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Polyethylene Polymer Modified Bitumen: Process Optimization and Modeling of Linear Viscoelastic Rheological Properties Using Response Surface Methodology

Nura Bala, Ibrahim Kamaruddin, Madzlan Napiah and Nasiru Danlami
Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS,
32610 Bandar Seri Iskandar, Perak, Malaysia

Abstract: Polymers are generally, applied to improve the durability and performance of asphalt pavement structures against premature defects. In this study, the optimization of polyethylene polymer for bitumen modification has been investigated to determine optimum proportions for higher linear viscoelastic properties. A Response Surface Methodology (RSM) Central Composite Design (CCD) design was applied with two with two independent variables polyethylene content and temperature and three linear viscoelastic responses Complex Modulus (CM), Phase Angle (PA) and Viscosity (V). The results showed that a high correlation coefficient (R^2) of 0.9998, 0.9962 and 0.9998 were obtained for complex modulus, phase angle and viscosity which indicates that, the model's values are in strong correlation with the values of the experiment. The model also indicates that temperature is the most influencing factor among the two independent variables responsible for linear viscoelastic properties of the modified binder. Based on numerical optimization using proposed quadratic model, the optimum mix can be achieved with a 4% polyethylene at a temperature of 25°C.

Key words: Modelling, polymer modified bitumen, linear viscoelastic properties, linear low-density polyethylene, optimization, independent variables

INTRODUCTION

Bitumen composed of different characteristics based on its chemical composition which varies at both molecular and intermolecular level and with the crude oil origin and process of distillation (Read and Whiteoak, 2003; McNally, 2011; Olutaiwo and Adedimila, 2008). Bitumen being a viscoelastic and heterogeneous substance consist of a complex mixture of different organic molecules namely asphaltenes, resins, aromatics and saturates (Masson and Polomark, 2001; Navarro *et al*., 2009; Ekott and Akpabio, 2011).

Polymers such as thermoplastic elastomers and plastomers were found to be among the best materials for bitumen modification after yielding several improvements (Airey, 2003). The major benefits recorded in applying polymers are a reduction in temperature sensitivity, increasing resistance to permanent deformation, higher stiffness during high temperature, good resistant to moisture, resistance to cracking at lower temperatures as well as longer fatigue life (Zhu *et al*., 2014). Some among the best polymers applied for bitumen modification are polyolefins group of polymers such as polyethylenes, these includes; high-density, low-density as well as linear low-density polyethylene polymers and polypropylenes with their copolymers (Punith and Veeraragavan, 2010). Polyolefins polymers when added to bitumen provide several benefits such as enhancement in properties during the service life of the pavement, improvement in thermo-mechanical resistance, increase in adhesion as well as elasticity of binder (Fang *et al*., 2008a, b; Auden *et al*., 2008; Lepe *et al*., 2005).

The rheological behavior of bitumen binders varies from Newtonian behavior (sol) to non-Newtonian behavior (gel). Even though several methods are used for determining bitumen rheological properties, the Dynamic Shear Rheometer (DSR) oscillatory test becomes the best method for presenting full bitumen rheology (Fawcett *et al*., 1999).

The DSR was accepted as the best instrument for determination of viscous, elastic and viscoelastic properties of bitumen especially if modified. However, the DSR being the best instrument has limitations in its applications as it is unable to reach extremely high temperatures (Benedetto and Olard, 2009). Recognizing that, equations or predictive models becomes best alternative methods for determining the Linear ViscoElastic (LVE) rheological properties of bitumen

Corresponding Author: Nura Bala, Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia

binders (Yusoff *et al*., 2013). The main benefits of applying models are acceptable accuracy, less time consuming, inexpensive and easy to use (Benedetto and Olard, 2009). Application of models becomes very useful in describing LVE rheological properties of bitumen binders such as complex modulus and phase angles at any given frequency or temperature that cannot be achieved through experimental works.

