Proceedings of the 10th World Congress on Civil, Structural, and Environmental Engineering (CSEE 2025)
Barcelona, Spain - April, 2025
Paper No. ICGRE 181
DOI: 10.11159/icgre25.181

Rheological Investigation of Bitumens Obtained From Different Refineries Modified With SEBS: Response Surface Methodology (RSM) Analysis

Erkut Yalçın[1], Ahmet Münir Özdemir[2]
[1]Firat University, Engineering Faculty, Civil Engineering Department, Elazig, Turkey
erkutyalcin@firat.edu.tr;
[2]Bursa Technical University Engineering and Natural Sciences Faculty, Civil Engineering Department, Bursa, Turkey
ahmet.ozdemir@btu.edu.tr

Abstract - The durability and performance of hot mix asphalts are highly dependent on the rheological properties of the bitumen. However, the diversity in the composition of crude oil from different regions, combined with the effects of the refining process, leads to significant differences in the properties of bitumen. This shows that modification methods can produce different results for each type of bitumen. Bitumen modification, especially with elastomeric additives, is an effective method to improve the deformation resistance and long-term performance of asphalt pavements. In this study, bituminous binders of penetration class 160/220 were obtained from two different refineries in Turkey-Batman and Iraq-Lanaz. Bitumens were modified with SEBS at different percentages (2,3 and 4%) and their rheological properties were determined by Dynamic Shear Rheometer (DSR) test. The effect of temperature and additive ratios on bitumens of different origin was investigated by Response Surface Methodology (RSM) analysis. The results revealed the importance of bitumen origin and showed that the addition of SEBS significantly increased the rutting strength for both binder types. The RSM analysis revealed that the effect of temperature was higher than that of the additive.

Keywords**:** Bitumen origin, modification, SEBS, Response Surface Method (RSM)

1. Introduction

Hot mix asphalts (HMAs), which form the superstructure of the highway, consist of aggregate and bituminous binder material. Various deformations occur in asphalt pavement over time due to traffic load and environmental effects. In order to reduce the deformations occurring in the asphalt pavement and to improve the performance of the pavement, HMAs are modified by using different additives. The modification process can be performed as modified bitumen by adding the additive material to the bitumen material or as a modified mixture by adding it to the mixture [1], [2].

Bitumen shows viscoelastic material properties. This viscoelastic behaviour causes the bitumen material to show viscous liquid behaviour at high temperatures or long loading times, while it shows elastic solid behaviour at low temperatures or short loading times [3]. Due to this behavioural characteristic of bituminous materials, rutting deformation of asphalt pavement increases at high service temperatures and due to slow moving vehicles in traffic [4]. Various additives are used to reduce deformations in asphalt pavement due to high temperature [5]. Bitumen material is produced according to the specification class during the distillation of crude oil in refineries. It is generally accepted that crude oil is formed over millions of years from the remains of marine organisms and accumulated mud and rock fragments on the ocean floor and accumulated plant matter deposits [3]. In the modification process, polymer additives are the most preferred additives [6], [7]. Styrene butadiene styrene (SBS) and styrene ethylene butadiene styrene (SEBS) polymers were used as additives in the modification process and were found to contribute positively to many rheological and mechanical properties of bitumen [8]. SBS additive is a good modification material. Because of its chemical structure and polymericity, it can be mixed with many types of asphalt without causing significant solubility and phase separation problems. However, SBS, like all unsaturated rubbers, ages, limiting the possibility of recycling after the end of the life of the asphalt pavement [9]. Therefore, there is an increasing interest in SEBS (styrene ethylene butadiene styrene block copolymer) saturated polymers, which have similar modifying properties to SBS and are produced by simple hydrogenation of SBS [10]. It has been determined that SBS additive improves the performance of the coating against permanent deformation, moisture damage and fatigue life of bituminous hot mixtures [11]. In the studies, it has been determined that SEBS additive positively contributes to the high temperature resistance and aging effect of bituminous binder [12].

