shapiro–Wilk test was used to check whether the data were normally distributed. As a result, it was determined that all data in the study were normally distributed. Then, results for duplicate samples were grouped and ANOVA analysis was performed to test for similarity between the groups. When conducting the ANOVA test, the statistical significance level (p) was set to be less than 0.05.

4 Results and Discussion

4.1 Results of FT-IR Analysis

The FT-IR spectra of the BASE, BO, and BW are shown in Fig. 2. While a C–H stretching band appears at 2926 cm^{-1} in base bitumen, the deformation bands of the CH_3 and CH_2 groups in the hydrocarbon chain are observed at 1456–1375 cm^{-1}, respectively. In the BO spectrum, B–OH and B–O tension bands are observed at 3189 and 1191 cm^{-1}, respectively. In the BW fraction, the vinylic C=C–H stretching band is observed at 2954 cm^{-1}, while C–H stretching bands are observed at 2916 and 2848 cm^{-1}, belonging to different hydrocarbon functions in wax, due to the partial difference in the hydrocarbon chain compared to base bitumen. The C=O stretching band of the monoester, diester, or triester function of the BW fraction is observed at 1735 cm^{-1}, and the peak of the O–C=O fraction of the same function is observed at 1170 cm^{-1}. Again, the CH_3 tension band in the hydrocarbon chain is observed at 1463 cm^{-1} and the CH_2 group stretching band at 1375 cm^{-1}. Unlike the BASE, the presence of the unsaturated function in BW can be understood from the double peak observed at 730–719 cm^{-1} in the fingerprint region. These peaks are out-of-plane absorption bands originating from the unsaturated part of the carbon chain.

In Fig. 3a, the FT-IR spectra of the selected samples are given together. The FT-IR test was not applied to all samples, but only to BASE, 3BO, 3BW and 3BO + 3BW bitumen samples. Thus, the complexity caused by having too much data in a graph was avoided. Also, it was possible to more clearly examine the effects of additives separately or together on base bitumen. When this figure is examined, no significant a new peak was observed except for the peaks from BO, BW and BASE content. In addition, when the effect of the addition of BO and/or BW to the BASE on the peak densities is examined in Fig. 3a, it can be said that the depth of the S=O (sulfoxide) band around 1030 cm^{-1} tends to increase with the addition of the BO and there is a trend that is not significantly affected by the addition of the BW. On the other hand, it is seen that the depth of the C=O (carbonyl) band around 1720 cm^{-1} tends to decrease with the addition of the BO, and to increase with the addition of BW. A quantitative analysis aimed to more accurately evaluate the effect of BO and BW on the S=O and C=O bands. For this purpose, $I_{c=o}$ and $I_{s=o}$ indices (aging and hardness indicators) are frequently used in the literature for quantitative analysis of FT-IR spectra [56–59]. In this study, $I_{c=o}$ and $I_{s=o}$ were calculated with Formula 3 and Formula 4 given below, respectively. While calculating the areas around the peak, horizontal and vertical lines were created at the starting and ending points of the peaks. Then, vertical lines were used directly as vertical boundaries, while the lower numerical value of horizontal

