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Optimization of Polypropylene Dosage for Improved Rheological, Physical and Mechanical Properties of Agbabu Bitumen

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ABSTRACT

The vast majority of road infrastructure deformations are irreversible. They shorten the lifespan of flexible pavements and add to road safety concerns. Viscoelasticity is required for natural bitumen to function as a binder in pavements. However, when exposed to climate and heavy loads, natural bitumen's ability to undergo elastic deformation reduces. Consequently, road researchers have focused on modifying bitumen using polymers and nanomaterials to enhance pavement performance. Polymeric bitumen is extremely sensitive to Polypropylene (PP) dosage. Excessive use of PP leads to high viscosity. This study examines the impact of PP doses on the physical, rheological, and mechanical properties of Agbabu natural bitumen. The bitumen was dehydrated and analyzed for conventional characteristics using established techniques. The purified material was treated with PP at varying dosages (1.5 - 6 wt percent), and a binary mixture of bitumen and PP was optimized using D-Optima experimental design and response surface approach. The result shows that the mechanical properties, flash, and softening points of the raw bitumen were enhanced after modification. However, the penetration point of the modified bitumen decreases while viscosity increases as PP dosage increased from 2 to 3.75 wt percent. Therefore, the optimum dosage of 2.75 wt percent PP is recommended.

INTRODUCTION

Many developing countries relied on imported modified bitumen and refinery asphalt residue for the construction and maintenance of road infrastructure (Ogbuigwe, 2018). This over-reliance on importation has reduced the extent of asphaltic road coverage and negatively impacted the safe transit of goods and services. Due to exposure to unfavourable climate conditions that have caused volatile compounds to oxidize, naturally occurring bitumen has been determined to be unsuitable for use as a binder in its original form (Olabemiwo et al., 2020). Previous studies have, however, shown that, with the right modification, naturally occurring bitumen can serve as an alternate binder for aggregates in the construction of asphaltic pavements (Salawudeen et al., 2020). For instance, a significant amount of bitumen has been found in the Ogun-Lagos corridor, Edo, and Ondo in southwest Nigeria. This bitumen, if properly modified, can be utilized as a binder and a waterproofing agent in the road and building sectors, respectively (Salawudeen et al., 2024).

Bitumen is modified by adding additives to enhance its mechanical, physical, and viscoelasticity properties (Mashaan et al., 2021). Several attempts have been made to improve the properties of Nigerian bitumen by using different additives, such as crumb rubber, polyphosphoric acid, silver nanoparticles, sulfur, and polymers (Olabemiwo et al., 2015). But no single modified bitumen has provided all the required properties, especially when subjected to high traffic densities and axle loadings. Road engineers typically have to choose the combinations that are the strongest and most resistant to deformation (Hu et al., 2020). Bituminous pavements need to be flexible at low and moderate temperatures to avoid cracking, and tough enough to resist rutting in hot weather (Sani et al., 2021). Although polymers were not initially designed for bitumen modification, various investigations have shown some improved properties of bitumen, such as higher stiffness at high temperatures, higher cracking resistance at low temperatures, better moisture resistance, or longer fatigue life (Enfrin & Giustozzi, 2022). Different classes of polymers, including plastomers (e.g. polyethylene (PE), PP, ethylene–vinyl acetate (EVA), ethylene–butyl acrylate (EBA)) and thermoplastic elastomers (e.g. styrene–butadiene–styrene (SBS), styrene–isoprene–styrene (SIS), and styrene–ethylene/butylene–styrene (SEBS)) have been investigated (Al-Rabiah et al., 2016; Kunanusont et al., 2020).

Polypropylene has been widely used in bitumen modification due to its impressive properties. Its high working temperature and tensile strength contribute to an increase in the softening point of modified bitumen, making it more resistant to deformation under heavy loads (Salawudeen et al., 2020, 2024). However, the polypropylene-modified bitumen is highly sensitive to dosage (Brasileiro et al., 2019). A significant drawback is its tendency to cause an increase in viscosity of bitumen, which is not desirable as it affects workability with high energy demand. Additionally, PP is prone to phase separation (Ortega et al., 2017), which can result in an inconsistent blend and negatively impact the performance of the modified bitumen. By optimization of polymer doses and mixing conditions, this study aims to produce bitumen batches with a general improvement of conventional properties. Furthermore, a new optimization process is urgently needed because the traditional optimization methodology, which has been emphasized in several publications (Reddy et al., 2019; Salawudeen et al., 2025) is limited.

