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# Prediction of Linear Viscoelastic Rheological Properties for Composite Nanosilica/Polyethylene Modified Bitumen Using Response Surface Methodology

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## *Abstract*

*This study evaluates the suitability of response surface methodology (RSM) to describe the linear viscoelastic (LVE) rheological properties of composite nanosilica/polyethylene modified binder. Two independent and three response variables were investigated, the independent variables were temperature and nanosilica content whilethe response variables are phase angle and complex modulus. Each of the independent variables was varied over three levels. The temperature was varied in the range of 35 to 55* $^{O}$*C and nanosilica was varied from 2 to 6%. RSM was used for the evaluation based on Central Composite Design (CCD) design. From the results, a high correlation coefficient (*$R^2$*) of 0.9999 and 0.9953 were obtained for complex modulus and phase angle. This confirms that the experimental values obtained are in real agreement with the developed quadratic models. Analysis of the individual effects of temperature and nanosilica content reveals that all the responses are influenced by the interaction of both the two independent variables but highly influenced by temperature than nanosilica content.*

**Keywords:** *Composite modified bitumen, linear viscoelastic properties, nanosilica, linear low density polyethylene*

## INTRODUCTION

Bitumen is a viscoelastic material which has been in used for various engineering applications especially in the construction of flexible highway pavements. Due to its viscoelastic properties, bitumen behaves similarly to an elastic material under rapid loading or at low temperatures like a viscous fluid under slow loading or at high temperatures [1, 2].

Previously, conventional unmodified bitumen has been applied satisfactorily in most flexible highway pavements constructions[2]. However, in the last two decades increase in axle loads, heavy traffic, severe climatic conditions, and construction failures brings about a need to enhance the performance properties of the base bitumen. In order to obtain bitumen with improved properties, several performance enhancers such as polymers have been investigated [3].Application of variouspolymer additives into bitumen binders is a common way to improve asphalt mixture performance [4]. Among the best polymers applied for bitumen modification are polyethylene (high, linear low and low densities polyethylene), acrylonitrile butadiene styrene, polypropylene, ethylene vinyl acetate, styrene-butadiene-styrene, polyvinyl chloride and polyethylene terephthalate[5, 6].

However, despite the improvements achieved with the application of polymers, several challenges still exist. The major problems includes lack of morphological stability due to phase separation under storage conditions, poor resistance to aging(oxidation), poor compatibility with bitumen and high cost of modification among others[7].

Recently, composite nanomaterial/polymer modification draws attention as the best alternative to polymers for bitumen modification [8]. Composite nanomaterial/polymer modification is generally more cost effective, as it reduces the quantities of polymer and nanomaterial used, and at the same time increasing compatibility of polymers with bitumen [9]. Common nanomaterials applied in bitumen modification are carbon nanotubes, titanium dioxide, nanoclay (organic montmorillonite), nano calcium trioxocarbonate, nanosilicon oxide and nano zinc oxide [10].

Statistical analysis was found to be an alternative for describing the interactions among dependent variables that affects a particular response. Application of statistical methods in the analysis of pavement helps to provide a better understanding of the parameters which determines the pavement performance during service life [11]. For rheological analysis, predictive models such as RSM have become the best alternative technique that quantifies the LVE rheological parameters of bitumen binders [12, 13].

Response Surface Methodology (RSM) is an accepted and important statistical technique mainly employed for designing experiments, modeling and process optimization through evaluation of both individual effects and interaction effects of different factors (independent variables) under less number of experimental runs [14].

This study was carried out to develop a statistical predictive model based on rheological parameters using RSM. The study was also aimed to investigate the interaction effect of temperature and nanosilica additive on composite modified binder rheological parameters.

## Materials

The base bitumen binder used for this study is grade 80/100 penetration, the bitumen was obtained from PETRONAS refinary Melaka, Malaysia. Polyethylene polymer linear low density polyethylene (LLDPE) in pellet form was used for the modification. LLDPE were produced by Etilinas Polyethylene factory, Kerteh, Malaysia. Nanosilica was supplied by Benua Sains chemical Sdn Bhd Malaysia with $SiO_2$ content and purity of 99.8% 99.9%.

## Methodology

### Preparation of composite nanosilica/polyethylene modified binder

Composite nanosilica/polyethylene modified binders was prepared by adding nanosilica into the optimum concentration of 6% LLDPE polymer at concentrations of 1-6% by weight of bitumen binder. Bitumen binder was first heated in an oven at a temperature of 150°C until it became sufficiently fluid, LLDPE were first added to the base binder before the composite modification, after LLDPE dissolves completely on the base binder, nanosilica were added gradually and sheared at high shearing rate. Composites mixing were done using a propeller blade bench top multimix high shear mixer at ahigh shearing rate of 4000 rpm for 2 hours duration. Throughout the mixing period, the temperature was maintained at a rate of 150 ± 5°C.