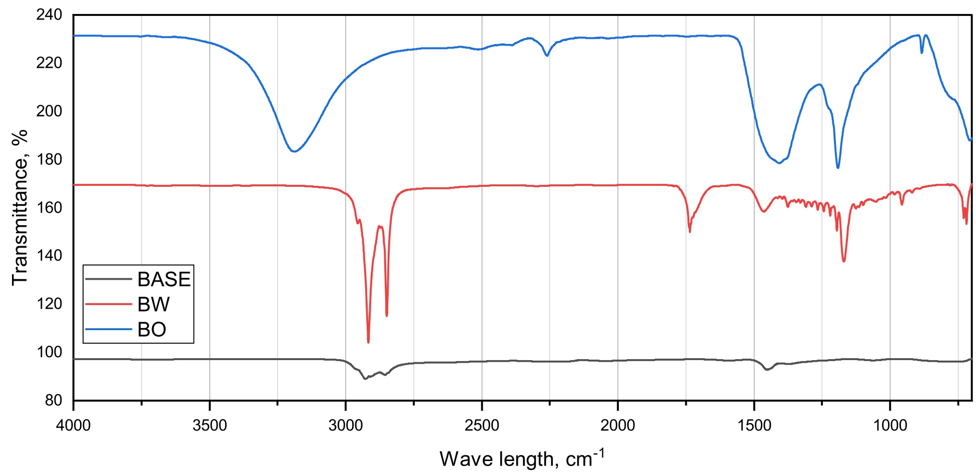

Fig. 2 FT-IR spectra of base bitumen and additives

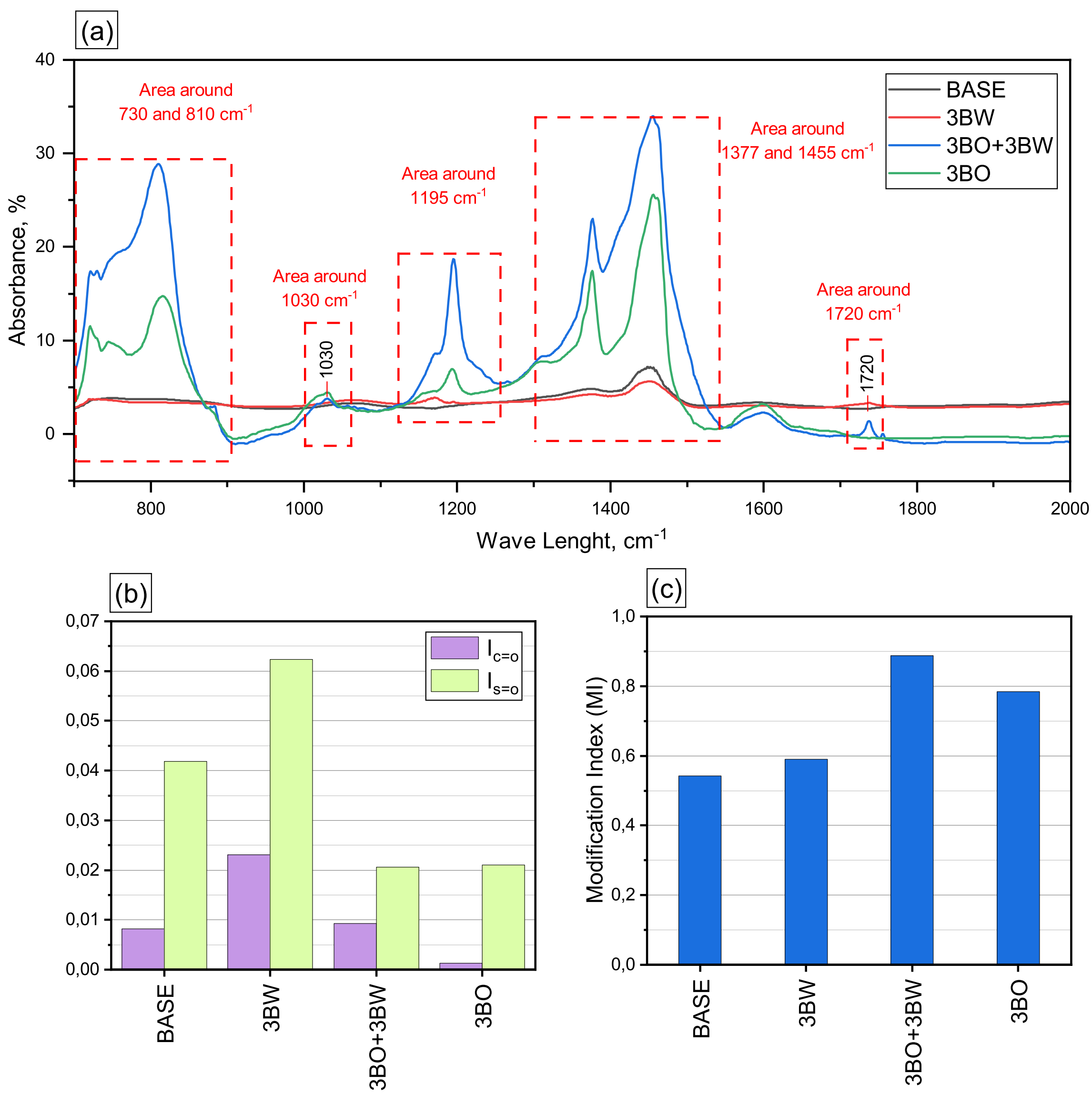

Fig. 3 **a** FT-IR areas, **b** aging indices of bitumen, and **c** modification indices

lines was preferred as the baseline. Thus, the area around the peak has been limited and made calculable.

$$I_{c=o} = \frac{\text{Area}\left(1720\ \text{cm}^{-1}\right)}{\text{Area}\left(1377\ \text{and}\ 1455\ \text{cm}^{-1}\right)} \quad (3)$$

$$I_{s=o} = \frac{\text{Area}\left(1030\ \text{cm}^{-1}\right)}{\text{Area}\left(1377\ \text{and}\ 1455\ \text{cm}^{-1}\right)} \quad (4)$$

When Fig. 3b is examined, it seen that the $I_{c=o}$ and $I_{s=o}$ indices tend to decrease with the addition of the BO. there is an upward trend with the addition of BW. $I_{c=o}$ and $I_{s=o}$ indexes of 3BO + 3BW bitumen are similar or lower oxidation than the BASE. Therefore, it is thought that there is a trend that pavements constructed with bitumen containing the BO will undergo less oxidation than the BASE. In other words, the oxidation that occurs with the reaction of different organic molecules in the bitumen with oxygen tends to decrease when BO is added to the bitumen. It is thought that this may be due to the fact that BO is both an inorganic substance and a compound that already contains oxygen in its structure (B_2O_3), so it is less likely to react with oxygen in the air. On the other hand, it is seen that there is a tendency towards a decrease in the oxidation resistance of base bitumen with the addition of BW. It is thought that this may be due to the possibility that BW contains more organic molecules that can react with oxygen compared to BASE, or that the reaction rate of organic molecules with oxygen is higher. Also, it is thought that there may be a relationship between the aging indices of bitumen and their viscosity. In this respect, with increasing viscosity, resistance to aging may increase due to decreased molecular mobility and/or the amount of light component. In this context, it has been observed in various studies that binders with higher viscosity show higher aging resistance, and vice versa [60–62]. Accordingly, the viscosity values given in Sect. 4.3 also support the above-mentioned findings.

In addition to aging indices, this study produced a modification index (MI) to evaluate the effect of additives on the BASE quantitatively with FT-IR. MI was calculated with Formula 5, considering the areas where significant differences in peak intensities of the base and modified bitumen spectra were observed.

$$\text{Modification Index,}\ \ \text{MI} = \frac{\text{Area}\ \left(1195\ \text{cm}^{-1}\right) + \text{Area}\ \left(730\ \text{and}\ 810\ \text{cm}^{-1}\right)}{\text{Area}\ \left(1377\ \text{and}\ \ 1455\ \text{cm}^{-1}\right)} \quad (5)$$

In Fig. 3c, it is seen that the MI value of the BASE increases significantly with the addition of the BO, while it increases slightly with the addition of the BW. The highest MI value belongs to the 3BO + 3BW bitumen. From these results, it can be concluded that the effect of the BO modification on base bitumen is quite evident, and this effect is further increased by BO + BW modification.

4.2 Results of Conventional Bitumen Tests

The results of conventional tests applied to BASE and modified bitumen samples are given in Fig. 4 collectively. When Fig. 4a is examined, it can be said that when both additives are used separately or together, the penetration value of BASE decreases. When 3% BO was added to the BASE, the penetration value decreased by 41.2%. On the other hand, when 3% BW was added, it decreased by 9.8%. This result shows that the hardening effect of the BO on base bitumen is more pronounced than the BW. When the softening point values given in Fig. 4a are examined, it can be seen that using both additives separately or together increase the softening point value of the BASE. The softening point value of the 3BO + 3BW is higher than 3BW but lower than 3BO. This result shows that the effect of using 3% BO on the softening point is more pronounced. The softening point value increased by 28% with the addition of 3% BO to the BASE. The PI values of the BASE and modified bitumen are given in Fig. 4b. The PI of the BASE increased with the addition of BO or BW. This result shows that both additives reduce the temperature susceptibility of the base bitumen. However, it is seen that the PI values of BO + BW modified bitumens with lower wax content are higher. This result indicates that the effect of BO on the temperature susceptibility of bitumen is improving more than BW.

4.3 Results of RV Tests

The results of the RV tests at 135 °C are given in Fig. 5. In this figure, it is seen that the viscosities of all bitumen samples are lower than 3000 cP, which is the upper limit of the specification. This result indicates that these bitumen samples will have sufficient fluidity under conditions of mixing and compaction with the aggregate during pavement construction.

The results of the RV test carried out at 120 °C, 135 °C, 165 °C, and 180 °C are given in Fig. 6a. The viscosity values of 3BO at all temperatures are higher than BASE. This is due to the fact that the melting temperature of BO (450 °C) is considerably higher than the measurement temperatures. In other words, it is thought that the BO grains, which are homogeneously dispersed in the bitumen, cause an increase in the viscosity of the base bitumen by maintain their thermal stability at test temperatures. On the other hand, the viscosity values of BW modified bitumens are lower than BASE. Since the test temperatures are higher than the melting point of BW (63.3 C), BW melts causing an increase in entropy and turns into liquid form in bitumen. As a result, the viscosity of base bitumen decreases. In Fig. 6a, the viscosity values of bitumen samples at different temperatures are combined with a curve.