During the last decades, rheological properties (LVE) for bituminous binders are usually presented using nonlinear multivariable methods or nomographs (Ferry, 1980; Mohammad *et al*., 2005). Currently, the nomographs are no more applicable due to the recent computational techniques approaches or various models that are more accurate and reliable. A bitumen rheological model mostly relies on Time-Temperature Superposition Principle (TTSP) through the construction of master curves for main rheological parameters (complex modulus and phase angle) (Heukelom and Klomp, 1964; Yusoff *et al*., 2011).

RSM is a statistical tool applied for optimization and modeling of various problems where by the responses or parameters of interest are influenced by different factors (Yusoff *et al*., 2011; Anderson *et al*., 1994). RSM is commonly used for the design of experiments in such a way to establish a relationship among different factors as well as to optimize all the related conditions of parameters for the prediction of best response (Bas and Boyaci, 2007). RSM eases to understand the various interactions between the parameters under study at less number of experimental runs.

This investigation evaluates the suitability of Response Surface Method (RSM) Model for describing the LVE rheological behaviors of polymer modified binder studied using DSR test. The correlations existing between measured phase angle, complex modulus as well as viscosity data were evaluated using ANOVA, graphical and goodness of fit statistical methods.

Bitumen rheology: Considering vast research conducted for rheological evaluation of bituminous binders, bitumen rheology can be regarded to be the major fundamental measurements that relate the flow and deformation properties of the binder (Zhang *et al*., 2016).

Full understanding and evaluation of bitumen rheological properties become necessary for assessing the performance of pavements since bitumen binders that easily deforms and flows can be highly susceptible to deformation and bleeding and for a binder that is highly stiff will be more susceptible to crackings and fatigue failures. Currently, bitumen LVE rheological behaviors are found using a Dynamic Shear Rheometer (DSR) which is an oscillatory type testing apparatus. DSR equipment is able to evaluate both viscous, elastic and viscoelastic behaviors of bitumen binders over large temperature and frequency ranges (Airey, 2003).

The main viscoelastic parameters found from DSR are complex modulus denoted as G* and phase angle denoted as (Montgomery, 2008). Complex modulus is described to be the ratio between maximum stress and a resulting strain of bitumen binder which measures a full susceptibility to deformation of binder under the condition of shear loading. The complex modulus is made of two main components, respectively; storage modulus G' or elastic component and loss modulus G" or viscous component. Phase angle is the time lag between applied stress and strain in an oscillatory test that measures the viscoelastic balance of the binder behavior. For a bitumen binder, if G' equals 90° the bitumen binder nature can be regarded as purely viscous material, while if G" equals to 0° the binder is purely elastic in nature. Any value obtained within these two extremes ranges; the nature of the material is viscoelastic behavior which consists of both viscous and elastic characteristics (Van der Poel, 1954).

MATERIALS AND METHODS

Bitumen: The control bitumen grade 80/100 penetration obtained from PETRONAS refinery Malacca, Malaysia was used for the blend preparation in this investigation. Physical properties of the base control binder are described in Table 1.

Polymer: Linear Low-Density Polyethylene (LLDPE) polymer in pellet form was used for the preparation of polymer-bitumen blend. LLDPE were produced by Etilinas Polyethylene factory, Kerteh, Malaysia.

Bitumen modification: In this research, three different modified binder samples were prepared at varying concentrations of LLDPE polymer. The samples were prepared by placing the control binder inside oven at a temperature of 150 °C until it becomes completely melted, upon reaching temperature, a weighted 4, 5 and 6% LLDPE polymer by weight of bitumen binder are gradually added to the bitumen while mixing using a multi mix bench top high-speed propeller blade shear mixer under high blending rate of 4000 RPM for 2 h period.

