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Optimizing activated carbon size and ratio in bitumen modification

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Professional paper

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Optimizing activated carbon size and ratio in bitumen modification

The aim of the study is to investigate the effects of activated carbon (C_A) on the rheology of bitumen, and to optimize the activated carbon size and ratio in bitumen modification. The use of C_A produced from waste hazelnut shells in bitumen modification is evaluated. Different sizes and ratios of C_A are used. Test results show that a C_A particle size smaller than 0.063 mm is the most effective, and that the C_A modification increases the bitumen consistency and high temperature performance, while reducing the temperature susceptibility and weight change.

Key words:
activated carbon, modification of bitumen, dynamic shear rheometer, ageing

Stručni rad

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Optimiziranje veličine i udjela aktivnog ugljena pri modifikaciji bitumena

Svrha je ovog rada istražiti učinke dodatka aktivnog ugljena (C_A) na reološka svojstva bitumena te optimiziranje veličina i udjela aktivnog ugljena pri modifikaciji bitumena. Za modifikaciju bitumena vrednovana je primjena aktivnog ugljena proizvedenog iz otpadnih ljuski lješnjaka. Upotrijebljene su različite veličine i udjeli aktivnog ugljena. Rezultati ispitivanja pokazuju da je veličina čestica aktivnog ugljena manja od 0,063 mm najučinkovitija, a da modifikacija s aktivnim ugljenom povećava bitumensku konzistentnost i radna svojstva pri visokim temperaturama te umanjuje osjetljivost na temperaturu i promjenu mase.

Ključne riječi:
aktivni ugljen, modifikacija bitumena, dinamički smični reometar, starenje

Fachbericht

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Optimierung von Größe und Anteil der Aktivkohle bei Bitumenmodifikationen

Das Ziel dieser Arbeit besteht darin, die Auswirkungen des Zusatzes von Aktivkohle (C_A) auf rheologische Eigenschaften von Bitumen zu untersuchen, sowie Größe und Anteil von Aktivkohle bei Bitumenmodifikationen zu optimieren. Dabei wurde der Zusatz aus Abfällen von Nussschalen gewonnener C_A bewertet. Es wurden verschiedene Größen und Anteile von C_A untersucht. Die Resultate der Untersuchungen zeigen, dass bei Größen unter 0,063 mm die C_A Teilchen am wirksamsten ist. Ebenso erhöht eine Modifikation mit C_A die Konsistenz des Bitumens, erleichtert die Bearbeitung bei hohen Temperaturen und mindert die Empfindlichkeit auf Temperaturänderungen sowie die Massenschwankung.

Schlüsselwörter:
Aktivkohle, Bitumenmodifikation, DSR, Alterung

1. Introduction

Bitumen is an organic mixture of various chemical elements and compounds. It is widely used for the construction of roads due to its good adhesion to mineral aggregates and its viscoelastic properties [1-3]. Unfortunately, bitumen assumes the form of liquid at high temperatures and becomes brittle at low temperatures, which can limit its application by causing high temperature rutting and low temperature cracking of pavement [1, 4]. Continuous increase in traffic volume and load on roadways, combined with adverse climatic effects, result in serious rutting and cracking occurrences. The improvement of bitumen and bituminous mixture properties by means of appropriate additives is an important issue in bitumen industry [5].

The additives used for bitumen modification include polymers, carbonaceous materials, and other materials of various origin [6]. Pavements with modified bitumen exhibit greater resistance to permanent deformation, fatigue damage, thermal cracking, stripping, and temperature susceptibility [1, 4].

$C_{A,}$ the additive used in this research, is a highly porous and amorphous carbon-based material. Due to its high degree of microporosity, it is used in the absorption of gases and soluble substances from water. C_A is produced from carbonaceous source materials such as nut shells, coconut husk, wood, and coal [7-10].

The purpose of the present study is to investigate the effects of C_A addition on the rheology of modified bitumen through conventional softening point and penetration tests, thin film oven test (TFOT), and Superpave methods (rotational viscometer (RV) and dynamic shear rheometer (DSR)). The C_A used in this study has been obtained by pyrolysis of hazelnut shells. The effects of C_A size and ratio on the rheology are also evaluated.

2. Materials and methods

The 50/70 penetration grade bitumen (original bitumen) obtained from the Kırıkkale terminal of the Turkish Petroleum Refinery was used throughout the study. Physical and rheological properties of the original bitumen are given in Table 1.