### Dynamic shear rheometer test

DSR was applied for characterization of the viscoelastic behavior of bitumen binders at varying service temperature conditions. DSR measurements were performed using a Kinexus Malvern Instruments rheometer. An 8mm diameter parallel plate geometry and 2mm diameter gap for testing were applied for low and intermediate temperature tests from 10°C to 35°C. At higher temperatures beyond 35°C, a parallel plate of 25mm diameter and 1mm gap for testing were applied. Temperature sweeps were performed within the linear viscoelastic region (LVE) at temperatures ranging from 20°C to 60°C within an interval of 5°C.Samples for rheological tests were prepared using both silicone mold and hot pour method. Rheological characterization test was conducted based on conditions described in Table 1.

***Table 1:** Rheological test conditions*

| Parameter | Condition |
|---|---|
| Mode of loading | Controlled strain |
| Test temperatures | 35–55°C (with the interval of 5 °C) |
| Frequency | 10 rad/sec |
| Temperature rise rate | $2^oC$/min |
| Spindle geometry | 25mm diameter and 1mm testing gap |
| Strain | (0.2%)within the LVE response |

**Design of experiments using RSM**

In this study, an experimental program based on central composite design (CCD) were utilized to evaluate the effects of independent variables (temperature and nanosilica) on LVE rheological properties of composite nanosilica/polyethylene modified binder. Experiments were designed using face centered central composite design (FCCCD) with alpha equals to 1.0 as it allows for areduction in a number of experimental levels.The responses considered are complex modulus (Pa.s) and phase angle ($^o$).

***Table 2:** Code level and actual values of independent variables for CCD*

| Factors | code | unit | coded variables | | |
|---|---|---|---|---|---|
| | | | -1 | 0 | 1 |
| Temperature | A | $^OC$ | 35 | 45 | 55 |
| Nanosilica | B | % | 2 | 4 | 6 |

(-1) is the low level; (0) is the mean level; (1) is the high level.

The possible combinations of response factors for the actual experimental design variables were obtained through running an experiment for the possible combinations suggested by FCCCD design. For each of the responses used, 13 numbers of experiments were performed in randomized order. Numerical variables for the experiments are transformed into coded form using Eq. 1.

$$x_i = \frac{(X_i - X_o)}{\Delta X} \qquad (1)$$

Where $x_i$ is the coded value of the ith independent factor, $X_i$, $X_o$ is the center point actual values and $\Delta X$ refers to the step change for theith variable.

For fitting of the experimental data into second order polynomial model, terms presented in equation (2) are used.

$$y = \beta_o + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i\angle j}^{k} \beta_{ij} x_i x_j + e$$

(2)

## Results and discussion

### Model fitting

Table 3 presents model summary statistics for all the responses. From Table 7 it can be seen that cubic models have the least values of standard deviation (SD), but aliased by the RSM software. Quadratic model fits to be the best for analysis of the responses due to its lower values of SD, press and larger $R^2$ values compared to other models.

A predicted $R^2$ value of 0.9993 for complex modulus and 0.9872 for phase angle presented in Table 3 are all in real agreement with the adjusted $R^2$ values of 0.9999 for complex modulus and 0.9920 for phase angle. There difference has been lessthan 0.2.

***Table 3:*** *Model summarystatistics for different models*

| | Source | SD* | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | PRESS |
|---|---|---|---|---|---|---|
| Complex Modulus ($Y_1$) | Linear | 0.067 | 0.7994 | 0.9972 | 0.9953 | 0.091 |
| | 2FI | 0.070 | 0.9977 | 0.9969 | 0.9892 | 0.21 |
| | Quadratic | 0.015 | 0.9999 | 0.9999 | 0.9993 | 0.014 |
| | Cubic | 7.14E-3 | 1.0000 | 1.0000 | 0.9999 | 2.2E-3 |
| Phase angle ($Y_2$) | Linear | 0.95 | 0.9706 | 0.9647 | 0.9441 | 17.04 |
| | 2FI | 0.98 | 0.9717 | 0.9622 | 0.8905 | 33.35 |
| | Quadratic | 0.45 | 0.9953 | 0.9920 | 0.9872 | 3.91 |
| | Cubic | 0.50 | 0.9960 | 0.9903 | 0.9908 | 2.80 |