In this study, two different bitumen obtained from Iraq and Turkey were modified with 2,3 and 4% SEBS and DSR test was performed on the modified bitumen. The detailed analysis of the temperature and additive ratio which are effective on the rutting parameter obtained after the DSR test was carried out by Response Surface Methodology.

2. Materials and Method

2.1. Bitumens and additive

Bitumens (penetration grade B 160/220) supplied from Iraq LANAZ and Batman TÜPRAŞ refineries were used as binder in the study. The physical properties of the bitumens used are given in Table 1. The physical properties of the additive SEBS used for bitumen modification are given in Table 2.

Table 1. Properties of pure Iraq-Lanaz and Turkey-Batman bitumens

Property	Iraq-Lanaz Bitumen	Turkey-Batman Bitumen
Penetration (dmm)	177	189
Softening Point (°C)	40.65	42.2
Viscosity (cP, 135°C)	237.5	262.5

Table 2. Properties of SEBS

Property	SEBS
Density (g/cm3)	0.88-1.25
Styrene content (%)	%30
Tensile strength (MPa)	34
Stiffness	75

2.2. Dynamic Shear Rheometer (DSSR)

The dynamic shear rheometer test is used to evaluate the viscoelastic properties of asphalt binder at medium and high service temperatures. This test is used to determine the resistance of bitumen to rutting and fatigue strength [13]. To measure the resistance of the binder against rutting, the test is performed on pure or RTFOT-aged bitumen specimens, while for the fatigue strength of the binder, the test is performed on PAV-aged bitumen specimens.The summary of the dynamic shear rheometer test method according to AASHTO TP5 standard is listed below.

- It includes the procedure used to measure the complex shear modulus (G*) and phase angle (δ) of asphalt binders.

- The test standard is suitable for use when the dynamic shear modulus ranges between 100 Pa and 10 MPa, which is usually achieved between 5 °C and 85 °C and depends on the grade of bitumen used, ageing and temperature.

- Test specimens are formed with a thickness (height) of 1 mm and a diameter of 25 mm or a thickness (height) of 2 mm and a diameter of 8 mm. During the test, one of the plates oscillates relative to the other plate at predetermined rotational deformation amplitudes and frequencies. The required amplitude depends on the complex shear modulus (G*) of the binder and the required amplitudes are selected so that the measurements remain within the linear behaviour region.

- The test specimen is kept at a test temperature of ± 1 °C by heating and cooling the plates.

- Oscillatory loading frequencies can range from 1 to 100 rad/s using a sinusoidal waveform. The specification test is performed at a test frequency of 10 rad/s and the shear modulus (G*) and phase angle (δ) are calculated automatically using computer software.

The dynamic shear rheometer test apparatus used in the study is shown in Figure 1.

Fig. 1. Dynamic Shear Rheometer (DSR)

2.3. Response Surface Method (RSM)

Response Surface Method (RSM) is a statistical analysis method used to model and optimise the effect of one or more independent variables on one or more dependent variables [14], [15]. This method was developed to analyse experimental data and express it in a mathematical model. RSM is used to determine the optimum values of dependent variables, especially in complex systems. When applied in conjunction with experimental design methods such as Central Composite Design (CCD), RSM provides both an understanding of system behaviour and identification of optimal conditions for targeted outputs.

In this study, RSM was applied to evaluate the rheological properties of SEBS (Styrene-Ethylene-Butadiene-Styrene) modified asphalt binders. The analyses were performed based on Dynamic Shear Rheometer (DSR) data. The experimental design was established by CCD method and temperature (52, 58, 64 and 70°C) and SEBS ratios (2%, 3%, 4%) were selected as independent variables. The rutting resistance parameter obtained from DSR tests was selected as the dependent variable.

The experimental data obtained were analysed with a cubic parabola model. The statistical validity and degree of fit of the model were evaluated by analysis of variance (ANOVA). The regression model was validated using R2 and p-value values and the significance of the model parameters was analysed. RSM analyses were performed separately for Iraqi and Turkish bitumen.