2.1. Production and characterization of C_A

C_A was produced from hazelnut shells obtained from the Giresun region of Turkey. The hazelnut shells were dried, crushed, and sieved to a particle size fraction of 1.0-2.0 millimetres. Chemical activation was applied in order to obtain a porous surface texture. During the activation procedure, hazelnut shells were saturated with 30 % H_2SO_4. The resulting chemical-loaded sample was placed in a furnace and heated (12.5°C min^{-1}) to the final carbonization temperature of 450°C for 2 hours [7, 8, 10, 11]. After cooling to room temperature, the resulting products were taken out and leached with distilled water until the pH 7.0 was reached [7, 12, 13]. The porous surface texture of $C_{A,}$

Table 1. Fundamental properties of original bitumen

Properties	Standard	Results
Penetration (0.1 mm). 100 g. 5 s	ASTM D5	57
Softening point [°C]	ASTM D36	48
Viscosity (cP. 135 °C)	ASTM D4402	675
Viscosity (cP. 165 °C)	ASTM D4402	175
G*/sinδ (kPa. 58 °C)	AASHTO T5	4.37
Penetration Index (PI)*	-	-1.41
After TFOT		
Mass loss [%]	ASTM D2872	0.93
Penetration (0.1 mm). 100 g. 5 s	ASTM D5	33
Retained penetration [%]	-	58
Softening point [°C]	ASTM D36	56
Increase in softening point [°C]	-	8
Penetration Index	-	-0.72

* PI calculated with the following equation:

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

where Pen_{25} is the penetration at 25 °C. and SP is the softening point temperature.

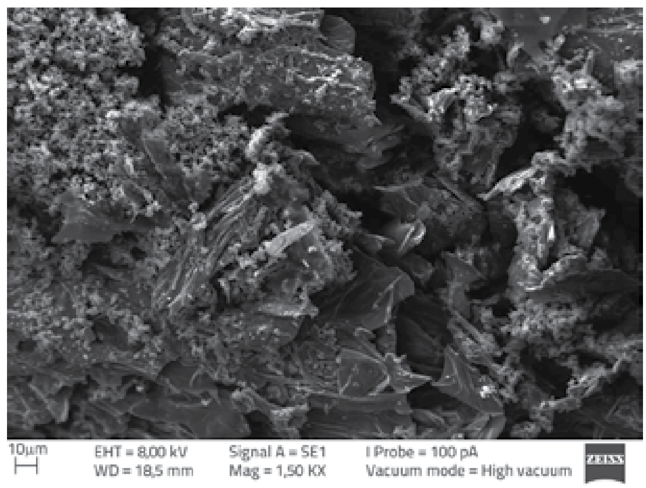

Figure 1. Surface texture of C_A

Table 2. Specifications of C_A

Specification	C_A
Fixed carbon [%]	49.2
Volatile matter [%]	44.6
Ash [%]	6.0
Moisture content [%]	4.9
Density [g/cm³]	1.96
Appearance	Black
Shape of grains	Amorphous

with macropores, micropores, and mesopores that disperse to the surface heterogeneously, is shown in a scanning electron microscope photograph (Figure 1). The specifications of C_A are summarized in Table 2.

2.2. Preparation of modified bitumens

Modified bitumens were prepared at a mixing temperature of 150°C by means of a laboratory Marshall mixer rotating at 500 rpm. C_A was added to hot bitumen at ratios varying between 1 and 25 % (w/w) and mixed for 45 minutes. C_A size categories were chosen as size 1 (< 0.063 mm), size 2 (0.063-0.125 mm), and size 3 (0.125-0.25 mm) (Figure 2). To avoid agglomeration of C_A in the bitumen, and to ensure the homogeneity of mixtures, C_A was added in small amounts [4, 6].

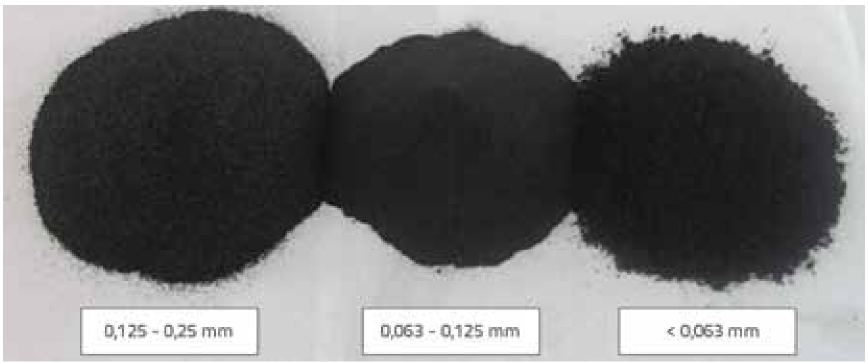

Figure 2. C_A sizes

3. Results and discussions

3.1. Softening point and penetration test results

Original and modified bitumens were subjected to a standard ring and ball softening point test [14, 15] in order to determine consistency parameters. The softening point of the original bitumen amounted to 48°C. As shown in Figure 3, softening point values of modified bitumens are higher than those of the original bitumen.

