Effects of various biochars on the high temperature performance of bituminous binder

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ABSTRACT

Bituminous binders as one of the two main elements which constitute flexible pavement friction layers, are obtained through refining of petroleum. Highway industry is faced with the problem of gradually increasing prices and decreasing bituminous binders which are used in flexible pavement construction. Depending on the economic growth and population increase; new highways constructed due to constantly increasing transportation demand and maintenance of current roads result in increase of the amount of required bituminous binders. Economic and environmental problems caused by using fossil-based materials revealed the need of miscellaneous alternative materials to be considered in terms of sustainability in highway industry. Biomass is one of the greatest and renewable energy resources of the world. After applying pyrolysis to biomass, bio-chars has the potential of being used with conventional petroleum products. Vegetable based materials having the structure of hydrocarbon and renewability in short time exposed that these materials can be used as pavement materials. Liquid product obtained after pyrolysis is called as bio-oil, solid product is called as biochar. In this study, usability of biochars obtained through pyrolysis of walnut crust and apricot seed shell whose economic value is low, as additive for bituminous binders were investigated in order to improve the performance of highway pavements. Modified bitumen samples were produced by mixing base bitumen with biochars at three different additive contents. The conventional properties of the modified binders were evaluated in terms of their properties using penetration, softening point and dynamic viscosity tests. The fundamental viscoelastic properties of the modified binders were determined using dynamic (oscillatory) mechanical analysis and were presented in the form of temperature- and frequency-dependent rheological parameters. It was determined by the results obtained from the conventional tests that the softening point and the viscosity increased and the penetration and the thermal sensitivity decreased with increased biochar contents. Dynamic shear rheometer test results indicated that the complex modulus values of modified binders increased and phase angle values decreased with biochar usage. Test results are an indication that the biochars have promising potential to reduce the permanent deformation or rutting of asphalt pavements.

Keywords: Additives, Rheology, Waste

1. INTRODUCTION

Bituminous binders, one of the two main components that form flexible pavement courses, are obtained by refining the petroleum. A non-renewable resource, petroleum has reserves for only 48.8 years based on the 2012 data [1]. Highway industry faces the problems of the continuous reduction of bituminous binder resources, which are used in flexible pavement production and are a petroleum byproduct, and the increase in prices. Increasing demand for transportation due to economic development and increasing population fuels the demand for bituminous binders, which are required for building new roads and maintaining the existing ones. Economic and environmental problems induced by the use of fossil resources created a need for the assessment of various alternative materials in highway industry for sustainability.

Biomass, one of the largest and renewable energy sources on earth, has the potential for use with or in parallel to the conventional petroleum products after various thermochemical treatments [2]. The rapidly renewable properties and hydrocarbon structure of vegetative materials increased the prominence of these as pavement material. The most frequently used method to produce material with high economic value from agricultural biomass is pyrolysis. Pyrolysis (carbonization) is the thermochemical degradation of organic material in oxygen-free environment and under high temperatures. As a result of this degradation, products in solid, liquid and gas phases are obtained. The liquid product obtained as a result of pyrolysis is called bio-oil and the solid product is called bio-char.

Studies on the use of products obtained from the pyrolysis of agricultural biomass with bituminous binders started in the 2000's and there are several studies on the subject matter. These alternative binders that are both sustainable and ecological are called bio-asphalt by the highway industry. Various research industries in certain European countries and especially the USA conduct studies to produce bio-asphalt using biomass and bio-waste [3 – 7].

Yang et al. investigated the usability of bio-oil obtained from the pyrolysis of tree waste together with the bituminous binders in the study they conducted. Bio-oil obtained from the tree waste was added to neat bitumen in the rates of 5% and 10%, and Superpave binder tests were conducted on bio-modified binders. Results showed that use of bio-oil that was produced with tree waste decreased the viscosity of the bituminous binders and improved high temperature performance and affected the low temperature resistance adversely and increased ageing of the bituminous binders [8].