MATERIALS AND METHODS

Materials and Equipment

The primary materials used were 50/70 penetration grade bitumen and polypropylene. The former was sourced from Agbabu (longitude 3°45E and 5°45E and latitude 6°00N and 7°00N) bitumen deposits in Ondo State, Nigeria, while the latter was purchased. The major equipment used for analyzing the modified bitumen are shown in Figure 1.

Characterization of Bitumen

Characterization of bitumen was carried out using ASTM standard techniques shown in Table 1. Table 1 shows the primary properties of the raw bitumen. The polypropylene sample supplied by Loba Chemie PVT Ltd has the following properties: 25 g/10 min MFI, 0.925 g/cm3 density, and a melting point of 150 ◦C.

Material Preparation

The bitumen sample was collected into an iron container from a dug oil well at Agbabu, Ondo state and transported to the laboratory. To remove sand and moisture, the sample was boiled in a beaker at 110 degrees Celsius for 30 minutes. The molten bitumen was filtered using iron filter to get rid of sand and other contaminants according to Salawudeen et al. (Salawudeen et al., 2020).

Experimental Design for Polymeric Bitumen

A randomized D-Optimal Mixture Design of the experiment was used to simulate bitumen - PP mixture.

Figure 1. Laboratory equipment used for bitumen modification: (a) Variable speed high shear mixer (b). Asphalt Penetration tester (c). LR-A018 No Rotor Rheometer (d). Softening point analyzer (Bitumen Laboratory, Chemical Engineering Department, LAUTECH, Ogbomoso, Nigeria)

Table 1 Properties of Base Bitumen

Physical properties	Penetration	Softening point	Flash point	Density	Ductility
Units	0.1 mm	(°C)	(°C)	g/cm^3	(cm)
Standard	ASTM D5–06e1	ASTM D−36	ASTM D−92	ASTM D−70	ASTM D−113
Standard value	50–70	46–54	-	-	≥ 100
Test value	53	48	279	1.16	110

Thirteen (13) random samples were simulated for the range of bitumen (94–98.5 wt%) and PP (1.5–6 wt%). D-optimal, axial, simplex-lattice, and simplex-centroid designs are some of the several types of mixed designs. In this work, the D-optimal mixed design was used to minimize the total variance of the objective functions (Izzati et al., 2015). Furthermore, compared to other designs, the D-optimal design requires a smaller number of runs, thereby reducing the cost and time of testing (Carneiro et al., 2020).

Preparation of PP-Modified Bitumen

For each of the experimental runs, a predetermined quantity of bitumen was weighed into a beaker according to the experimental design and placed under a thermostatically controlled hot plate set at 160 ◦C(Celauro et al., 2020). A measured quantity of PP was added to the molten bitumen, and content was mixed using a high-shear mixer, agitated at 1200 rpm for 30 minutes. After 30 minutes, each the PP- bitumen mix was removed and kept in a beaker at ambient conditions for characterization. Table 2 presents the design matrix and responses in the 13 tests resulting from the experimental D-optimal design.

Determination of Conventional Properties

Standard methods were used for the analysis of raw and modified samples. The method is described as follows:

Softening point determination

The softening point of the raw and modified samples was determined using ASTM D36 (ASTMD36/D36M-14, 2014). A measured quantity (50 g) of bitumen samples were put in a ring and hanged in a cup filled with 75 cl of water. Glycerine was applied on the metal plate below the hanger to prevent bitumen from sticking to the plate. A ball was suspended on the bitumen in the ring, and the heater was put in an "ON" mode. As the temperature of the water increased, the bitumen melted. The weight of the ball fell through the melted bitumen on the plate. The temperature and time at which the ball fell on the plate were noted and recorded. The procedure was repeated for all the samples and the modified bitumen.

Penetration point determination

Penetration test is an empirical test which is used to measure the consistency (hardness) of bitumen mixture at a specified test condition. The ASTM-D5-97 standard (ASTMD5-97, 1998) was followed in carrying out the experiment. Penetration was measured by means of a penetrometer in which a needle with a load was applied to the surface of the bitumen sample at 25 ^{o}C for 5 seconds. The penetration reading was taken in triplicate for each sample and recorded. The sample procedure was repeated for all the modified samples.