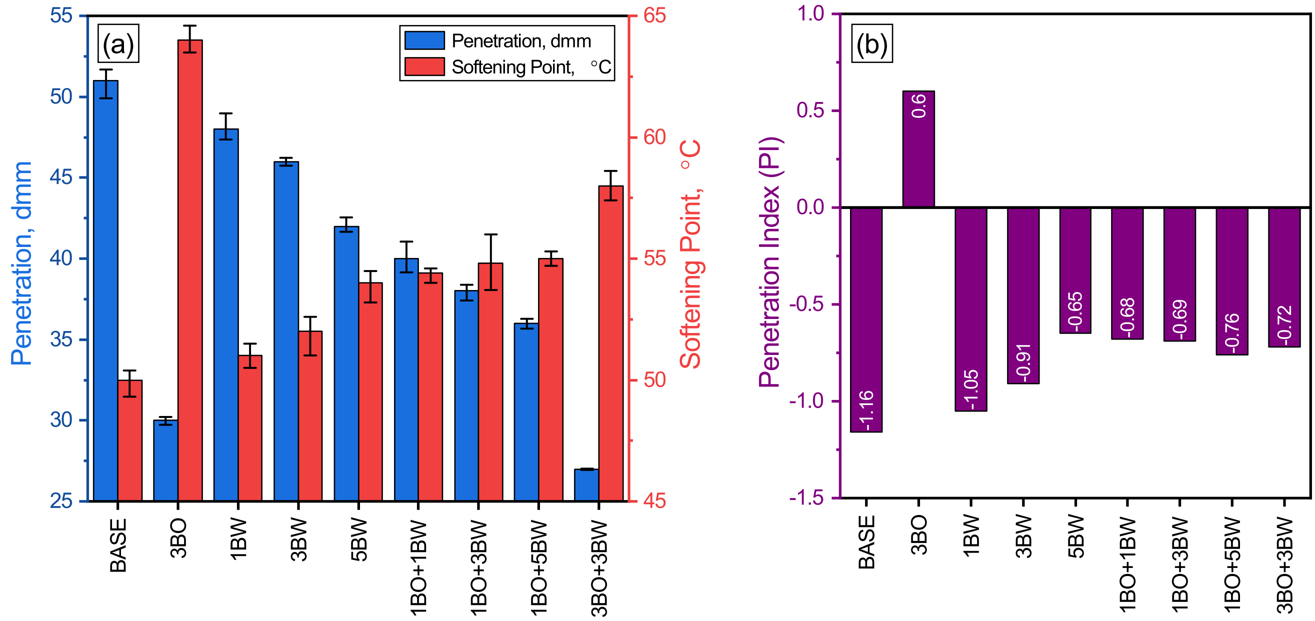

Fig. 4 Results of conventional tests: **a** Penetration and softening point values and **b** PI values

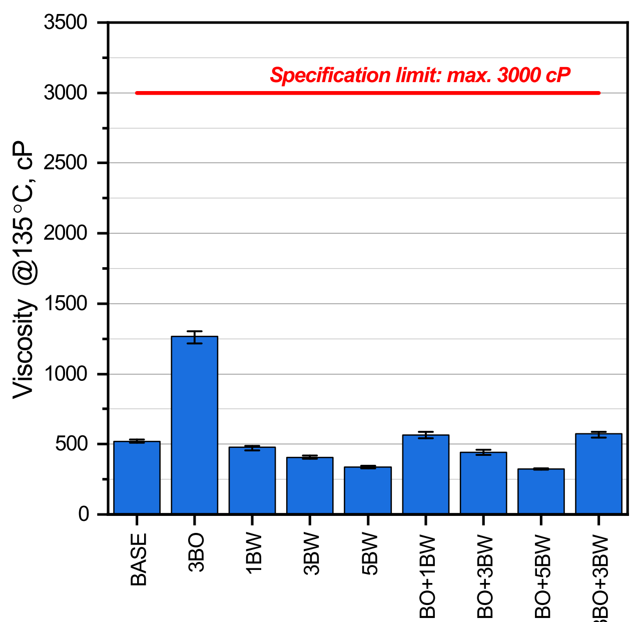

Fig. 5 Results of RV test conducted at 135 °C

Mixing and compaction temperatures were determined on this curve, and these temperatures are given in Fig. 6b. With the addition of the 3% BO to the BASE, the mixing and compaction temperatures increased from 163 and 154 °C to 171 °C and 163 °C, respectively. This result indicates that the 3BO will increase energy consumption during pavement construction, resulting in higher carbon emissions than the BASE.

On the other hand, the mixing and compaction temperatures of the BASE decreased in parallel with the addition of the BW. When 5% BW was added to the BASE, the mixing and compaction temperatures decreased to 155 °C and 142 °C, respectively. While the mixing and compaction temperatures of 1BO + 1BW and 3BO + 3BW are similar to the BASE, 1BO + 3BW and 1BO + 5BW are 2–4 °C and 6–10 °C less, respectively. From these results, it can be concluded that the negative effect of the BO modification on the workability and the amount of carbon released to the environment can be reduced by adding BW.

4.4 Results of Short-Term Aging

Mass losses of bitumen samples calculated with Formula 2 are given in Fig. 7. The mass losses of all bitumen samples are well below the specification upper limit of 1%. The mass loss of the BASE decreased with the addition of BO or BW. For this reason, it is thought that modified bitumen will age less during pavement construction compared to the BASE, and pavements built with these bitumens will maintain their performance more.

4.5 Results of DSR Tests

4.5.1 DSR Test Results of Unaged Binders

The G* and δ values obtained from DSR tests are given in Fig. 8. When BO was added to the BASE, the G* value increased significantly. On the other hand, the G* value of the BASE decreased in parallel with the addition of the BW.