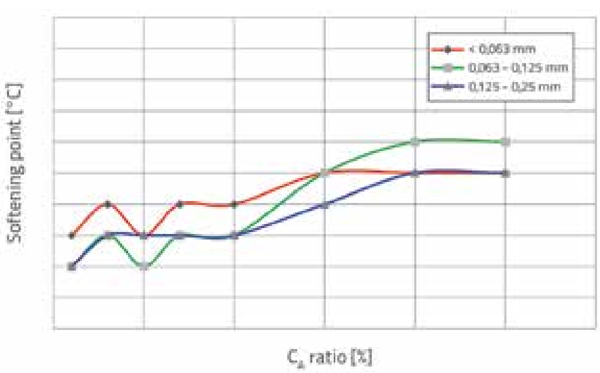

Figure 3. Softening point test results for modified bitumens

Table 3. Effective C_A sizes and ratios

Mixture number	C_A size [mm]	C_A ratio [%]
1	< 0.063	10
2	< 0.063	15
3	< 0.063	20
4	0.63 - 0.125	10
5	0.63 - 0.125	15
6	0.63 - 0.125	20
7	0.125 - 0.25	15
8	0.125 - 0.25	20

The increase in softening point, especially at 10, 15, and 20 % ratios, is an indicator of the stiffening effect of C_A. The most effective C_A sizes and ratios were determined based on the softening point test results for use in the latter tests. These values are given in Table 3.

The standard 100 gram, 25°C, 5 second penetration test was carried out on the bitumens given in Table 3. In addition, the temperature susceptibility of the bitumens was calculated in terms of penetration index (PI) using the results obtained during the penetration and softening point tests. Temperature susceptibility is defined as the change of consistency parameter as a function of temperature [14].

The effect of C_A modification on the properties of original bitumen can be seen in Figure 4, a decrease in penetration values and an increase in softening points occurs with an increase in C_A content.

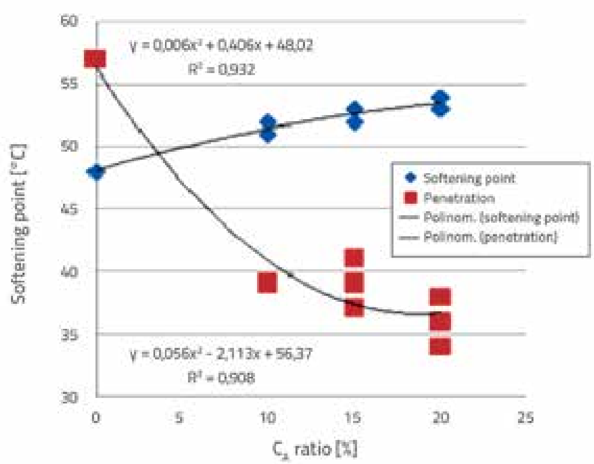

Figure 4. Correlations between softening point and penetration values and C_A content

Correlations between the softening point and penetration values and the C_A content are given in Figure 4. High values of correlation coefficients (0.93 and 0.91) confirm the C_A dependence on penetration and softening point values. The increase in softening point is favourable since bitumen with a higher softening point is more resistant to rutting. C_A modification reduced the temperature susceptibility (as determined by PI) of the original bitumen, especially at the 20 % ratio. Lower values of PI indicate higher temperature susceptibility [14]. Size 1 was determined as the most effective size for PI increase. The 20 % C_A ratio with size 1 increased the PI value from -1.41371 to -0.96942.