Lignin found in the structure of the bio-char obtained as a result of the pyrolysis of vegetable and organic waste could be used as a bio-polymer and has an inhibitor effect on the ageing of asphalt coatings. Use of bio-char with a 7% lignin content by binder weight decreases the ageing of bituminous binder significantly [9 – 11]. By addition of corn lignin to the bituminous binders in the rates of 3%, 6%, 9%, and 12%, 52 different binders were obtained. Results demonstrated that lignin use decreased ageing, rutting resistance increased and low temperature cracking resistance remained constant [12]. Bio-char obtained by the pyrolysis of switch grass plant (in the rates of 5%, 10%, 15%, and 20%) and a commercial product, active carbon (10%) were used as an additive in PG 64-22 performance degree neat bitumen, and the performance properties of the modified binders were investigated. Results of the study demonstrated that bio-char use was generally beneficial for the principal degradation types observed on the pavements. Active carbon modified binders demonstrated an increase in fatigue resistance, however no changes were observed with the bio-char modified binder, and it was determined that bio-char modified binders were more effective when compared to the commercial active carbon modified binders [13].

Bostancıoğlu scrutinized the availability of active carbon produced by chemical activation from nutshell waste and furan resin produced from furfural obtained by acidic hydrolysis of vegetal waste in bitumen modification. Test results demonstrated that both active carbon and furan resin increased the toughness, lowered temperature sensitivity, and developed rheological properties of the bitumen. Based on the results obtained from mixture experiments, both additives increased the rutting resistance and fatigue endurance under repeated loads of the mixtures [14].

Turkey, which is an agricultural country due to its geographical location and the climate, could cultivate various crops. As a result, great amounts of biomass are created in the agricultural lands (40-53 million tons per year). In this study, ground walnut shells and apricot seed shell granules, which are found in large amounts in Turkey and have little economic value, were sifted through a sieve No 200, and the process of pyrolysis was implemented to produce different bio-chars. These bio-chars were added to bitumen in 3 different ratios (5 – 10 – 15%) to obtain modified bitumen. Conventional and Superpave binder tests were conducted on the neat and modified binders. Thus, the effects of bio-chars produced via the pyrolysis of the biomass on the rheological properties of bituminous binders were assessed.

The objective of the study was to research the usability of bio-chars produced with the pyrolysis of ground walnut shells and apricot seed shell granules, which are found in large amounts in Turkey and have little economic value, with bituminous binders to improve the performance of highway pavements. The determination of its positive effects on bituminous binders would decrease or delay the maintenance and repair expenses of the roads. The study aims to create benefits in economic and environmental sustainability by utilizing these waste materials in a previously unchartered field.

2. MATERIALS AND METHODOLOGY

The study utilized B160/220 class bituminous binder procured from Batman TÜPRAŞ refinery as the main binder. Bio-chars produced by the pyrolysis (carbonization) of the filler that was sifted through a No 200 sieve of walnut and apricot seed shells procured from Elazığ as additive. Bio-char pyrolysis (carbonization) process was conducted in compliance with ASTM E 897-83 standard procedure. In the process, approximately 1 g sample (ground walnut or apricot seed shell) with 0.01 mg precision was placed in crucibles, which were brought to constant weigh; the crucible lid was closed and it was placed in muffle furnace at 900±50°C (Figure 2.1). The crucibles were kept in the furnace for 7 minutes and taken out and cooled in a desiccator and weighed. Volatile substance amount determination by the weight loss (including the moisture that the sample contains) and carbonized product (solid product) amount were identified using Equations 2.1 and 2.2.

Figure 2.1: Placement of the crucibles containing the samples in muffle furnace and the process of pyrolysis [15]

$$Volatile.Matters(\%) = (\frac{g_1 - g_2}{g_1}) \times 100 \quad (2.1)$$

$$Solid.Matters(\%) = 100 - (\frac{g_1 - g_2}{g_1}) \times 100 \quad (2.2)$$

where;

g_1= The weight of the sample used in carbonization test, (g)
g_2= The weight of the sample at the end of carbonization process, (g)

Carbonized products obtained were kept in lidded plastic containers until they were used in bitumen modification. Images of ground walnut and apricot seed shells before and after they were subjected to pyrolysis are shown in Figure 2.2.