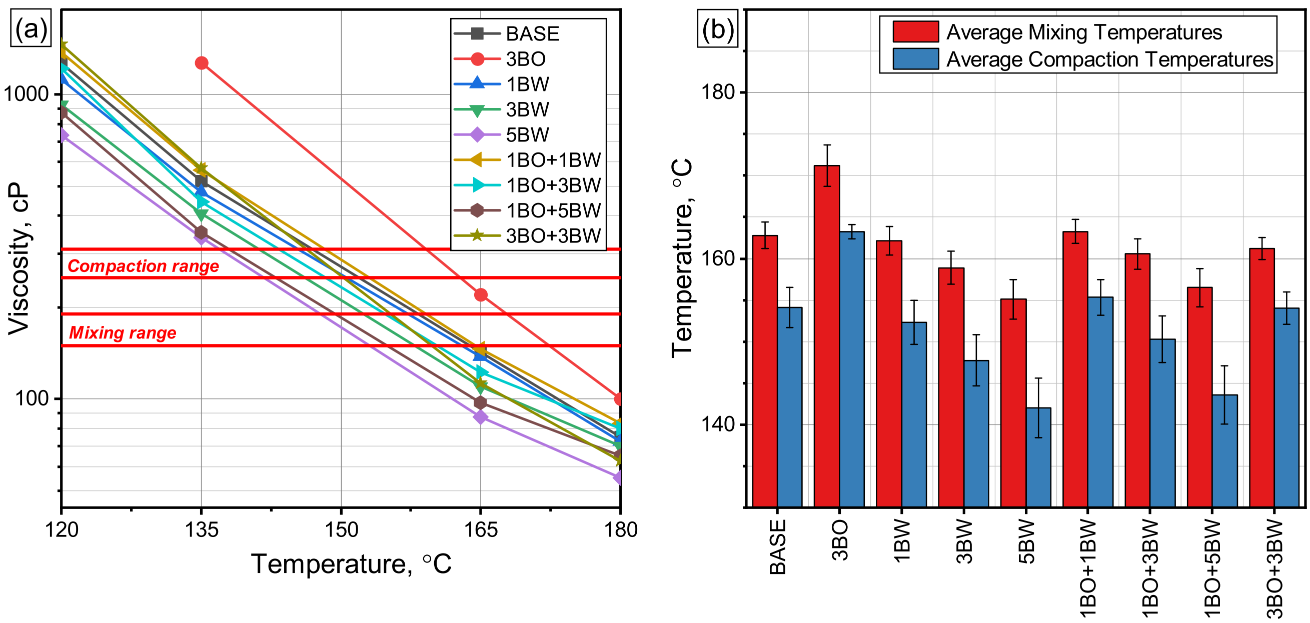

Fig. 6 Results of RV tests: **a** temperature-viscosity graphic and **b** average mixing and compaction temperatures

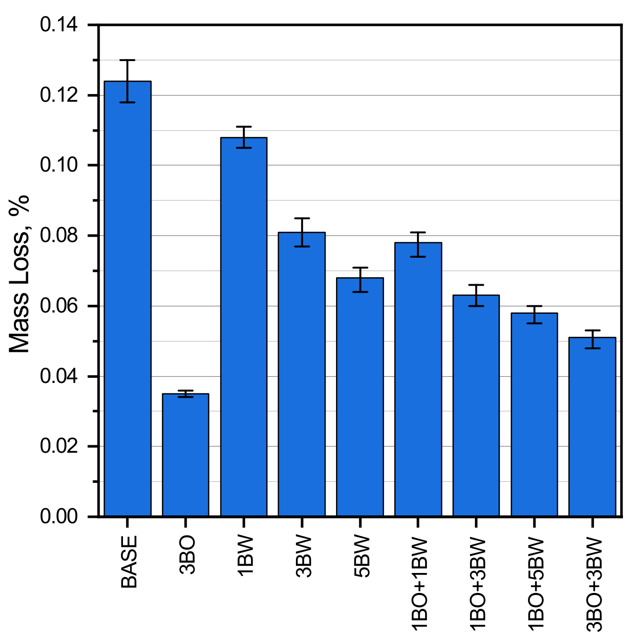

Fig. 7 Mass loss percentages after RTFO test

For the bitumen modified with two additives, 1BO + 1BW and 3BO + 3BW gave higher, and 1BO + 3BW and 1BO + 5BW gave lower G* value than the BASE. These results show that 3BO, 1BO + 1BW, and 3BO + 3BW will show higher, and other modified bitumen samples will show lower strain resistance compared to the BASE.

In Fig. 8b, it is seen that the addition of the BO to the BASE significantly decreases the δ value and the addition of the BW increases it. These results show that the addition of BO significantly improves the elastic properties of the base bitumen at high temperatures, while the addition of the BW affects it negatively. In addition, the δ values of all bitumen samples containing both additives are lower than the BASE, indicating that the effect of the BO on the elastic properties of the BASE is more pronounced and improving than BW.

G*/sinδ parameters of bitumen samples are given in Fig. 9. While the G*/sinδ parameter increased with the addition of the BO to the BASE, it decreased with the addition of the BW. This result shows that BO improves the rutting resistance of BASE, but BW negatively affects it. Although the hardening effect of the BW was observed in conventional bitumen tests, this effect was not observed at high temperatures. The impact of waxes (natural or commercial) on the properties of bitumen is a complex issue that depends on the amount and chemical structure of the wax and the bitumen [29]. While the wax hardens the bitumen by crystallizing at low temperatures, it can melt at high service temperatures and soften the bitumen [30]. The key word in this wax behavior is its chemical composition/melting point. In this study, it is thought that adding BW reduces the rutting resistance of the BASE relatively since the melting temperature of BW (63.3 °C) is close to high service temperatures. This effect of the BW is indirectly due to its chemical structure. Due to a large number of polar groups and short chain fractions in the structure of the BW, the melting point of BW is low, and the overlap of the short chain fractions of the BW with the long hydrocarbon chains of bitumen (electrostatic effect) is weak. For this reason, it is thought that adding BW to the BASE has a negative impact on the rutting performance.

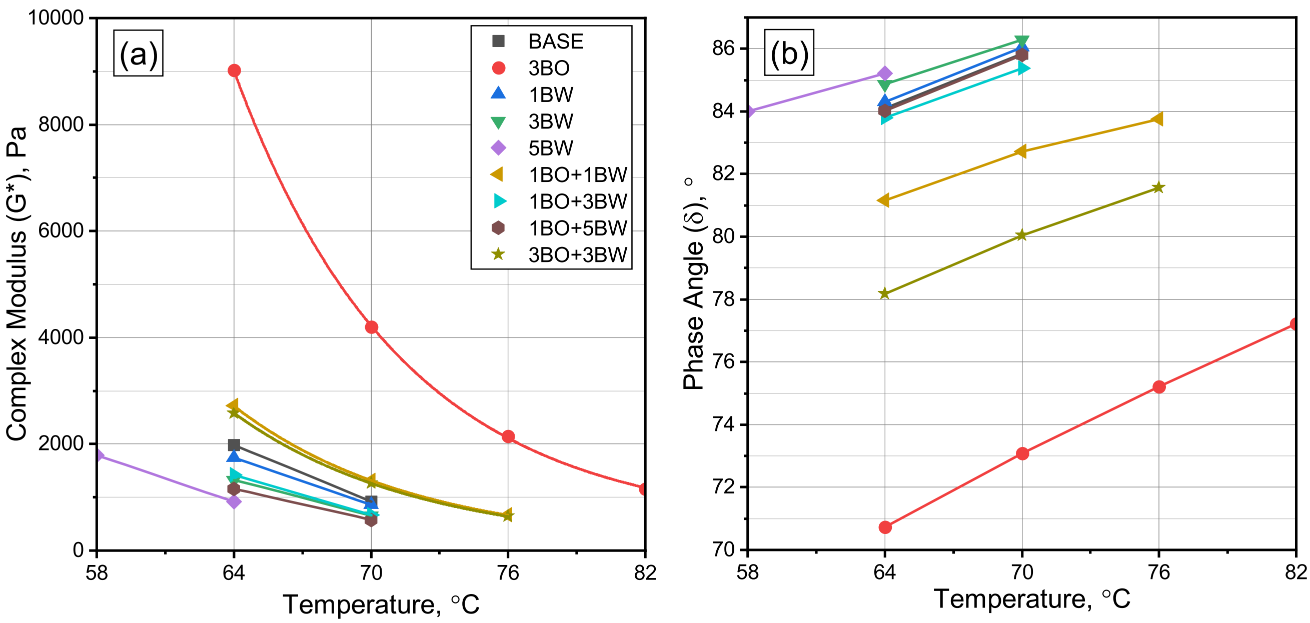

Fig. 8 DSR test results of unaged samples: **a** complex modulus and **b** phase angles