Determination of flash point

The flash point of the bitumen was determined according to the ASTM D92 (ASTMD92-01, 1965). The cup was filled with a sample of the bitumen up to the mark (75 ml), and the cup was heated with a Bunsen burner, maintaining a small open flame from an external supply of natural gas. Periodically, the flame was allowed to pass over the surface of the bitumen using a flame lighter. When the flash temperature is reached, the bitumen catches fire. The temperature (at the moment) at which this occurred was noted and recorded as the flash point temperature.

Procedure for Viscosity determination

ASTMD2170-95 was used for measuring the viscosity of raw and modified bitumen (ASTMD2170-95, 1995). A measured quantity (0.3 g) of modified bitumen samples was measured using analytical weighing balance. Each sample was wrapped in a specially made nylon that came from the manufacturer. The rheometer was connected to a computer with rubber and polymer software installed on it. The rheometer opens and closes based on pressure due to the pressure cylinder attached to the rheometer. The weighed sample was then placed on the spindle when the rheometer was opened and thereafter, the chamber was closed. The rheometer was initially set at 130 ^{o}C and 240 seconds. The sample was allowed to be heated at that temperature for 240 seconds. The viscosity reading was then taken and recorded.

Determination of bitumen ductility

Ductility was measured using the ASTM D− 113. The description of the procedure is available elsewhere (Salawudeen et al., 2020).

Statistical Analysis and optimization study

For data analysis, Analysis of variance (ANOVA) was used at 95% confidence level. Coefficient of determination (R^2), adjusted coefficient of determination (adjusted R^2), predicted coefficient of determination (predicted R^2), coefficient of variation (C.V.), standard deviation, predicted residual sum of squares (PRESS), lack-of-fit, and regression data (p and F values) are the statistical parameters used to evaluate and choose the best-fitted model for the binary systems(Salawudeen et al., 2025).

The aforementioned correlation coefficients, which demonstrate the agreement between the anticipated and experimental responses, were used to calculate the degree of significance for the mean, linear factorial (2F1), quadratic, cubic, and quartic models using the ANOVA. Following the fitting procedure, the Design Expert also displayed the contour, 3D model, factors, and interaction graphs based on the correlation of design factors.

Using the ANOVA, the best mathematical model that described the experimental data of various responses was selected as the objective function. Optimization was thereafter carried out by employing the numerical approach involving solving the multi-objective functions subjected to inequality constraints. Three repetitions of the experimental verification of the numerical optimization solution were conducted.

RESULT AND DISCUSSION

Effects of PP Dosage on Penetration

Figure 2 (a) shows the effect of PP dosage on the penetration point of the modified bitumen. The analysis in this study shows that all the modified samples exhibited lower penetration values in the range of 36.25 – 44.50 cm compared with the 53 cm obtained in the raw bitumen. The reduction of penetration as PP dosage increases between 2-6 wt%. may be attributed to the rigidity of bitumen on the addition of PP, as earlier posited by previous studies (Aljanadi et al., 2020; Olukanni & Olugbenga, 2018). The resistance to penetration is an indication of improved rigidity of the binder at 25 ^{o}C (Feng et al., 2016; Mashaan et al., 2022). But the variation in the observed values suggests that PP dosages have effects on the rheological properties of bitumen. Previous authors have observed that the chemical composition (SARA fraction) of bitumen had a significant effect on penetration (Hu et al., 2020).

Effects of PP Dosage on Softening Point

Figure 2(b) shows the effects of PP dosage on the softening point of the bitumen sample. It is observed from Table 2 that the sample's softening point ranged from 51.81 to 68.79 ^{o}C, which differed remarkably from that of the raw sample (48 ^{o}C). Softening point may vary depending on the composition of the bitumen samples. Abdul et al. (Abdul et al., 2019) reported 40°C for a Malaysian bitumen. Olabemiwo et al (Olabemiwo et al., 2015) also reported a softening point of 47°C for unmodified Agbabu bitumen from Nigeria, which confirmed the observation of this present study. Thus, softening points for raw bitumen are generally low when compared with standard (ASTM D-36) (Abdul et al., 2019; Salawudeen et al., 2024). However, the highest softening point of 61^{o}C was recorded after modifying the sample with 3.75 wt% PP. thus, a further increase in the dosage of PP beyond this threshold value lowers the softening point. Thus, the softening point is sensitive to PP dosages.