(a) (b) (c)

Figure 2.2: Walnut shell grinded and sifted through No 200 sieve (a), the images of apricot seed shell granule before (b) and after (c) the pyrolysis

Modified bitumen were obtained by the addition of bio-chars produced by the pyrolysis (carbonization) process in the rates of 5%, 10%, and 15% per bitumen weight to the bitumen. Mixing temperature was selected as 180°C during the preparation of modified bitumen. Neat bitumen and the bitumen modified with the selected ratios of additive were stirred at 1000 rpm rate of rotation for 1 hour (Figure 2.3).

Figure 2.3. Modified bitumen mixer and mixing cap

Penetration (EN 1426), softening point (EN 1427), rotational viscometer (ASTM D 4402), and dynamic shear rheometer (AASHTO TP5) tests were conducted on the modified bitumen prepared. Modified bitumen containing 5%, 10%, and 15% ground walnut shell char were displayed as CW5%, CW10%, CW15%; %5, %10 and %15, in the figures; and modified bitumen containing 5%, 10%, and 15% ground apricot seed shell char were displayed as CA5%, CA10%, CA15% in the figures, respectively.

Results of the penetration tests conducted on binders are displayed in Figure 2.4. The figure demonstrates that the lowest penetration value was observed with the bitumen modified by 15% apricot seed shell and walnut shell, while the highest penetration value was obtained with the neat binder.

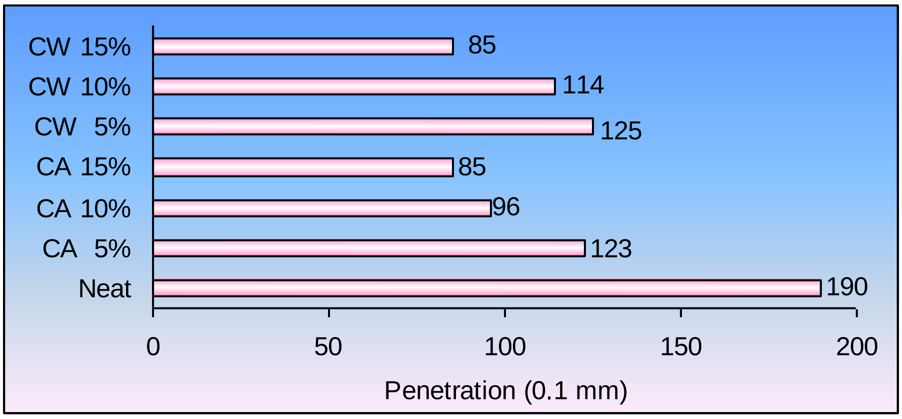


Figure 2.4: Change in binder penetration values with the additive type and content

It was determined with the penetration test results that when ground apricot seed or walnut shell chars were used in the modification of bitumen, the penetration values would decrease, increasing the stiffness of the binders. Test results obtained from the softening point tests conducted on binders are displayed in Figure 2.5. The figure shows that the highest softening point value was obtained with the bitumen modified with 15% granulated walnut shell char, while the lowest value was obtained with the neat binder. As the additive content increased, softening point values increased steadily.

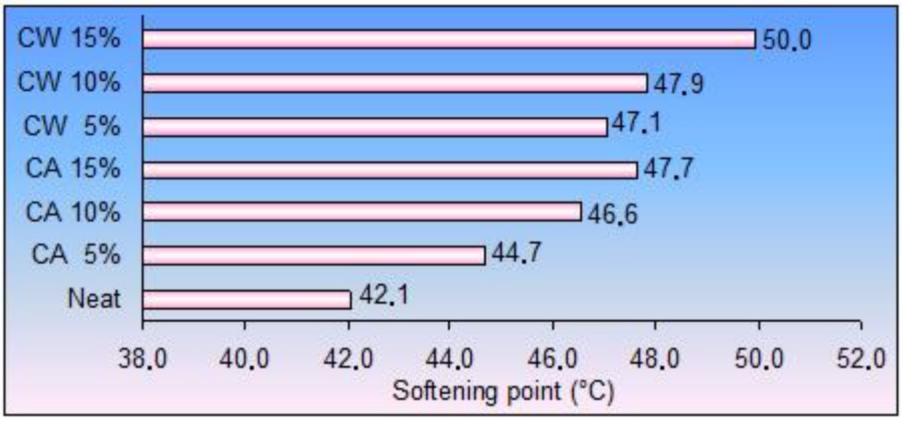


Figure 2.5: Change in binder softening point values with additive type and content