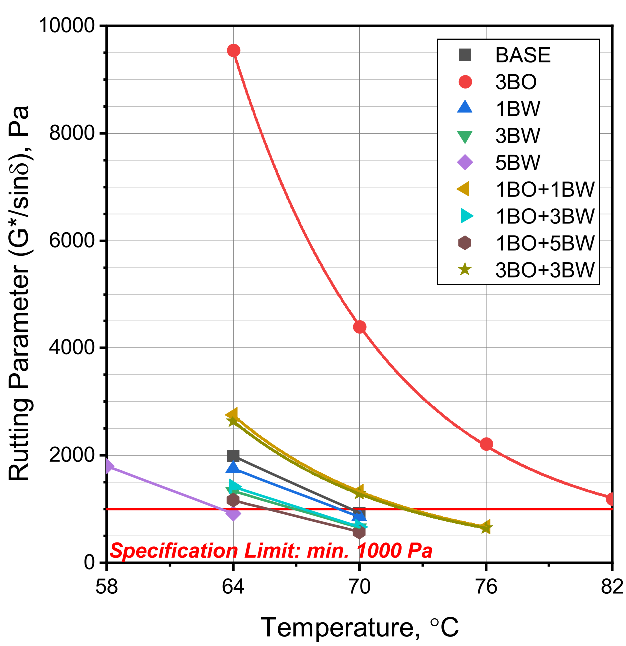

Fig. 9 Rutting parameters of unaged samples

When the G*/sinδ parameters of bitumens are compared with the specification criteria (Fig. 9), all bitumen samples are at 58 °C, except for BW at 64 °C; 3BO, 1BO + 1BW, and 3BO + 3BW at 70 °C; and only 3BO at 76 °C and 82 °C met the specification criteria.

4.5.2 DSR Test Results of Aged Binders

G* and δ values of RTFO aged samples are given in Fig. 10. Compared to the BASE, like unaged binders, 3BO, 1BO + 1BW, and 3BO + 3BW bitumens gave a higher G* value, while other modified bitumens gave lower. Similar to unaged binders in terms of δ, all bitumen samples containing BO have lower values than the BASE, while 1BW, 3BW, and 5BW samples have higher values. Hence, it can be concluded that BO and BW maintain their effects on bitumen after short-term aging.

When the G*/sinδ parameters of the RTFO aged samples are examined (Fig. 11), it is seen that all bitumen samples at 64 °C, 3BO, 1BO + 1BW, and 3BO + 3BW at 70 °C, and only 3BO at 76 °C met the specification criteria (2.2 kPa).

G*·sinδ parameters of PAV aged bitumens are given in Fig. 12. When this figure is examined, it is seen that 1BW shows a lower G*·sinδ than BASE, unlike 3BW and 5BW. This result shows that adding 1% BW to BASE has an improving effect on fatigue resistance, but adding BW at increasing rates has a negative effect. However, further research is needed to make a more precise judgment about the effect of adding low rates of BW to BASE on fatigue resistance and to determine the optimum BW contribution rate for fatigue resistance. On the other hand, although all bitumen samples containing BO met the specification criteria (maximum 5000 kPa) at tested temperatures, they have a higher G*·sinδ value than BASE. This result shows that the addition of BO negatively affects the fatigue resistance of BASE, but this effect remains at a level that does not exceed the specification limit.

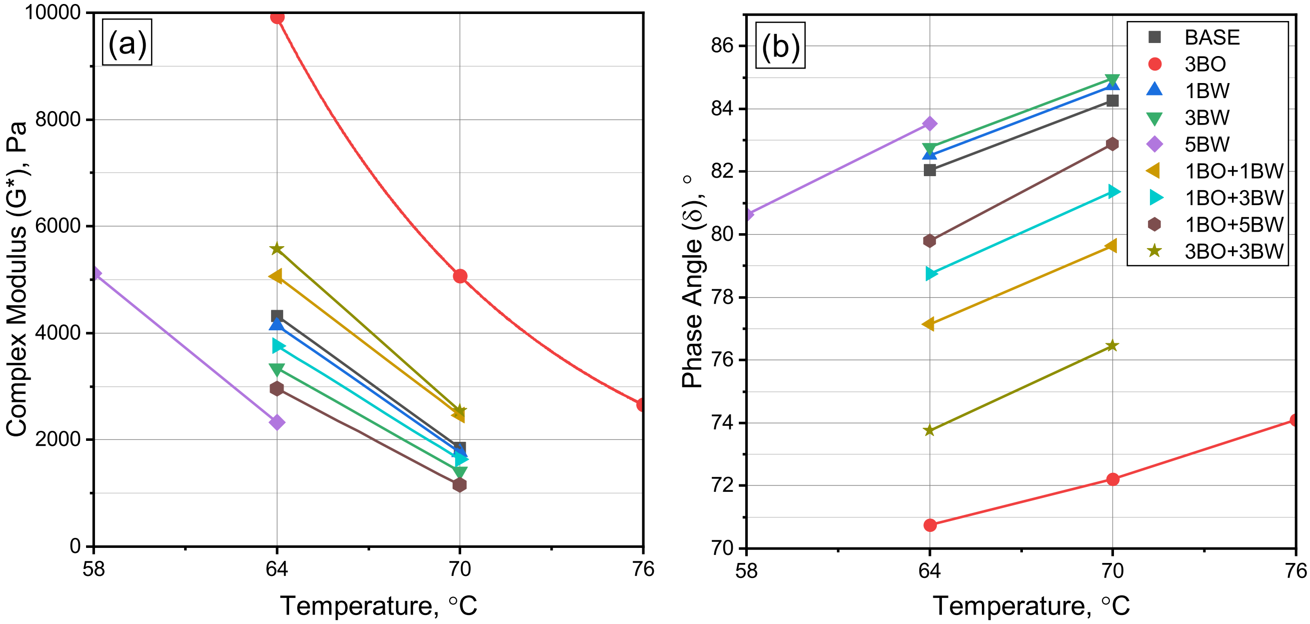

Fig. 10 DSR tests result of RTFO aged samples: **a** complex modules and **b** phase angles

