Design and optimization of polyurethane modified bitumen (PUMB) using response surface method

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Abstract. This paper discusses the utilization of Response Surface Method (RSM) statistical tool to determine the optimal amount of polyurethane (PU) for modifying 80/100 penetration grade bitumen. Central composite design (CCD) was used to develop an experimental design matrix where bitumen and PU are designated as the factors while penetration, softening point and viscosity are designated as the response. Numerical analysis of polyurethane modified bitumen (PUMB) shows that the optimal amount of PU in the modification of the bitumen is 5%. Verification of the chosen model shows that it is consistent with the experimental value since the percentage error is less than 5%. Result of the consistency test shows that the addition of 5% PU resulted in higher penetration and viscosity values but lower softening point value, which in consequence improve bonding strength as the flow of bitumen is reduced.

1. Introduction

Bitumen is a viscous thermoplastic material with a strong adhesive property and is commonly used in the construction of flexible pavements [1]. However, excessive heavy traffic, heavy axle load and changes in environmental conditions cause a deterioration of the properties of bitumen, thereby reducing its performance as well as its service life [2]. The most commonly observed pavement failures are rutting, fatigue and cracking. One of the methods for extending the service life of pavements is by improving bitumen properties through the addition of a modifier.

Previous studies on bitumen modification have been conducted using various types of additives, such as epoxidized natural rubber, nanoclay, bio-oil, polymer, geopolymer and other promising materials. Researchers have experimented with using bio-renewable material such as biomass and bio-oil in an attempt to improve bitumen properties and reduce bitumen consumption. Mohab et al. [3] used palm kernel oil polyol (PKO-p) as a replacement in conventional bitumen and found that, in addition to the lower temperatures required for the mixing and compaction of the modified bitumen, the physical properties of the bitumen are similar with those of the unmodified bitumen. Khairuddin et al. [4] have shown that the addition of the PKO-p and 2,4-diphenylmethane diisocyanate (MDI) imparted a higher resistance towards rutting due to the higher softening point and lower penetration
values of the 60/70 penetration grade bitumen. Investigation has also been carried out to determine the effect of PKO-p and MDI on aging and results show improved bitumen resistance towards aging [5].

Researchers are increasingly employing statistical analysis to analyse bitumen content, asphalt mixture performance parameters, and pavement performance during its service life [6]. Response surface method (RSM) is a statistical method used to design experiments, develop models, evaluate the interaction between the factors and the response as well as to run the optimization process with minimal number of experiments runs [7]. Nassar et al. [8] used RSM to determine bitumen emulsion content, pre-wetting water content and curing time to optimize the mix design parameters of the pavement. Another research utilize RSM to establish the optimum content of Warm Mix Asphalt (WMA) additive on asphalt mixture compaction temperature [9]. Bala et al. [10] investigated the optimum amount of nanosilica and bitumen by using RSM in an endeavour to obtain high performance nanocomposite-modified asphalt mixture. Therefore, RSM can be used as an alternative technique for optimizing the mix design parameters of pavements as well as for reducing the number of samples required for testing.

The objective of this study is to determine the optimal percentage of polyurethane (PU) for modifying 80/100 penetration grade bitumen. The design and optimization were done using RSM run by Design Expert Software. The effects of this new material were investigated through penetration, softening point and viscosity tests that are designated as the response. Validation of predicted model and optimization of the results were conducted to ensure the accuracy of the predicted model.

2. Experimental designs

2.1. Materials

The 80/100 penetration grade bitumen used as the control sample in this study is supplied by Cenco Science Malaysia. The PU was produced using palm kernel oil polyol (PKO-p) and 2,4-diphenylmethane diisocyanate (MDI) using a pre-polymerization method. Both PKO-p and MDI were supplied by the School of Chemical Sciences, UKM, Malaysia. The physical properties of the control sample is presented in Table 1.