Effects of PP Dosage on Ductility

The ductility is a mechanical property that measures the extent of stretches when bitumen is under stress at standard conditions (5 cm/min at 25 ^{o}C). It is also an indicator of bitumen viscoelasticity during deformation. A minimum of 100 (ASTM D113) is the ASTM specification for binders. Ass shown in Table 1, the ductility of unmodified samples obtained ranged from 101-110 mm, which satisfied the minimum requirement. After modification the maximum ductility value of 119 cm was observed.

This shows that using PP modifier, the mechanical property of bitumen was enhanced.

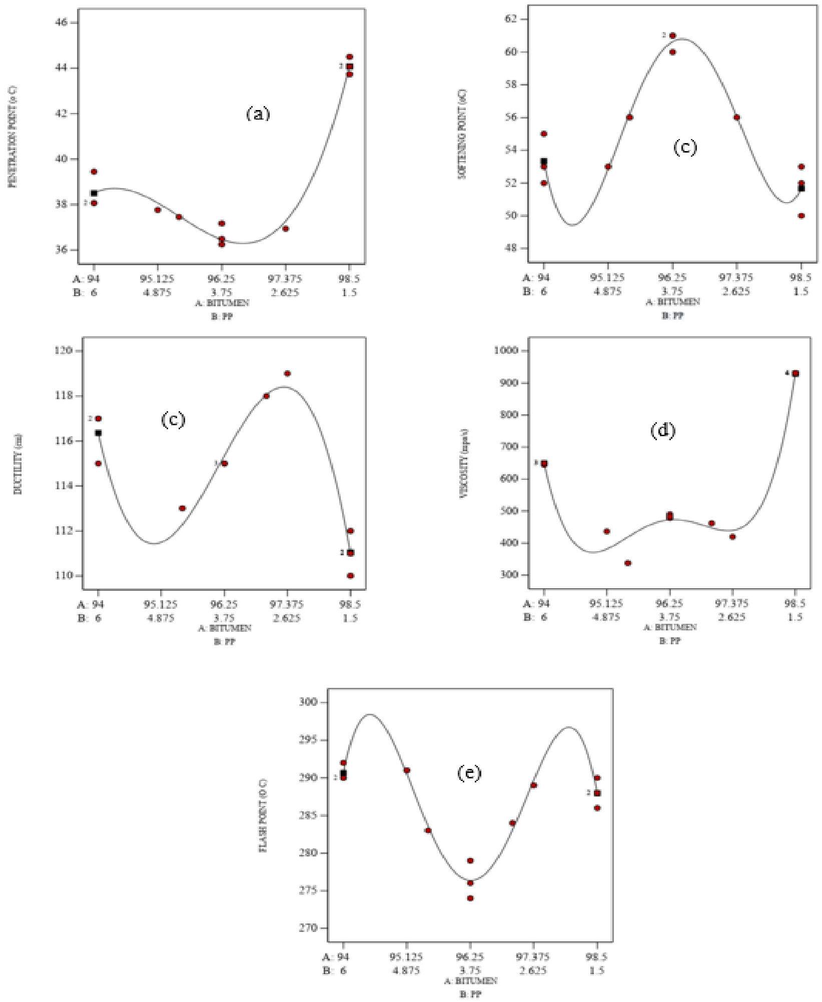

Figure 2. Sensitivity of PP dosage to (a). Penetration point (b). Softening point (c). Ductility (d). Viscosity and (e). Flash point

It is, however, observed that PP modifiers in the range between 2.76 and 3.75 wt.% are adequate. Previous research (Desidery & Lanotte, 2021) has indicated a disproportionate increase in ductility with PP, as observed in this study.

Effects of PP Dosage on Viscosity

Figure 2 (d) shows the effects of PP dosage on the viscosity of the bitumen sample. Differences were observed in viscosity when bitumen samples were modified with varying quantities of PP. The differences in viscosities can be linked to the SARA composition, especially the resin fraction of the bitumen (Cui et al., 2014; Salawudeen et al., 2024). It can also be seen vividly that the addition of PP increased the viscosity values higher than those of the raw sample. According to a previous study, the presence and quantity of asphaltenes in bitumen may influence the polymeric wax formation and pour point (Yang et al., 2014).