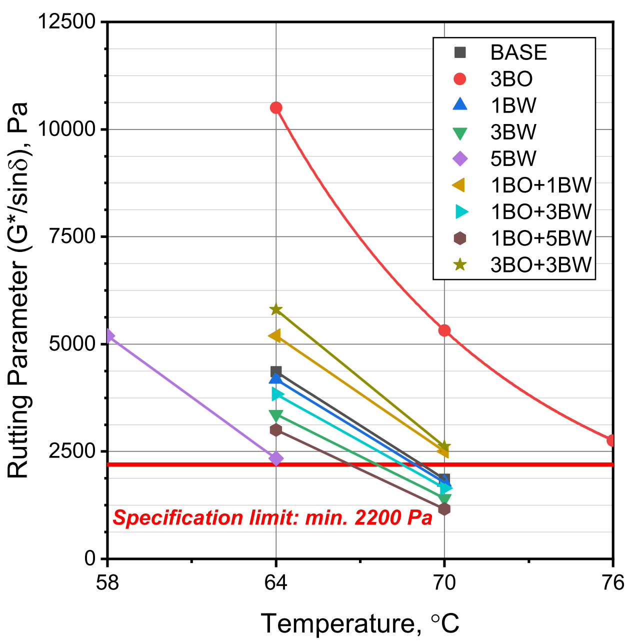

Fig. 11 Rutting parameters of RTFO aged samples

4.6 Performance Grades

In this study, bitumen samples were classified using the results obtained from DSR tests. Firstly, the performance grades (PGs) of the bitumen samples, which are expressed with 6 °C temperature ranges, were determined according to the Superpave classification. Secondly, the continuous grades (CGs) of samples, the temperature at which the G*/sinδ parameter is equal to the Superpave specification limit value (for unaged 1.0 kPa and RTFO-aged 2.2 kPa) were calculated.

The PGs and CGs calculated for unaged samples at high temperatures are shown in Fig. 13a. In this figure, it is seen that there is a significant increase in the high-temperature performance of the BASE with the addition of BO. While the PG of BASE did not change with adding 1% and 3% BW, it decreased with adding 5% BW. For bitumen samples containing BO and BW, 1BO + 1BW and 3BO + 3BW outperform BASE, while PG of 1BO + 3BW and 1BO + 5BW is the same as the BASE. When the CGs in Fig. 13a are examined, it is seen that the CG of the BASE increases significantly with the addition of BO but decreases in parallel with the addition of BW. CG of the BASE increased by about 14 °C with 3% BO, while it decreased by approximately 6 °C with 5% BW. When CGs of bitumen samples containing both additives are examined, it is seen that 1BO + 1BW and 3BO + 3BW are about 4 °C higher, and 1BO + 3BW and 1BO + 5BW are 2 °C and 4 °C lower, respectively, compared to the BASE.

Figure 13b shows the PGs and CGs of RTFO-aged samples. Compared to unaged samples, PG of the 5BW increased by one grade, while PG of 3BO decreased by one grade and the other samples retained the PGs. However, the performance of 3BO is still significantly superior to the BASE. When the CGs of samples are examined, the CG of 3BO is the highest and that of 5BW the lowest among all samples. Compared to the BASE, the CG of 3BO is 8 °C higher, and that of 5BW is 5 °C lower.