Softening point test results indicated that use of both ground apricot seed and ground walnut shell chars in bitumen modification increased the softening point values, thus increasing high-temperature resistance of the bituminous binders. Comparison of the results for additive types demonstrated that the softening points of modified bitumen that

included ground walnut shell char in the same ratio were higher than the softening point values of the modified bitumen including apricot seed char. Based on the softening point values, use of 10% walnut shell char in bitumen modification produced similar softening points when compared to the modified bitumen including 15% apricot seed char. This demonstrated that walnut shell char was more effective than apricots seed with respect to the softening point.
Penetration indices showing the temperature sensitivity of neat and modified bitumen were determined using Formulas 2.3 and 2.4. Penetration index values for the binders are displayed in Figure 2.6. Where P_{25} is the penetration values at 25°C and T_{SP} is the softening point values of binders.

$$A=\frac{\log 800-\log P_{25}}{T_{SP}-25} \tag{2.3}$$

$$PI=\frac{20-500A}{1+50A} \tag{2.4}$$

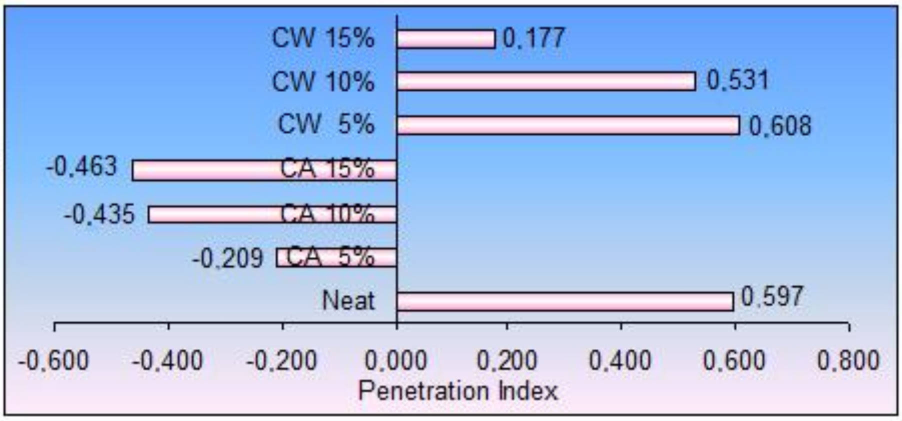
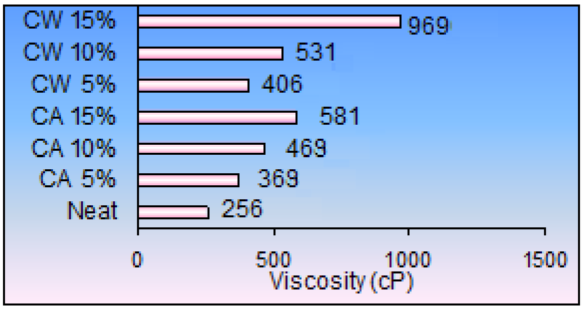
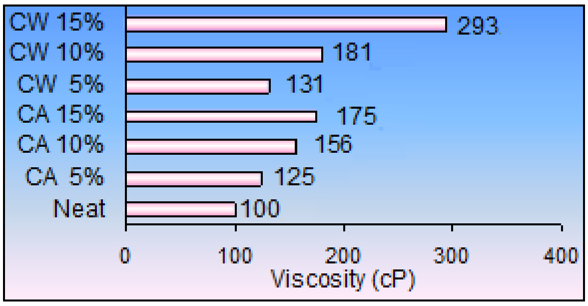


Figure 2.6: Penetration index values for the binders

Generally, penetration index values decreased with the use of additive as presented in Figure 2.6. Penetration index values especially decreased due to the use of walnut shell char. This was due to the fact that, although the utilization of especially the ground apricot seed shell reduced the penetration values in all bitumen modifications, it did not have significant effects on softening point values. It was determined as a result of penetration index values that utilization of ground walnut shell or apricot seed shell chars increased the temperature sensitivity of the binders. Although the decrease in penetration and the increase in softening point of the binder by the use of ground apricot seed or walnut shell chars in bitumen modification has rheological benefits, it was determined as a result of penetration index values that the use of these additives had a negative effect on sensitivity to temperature.
Results of the rotational viscometer experiments that were conducted on the binders under the temperatures of 135°C and 165°C are presented in Figure 2.7.