3. Results and Discussions

3.1. Test results of Iraq-Lanaz bitumen

The descriptive data of the factors and the descriptive data of the responses for the RSM model for Iraq-Lanaz bitumen are given in Table 3 and Table 4, respectively.

Table 3. Descriptive data for Iraq-Lanaz bitumen (factors)

Factor	Name	Units	Type	SubType	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Temperature	°C	Numeric	Continuous	52	70	-1 ↔ 52.00	+1 ↔ 70.00	61.00	6.93
B	SEBS	%	Numeric	Continuous	0	4	-1 ↔ 0.00	+1 ↔ 4.00	2.25	1.53

Table 4. Descriptive data for Iraq-Lanaz bitumen (responses)

Response	Name	Units	Observations	Minimum	Maximum	Mean	Std. Dev.	Ratio
R1	$G^*/\sin\delta$	Pa	16	322	9873.28	2845.19	2711.04	30.66

The independent variables are temperature and additive ratio, while the dependent variable is the wheel track parameter. The ANOVA results obtained in the study using DSR data are given in Table 5. The ANOVA results showed that the model was highly significant overall ($p < 0.0001$). Among the main effects, temperature (A) and SEBS ratio (B) have a significant effect on rheological properties with $p < 0.0001$ and $p = 0.0013$, respectively. Furthermore, the interaction between temperature and SEBS ratio (AB) was also highly significant ($p < 0.0001$). The non-linear terms (A^2, B^2, A^2B, AB^2) and the third-order effect of temperature (A^3) were below significance levels ($p < 0.01$), while the third-order effect of SEBS ratio (B^3) was not significant ($p = 0.6442$). These results suggest that it is important to consider non-linear effects and interactions between factors in the model.

Table 5. ANOVA results for Iraqi bitumen

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.10E+08	9	1.22E+07	769.18	< 0.0001	significant
A-Temperature	1.75E+06	1	1.75E+06	110.23	< 0.0001	
B-SEBS	5.15E+05	1	5.15E+05	32.39	0.0013	
AB	1.09E+07	1	1.09E+07	683.24	< 0.0001	
A^2	6.77E+06	1	6.77E+06	425.15	< 0.0001	
B^2	1.04E+06	1	1.04E+06	65.17	0.0002	
A^2B	1.15E+06	1	1.15E+06	72.02	0.0001	
AB^2	4.39E+05	1	4.39E+05	27.61	0.0019	
A^3	2.75E+05	1	2.75E+05	17.29	0.006	
B^3	3759.36	1	3759.36	0.2363	0.6442	
Residual	95470.52	6	15911.75			
Cor Total	1.10E+08	15				

2D and 3D RSM plots are given in Figure 2. The graphs show the effect of SEBS ratio (B) and temperature (A) variables on G*/sinδ values for Iraqi bitumen. G*/sinδ varies with temperature and SEBS ratio. As the temperature increases, the G*/sinδ value tends to decrease; this indicates that the stiffness of the asphalt decreases and becomes more prone to deformation at high temperatures. A significant increase in G*/sinδ value is observed as the SEBS ratio increases, indicating that SEBS improves the performance of bitumen by increasing the elastic properties. The graph shows that the G*/sinδ value peaks near the optimum SEBS ratio and temperature. When the 2D graph is analysed, it is clearly seen that high G*/sinδ values are obtained at low temperatures and high SEBS ratios in this graph where G*/sinδ values are shown with isoclines according to SEBS ratio and temperature combinations. For example, when the SEBS ratio approaches 4% and the temperature is in the range of 52-58°C, G*/sinδ values exceed 8000 Pa. In general, increasing the SEBS content significantly improves the elastic modulus of Iraqi bitumen and increases its resistance to deformation at high temperatures. However, the stiffness of bitumen decreases as the temperature increases. This highlights the modification effect of SEBS and shows the importance of determining the appropriate SEBS ratio and temperature range for optimum performance.