Effects of PP Dosage on Flash Point

The temperature at which the bitumen flashes in the presence of an open fire is the flash point (Salawudeen et al., 2020). A minimum flash point of 250 °C and 225 ºC for 60/70 and 80/100 penetration grades is specified for bitumen (Osuolale & Agbalaya, 2012). The average flash point measured ranged between 277 and 279 ºC, which is higher than the recommended minimum value. It was, however, observed that an increase in dosage of PP marginally caused an increase in flash point of the bitumen. Thus, a small PP quantity as low as 2 wt.% is sufficient to cause a significant improvement in the flash point.

Optimization Study

Model Selection

Table 2 presents the 13 experimental runs comprising varying PP dosage (1.5 - 6 wt%) and bitumen quantity (94 – 98.5 wt%). A high value is desired for softening, flash, and ductility values, while a lower penetration value is anticipated following modification with PP. This study developed predictive empirical correlations for these responses, which were used for optimization of PP dosages for the formulation of binary PP-bitumen mix.

Analysis of variance (ANOVA) was used to assess the significance of the interaction of dosage with bitumen. Using the regular coefficient of determination, the suitability of regression models was confirmed for each of the responses as indicated in **Table 3**. For all the responses measured, polynomial models were suggested.

Model Development

Table 4 shows the ANOVA table for the developed models for all the properties. The F-value, p-values, and lack of fit recorded for various responses indicate that the associated models are reasonably accurate with a 95 % confidence level since noise is unlikely to produce an F-value greater than 0.01%. Furthermore, the Lack of Fit is not significant ($p>0.05$), an indication of the adequacy of the chosen polynomial models. The redundant quadratic and interaction terms were omitted because they are not significant ($p>0.05$). The final models are presented in Eqs. 1 - 5, where A and B denote bitumen and PP, respectively.

Table 2 Design Matrix and Response for Binary PP-Bitumen Mix

Run	A:Bit	B:PP	Flash Point (oC)	Ductility (cm)	Penetration Point (mm)	Softening Point (^oC)	Viscosity Mpa.s
1	98.5	1.5	286	112	44.50	53	931
2	94	6	290	115	39.45	55	650
3	97.375	2.625	289	119	36.94	56	420
4	95.125	4.875	291	115	37.77	53	437
5	94	6	290	117	38.07	53	650
6	98.5	1.5	288	110	44.07	52	929
7	96.25	3.75	279	115	36.49	60	483
8	94	6	292	117	38.07	52	645
9	97	3	284	118	35.81	49	462
10	95.5	4.5	283	113	37.45	56	338
11	96.25	3.75	274	115	37.17	61	478
12	98.5	1.5	290	111	43.74	50	930
13	96.25	3.75	276	115	36.25	61	490

Table 3: Summary statistics for flash point, ductility penetration values, softening values, and viscosity of PP-bitumen models

Properties	Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	Remarks
Flash point	Quartic	<0.0001	0.7934	0.9111	0.8572	Suggested
Ductility	Cubic	<0.0001	0.4842	0.4842	0.9053	Suggested
Pen. Point	Cubic	<0.0001	0.6641	0.9699	0.9490	Suggested
Soft. point	Quartic	0.0003	0.8340	0.8969	0.8055	Suggested
Viscosity	Quartic	<0.0001	<0.0001	0.9692	0.8880	Suggested

$$Penetration = 44.08A + 38.50B - 19.29\,AB(A-B) \quad (1)$$

$$Softening = 51.67A + 53.34B + 32.51AB + 21.42\,AB(A-B) - 88.69AB(A-B)^2 \quad (2)$$

$$Ductility = 111.05A + 116.36B + 6.58AB + 50.95AB(A-B) \quad (3)$$

$$Viscosity = 929.25A + 649.54B - 1267.10AB - 435.21AB(A-B) - 3007.75AB(A-B)^2 \quad (4)$$

$$Flash\,point = 287.98A + 290.68B - 51.78AB + 2.79AB(A-B) + 223.20AB(A-B)^2 \quad (5)$$

