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Evaluation of the Rheological Properties of Bituminous Binders Modified with Biochars Obtained from Various Biomasses by Pyrolysis Method

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***Abstract*—**In this study, apricot seed shell, walnut shell, and sawdust were chosen as biomass sources. The materials were sorted by using a sieve No. 50 and the sieved materials were subjected to pyrolysis process at 400 °C, resulting in three different biochar products. The resulting biochar products were added to the bitumen at three different rates (5%, 10% and 15%), producing modified bitumen. Penetration, softening point, rotation viscometer and dynamic shear rheometer (DSR) tests were conducted on modified binders. Thus the modified bitumen, which was obtained by using additives at 3 different rates obtained from biochar produced at 400 °C temperatures of 3 different biomass sources were compared and the effects of pyrolysis temperature and additive rates were evaluated. As a result of the conducted tests, it was determined that the rheology of the pure bitumen improved significantly as a result of the modification of the bitumen with the biochar. Additionally, with biochar additive, it was determined that the rutting parameter values obtained from softening point, viscometer and DSR tests were increased while the values in terms of penetration and phase angle decreased. It was also observed that the most effective biomass is sawdust while the least effective was ground apricot seed shell.

***Keywords*—**Rheology, biomass, pyrolysis, biochar.

I. Introduction

HOT-mix asphalts (HMA) used in highway pavements is one of the most conspicuous and studied fields in highway constructions due to their high cost. HMAs that are not prepared with suitable materials, under suitable conditions and in suitable fashions cause reduction in the service lives of highway pavements and thus cause problems in terms of security, comfort and economics.

Bitumen, a petroleum product, is usually obtained following the refining of petroleum. Declining oil reserves and problems experienced in countries with oil bring about an increase in the price of the oil and due to this factor; studies conducted on this topic are of great importance [1]. Thus, materials as alternatives to bitumen or inclusion of additives in order to improve the service lives of pavements are studied at a growing number every day. The resultant concerns about environment, reserves and economics of using petroleum-based materials raised the need for utilizing various alternative materials in the highway industry.

Biomass, which is one of the widest and most sustainable sources in the world, is a significant renewable energy source due to its stable carbon content just as petroleum-based materials. Biomass can be used in place of traditional petroleum products following the applications of various thermochemical methods [2]. Biomass sources are classified as agricultural (vegetable, animal and water) forest (sawdust, bark and pinecone), urban and industrial (municipality garbage dump sites, sewage and industrial wastes) based sources. Sources of biomass are presented in Fig. 1.

In this study, asphalt additives were attempted to be produced from biomasses of ground apricot seed shells, ground walnut shells and sawdust biomass. Approximately 3.500.000 tons of fresh apricots are being produced in the world. Turkey is at the top of the apricot production with approximately 20% share. Turkey is followed by Pakistan, Iran, Uzbekistan and Italy in apricot production. The seed shell constitutes a 20% portion of a fresh apricot. This fact suggests that approximately 700.000 tons of apricot seed occur in our country on a yearly basis. The economic value of the apricot seed shell is low and it is used for domestic heating [3]. Turkey is the 4th country in the walnut production, following the USA, China and Iran, with approximately 200.000 tons of walnut and 100.000 tons of shelled walnuts produced annually and meets the 6% portion of the walnut production demand of the world [4]. Walnut, which is the 2nd most produced hard-shelled fruit in Turkey after hazelnut, was produced at approximately 136.000 tons in 2002. This amount is 177.298 tons according to Turkey's walnut production data. The estimated amount for the walnut's shells is 48.4% (85.847 tons) for the walnuts produced in Turkey. Because the economic value of the walnut shell is low it is generally used as low-calorie fuel in industrial facilities, bakeries and breeding farms for heating purposes [5]. The biomass sources that can be used for bioenergy in Turkey's forests are approximately 5-7 million tons [6]. These wastes are used for heat generation in factories unless there is a more profitable possibility arises [7].