Table 1. Physical properties of control sample.

| Bitumen test               | Bitumen Grade 80/100 | Standard Test |
|----------------------------|----------------------|---------------|
| Penetration (0.1 mm) at 25 °C | 86                   | ASTM D5       |
| Softening point (°C)       | 46                   | ASTM D36      |
| Ductility(cm) at 25 °C     | 180                  | ASTM D113     |
| Viscosity (mPa.s) at 135 °C | 332                  | ASTM D4402    |
| Specific gravity (g/cm³) at 25 °C | 1.03                | ASTM D70      |

2.2. Sample preparation

The control sample was heated at 145°C until it turns into liquid. PKO-p was added to the liquid and mixed using mechanical shear mixer at 2000 revolutions per minute for 15 minutes at 110°C; this is followed by the addition and mixing of MDI using the same parameters. In order to obtain a homogeneous PUMB, the temperature, mixing rate and time were evaluated through softening point and viscosity tests until stable results were obtained for both tests [11, 12]. The modifier for the control sample, PU, was added in varying percentages of between 5-20% [4].

2.3. Laboratory testing

Penetration, softening point and viscosity were designated as the response variable; these tests were carried out at 135 °C to determine the effect of adding PU to the control sample. All three tests were conducted in accordance with ASTM D5, ASTM D36, and ASTM D4402, respectively.
2.4. Response surface method

RSM is a combination of statistical and mathematical techniques. This technique is able to reduce the amount of experimental work carried out in determining the factors that interact with response variables. Additionally, the optimum condition can be determined for the selected factor and responses by developing a regression model [13]. In the present study, the regression model for the two factors is given by equation 1:

\[ Y = b_0 + [b_iX_i + b_jX_j] + [b_{ij}X_i^2 + b_{ij}X_j^2] \]  

(1)

where Y is response variable (i.e., penetration, softening point, and viscosity); \( X_i \) and \( X_j \) are bitumen and PU, respectively; \( b_0, b_i, b_j, b_{ij} \) and \( b_{ij} \) are the constant coefficients of the intercept, linear, quadratic, and interaction terms, respectively.

Optimization of bitumen and PU were analyzed using Design Expert software 7.0. Analysis of variance (ANOVA) was used to examine the developed regression model. The possible interactions between the factors and the responses were determined by conducting the experiment suggested by the central composite design (CCD) [14]. In this study, the percentage of bitumen range between 80-95% and PU was added in varying percentages, with 5% being the low limit of the factorial design and 20% being the highest limit. Following this, 13 experimental runs were randomly run in five replicates at the central point. This is to ensure that there is an interaction between the factors and the responses. Table 2 presents the experimental design and the results for all responses. Finally, the Design Expert Software designed, modeled, and performed the ANOVA analysis and optimization process for the selected parameters.

| No. | Bitumen (%)a | PU (%)b | Penetration (dmm) | Softening Point (°C) | Viscosity @ 135°C (mPa.s) |
|-----|--------------|---------|-------------------|----------------------|--------------------------|
| 1   | 80.0         | 5.0     | 88                | 45.9                 | 1058                     |
| 2   | 90.0         | 10.0    | 93                | 46.5                 | 875                      |
| 3   | 80.0         | 20.0    | 89                | 48.5                 | 1375                     |
| 4   | 87.5         | 12.5    | 91                | 46.9                 | 954                      |
| 5   | 80.0         | 12.5    | 89                | 46.2                 | 991                      |
| 6   | 87.5         | 12.5    | 92                | 47.5                 | 969                      |
| 7   | 95.0         | 5.0     | 90                | 45.7                 | 513                      |
| 8   | 95.0         | 12.5    | 98                | 48.6                 | 1005                     |
| 9   | 87.5         | 12.5    | 90                | 47.9                 | 975                      |
| 10  | 95.0         | 20.0    | 100               | 50.2                 | 1050                     |
| 11  | 87.5         | 12.5    | 92                | 47.2                 | 954                      |
| 12  | 87.5         | 20.0    | 99                | 49.3                 | 988                      |
| 13  | 87.5         | 5.0     | 90                | 46.1                 | 890                      |

\( ^a \) The % of PUMB used for each blend is based on 200g/blend where 80.0% Bitumen = 80.0/(80.0+5)/200g =188.2g

\( ^b \) PU=5.0/(5.0+80.0)/200g=11.8g.