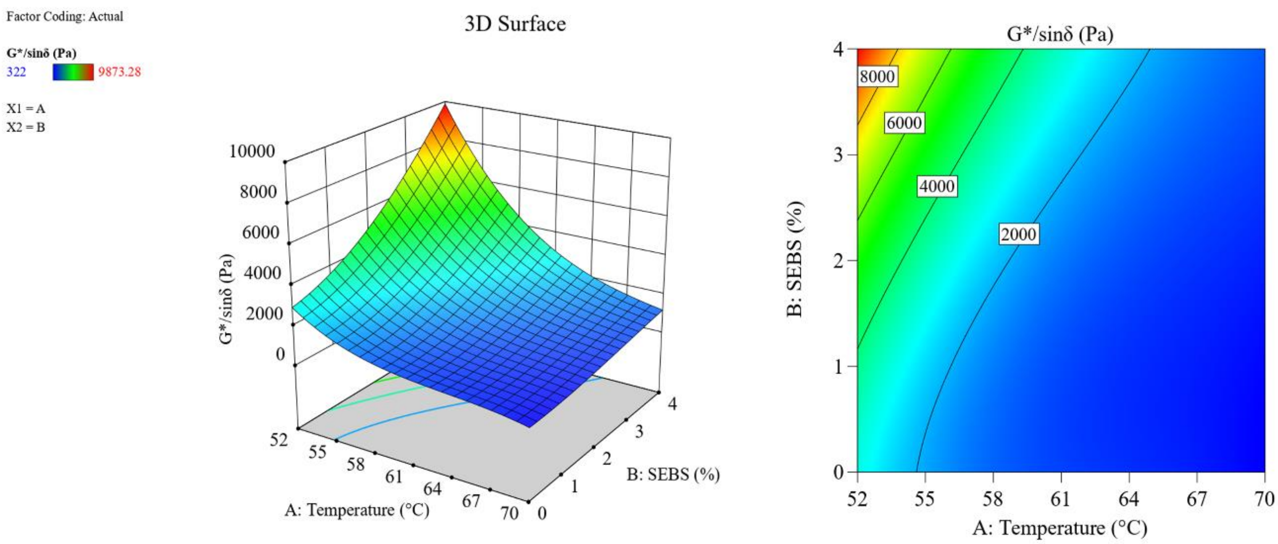

Fig. 2. 2D and 3D RSM plots for Iraqi bitumen

Figure 3 shows the perturbation curves. These curves are used to more clearly describe the effect of inputs on the response and represent deviations from the reference point to compare the effect of a factor on the response variable. The green curve shows the effect of temperature change (A) on G*/sinδ. The curve exhibits a negative slope, indicating that G*/sinδ decreases rapidly as temperature increases. This is consistent with the fact that bitumen becomes more flexible and its stiffness decreases at higher temperatures. Temperature has a significant effect on G*/sinδ and the magnitude of this effect is greater than that of the SEBS ratio. The blue curve shows the effect of a change in the SEBS ratio (B) on G*/sinδ. This curve has a positive slope, i.e. G*/sinδ increases with increasing SEBS content. SEBS improves the elastic properties of bitumen, resulting in higher performance. However, compared to the effect of temperature, the effect of SEBS is more moderate.

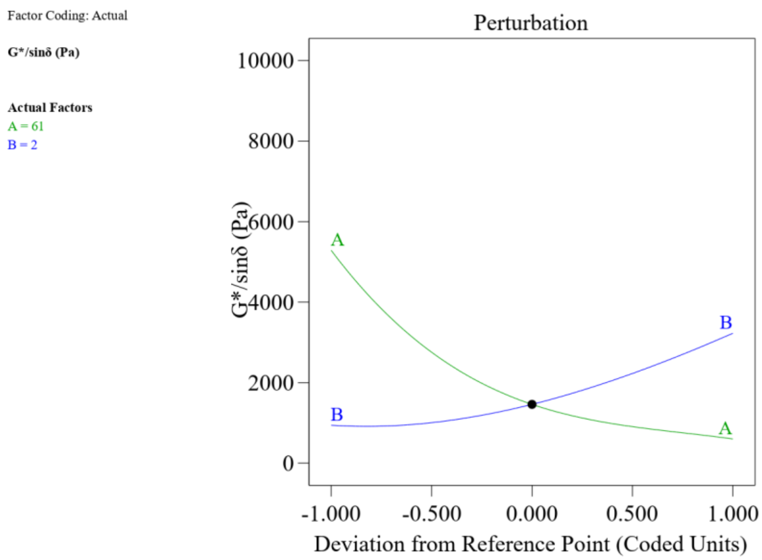

Fig. 3. Perturbation curves for Iraqi bitumen (A:temperature, B:SEBS ratio)