(a)



(b)

Figure 2.7: Change in viscosity values with additive type and content under 135°C (a) and 165°C (b)

Figures 2.7 (a) and (b) shows that viscosity values increased with the use of additive under both temperature values. As the additive content increased, viscosity values increased constantly as well. The highest viscosity value was obtained with the modified bitumen that contains 15% ground walnut shell char per bitumen weight; and the lowest viscosity value was obtained with the neat binder.
Viscosity tests indicated similar results with penetration and softening point experiments. It was determined that use of walnut and apricot seed shell chars in the modification of bitumen increased the viscosity, thus increasing the stiffness of the binders.

Temperatures at recommended viscosity values (equiviscous temperature of 280±30 cP for compaction and 170±20 cP for mixing) to determine the mixing and compaction temperatures in hot mix asphalt (HMA) production using apricot seed shell and walnut shell chars were determined. These values are presented in Table 2.1.

Table 2.1: Temperature ranges for mixture-compaction temperatures for neat and modified bitumen

		Mixing range temperatures (°C)	Average values for mixing temperatures (°C)	Compaction range temperatures (°C)	Average values for compaction temperatures (°C)
Neat Bitumen		146.2-153.9	150.1	130.5-137.4	134.0
Apricot shell char	**5%**	153.6-160.2	156.9	140.0-146.0	143.0
	10%	158.0-164.4	161.2	144.8-150.6	147.7
	15%	163.0-168.9	166.0	150.7-156.1	153.4
Walnut seed shell char	**5%**	153.8-160.0	156.9	140.9-146.6	143.8
	10%	162.9-169.6	166.3	149.4-155.4	152.4
	15%	174.9-180.9	177.9	162.7-168.1	165.4

It was determined by the examination of mixing temperatures that mixing temperature differed 27.8°C the most in modified bitumen containing ground walnut shell char (15% usage); and the mixing temperature differed 15.9°C the most in modified bitumen containing apricot seed shell char (15% usage). It was determined that at compaction temperatures, modified bitumen containing walnut shell char required higher temperatures during mixing when compared to the modified bitumen containing apricot seed char.
Results identified that modified bitumen containing both ground walnut shell and apricot seed shell chars required more heat, thus requiring more energy during mixing with the aggregate. Furthermore, it was determined that modified bitumen containing walnut shell char required more energy when compared to the modified bitumen containing apricot seed shell char.
High temperature performance levels of neat and modified non-aged binders based on Superpave method were determined by DSR tests conducted on binders. Modified bitumen samples prepared were filled into silicon containers with a 25 mm diameter and cooled until they reached the ambient temperature. Later on, the samples were placed in the DSR test equipment and kept there until they gain the test temperature and tested under different temperatures. DSR test results are presented in Table 2.2.

Table 2.2: DSR test results for neat and modified binders

Binder Type		Temperature (°C)	G*/sin δ (Pa)	Phase Angle (°)	High Temperature PG
Neat Bitumen		**52**	**2073**	**80.7**	PG 52-Y
		58	977	83.2	
		64	496	85.4	
Walnut shell char	**5%**	52	4283	78.4	PG 58-Y
		58	**1991**	**81.5**	
		64	946	83.8	
	10%	52	5659	78.4	PG 64-Y
		58	2562	81.5	
		64	**1244**	**83.8**	
		70	625	85.0	
	15%	52	6853	79.1	PG 64-Y
		58	3163	82.0	
		64	**1546**	**84.3**	
		70	820	86.1	
Apricot seed shell char	**5%**	52	3658	78.2	PG 58-Y
		58	**1715**	**81.1**	
		64	837	83.3	
	10%	52	5264	77.5	PG 64-Y
		58	2351	80.7	
		64	**1144**	**82.8**	
		70	573	83.6	
	15%	52	5371	79.1	PG 64-Y
		58	2532	81.9	
		64	**1253**	**84.3**	
		70	659	86.1	