Table 1: Physical properties of base binder

Physical property	Values	Units
Penetration (25°C, 100 g, 5 sec, 0.1 mm)	84	dmm
Softening point temperature	42	°C
Ductility at 25°C	>150	cm
Viscosity at 135°C	0.64	Pa.s

Dynamic shear rheometer test: Rheological behaviors of modified samples were obtained using an oscillatory mode DSR with two parallel plate testing geometries of 8 and 25 mm diameter. The opening in between the plates was first set at the required height of 50 μm with the addition of testing gap distance at selected testing temperature. After setting the gap, a sufficient quantity of heated binder was poured on the surface of the lower DSR plate and ensured there is a slight excess of binder around the selected testing geometry. The DSR upper plate was then lowered slowly until it reaches the selected testing gap plus 50 μm. Excess binder surrounding the upper and lower plates was then trimmed off using a sharp hot knife. Immediately after sample trimming, the extra 50 μm gap between plates was then closed to have the required testing gap. Temperature sweep test was conducted at a temperature range of 20-60°C with a temperature rise of 2°C/min.

Experiment design using RSM and data analysis: The experimental design as well as analysis was conducted using a design expert software version 9.0.6.2 (Stat Ease Inc., Minneapolis, USA). In RSM, a fractional factorial design like CCD is generally, applied due to its potential approach that provides acceptable functional relationship among the independent variables and responses (Goodrich, 1988).

In this study, a three-level face-centered CCD factorial design was applied to evaluate the interaction and response surface nature of the experimental design. Two significant modification parameters (independent variables) considered were LLDPE content (A) and temperature (B). LVE rheological parameters complex modulus (Pa), phase angle (°) and viscosity (Pa.s) were chosen as response parameters. Selecting the ranges for the independent variables LLDPE content 4-6% (Lu *et al*., 2016; Khodaii *et al*., 2016; Polacco *et al*., 2008) and temperature 20-60°C (Benedetto and Olard, 2009) was based on the preliminary study in addition extant review of the literature.

The independent variables were studied at three levels -1, 0 and +1 designated as low, mean and high levels for the variables. For the statistical analysis, Eq. 1 was used to convert the independent variables into dimensionless codified values for the factors comparison with different units and also for decreasing error in the model fitting:

$$x_i = \frac{(X_i - X_0)}{\Delta X} \quad (1)$$

Where:

x_i = The ith independent factor coded value
X_i, X_0 = The actual values of the center point
ΔX = The step change for ith variable

The total number of experiments conducted was thirteen with five replication of the central point to increase the precision of the experiment as well as any possible error. The two independent variables together with their respective levels are shows in Table 2.

Goodness of fit of the data to the models was estimated by the coefficient of determination (R^2) in relation to its agreement with adjusted R^2. Fisher's F test was applied for checking of statistical significance for the models and its terms which are expressed by (p-value) with 95% confidence level. A data variation around the fitted model was also checked by F-test (lack of fit). Adequate Precision (AP) was used to evaluate signals to noise ratios and Standard Deviation (SD) was used for checking the set of data spread from its mean value. For determination of Reproducibility for the models a Coefficient of Variance (CV) was used which is regarded as the ratio between standard error and mean value of the observed response.

Table 2: Code level and actual values of factors and experimental matrix for face centered CCD

	Factors						
	LLDPE (%) A		Temperature (°C) B		Responses		
Run	Uncoded	Coded	Uncoded	Coded	Complex modulus (Pa)	Phase angle	Viscosity (Pa.s)
1	5	0	20	-1	224957	51	68854
2	5	0	40	0	11298	74	2344
3	5	0	60	1	292.13	83	86.99
4	5	0	40	0	11117	73	2327
5	6	1	20	-1	525056	48	113740
6	5	0	40	0	11341	76	2311
7	5	0	40	0	11399	75	2279
8	4	-1	60	1	71.84	85	26.76
9	5	0	40	0	11279	75	2344
10	4	-1	20	-1	75901	56	29622
11	6	1	40	0	27367	71	4647
12	6	1	60	1	6714	80	186
13	4	-1	40	0	3545	77	972

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

RESULTS AND DISCUSSION

Model fitting: Fitting of the experimental data in terms of significant influencing factors for final regression model is done based on several factors suggested by RSM. Table 3 presents a summary of the different models, it can be seen that both quadratic and cubic models are suitable for all the independent variables, their suitability is based on the Prob >F-value of <0.05. The quadratic model was considered to navigate the design space. The cubic model was not considered because it was initially aliased by the software. Therefore, quadratic models were selected according to their highest polynomial order where additional terms were significant and the models are not initially aliased.