Figure 4 shows the curve comparing the prediction values with the actual values. When Figure 4 is analysed, it is seen that prediction is made with high accuracy.

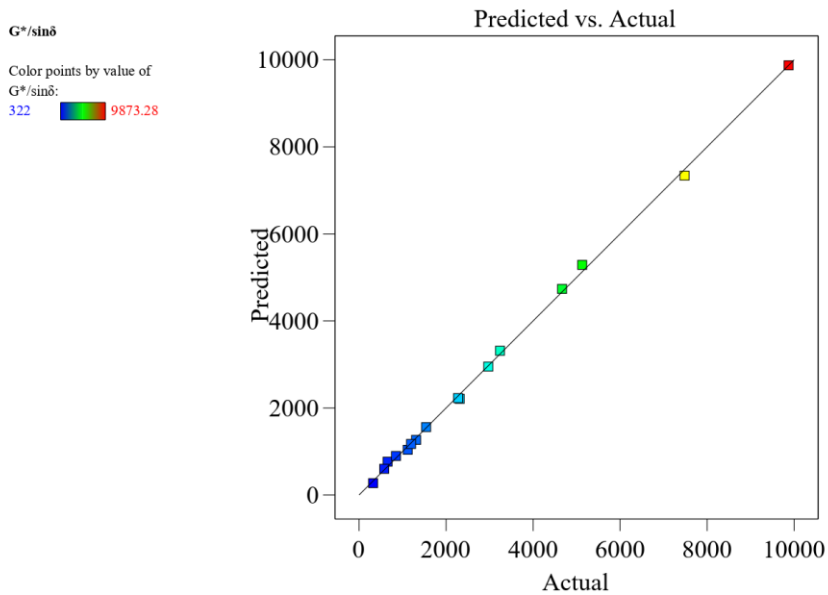

Fig. 4. Comparison of predicted and actual values

3.2. Test results of Turkey-Batman bitumen

The descriptive data of the factors and the descriptive data of the responses for the RSM model for Turkey-Batman bitumen are given in Table 6 and Table 7, respectively.

Table 6. Descriptive data for Turkey-Batman bitumen (factors)

Factor	**Name**	**Units**	**Type**	**SubType**	**Minimum**	**Maximum**	**Coded Low**	**Coded High**	**Mean**	**Std. Dev.**
A	Temperature	°C	Numeric	Continuous	52	70	-1 ↔ 52.00	+1 ↔ 70.00	61.00	6.93
B	SEBS	%	Numeric	Continuous	0	4	-1 ↔ 0.00	+1 ↔ 4.00	2.25	1.53

Table 7. Descriptive data for Turkey-Batman bitumen (responses)

Response	Name	Units	Observations	Minimum	Maximum	Mean	Std. Dev.	Ratio
R1	G*/sinδ	Pa	16	214	11724.5	3371.15	3443.85	54.79

Table 8 shows the ANOVA results for Batman bitumen. The ANOVA results show that the model used for Turkish Batman bitumen is highly significant overall ($p < 0.0001$). Among the main effects, temperature (A) and SEBS ratio (B) have a significant effect on G*/sinδ with $p = 0.0002$ and $p = 0.0354$, respectively. The interaction between temperature and SEBS ratio (AB) is very significant ($p < 0.0001$) and the non-linear effect of temperature (A^2) is also highly significant ($p < 0.0001$). However, the non-linear effect (B^2) and the third-order effect (B^3) of SEBS ratio were not significant ($p = 0.2162$ and $p = 0.4453$). The third order effect of temperature (A^3) was significant with $p = 0.0438$. Also, the interaction A^2B was significant ($p = 0.0008$), while the effect of AB^2 was insignificant ($p = 0.1433$). These results indicate that the effect of temperature on rheological properties is dominant and the effects of SEBS ratio should also be considered, but the non-linear SEBS terms can be removed from the model.