3. Results and discussion

3.1. Statistical analysis

In this study, the model equation for penetration, softening point and viscosity are given by equations (2), (3) and (4), respectively. All three models fit the quadratic polynomial regression model where the model is not aliased by RSM and were selected based on the highest order of significant condition. The results of ANOVA for the proposed models are presented in Table 3. Before verifying the
adequacy of the models, the p value, determination coefficients ($R^2$) and $R^2$ adjusted value, and lack of fit (LOF) values have to be evaluated. It is crucial to ensure the adequacy of each model since they may affect the quality of the developed model for each response [6].

Table 3 shows that the p-values for all three models are less than 0.05, indicating that the models are statistically significant. This shows that a 95% confidence interval is established for the model and the term. This is followed by evaluation of the determination coefficients. Results shows that the $R^2$ for penetration, softening point and viscosity are 0.8594, 0.8914 and 0.7185, respectively. The $R^2$ adjusted values are fairly congruent with the $R^2$ values of all models, where the $R^2$ adjusted are 0.8212, 0.8310 and 0.6922 for penetration, softening point, and viscosity, respectively. The value of LOF was evaluated to determine the discrepancy of data around the model. The LOF values for the penetration and softening points are insignificant with a p-value > 0.05, 0.1259 and 0.3887 respectively, while the p-value for viscosity is 0.0003 (significant). According to Myers [15], errors in LOF are generally related to model selection because LOF error is small and insignificant for correctly selected models. Results of the three evaluations confirm that the selected models are significant and can be used to describe the correlations between the factors and the responses [6, 16, 17].

Penetration $= + 92.24 + 3.76A + 3.24B + 2.25 AB - 0.34 A^2 + 0.66 B^2 \tag{2}$
Softening point $= + 47.36 + 0.66A + 1.71B + 0.50 AB - 0.039 A^2 + 0.26 B^2 \tag{3}$
Viscosity $= + 953.88 - 136.67A + 152.67B + 56.92 AB + 49.70 A^2 - 9.30 B^2 \tag{4}$

where $A$ represents bitumen and $B$ represents PU.

| Source              | SS   | DF | MS   | F value | p-value | Model      |
|---------------------|------|----|------|---------|---------|------------|
| Penetration         |      |    |      |         |         |            |
| Regression          | 169.58 | 5  | 33.910 | 10.999  | 0.0013  | Quadratic  |
| Residual error      | 27.75105 | 9  | 3.0834 |         |         |            |
| Lack of Fit         | 22.55105 | 5  | 4.5102 | 3.4693  | 0.1259  |            |
| $R^2$               | 0.8594 |    |       |         |         |            |
| $R^2$ adjusted      | 0.8212 |    |       |         |         |            |
| Softening point     |      |    |      |         |         |            |
| Regression          | 21.63982 | 5  | 4.3279 | 14.7683 | 0.0004  | Quadratic  |
| Residual error      | 2.637518 | 9  | 0.2930 |         |         |            |
| Lack of Fit         | 1.669518 | 5  | 0.3339 | 1.37976 | 0.3887  |            |
| $R^2$               | 0.8914 |    |       |         |         |            |
| $R^2$ adjusted      | 0.8310 |    |       |         |         |            |
| Viscosity           |      |    |      |         |         |            |
| Regression          | 291343.3 | 5  | 58268.67 | 4.5950  | 0.0233  | Quadratic  |
| Residual error      | 114127.1 | 9  | 12680.79 |         |         |            |
| Lack of Fit         | 113201.9 | 5  | 22640.37 | 97.8831 | 0.0003  |            |
| $R^2$               | 0.7185 |    |       |         |         |            |
| $R^2$ adjusted      | 0.6922 |    |       |         |         |            |