SD; Standard deviation

The final regression models equations in terms of coded factors are expressed in Eq. 3 and 4 respectively.

$$Y_1 = 17.11 - 0.19A + 0.17B - 3.54AB + 3.02A^2 + 0.025B^2 \quad (3)$$

$$Y_2 = 27.88 + 1.81A - 1.85B + 0.015AB - 0.014A^2 - 0.058B^2 \quad (4)$$

The $R^2$ values for Eqns. 3 and 4 are 0.9999and 0.9953 forcomplex modulus and phase angle respectively. The $R^2$ values obtained indicates that 99.9% and 99.6% of the total variations in the responses were attributed to the experimental variables investigated. A high $R^2$ value close to 1.0 indicates a reasonable and desirable agreement between experimental and predicted values. The two models equations have SD values of 0.015 and 0.45 for $Y_1$ and $Y_2$, respectively. $R^2$ and SD values were used to evaluate the quality of the models developed. The positive and negative signs before the terms in the equations show the synergistic and antagonistic effects of the individual variables on the responses.

## ANOVA analysis for the models

ANOVA analysis was used for assessing the suitability of the selected models and evaluating the significances of each of the variable factor. Table 4 presents ANOVA statistics for the responses. From the Table, it can be seen that for all the models, temperature was found to be the most influencing and significant factor among the two independent variables, showing the highest F-values of 70439.32 and 1121.56 for complex modulus and phase angle. The required Prob>F of lessthan 0.05 was obtained in all the models. The model F-values of 336.86 and 392.52 for the responses together with Prob>F of less than 0.0001 proves that the models are statistically significant for the rheological responses. Generally, a P>F values of lessthana 0.05 signifiesthat terms in the model are significant [15]. From these results, Nanosilica and temperature both have a significant effect on rheological responses. For values larger than 0.1 (P>0.1), it indicates that terms in the model are not significant.

Validation of the models is necessary for the process of data analysis; this is because poor model ends up giving ambiguous results. Appropriate accuracy for model quantifies the signal to noise ratio. Adequate Precision (AP) compares the range of the predicted values at the design points to the average prediction error. Basic requirement defines AP ratio higher than 4 as acceptable. In this study, AP ratios of 457.04 and 61.97were obtained for all the responses variables. These values indicate adequate signal and confirm that the models chosen can satisfactorily navigate the design space define by CCD to provide parameters for optimum mix design.

*__Table 4:__ Analysis of ANOVA for responses*

| Source | S.S | D.F | Mean square | F value | P value | A.P |
|---|---|---|---|---|---|---|
| **Complex Modulus** | | | | | | |
| Model | 19.31 | 5 | 3.56 | 16764.42 | <0.0001 | |
| A | 16.23 | 1 | 16.23 | 70439.32 | <0.0001 | |
| B | 3.04 | 1 | 3.04 | 13196.90 | <0.0001 | |
| AB | 2.0E-04 | 1 | 2.0E-04 | 0.87 | 0.3823 | 457.04 |
| $A^2$ | 2.5E-03 | 1 | 2.5E-03 | 10.95 | 0.0130 | |
| $B^2$ | 0.028 | 1 | 0.028 | 119.62 | <0.0001 | |
| Residual | 1.6E-03 | 7 | 2.3E-04 | | | |
| **Phase angle** | | | | | | |
| Model | 303.24 | 5 | 60.65 | 296.99 | <0.0001 | |
| A | 229.03 | 1 | 229.03 | 1121.56 | <0.0001 | |
| B | 66.67 | 1 | 66.67 | 326.47 | <0.0001 | |
| AB | 0.34 | 1 | 0.34 | 1.65 | 0.2402 | 61.97 |
| $A^2$ | 5.32 | 1 | 5.32 | 26.07 | 0.0014 | |
| $B^2$ | 0.15 | 1 | 0.15 | 0.74 | 0.4190 | |
| Residual | 1.43 | 7 | 0.20 | | | |

SS is sum of squares, DF is degree of freedom and AP is adequate precision

## Effects of parameters: Analysis of response surface

Fig. 1a and 2a present the 3D response surfaces plots for complex modulus and phase angle based on the effects of independent variables temperature and nanosilica content. From the plots, it can be observed that the surface plot curvature indicates that both temperature and nanosilica have asignificant interaction effect on complex modulus and phase angle. It can also be observed that, as temperature increases, complex modulus decreases, and phase angle increases.