Numerical Optimization

It is possible to select a mix among several designs using a method that simultaneously considers the effects of multiple factors at different levels using regression equations. In this case, equations 1 – 5 are considered in a single optimization framework available in the Design Expert software. The optimization problem was set up to minimize or maximize the objective functions, subject to a selected set of constraints (Baghaee et al., 2015). Equations 1 – 5 serve as the objective functions, with the set of constraints set as ranges of variables used during the experiment. These equations were used for searching combinations of factors that satisfy the constraint placed on each of the responses. The solution is achieved by maximizing flashpoint, ductility, and softening point while simultaneously minimizing the penetration point and viscosity. Design-Expert performed multi-objective function optimization by transforming each of the regression equations to a desirability function, d_i (Arinkoola et al., 2022).

The overall desirability (D) is obtained as the multiplicative mean of all individual desirability (Equation 6) after the specified number of iterations.

$$D = \left[\prod_{i=1}^{n} d_i\right]^{1/n} \quad (6)$$

where n is the number of random samples and d_i are the desirability for different realizations. At the optimum conditions A (97.25 wt.%) and B (2.75 wt.%), the corresponding flash point, ductility, penetration point, softening point, and viscosity are 287.42 ºC, 118.39 cm, 36.95 mm, 57.05 ºC, and 439.36 MPa.s, respectively. Design Expert also displays the result of the optimization as depicted on the ramps diagram shown in Figure 3. The validity of this result was established experimentally through analysis of three different batches of bitumen mixes prepared with 97.25 wt.% bitumen and 2.75 wt.% PP. The mean properties obtained from the experimental mixes yielded 280.02± 3.2 ºC, 120.12±1.23 cm, 37.87±08 mm, 59.55±1.0 ºC, and 440.15±3.52 MPa.s, respectively, for flash point,

Table 4: ANOVA of developed models for binary PP-bitumen properties

	Sum of Squares	df	Mean Square	F-value	p-value	
Flash point						
Model	400.03	4	100.01	31.74	< 0.0001	significant
(1)Linear Mixture	11.17	1	11.17	3.55	0.0964	
AB	363.67	1	363.67	115.43	< 0.0001	
AB(A-B)	0.1983	1	0.1983	0.0629	0.8083	
AB(A-B)^2	163.29	1	163.29	51.83	< 0.0001	
Residual	25.21	8	3.15			
Lack of Fit	1.87	2	0/9359	0.2406	0.7934	Not significant
Pure Error	23.33	6	3.89			
Cor Total	425.23	12				
			Ductility			
Model	80.31	3	26.77	36.09	<0.0001	Significant
(1) Linear Mixture	23.10	1	23.10	31.10	0.0005	
AB	6.93	1	6.93	9.33	0.0157	
AB(A-B)	45.35	1	45.35	61.05	<0.0001	
Residual	5.94	8	0.7428			
Lack of Fit	1.28	2	0.6380	0.8203	0.4842	Not significant
Pure Error	4.67	6	0.7778			
Cor Total	86.25	11				
			Penetration Point			
Model	103.9	3	34.36	119.00	<0.0001	Significant
(1) Linear Mixture	43.14	1	43.14	149.39	<0.0001	
AB	56.95	1	56.95	197.21	<0.0001	
AB(A-B)	7.38	1	7.38	25.56	0.0010	
Residual	2.31	8	0.2888			
Lack of Fit	0.2947	2	0.1473	0.4386	0.6641	Not significant
Pure Error	2.02	6	0.3359			
Cor Total	105.40	11				
			Softening Point			
Model	143.59	4	35.90	24.93	0.0003	Significant
(1)Linear Mixture	2.16	1	2.16	1.50	0.2601	
AB	137.19	1	137.19	95.28	<0.0001	
AB(A-B)	9.227	1	9.22	6.40	0.0392	
AB(A-B)^2	25.23	1	25.23	17.52	0.0041	
Residual	10.08	7	1.44			
Lack of Fit	0.0798	1	0.0798	0.0479	0.8340	Not significant
Pure Error	10.00	6	1.67			
Cor Total	153.67	11				
			Viscosity			
Model	5.1024E+05	4	1.276E+05	95.31	<0.0001	significant
(1)Linear Mixture	1.146E+05	1	1.146E+05	85.66	<0.0001	
AB	2.178E+05	1	2.178E+05	162.72	<0.0001	
AB(A-B)	4830.76	1	4830.76	3.61	0.0940	
AB(A-B)^2	29650.73	1	29650.73	22.16	0.0015	
Residual	10706.44	8	1338.30			
Lack of Fit	10615.10	2	5307.55	348.67	<0.00015	Significant
Pure Error	91.33	6	15.22			
Cor Total	5.209E+05	12				