Where $a$ is sum of squares; $b$ is degree of freedom; $c$ is mean square

The 2D and 3D contour plots in Figure 1 (a-c) shows the effect of PU and bitumen on penetration, softening point and viscosity, respectively. The colours in these plots represent the interaction effect between the factors and the responses. In all graph, the colour blue to red indicate higher response value. Figure 1(a) shows the addition of 5 to 20% PU into bitumen resulted in higher penetration value. A higher penetration value may result in lower softening point, as shown in Figure 1(b). The viscosity test was conducted at 135 °C, and Figure 1(c) shows the addition of PU resulted in a proportional increase in viscosity value. The increase in viscosity is due to the hardening effect of MDI during the
pre-polymerization process that form the hard segment [16]. It can be concluded that the addition of between 5 to 20% PU increased the penetration and viscosity values but decreased the softening value, thereby resulting in a better bonding strength as the flow of bitumen was reduced.

Figure 1. Contour plots on the effect of PU and bitumen content for each response.
4. Optimization of PU

The objective of this study is to establish the optimum amount of PU to be incorporated into bitumen in an effort to obtain properties within the limitation or better than the control sample. In the present study, numerical optimization was done based on the interaction between the factors and the response that meet the targeted response. Therefore, the response for penetration were set at (80-100 dmm), softening point at (45-52 °C), and minimum viscosity value (513 mPa.s). The three solutions proposed by RSM are presented in Table 4. Figure 2 (a-c) presents the contour plots of desirability for the three proposed solutions. Based on this result, the first solution, which has the highest desirability of 0.843, was chosen. A desirability approaching 1 is the ideal optimization value while a value of 0 indicates that one or more response is not within the limits. For this solution, the 95% bitumen incorporated with 5% PU produced the optimum combination which meet the targeted responses for penetration, softening point and viscosity values.

Table 4. Solutions for optimization.

| Number | Bitumen | PU | Penetration | Softening Point | Viscosity | Desirability |
|--------|---------|----|-------------|-----------------|-----------|--------------|
| 1      | 95.00   | 5.00 | 91          | 46.0            | 648       | 0.843        |
| 2      | 95.00   | 5.40 | 91          | 46.1            | 660       | 0.829        |
| 3      | 93.89   | 5.00 | 91          | 46.0            | 663       | 0.826        |

Figure 2. Contour plot of desirability for the proposed solutions.

5. Validation of optimization result

In order to validate the predicted optimum combination proposed by RSM, penetration, softening point and viscosity test were conducted twice using the optimum percentages of bitumen and PU. The averaged result was used for each test and the percentage of error was calculated using equation (5). Table 5 presents the predicted and observed value for each testing; it can be seen that all percentage error difference are less than 5%. Thus, it can be concluded that the developed models are in good agreement with the experimental result [18].

\[
\text{Error} \% = \left| \frac{\text{Experimental} - \text{Model}}{\text{Experimental}} \right| \times 100\%
\]
Table 5. Validation results for optimal bitumen and PU percentages.

| Parameter       | Unit  | Predicted | Observed | Error (%) |
|-----------------|-------|-----------|----------|-----------|
| Penetration     | dmm   | 91        | 90       | 1.11      |
| Softening point | °C    | 46.0      | 45.7     | 0.66      |
| Viscosity       | mPa.s | 648       | 635      | 2.05      |

6. Conclusion

This research has investigated the design and optimization of a new material which used PU as a bitumen modifier through the RSM statistical approach. Based on the RSM analysis using CCD method, the optimal combination has been determined to be 95% bitumen and 5% PU. This is based on the results of penetration, softening point and viscosity tests that have been designated as the response. Results showed that the experimental data were accurately analyzed using the developed quadratic regression model. In conclusion, the predicted models proposed by RSM are in agreement with the experimental laboratory results since the percentage of error of less than 5% was achieved for all responses.

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