As Table 2.2 demonstrates, all binders met the original binder G*/sin δ condition (min 1000 Pa) at 52°C temperatures. At 58°C temperatures, all binders except the neat binder met non-aged binder condition G*/sin δ (min 1000 Pa). All modified binders except the modified bitumen with 5% ground apricot seed and walnut shell chars at 64°C met the specification limits. None of the binders at 70°C temperatures met the specification limits. The findings demonstrated that the performance level of neat binders was PG 52-Y, performance levels of the modified bitumen that contained 5% ground walnut shell and apricot seed shell chars were PG 58-Y, and performance levels of the modified bitumen that contained 10% and 15% ground walnut shell and apricot seed shell chars were PG 64-Y. Results showed that use of apricot seed and walnut shell chars increased the endurance parameter of bituminous binders against permanent deformation.
Furthermore, DSR tests under different frequencies and temperatures were conducted on all modified bitumen. DSR tests were conducted under 4 different temperatures (40, 50, 60 and 70°C) and 10 different frequencies that increased logarithmically between 0.1 Hz and 4 Hz (0.1; 0.15; 0.23; 0.34; 0.52; 0.78; 1.17; 1.77; 2.66; 4 Hz). To assess the effects of additive types, complex modules values for different temperatures and frequencies are presented below. Complex modulus values at 40°C temperatures, and 0.1 Hz and 4 Hz frequencies are presented in Figure 2.8; and complex modulus values at 70°C temperatures, and 0.1 Hz and 4 Hz frequencies are presented in Figure 2.9. It isn't determined a meaningful change or big differences in phase angles of modified binders. So, phase angle values aren't evaluated.

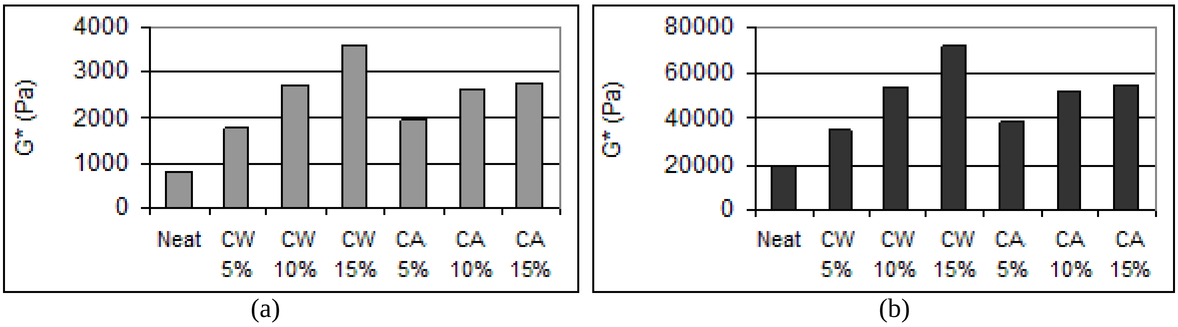


Figure 2.8: Complex modulus values at 40°C temperatures, and 0.1 Hz (a) and 4 Hz (b) frequencies

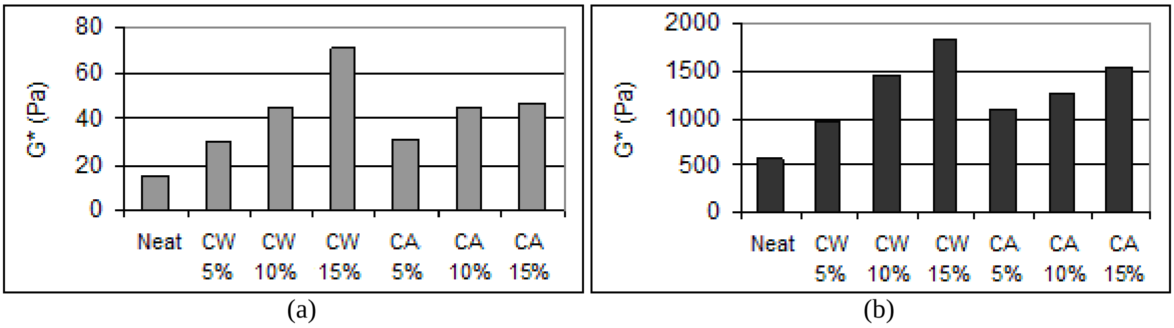


Figure 2.9: Complex modulus values at 70°C temperatures, and 0.1 Hz (a) and 4 Hz (b) frequencies