Organic materials' (biomasses') thermochemical degradation process in an anaerobic environment is called pyrolysis (carbonization). As a result of heat treatment, gases such as methane and hydrogen originate and the organic material turns into a structure such as that of petroleum or its derivatives [8]. Pyrolysis can be conducted in three manners as slow, fast and immediate (flash). The fact that a significant amount of biomass comprises of natural polymers suggests that this material can be used together with bituminous binders

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and mixtures after being subjected to appropriate thermochemical processes. These alternative binders, which are both sustainable and ecologically friendly in terms of highway industry, are called bioasphalts. Various research industries established in several European countries and especially in the USA have been conducting researches in order to produce biomasses and bioasphalts from the biowastes [9]-[13]. Besides, various studies are conducted on the use of biochar and bio-oils, which are obtained from the pyrolysis of the agricultural and natural wastes, in place of bituminous binders or as additive materials to bitumen. The studies conducted on this subject are new and up to date, and emerged after the 2000s in the international field. As a result of several studies conducted on this matter, it was determined that biochars can be used in place of bituminous materials or as additive materials to bitumen [14]-[20].

Fig. 1 Biomass sources

Fig. 2 Pyrolysis device

In this study, unlike previous studies, ground apricot seed shell, ground walnut shell and sawdust were sieved with a No.50 sieve and then the sieved materials were subjected to pyrolysis. Biochars, which were obtained from the pyrolysis of 3 different biomasses were included in pure bitumen at 3 different rates and modified bitumens were acquired. On pure bitumen and 9 different modified bitumens, penetration, softening point, rotational viscosity (at 135 and 165 °C) and DSR tests were applied in an attempt to determine the effects of biochars on the rheological properties of the bituminous binders.

A. Materials

In this study, asphalt cement, PG 58-34, obtained from Turkish Petroleum Refineries was used as the pure binder. Additionally, the biomass sources, apricot seed shell, walnut shell, and sawdust were obtained from Alesta Naturel and Tersun Limited. The biomasses were sieved by using a No.50 mesh sieve. Furthermore, the slow pyrolysis device, which was specifically manufactured for the study and presented in Fig. 2, was used in this study. 1000 g biomass was placed in the pyrolysis plate and kept at 400 °C for 1 hour. The gas exhaust was conducted with the help of a pipe and the bio-oil was obtained by condensing the exhaust gas via a special apparatus. When the gas exhaust concluded, the device was left for cooling and when the room temperature was reached, the lid was opened to obtain the carbonized product, biochar. By subjecting the same-sized materials to the pyrolysis process at the same temperature, the effects of size and temperature on the samples' properties were prevented. The obtained biochars were placed in containers and were covered in order to prevent air contact, and they were kept in an environment that was at room temperature and away from sunlight until the modification process. Modified bitumens were prepared by using biochars at 5%, 10% and 15% portions according to the weight of the pure bitumen. The abbreviations for the modified bitumen were presented below. For the purpose of preparing the modified binders, the pure bitumen and additives were mixed for 60 minutes at 180 °C inside a mixer with a rotation rate of 2,000 rpm (Fig. 3).

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Fig. 3 High shear mixer

After completion, the samples were removed from the flask and were divided into small containers, covered with aluminum foil and stored for testing.

TABLE I
ABBREVIATION OF MODIFIED BINDERS

Biochar type	Additive ratio (%)		
	%5	%10	%15
Walnut shell	5%WS	10%WS	15%WS
Apricot seed shell	5%AS	10%AS	15%AS
Sawdust	5%SD	10%SD	15%SD

B. Method

Following the preparation of the modified bitumen samples, conventional test methods (penetration, softening point and rotational viscosity) and dynamic mechanical analysis were performed on each of the modified bitumen samples.

In this study, the penetration test was conducted according to the EN 1426 standards while the softening point test was conducted according to the EN 1427 standards and the viscosity test was conducted according to the ASTM D4402 standards. The mixing and compaction temperatures were determined for binders by using 170 ± 20 and 280 ± 30 cP viscosity values, respectively. In addition, the temperature susceptibility of the modified bitumen samples was calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests. Temperature susceptibility is defined as the change in the consistency parameter as a function of temperature. A classical approach related to PI was given in the Shell Bitumen Handbook [21] as shown with:

$$PI = \frac{1952 - 500 * \log(Pen_{25}) - 20 * SP}{50 * \log(Pen_{25}) - SP - 120} \quad (1)$$

where, Pen_{25} is the penetration at 25 ^{o}C and SP is the softening point temperature of PMB.

At present the most commonly used method of fundamental rheological testing of bitumen is by means of dynamic mechanical methods using oscillatory-type testing, generally conducted within the region of linear viscoelastic (LVE) response. These oscillatory tests are undertaken using DSRs.