Table 4. Penetration, softening point, and PI results

Mixture number	Softening point (SP) [°C]	Penetration (0.1 mm)	Penetration Index (PI)
Original bitumen	48	57	-1.41371
1	52	39	-1.25281
2	53	39	-1.02576
3	54	36	-0.96942
4	51	39	-1.48483
5	53	37	-1.13404
6	54	34	-1.08428
7	52	41	-1.14902
8	53	38	-1.07951

3.2. TFOT results

The aging of bitumens was performed using the TFOT (thin film oven test) method (ASTM D 1754). Standardized conditions, that is, 163°C and 5 hours, were used [16]. The aged bitumens were evaluated by penetration and softening point tests. TFOT test results are presented in Figure 5 and Table 5. C_A modification to the original bitumen reduced the weight loss percentage. As can be seen in Figure 5, the aging characteristics of original bitumen improve with an increase in the C_A content.

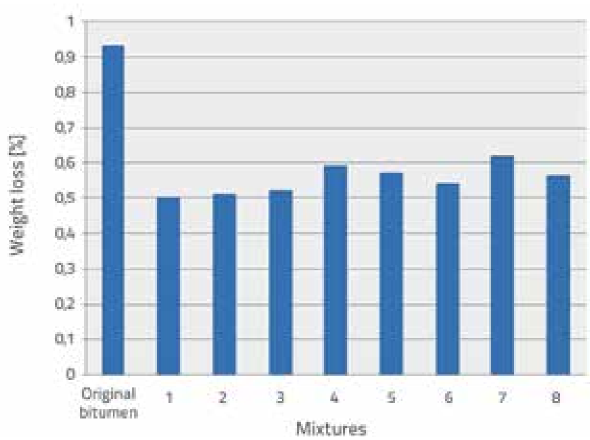

Figure 5. Weight loss percentages

This improvement can be explained by interactions between the functional groups of C_A and volatile components of bitumen. As is evident from Figure 5, size 1 is the most effective size in terms of characteristics. The penetration and softening point tests conducted according to the TFOT method show that penetration values decrease, while softening point and PI values increase, in comparison with original bitumen.

Table 5. Bitumen characteristics after TFOT

Mixture number	Penetration after TFOT (0.1 mm)	Softening point after TFOT [°C]	PI after TFOT
Original bitumen	33	56	-0.72123
1	30	59	-0.31324
2	27	59	-0.51924
3	29	59	-0.38049
4	28	58	-0.64242
5	25	59	-0.66425
6	24	60	-0.55279
7	27	60	-0.33027
8	27	60	-0.33027

3.3. DSR test results

The DSR test was performed on original and C_A-modified bitumens using a Bohlin DSRII rheometer under the 120 Pa controlled stress at temperatures varying between 58-76°C with an increment of 6°C and the 10 rad/s frequency, using a 25 millimetre diameter plate with a 1 mm gap opening. In order to determine the high temperature properties of bitumen, complex shear modulus (G*), and phase angle (δ), the principal viscoelastic parameters were determined during the testing. G*/sinδ, which indicates the bitumen resistance to rutting under elevated temperatures, was calculated and compared with the Superpave asphalt bitumen test specifications as defined in AASHTO TP5. The specification shows that the G*/sinδ parameter is less than 1000 Pa for unaged bitumens [17, 18]. DSR test results (G*/sinδ values) are given in Figure 6-7.

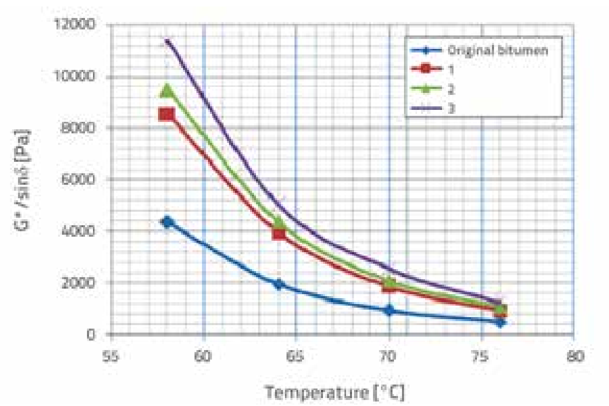

Figure 6. G*/sinδ for original bitumen and mixtures 1, 2, and 3 (Size 1)

Based on the Superpave PG grading system, the original bitumen exhibits 1000 Pa of G*/sinδ at 64°C. The high temperature performance of mixtures 1, 4, and 7 is 70°C, while it amounts to 76° for all other mixtures. As can be seen in Figures 6 and 7, the rutting parameter improves with an increase in the C_A content. Correlations between the C_A content and improvement of G*/sinδ values are given in Figure 8. The G*/sinδ values at 76°C with the 20 % additive ratio show that sizes 1 and 2 have similar effects on the rutting parameter, while the worst value is obtained with size 3. This can be explained by the separation of coarse C_A and the resulting deterioration of homogeneity.