Figures above demonstrate that complex modulus values increased with additive use at all temperatures and in all frequencies. This shows that additive use would increase the resistance of the binders against shear.
Furthermore in the study, reference temperature was selected as 40°C and master curve for each binder was plotted. Arrhenius equation, one of the most common methods to determine temperature-stiffness relationship for bituminous binders, was used in determination of the master curves. Figure 2.10 shows the master curves for ground walnut shell char modified bituminous binders, Figure 2.11 shows the master curves for apricot seed shell char modified bituminous binders. In addition, complex modulus values for master curves in different frequencies are given in Table 2.3.

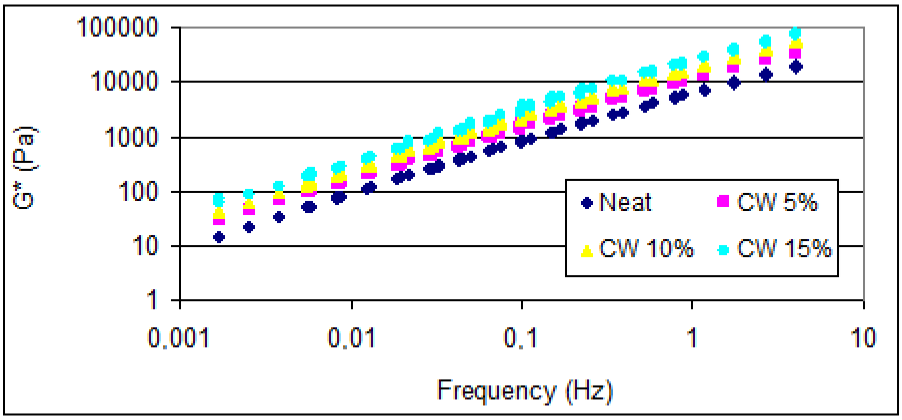


Figure 2.10: Master curves for modified binders that include walnut shell char at 40°C

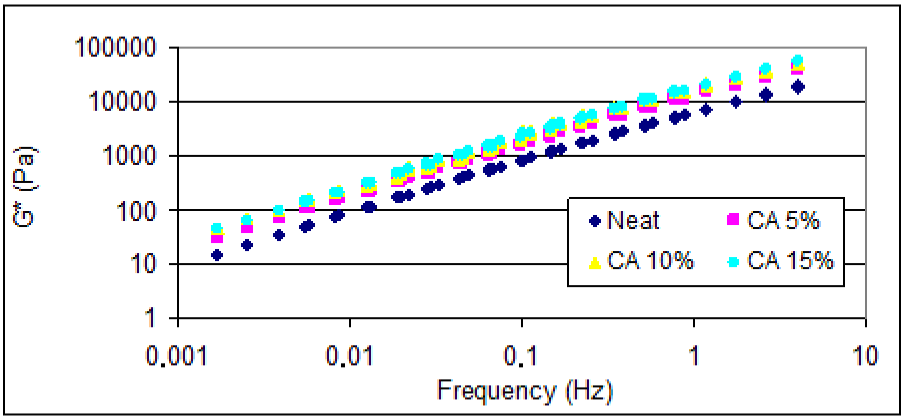


Figure 2.11: Master curves for modified binders that include apricot seed shell char at 40°C