The DSR test was performed on neat and modified bitumens by using a Bohlin DSRII Air Bearing rheometer. In the study, the original binder performance level high-temperature values were determined by the Superpave method. For this purpose, bitumen samples with 25 mm diameter and 1 mm gap geometry were subjected to tests at different temperatures. The principal viscoelastic parameters obtained from the DSR are the magnitude of the complex shear modulus (G^*) and phase angle (δ). G^* is defined as the ratio of maximum (shear) stress to maximum strain and provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading. It contains elastic and viscous components, which are designated as (shear) storage modulus (G') and (shear) loss modulus (G''), respectively. The elastic and viscous components in consideration are connected to both the complex (shear) modulus and to each other through the phase (or loss) angle (δ). Namely, the phase or time lag between the applied shear stress and the shear strain responses during a test [22]. According to the Superpave binder agreement, in the original binder, the G*/sin δ value should be 1000 Pa at the related test temperature.

II. RESULTS AND DISCUSSION

A. Conventional Binder Test Results

Penetration values of biochar modified binders were presented in Fig. 4. As it can be seen in the figure, the penetration values decreased with additive use; thus, the rigidity of the binders increased. In the event of using the biochar obtained from the pyrolysis of ground walnut shell at 5%, 10% and 15% portions, the penetration values, compared to the pure binder, decreased by 14.4%, 8.7% and 16.4%, respectively. By using the biochar obtained from the pyrolysis of ground apricot seed shell as the additive at 5%, 10% and 15% portions, the penetration values, compared to the pure binder, decreased by 10.8%, 3.4% and 6.7%, respectively. Furthermore, by using the biochar obtained from the pyrolysis of sawdust in the bitumen modification 5%, 10% and 15% portions, the penetration values, compared to the pure binder, were decreased by 6.9%, 12.1% and 21.7%, respectively. The obtained results suggested that the most effective additive in terms of penetration values is the biochar obtained from the pyrolysis of sawdust (15% use) while the least effective one was the biochar obtained from the ground apricot seed at the rate of 10%.

The softening point values of the bituminous binders were presented in Fig. 5. As it can be observed in Fig. 5, the softening point values were increased with additive use, thus, it was determined that the biochars improved the high-temperature resistances of bituminous binders. With the increased amount of additive, the softening point values also increased regularly. By using the biochars obtained from the pyrolysis of ground walnut shell, the softening point values, compared to the pure binder, increased by 2.9% at 5% biochar content while at 10% biochar content, the increase was 4.8% in addition to the 8.7% increase at 15% biochar content. In the event of using the biochars obtained from the pyrolysis of the ground apricot seed shell for the bitumen modification at 5%, 10% and 15%, the softening point values, compared to the pure binder, increased by 0.7%, 2.9% and 6.2%, respectively. By using the biochar obtained from the pyrolysis of the sawdust at the same portions, the softening point values, compared to the pure binder, increased by 2.6%, 7.7% and 15.3%, respectively. The obtained results suggested that the biochars obtained from the pyrolysis of the sawdust as an additive at 15% produced the most effective result in softening point test just as it did in the penetration test.

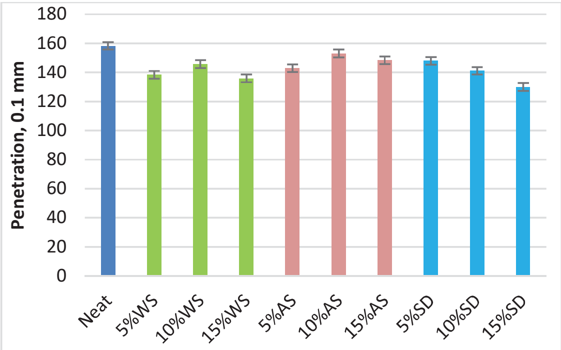

Fig. 4 Penetration values of pure and modified binders

The changes in the PI values, which were determined by the values of penetration and softening point test and were an indicator of the sensitivity of the bituminous binders to heat, were presented with additive type and the amount in Fig. 6. As it can be observed in Fig. 6, with increased amounts of additives, the PI of all of the modified bitumen increased and thus, the sensitivities of the bituminous binders to heat increased regularly. Additionally, it was observed that the process of using biochars obtained from the pyrolysis of ground walnut and apricot seed shells at a 5% biochar content rate produced modified binders with higher heat sensitivity, compared to pure bitumen while all of the other modifications yielded modified bitumen with lower heat sensitivity, compared to pure bitumen.