ductility, penetration and softening points, and viscosity, respectively. These values were found to agree with standard bitumen properties (Table 1) and compared favourably with what was obtained from the literature (Salawudeen et al., 2020).

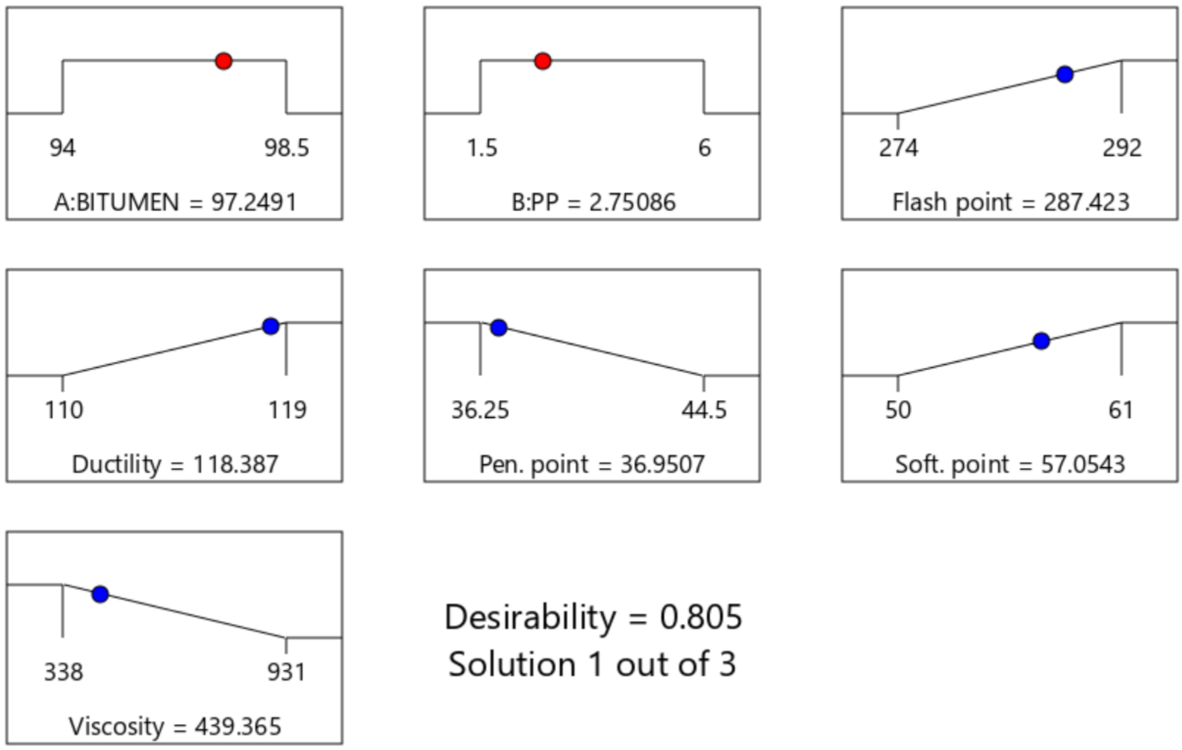

Figure 3. Ramp diagram showing optimal conditions

CONCLUSIONS

In this study, polymeric modification of the virgin bitumen was investigated using experimental design techniques. Statistical analysis and optimization of the PP and bitumen were investigated using RSM and physical characterization. The conclusions drawn from this study are as follows:

1. Models created for the binary modified bitumen showed good agreement between predicted and actual values, suggesting that the models could accurately predict the mix properties within the specified factor range.
2. According to the study's findings, adding optimal 2.75 wt% PP to virgin bitumen increased the softening point, ductility, and viscosity. However, the penetration point was reduced.

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DISCLOSURE OF ANY CONFLICT OF INTEREST

The authors declare that they have no other known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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