Table 8. ANOVA results for Batman bitumen

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	1.78E+08	9	1.97E+07	307.72	< 0.0001	significant
A-Temperature	3.88E+06	1	3.88E+06	60.48	0.0002	
B-SEBS	4.69E+05	1	4.69E+05	7.31	0.0354	
AB	2.14E+07	1	2.14E+07	333.58	< 0.0001	
A^2	9.56E+06	1	9.56E+06	149.18	< 0.0001	
B^2	1.23E+05	1	1.23E+05	1.91	0.2162	
A^2B	2.42E+06	1	2.42E+06	37.8	0.0008	
AB^2	1.82E+05	1	1.82E+05	2.83	0.1433	
A^3	4.15E+05	1	4.15E+05	6.48	0.0438	
B^3	42747.54	1	42747.54	0.6669	0.4453	
Residual	3.85E+05	6	64097.67			
Cor Total	1.78E+08	15				

Figure 5 shows 2D and 3D RSM plots for Turkey Batman bitumen. The RSM plots for Turkey Batman bitumen reveal the effects of temperature (A) and SEBS ratio (B) on G*/sinδ in detail. The 3D surface plot visually explains how G*/sinδ changes depending on the SEBS ratio and temperature changes. According to the graph, it is seen that G*/sinδ value decreases rapidly as the temperature increases, i.e. the stiffness of the bitumen decreases and becomes more prone to deformation at high temperature. On the other hand, the increase in the proportion of SEBS significantly increases the value, indicating that SEBS improves the elastic properties of bitumen and increases its high temperature resistance. The contour plot reveals this trend more clearly, showing that high G*/sinδ values are obtained at low temperatures and high SEBS ratios. For example, when the SEBS ratio reaches 3-4% and the temperature is between 52-58°C, G*/sinδ values exceed 8000 Pa. This emphasises the importance of determining the SEBS ratio and controlling the temperature for optimum performance. In conclusion, SEBS modification for Batman bitumen makes an important contribution to improve the rheological performance, especially by balancing the temperature effect.