The rotational viscosity test results of the bituminous binders were presented in Table II. As it can be observed in the table, the viscosity values regularly increased with additive use. At both 135 °C and 165 °C temperatures, the additive with the highest viscosity increase was the biochar obtained from the pyrolysis of sawdust. It was determined that sawdust's biochar was more effective at 135 °C compared to 165 °C. In the investigation of the mixing with aggregate and compaction temperatures of the bituminous binders, it was determined that with additive use, higher temperatures were needed and thus, more energy would be necessary. Especially in the event of using the biochar obtained from sawdust pyrolysis at 15%, in order to mix the bitumen with aggregate, a 25 °C higher temperature would be necessary compared to the pure bitumen.

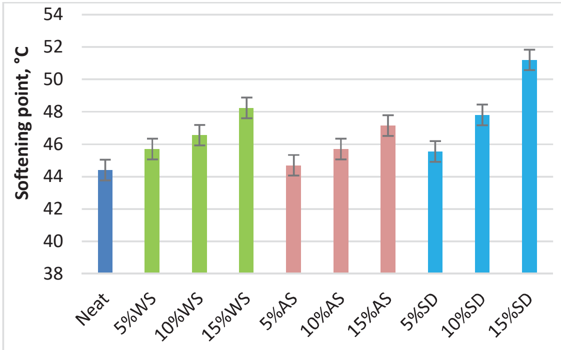

Fig. 5 Softening point values of pure and modified binders

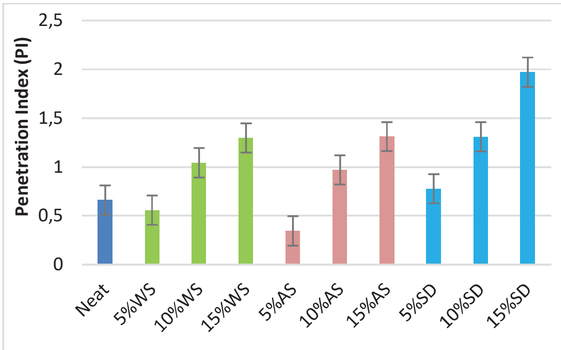

Fig. 6 PI values of the mixtures

TABLE II
ROTATIONAL VISCOSITY TEST RESULT

Properties	Standard	Neat	5% WS	10% WS	15% WS	5% AS	10% AS	15% AS	5% SD	10% SD	15% SD
Viscosity (cP, 135°C)	ASTM D4402	237,5	337,5	425	562,5	312,5	362,5	500	387,5	612,5	1138
Modification index @135 °C (η_{MB}/η_{base})		1,00	1,42	1,79	2,37	1,32	1,53	2,11	1,63	2,58	4,79
Viscosity (cP, 165°C)		87,5	112,5	137,5	187,5	125	125	162,5	137,5	187,5	350
Modification index @165 °C (η_{MB}/η_{base})		1,00	1,29	1,57	2,14	1,43	1,43	1,86	1,57	2,14	4,00
Mixing temperature range (°C)	-	142,9-150,1	135,9-141,7	141,9-147,6	149,7-155,5	133,3-140,2	141,4-147,5	149,6-155,4	139,6-145,7	154,1-159,6	169,4-174,9
Compaction temperature range (°C)	-	128,1-134,6	149,1-155,5	154,8-161,0	163,1-169,3	149,0-156,7	155,4-162,1	162,8-169,2	153,6-160,3	166,6-172,7	182,0-188,0

B. DSR Test Results

Within the scope of this study, performance grade high-temperature values unaged (original) pure and modified bitumen were determined according to the Superpave method.

Thus, in accordance with the agreement, the pure binder was subjected to test at 3 different temperatures (52 °C, 58 °C and 64 °C) while the modified bitumen were subjected to tests at 4 different temperatures (52 °C, 58 °C, 64 °C and 70 °C). The changes in the complex module value (G*) obtained from the conducted tests were presented in Fig. 7 while the changes in the phase angle values were presented in Fig. 8 and the changes in the rutting parameter values (G*/sin δ) were presented in Fig. 9.