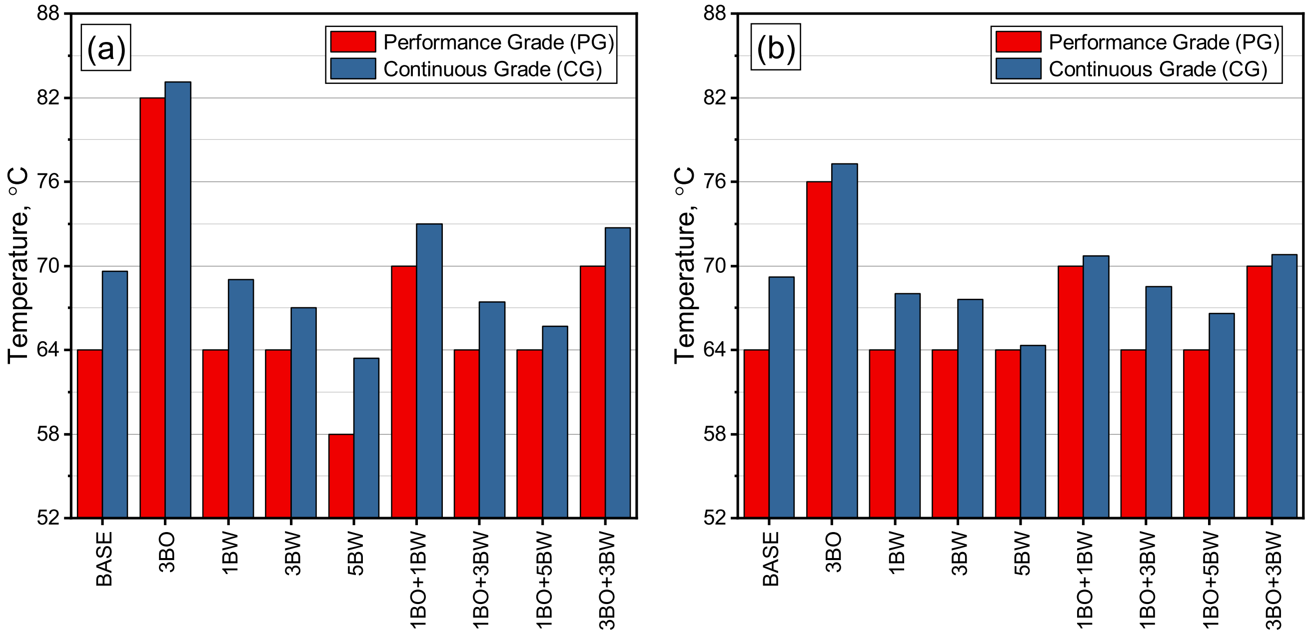

Fig. 13 High-temperature grades: **a** unaged samples **b** RTFO aged samples

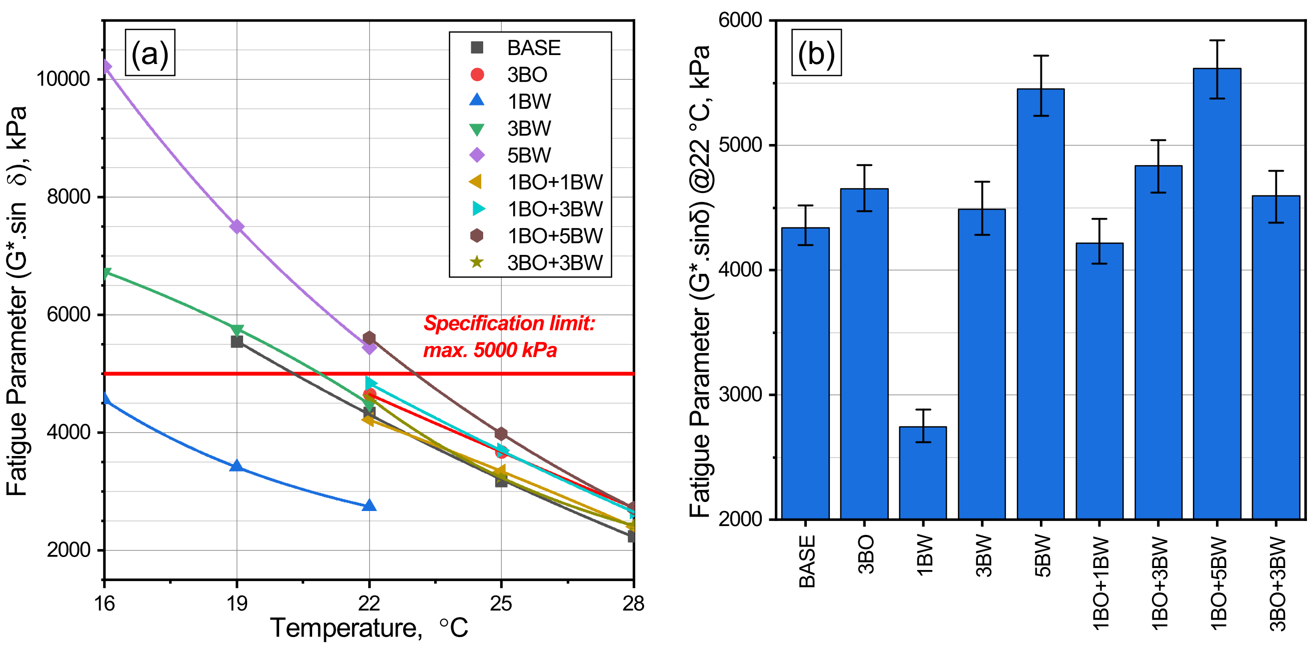

Fig. 12 Fatigue parameters of bitumen samples

4.7 Combined Evaluation of DSR and RV Tests

Bitumen with a high rutting parameter and a low viscosity has both good deformation resistance at high temperatures and good workability during the production of bituminous mixtures. A performance criterion can be determined by utilizing the DSR and RV test results to quantitatively evaluate this desired condition for the performance and production of the pavement. In this context, the G*/sinδ (G) value of bitumen at 64 °C is divided by the viscosity value at 135 °C, and the G/V performance criterion is calculated [7, 63, 64]. A high G/V value indicates that the bitumen has high resistance to permanent deformation and good workability for production. In this study, the G/V performance criterion of bitumen were calculated and given in Fig. 14. When this figure is examined, it is seen that 3BO has the highest G/V value and 5BW has the lowest G/V value. In bitumens containing both additives, the G/V values of 1BO + 1BW and 3BO + 3BW are

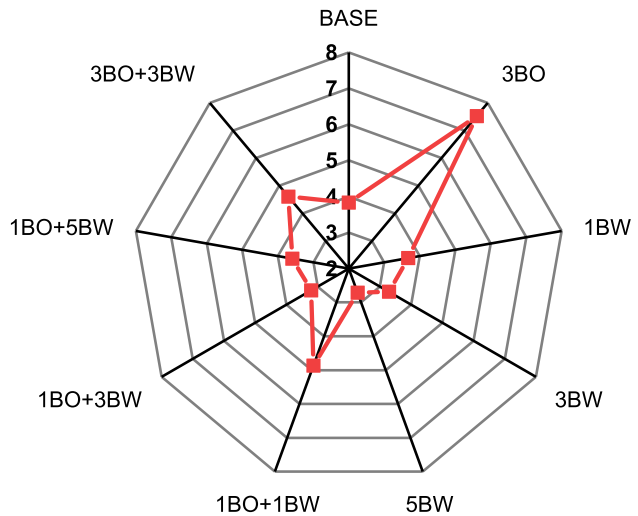

Fig. 14 Variation of G/V performance criterion

higher than BASE, while other bitumens are close to BASE. G/V performance criteria of 1BO + 1BW and 3BO + 3BW bitumens are 27% and 20% higher than BASE, respectively. Hence, it can be concluded that the rutting resistance and workability of the bitumen will be good with the addition of BO and BW in the same ratios to the base bitumen.

4.8 Statistical Evaluations

In the study, statistical analyses were applied on duplicate samples used in 4 different experiments. The experimental results to be used were determined as the results obtained from penetration, softening point, RV at 135 °C and DSR at 64 °C. For each experiment, statistical analyses were carried out between the results of the respective experiment.

The results of the ANOVA analyses are given in two different tables (Tables 3 and 4). Firstly, Table 3 gives an overview of the descriptive statistics and ANOVA results of the experimental results data. It was determined that each sample had a statistically significant difference in the result obtained from the relevant experiment compared to the other samples ($p < 0.001$). On the other hand, groups were obtained according to Tukey tests. The groups obtained are indicated by numbers and it is stated that the samples with the same number do not have a statistically significant difference. Accordingly, when the penetration test results are analyzed, there is no statistical difference between the averages of 5BW and 1BO + 1BW specimens. However, these specimens differ from the other specimens. In the softening point test, there is no statistical difference between the means of 5BW, 1BO + 1BW, 1BO + 3BW, and 1BO + 5BW specimens. On the other hand, although 1BW sample is similar to BASE and 3BW samples in terms of mean values, 3BW and BASE are statistically different from each other.

When evaluated for the RV results of another experiment, the mean of 5BW and 1BO + 5BW, 1BO + 1BW and 3BO + 3BW specimens are statistically similar. In addition, the 5BW specimen also shows similarity with BASE. On the other hand, although 1BO + 3BW is similar to 3BW and 1BW, these two samples are statistically different from each other. Moreover, the 1BW sample is also similar to BASE. Finally, according to the DSR test results at 64 °C, the 5BW sample is similar to 1BO + 5BW. The 1BO + 5BW sample is also similar to the 1BO + 3BW and 3BW samples, but these samples are statistically different from the 5BW sample. In addition, the 1BO + 3BW sample is also similar to the 1BW sample. The 1BW sample is also similar to the BASE sample in terms of mean. Also, the 1BO + 1BW sample and the 3BO + 3BW sample are statistically similar. However, the 3BO sample is statistically different from all other sample groups.

Table 4 shows the results of the two-way comparison carried out to statistically compare the effects of bitumen modification on neat bitumen. According to the results of the penetration test, the BASE sample and all other sample groups are statistically different. On the other hand, according to the results of the softening point test and DSR results at 64 °C, no statistical difference can be observed between BASE and 1BW, while the other samples are statistically different from BASE. In addition, according to the RV test results at 135 °C, there is no difference between BASE-1BW, BASE-1BO + 1BW, BASE-3BO + 3BW.

5 Conclusions

In this study, the effects of BO and/or BW on the chemical, physical, and rheological properties of base bitumen were investigated by adding different amounts of these additives to 50/70 penetration graded base bitumen. For this purpose, chemical analyses and conventional and rheological tests were applied to prepared bitumen samples. Results received from these tests and analyzes are summarized below:

- When the FT-IR spectrums of base and modified bitumen are compared, it is observed that a new peak occurs at approximately 1700 cm^{-1} in BW modified bitumens. On the other hand, no significant changes were observed in spectrums of BO-modified bitumen, except for peaks from BASE and BO content. In terms of quantitative indices calculated from FTIR results, $I_{c=o}$ and $I_{s=o}$ indices decrease significantly with the addition of the BO, while they increase with the addition of BW. On the other hand, MI increased with the addition of both additives to bitumen and the effect of BO was more pronounced.