Table 2.3: Master curve values for neat and modified binders

	Neat	CW5%	CW10%	CW15%	CA5%	CA10%	CA15%
Frequency (Hz)	**Complex Modulus (Pa)**						
0.001697	15	29.	44	61	30	46	45
0.002557	22	44.	63	84	45	67	64
0.005806	52.	98.	150	188	103	151	149
0.008748	78	145	213	275	154	218	214
0.01256	112	210	304	390	225	292	318
0.01892	168	308	452	578	336	416	476
0.03301	291	574	891	1158	626	857	860
0.04506	391	676	1015	1314	754	985	1042
0.06789	578	989	1492	1912	1104	1429	1526
0.07493	628	1225	1904	2483	1328	1893	1845
0.09761	796	1441	2179	2805	1606	2066	2247
0.1	820	1757	2709	3581	1920	2742	2615
0.1129	919	1771	2761	3612	1946	2726	2661
0.1507	1180	2492	3833	5067	2765	3891	3700
0.1702	1343	2543	3999	5201	2767	3905	3845
0.2271	1715	3557	5492	7237	3948	5487	5320
0.2567	1938	3634	5725	7444	3981	5551	5538
0.5155	3489	7062	10900	14370	7940	10850	10650
0.8762	5713	10250	15960	21210	10920	15220	16030
1.765	9807	19300	29830	38180	20940	28500	28680
2.655	13590	25990	39990	54820	28870	37430	39860
4	18800	35000	53840	71270	38230	51900	54730

As is observed in table and the figures, the increase in frequency resulted in increased in complex shear modulus values. Based on the master curves that represent all temperature values, it was determined that the additive that increased the complex shear modulus the most in all frequencies was the walnut shell subjected to pyrolysis. It was also determined that the highest complex shear modulus values were obtained with the modified bitumen that included 15% ground walnut shell char.
Comparison of additives demonstrated that modified bitumen including 10% ground walnut shell char and modified bitumen including 15% ground apricot seed shell char had similar complex shear modulus values.

3. RESULTS

The study scrutinized the availability of natural waste materials for bitumen modification after pyrolysis process. For this purpose, two different natural waste material; apricot seeds and walnut shells were used. These waste materials were used to obtain bio-chars through the process of pyrolysis. Bio-chars were used in bitumen modification in three different ratios (5%, 10%, and 15%). Penetration, softening point, rotational viscometer and DSR tests were conducted on the modified bitumen produced.
As a result of the penetration tests, it was determined that penetration values of the binders decreased by the use of additives, thus increasing the stiffness of the binders. The most effective additive on the penetration values was the walnut shell char.
Softening point test findings showed that both additives increased the softening point values, and as the additive content increased, softening point values increased constantly as well. It was determined that the most effective additive on the softening point values was also the walnut shell char.
Penetration index values that indicate the sensitivity of bituminous binders for temperature demonstrated that the sensitivity of bituminous binders for temperature increased by the use of both ground walnut shell and ground apricot seed chars. This was due to the fact that despite the significant decrease in penetration values, softening point values did not increase much with additive use. Sensitivity for temperatures increased more in modified bitumen containing apricot seed shell char when compared to walnut shell char.
Viscosity test results indicated that viscosity values increased with the use of additive, and as the additive content increased, viscosity values increased constantly. Using the viscosity values, temperatures for mixing with the aggregate and compaction in the field were determined. Since the use of ground apricot seed and walnut shell char increased the stiffness of the modified bitumen, it was determined that mixing with the aggregate and compaction temperatures increased as well. This shows that the use of these additives would necessitate use of more energy for the preparation of hot mix asphalts.
High temperature performance levels of the binders were determined using the Superpave method. Findings demonstrated that neat binder high-temperature performance level was PG 52-Y, the same value for modified bitumen with 5% additive was PG 58-Y, and performance level high-temperature value for modified bitumen containing 10% and 15% additive were PG 64-Y.
DSR tests conducted in different frequencies showed that additive use increased complex shear modulus values. Assessment of master curves demonstrated that 10% ground walnut shell char modified bitumen and 15% apricot seed shell char modified bitumen displayed similar properties.
All test results indicated that natural waste materials could be used as asphalt additive materials after the process of pyrolysis with the exception of the fact that they increased the sensitivity for the heat and the mixture temperature. It is considered that a comprehensive study should be beneficial on the mixture experiments for the study to gain validity. Also, low temperature performance tests should be done on the biochar modified binders and hot mix asphalt mixtures for determination usability of biomass in bitumen modification.

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