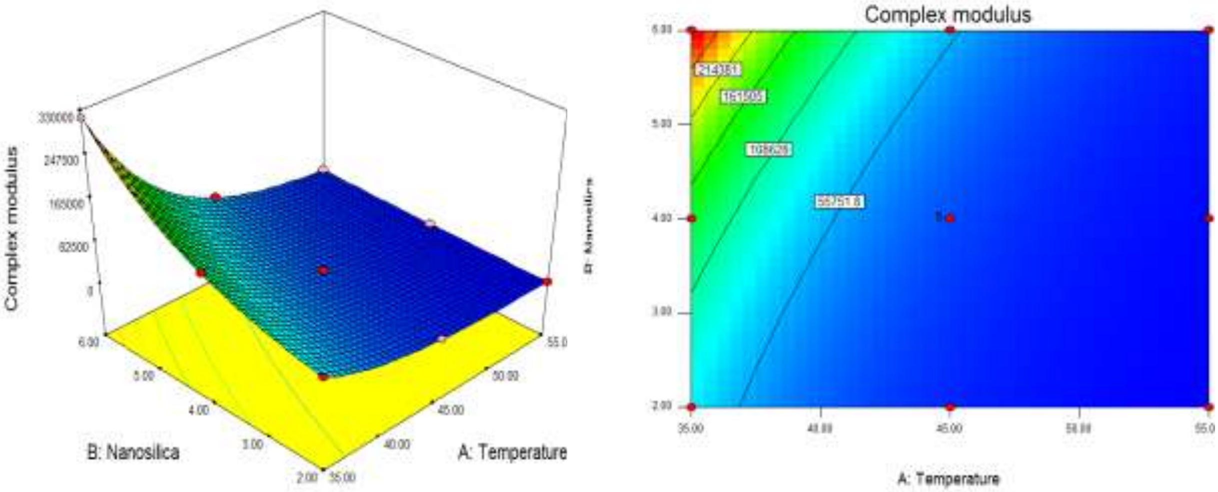

***Fig. 1.*** *Effect of temperature and nanosilica content on complex modulus (a) 3D and (b) 2D*

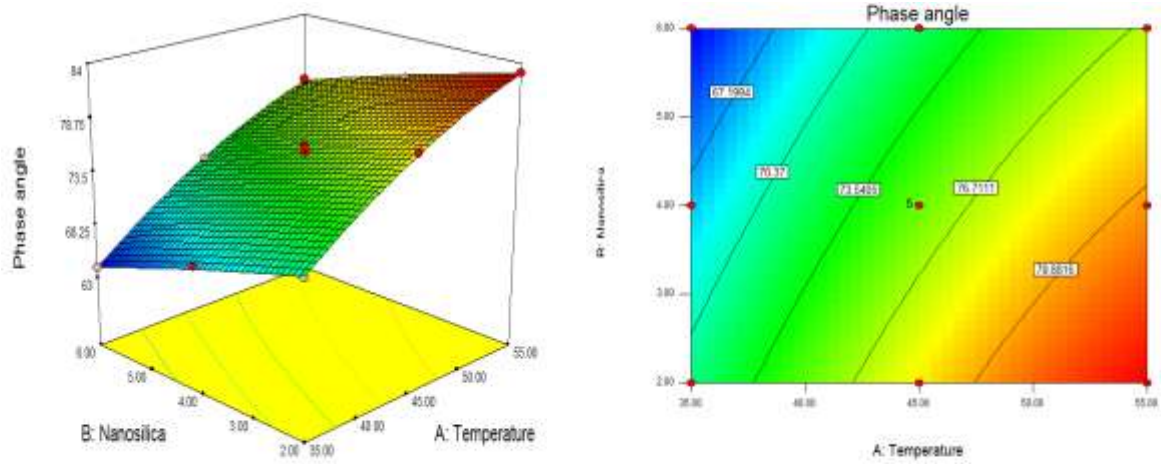

***Fig. 2.*** *Effect of temperature and nanosilica content on phase angle (a) 3D and (b) 2D*

However, with the addition of more nano silica content up to 6%, the complex modulus increases significantly and phase angle decreases. This indicates that both complex modulus and phase angle are strongly influenced by temperature than nanosilica content. Fig. 1b and 2b present 2D contour plot for the response function. It can be seen from the contour plot that there is good interaction between the independent variables.

## CONCLUSIONS

The results obtained in this study indicate that experimental data were interpreted accurately by developed regression quadratic models. High correlation coefficients ($R^2$) of 0.9999 and 0.9953 obtained for the responses confirm that the experimental data obtained are in real agreement with the developed quadratic models applied. Analysis of the individual effects of temperature and nanosilica content reveals that all the responses are influenced by the interaction of both the two independent variables but both complex modulus and phase angle are highly influenced by temperature than nanosilica content.

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