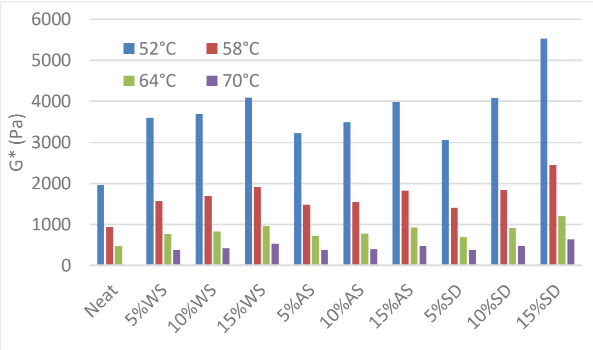

Fig. 7 Changes in the complex module values with additive type

In the evaluation of the complex shear module values, it was determined that with increased temperatures the G* value decreased and with additive use, these values were regularly increased and thus, with additive use, a benefit can be obtained in terms of resistance to shear. In the comparison of the complex shear modules, the most effective one was determined to be the biochar of sawdust while the least effective was that of the ground walnut shell. Furthermore, it was also determined that 10% sawdust biochar modification and 15% ground walnut shell and apricot seed shell biochar modifications had similar effects in terms of the G* value.

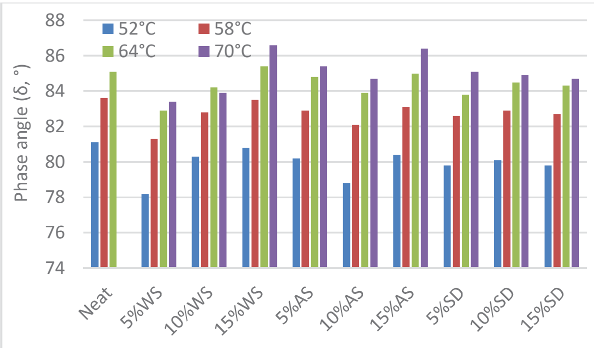

Fig. 8 Changes in the phase angle values with additive type

The phase angle value varies between 0 and 90 and the event when it is closer to 0, indicates that the elasticity is higher while the event when it is closer to 90, indicates that it is closer to viscous behavior. As it can be observed in Fig. 8, with increased temperatures, the phase angle values were regularly increased and thus, the binders exhibited more viscous behaviors. The fact that pure binders had the highest phase angles at every temperature indicates that additive use increases the elasticity.

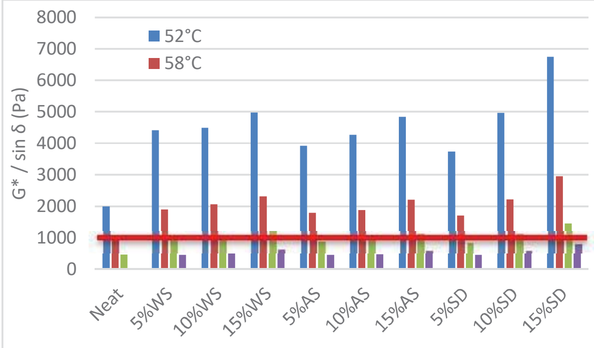

Fig. 9 Rutting parameters of the binders

In the investigation of the rutting parameters (G*/sin δ) presented in Fig. 9, it was determined that these values were regularly increased with additive use while with increased temperatures, they were regularly deceased. According to Superpave method, it is evaluated whether the original binders provide the value of 1000 Pa, which is the rutting tolerance value. It has been determined that all binders provide this value at 52 °C. Furthermore, the agreement criteria value was also provided by every modified binders at 58 °C temperature, except the pure binder while it was provided at 64 °C by 4 modified binders (15% ground walnut shell biochar, 15% ground apricot seed shell biochar, 10% and 15% sawdust biochar modified bitumens). At 70 °C temperature, none of the binders met the agreement criteria. According to the obtained results, it was determined that with biochar materials used as additive, the resistance of bituminous binders to rutting would increase and the most effective additive material was the sawdust biochar.

III. Conclusions

In this study, modified bitumens were prepared by adding biochars obtained from the pyrolysis of various biomasses (walnut shell, apricot seed shell and sawdust) at 3 different rates (according to the weight of the bitumen at 5%, 10% and 15%). Penetration, softening point, rotational viscosity and DSR tests were conducted on the modified bitumen.

It was determined that with additive use, penetration values were decreased while the softening point values increased and thus, the bituminous binders gained a hardener property and an improvement for high-temperature resistance. According to the PI values, it was determined that with additive use, the binders' sensitivities to heat were decreased.

The viscosity test results also indicated that additive use led to a reduction in the workability properties of the bituminous binders. Furthermore, the energy need was increased due to the increase in the process of mixing with aggregate. According to the DSR results, by using biomass biochars in the bitumen modification, the rutting resistances of binders were increased. In the comparison of the additive types, it was determined that the apricot seed shell biochars and walnut shell biochars had similar effects while the most effective additive type was that of sawdust biochar.

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