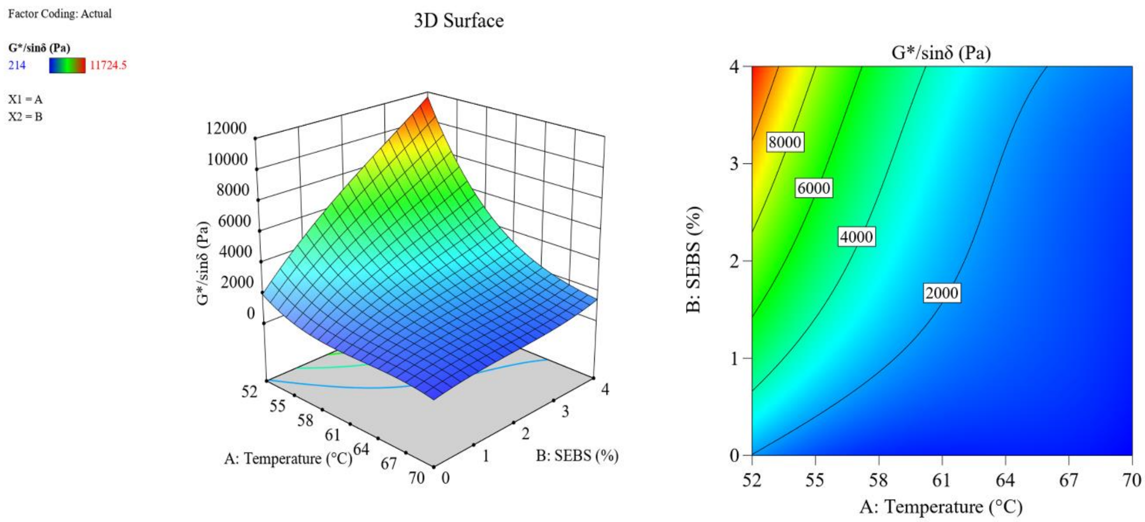

Fig. 5. 2D and 3D RSM plots for Turkey-Batman bitumen

Figure 6 shows the perturbation curves for Iraqi and Batman bitumen for comparison. When the perturbation curves generated by RSM (Response Surface Methodology) on the G*/sinδ (dynamic shear modulus) values obtained by modifying Iraqi and Batman bitumen with 2%, 3% and 4% SEBS (Styrene-Butadiene-Styrene) additives are compared, significant differences between the two bitumen types are observed. In Iraqi bitumen, the G*/sinδ value decreases significantly as the temperature (A factor) increases, indicating that temperature increase has a negative effect on viscoelastic properties. The steep structure of the curve indicates that the Iraqi bitumen exhibits a very sensitive behaviour to temperature changes. When the SEBS additive ratio (B factor) is increased, a limited increase in G*/sinδ value is observed, but the curve of this increase is slower and its effect is lower, indicating that the additive ratio has a more secondary role in Iraqi bitumen. On the other hand, as the temperature (A factor) increases in Batman bitumen, the G*/sinδ value decreases again, but this decrease is slower and linear. This indicates that Batman bitumen exhibits a more stable viscoelastic behaviour against temperature changes. Furthermore, a significant increase in the G*/sinδ value of Batman bitumen is observed as the SEBS additive ratio (B factor) increases, indicating that the additive provides a more effective modification of this bitumen. In general, Iraqi bitumen is more sensitive to temperature changes, while Batman bitumen adapts better to the SEBS additive and shows a more balanced response to temperature effects. These differences may be due to the chemical and physical structure of the bitumens; Batman bitumen can be considered to have a matrix that is better adapted to SEBS, while Iraqi bitumen loses its viscoelastic properties faster in the face of temperature. As a result, Batman bitumen can be considered as a more suitable option for wide application areas by exhibiting a more stable performance, while Iraqi bitumen can be considered as a material that requires careful handling.