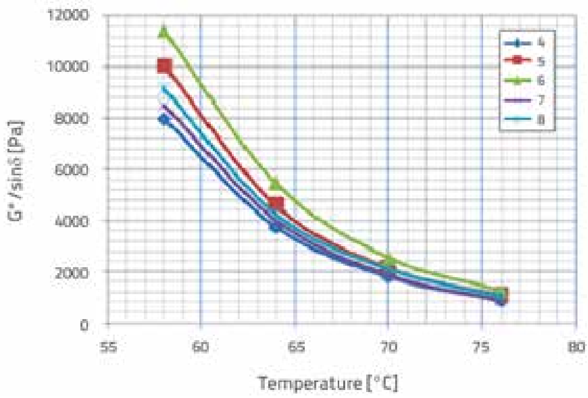

Figure 7. G*/sinδ for mixtures 4, 5, 6, 7, and 8 (Sizes 2 and 3)

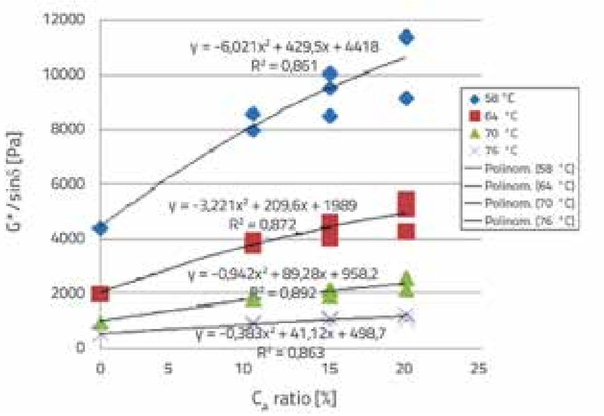

Figure 8. Correlations between G*/sinδ and C_A ratio

3.4. RV test results

The viscosity obtained by RV test is the measure of internal friction in bitumen. The viscosity at 135°C is usually used to measure workability according to Superpave specifications. The RV also measures rheological properties of bitumens to evaluate their ability to be pumped during delivery and plant operations. Therefore, elevated temperatures of 135° and 165°C were used in this study for testing purposes [17, 19]. The viscosity was determined by measuring the torque required to maintain constant rotation speed (20 rpm) of a cylindrical spindle submerged in bitumen maintained at a constant temperature [20]. RV test results at 135 and 165°C are given in Figure 9.

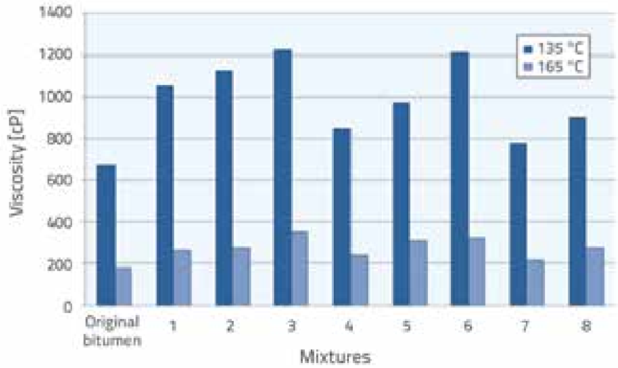

Figure 9. RV results of bitumens

The viscosities give a clear indication of the stiffening effect of C_A modification with a high additive content. Size 1 is the most effective size in terms of viscosity increase for all ratios. It was determined that the viscosity for size 3 C_A mixtures with a 20 % additive ratio at 135°C is by 26 % smaller compared to the remaining two sizes. The observed decrease in viscosity can be explained by the non-homogenous mixture evidenced in DSR results.

4. Conclusions

The following conclusions were drawn based on the test results:
- Bitumen stiffness and consistency clearly increase with an addition of C_A.
- According to softening point test results, the optimum additive ratio varies between 10 and 20 %.
- PI values show that the temperature susceptibility of original bitumen decreases with C_A modification. In particular, size 1 and the 20 % additive ratio are the most effective conditions for preventing temperature susceptibility.
- C_A modification affects the ageing characteristics of original bitumen and decreases the weight loss percentage.
- In the DSR test, C_A modification yields higher G*/sinδ values. When comparing the three different sizes, size 3 performs worse than the other two sizes. The reduction of rutting parameter in case of size 3 is a result of separation of coarse C_A and deterioration of homogeneity.
- Viscosity increases and workability decreases when bitumen is modified with C_A.

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