Table 3 Descriptive statistics and ANOVA resulst

Test	Sample codes	Mean ± Std. Dev	SEM	F	*p*	Groups
Penetration	BASE	51.30 ± 0.96	0.557	525.748	< 0.001	8
	3BO	30.07 ± 0.25	0.145			2
	1BW	48.13 ± 0.85	0.491			7
	3BW	46.07 ± 0.25	0.145			6
	5BW	42.03 ± 0.49	0.285			5
	1BO + 1BW	40.43 ± 0.97	0.561			5
	1BO + 3BW	38.00 ± 0.53	0.306			4
	1BO + 5BW	36.03 ± 0.31	0.176			3
	3BO + 3BW	27,06 ± 0.05	0.031			1
Softening Point	BASE	50.00 ± 0.48	0.242	229.402	< 0.001	1
	3BO	64.00 ± 0.5	0.248			5
	1BW	51.00 ± 0.44	0.220			1, 2
	3BW	52.00 ± 0.7	0.349			2
	5BW	54.00 ± 0.57	0.286			3
	1BO + 1BW	54.40 ± 0.28	0.141			3
	1BO + 3BW	54.80 ± 0.94	0.471			3
	1BO + 5BW	55.00 ± 0.26	0.129			3
	3BO + 3BW	58.00 ± 0.5	0.248			4
Rotational Viscosity@135 °C	BASE	520.00 ± 10.64	6.144	525.542	< 0.001	4, 5
	3BO	1268.70 ± 47.38	27.355			6
	1BW	476.67 ± 16.62	9.593			3, 4
	3BW	405.83 ± 12.34	7.126			2
	5BW	338.33 ± 9.75	5.630			1
	1BO + 1BW	564.20 ± 22.48	12.978			5
	1BO + 3BW	444.17 ± 17.57	10.142			2, 3
	1BO + 5BW	324.20 ± 2.88	1.665			1
	3BO + 3BW	572.50 ± 21.86	12.619			5
Rutting parameter @64 °C	BASE	1993 ± 84.54	48.809	1494.21	< 0.001	4
	3BO	9553 ± 324.07	187.104			6
	1BW	1752 ± 58.28	33.650			3, 4
	3BW	1335 ± 32.6	18.824			2
	5BW	917 ± 38.74	22.368			1
	1BO + 1BW	2748 ± 33.41	19.287			5
	1BO + 3BW	1423 ± 47.03	27.154			2, 3
	1BO + 5BW	1163 ± 38.51	22.234			1, 2
	3BO + 3BW	2639 ± 81.02	46.776			5

- As a result of DSC analysis, it has been determined that the melting temperature of the BW is lower than the mixing temperatures of the bitumen. Therefore, it is thermally suitable to be mixed with bitumen.
- The conventional test results show that both additives decrease the penetration of the bitumen and increase the softening point. Compared to BASE, 3BO, 3BW, and 3BO + 3BW have 41.2%, 9.8%, and 47% lower penetration and 28%, 4%, and 16% higher softening points, respectively. From these results, it can be concluded that the hardening effect of BO on base bitumen is more pronounced.
- It was determined that the viscosity of the BASE increased with the addition of BO but decreased in parallel with the addition of BW. By increasing the mixing and compaction temperatures, BO can increase the energy consumed during the construction of the pavement layer, resulting in more carbon emissions. On the other hand, it is thought

Table 4 Comparison results of the modified bitumen with the BASE

Test	Reference	Sample codes	Mean difference	Sig
Penetration	BASE	3BO	21.23	< 0.001
		1BW	3.17	< 0.001
		3BW	5.23	< 0.001
		5BW	9.27	< 0.001
		1BO + 1BW	10.87	< 0.001
		1BO + 3BW	13.30	< 0.001
		1BO + 5BW	15.27	< 0.001
		3BO + 3BW	24.24	< 0.001
Softening point	BASE	3BO	− 14.00	< 0.001
		1BW	− 1.00	0.253
		3BW	− 2.00	< 0.001
		5BW	− 4.00	< 0.001
		1BO + 1BW	− 4.40	< 0.001
		1BO + 3BW	− 4.80	< 0.001
		1BO + 5BW	− 5.00	< 0.001
		3BO + 3BW	− 8.00	< 0.001
Rotational Viscosity@135 °C	BASE	3BO	− 748.70	< 0.001
		1BW	43.33	0.311
		3BW	114.17	< 0.001
		5BW	181.67	< 0.001
		1BO + 1BW	− 44.20	0.289
		1BO + 3BW	75.83	0.010
		1BO + 5BW	195.80	< 0.001
		3BO + 3BW	− 52.50	0.133
Rutting Parameter@64 °C	BASE	3BO	− 7560.00	< 0.001
		1BW	241.00	0.312
		3BW	658.00	< 0.001
		5BW	1076.00	< 0.001
		1BO + 1BW	− 755.00	< 0.001
		1BO + 3BW	570.00	< 0.001
		1BO + 5BW	830.00	< 0.001
		3BO + 3BW	− 646.00	< 0.001

that BW may have an environmentally friendly effect by increasing the workability of the BASE.

- It was determined that the rutting resistance of the BASE at high temperatures improved significantly with the addition of BO, while it decreased with BW. The negative effect of BW on rutting performance is thought to be due to its melting point and chemical composition.
- It was observed that the fatigue resistance of BASE slightly decreased with the addition of BO. On the other hand, the fatigue performance of bitumen increased with the addition of 1% BW but decreased at higher ratios.
- It was determined that the PG and CG of base bitumen increased significantly with the addition of BO however decreased with the addition of BW. On the other hand, with the addition of two additives to the BASE in the same ratio, while the PG and CG of bitumen increased, bitumen containing higher ratios of BW (1BO + 3BW and 1BO + 5BW) gave results close to the BASE.
- When the G/V performance criteria were calculated, it was determined that 3BO had the highest value and 3BW had the lowest. In addition, from the G/V values of the 1BO + 1BW and 3BO + 3BW bitumens, it was determined that both the rutting resistance and the workability of these bitumens could be high.
- When the ANOVA analysis results were evaluated in general terms, it was determined that each sample showed a statistically significant difference compared to the other samples. As for the groups obtained according to Tukey

tests, there was no significant difference between the same number of samples. On the other hand, when modified bitumens were statistically compared to BASE, it was determined that BASE and all other sample groups were statistically different in terms of penetration test results. In the softening point and DSR test results, it was seen that there was no statistical difference between BASE and BW, but the other samples were statistically different from BASE. Finally, when the RV test results were evaluated, it was observed that there was no statistical difference between BASE-1BW, BASE-1BO + 1BW, BASE-3BO + 3BW.

Adding BO to base bitumen can increase high-temperature performance and viscosity. On the contrary, with the addition of BW, the workability can be improved while the rutting resistance can be reduced. By adding BO and BW together to the BASE, both the negative effect of BO on workability and the negative impact of BW on high-temperature performance can be eliminated. Thus, environmentally friendly bitumen with high rutting resistance can be obtained. In addition, it is thought that using BO + BW modified bitumen in areas subject to high service temperatures may be beneficial. In future studies, investigating the low-temperature performance of BO + BW modified bitumen and the performance of asphalt mixtures prepared with these bitumens with various tests will contribute to the literature.

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