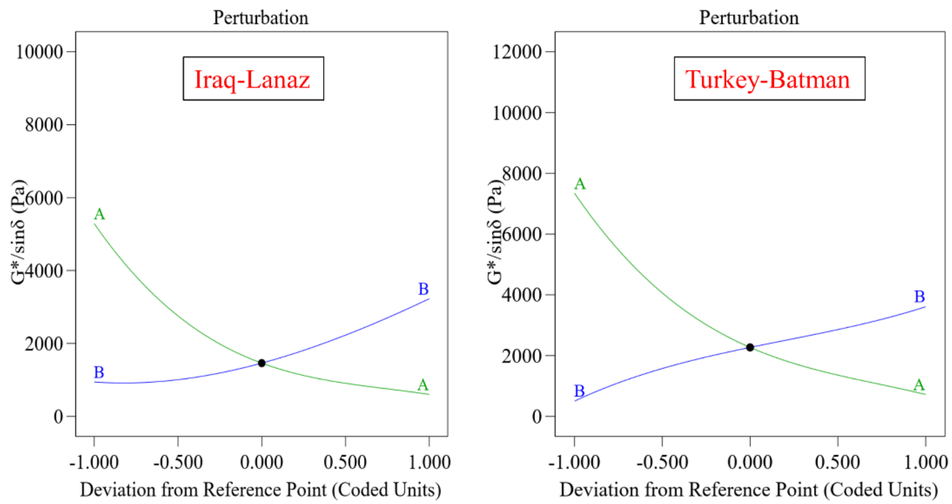

Fig. 6. Comparison of perturbation curves for both bitumen

4. Conclusion

This study examines the G*/sinδ values of Iraqi and Batman bitumen modified with 2%, 3%, and 4% SEBS (Styrene-Butadiene-Styrene) using Response Surface Methodology (RSM). The results showed significant differences in the viscoelastic properties of the two bitumens after modification. In Iraqi bitumen, G*/sinδ values decreased sharply with temperature (factor A), indicating high sensitivity to temperature changes. A slight increase in G*/sinδ was observed with higher SEBS ratios (factor B), showing limited additive effectiveness. For Batman bitumen, the decrease in G*/sinδ with temperature was slower and more controlled. Higher SEBS ratios significantly increased G*/sinδ values, suggesting greater additive compatibility. These findings highlight that Batman bitumen modified with SEBS offers more stable performance and broader application potential, while Iraqi bitumen requires careful evaluation due to its temperature sensitivity.

References

[1] Y. R. Kim, *Modeling of Asphalt Concrete*, First edit. New York: McGraw-Hill Education, 2009.
[2] D. N. Little, D. H. Allen, and A. Bhasin, *Modeling and design of flexible pavements and materials*. 2017.
[3] R. Hunter, A. Self, and J. Read, *The Shell Bitumen Handbook, 6th edition*. 2015.
[4] B. Javilla, L. Mo, F. Hao, B. Shu, and S. Wu, “Significance of initial rutting in prediction of rutting development and characterization of asphalt mixtures,” *Construction and Building Materials*, vol. 153, pp. 157–164, 2017.
[5] A. Subhy, “Advanced analytical techniques in fatigue and rutting related characterisations of modified bitumen: Literature review,” *Construction and Building Materials*, vol. 156, pp. 28–45, 2017.
[6] U. Isacsson and X. Lu, “Testing and appraisal of polymer modified road bitumens—state of the art,” *Materials and Structures*, vol. 28, no. 3, pp. 139–159, 1995.
[7] J. Zhu, B. Birgisson, and N. Kringos, “Polymer modification of bitumen: Advances and challenges,” *European Polymer Journal*, vol. 54, pp. 18–38, 2014.
[8] X. Lu and U. Isacsson, “Modification of road bitumens with thermoplastic polymers,” *Polymer Testing*, vol. 20, no. 1, pp. 77–86, 2000.
[9] G. Polacco, J. Stastna, D. Biondi, and L. Zanzotto, “Relation between polymer architecture and nonlinear viscoelastic behavior of modified asphalts,” *Current Opinion in Colloid & Interface Science*, vol. 11, no. 4, pp. 230–245, 2006.
[10] S. S. Galooyak, B. Dabir, A. E. Nazarbeygi, and A. Moeini, “Rheological properties and storage stability of bitumen/SBS/montmorillonite composites,” *Construction and Building Materials*, vol. 24, no. 3, pp. 300–307, 2010.
[11] B. V. Kok and M. Yilmaz, “The effects of using lime and styrene–butadiene–styrene on moisture sensitivity resistance of hot mix asphalt,” *Construction and Building Materials*, vol. 23, no. 5, pp. 1999–2006, 2009.

[12] S. Zapién-Castillo, J. L. Rivera-Armenta, M. Y. Chávez-Cinco, B. A. Salazar-Cruz, and A. M. Mendoza-Martínez, "Physical and rheological properties of asphalt modified with SEBS/montmorillonite nanocomposite," *Construction and Building Materials*, vol. 106, pp. 349–356, 2016.

[13] J. Zaniewski and M. Pumphrey, "Evaluation of Performance Graded Asphalt Binder Equipment and Testing Protocol," 2004.

[14] M. Ulucan, "From waste to sustainable production: Experimental design and optimization of sustainable concrete using response surface methodology and life cycle assessment," *Sustainable Chemistry and Pharmacy*, vol. 42, p. 101770, 2024.

[15] M. Ulucan and K. E. Alyamac, "An integrative approach of the use of recycled concrete aggregate in high-rise buildings: Example of the Elysium," *Structural Concrete*, vol. 24, no. 3, pp. 3329–3350, 2023.