Table 4 presents model summary statistics for all the responses, it can be seen that cubic models have the least values of 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 0.9983 for complex modulus, 0.9864 for phase angle and 0.9988 for viscosity presented in Table 4 are all in real agreement with the adjusted R^2 values of 0.9997 for complex modulus, 0.9935 for phase angle and 0.9997 for viscosity. There difference been 0.2 (Bas and Boyaci, 2007).

For fitting of the experimental data, the coefficients of the second-order polynomial model were calculated using Eq. 2:

$$y=\beta_0+\sum_{j=1}^{k}\beta_j x_j+\sum_{j=1}^{k}\beta_{jj}x_j^2+\sum_{j\angle 1}^{k}\beta_{ij}x_i x_j+e \quad (2)$$

Where:

y	= The predicted outcome
β_0	= The experiment central point fixed response value
β_j and β_{jj}	= First and the second order effects
β_{ij}	= Cross interaction effect
x_i and x_j	= The coded factors
e	= The model random error

The final regression model equations in terms of significant factors are expressed in Eq. 3 through 5, respectively. The models were presented after model reduction to exclude all the insignificant terms for the models:

$$Y_1 = 5.99+2.58A-0.112B+3.93AB-0.169A^2-9.12B^2 \quad (3)$$

$$Y_2 = 32.55-3.5A+2.18B-0.017B^2 \quad (4)$$

Table 3: Summary of different models

Variable /Source	SS*	df**	MS**	F-values	Prob>F
Complex Modulus (Y_1)					
Linear	75.050	2	37.530	525.050	<0.0001
2FI	0.025	1	0.025	0.320	0.5839
Quadratic	0.680	2	0.340	164.010	<0.0001
Cubic	0.011	2	5.35E-03	7.230	0.0334
Phase angle (Y_2)					
Linear	1577.67	2	788.830	48.720	<0.0001
2FI	0.25	1	0.250	0.014	0.9087
Quadratic	155.10	2	77.550	82.620	<0.0001
Cubic	0.83	2	0.420	0.360	0.7124
Viscosity (Y_3)					
Linear	13.500	2	6.750	2100	<0.0001
2FI	0.018	1	0.018	11.840	0.0074
Quadratic	0.012	2	5.86E-03	19.060	<0.0001
Cubic	6.4E-04	2	3.2E-04	1.060	0.4137

SS; Sum of Squares, DF; Degree of Freedom, MS; Mean Squares

Table 4: Model summary statistics for different models

Variable/Source	SD*	R^2	Adjusted R^2	Predicted R^2	PRESS
Complex Modulus (Y_1)					
Linear	0.270	0.9906	0.9887	0.9799	1.530
2FI	0.280	0.9909	0.9879	0.9531	3.560
Quadratic	0.045	0.9998	0.9997	0.9983	0.130
Cubic	0.027	1.0000	0.9999	0.9949	0.390
Phase angle (Y_2)					
Linear	4.020	0.9069	0.8883	0.8258	303.080
2FI	4.240	0.9071	0.8761	0.6640	584.490
Quadratic	0.970	0.9962	0.9935	0.9864	23.590
Cubic	1.070	0.9967	0.9921	0.9123	152.590
Viscosity (Y_3)					
Linear	0.057	0.9976	0.9972	0.9939	0.083
2FI	0.039	0.9990	0.9986	0.9948	0.070
Quadratic	0.018	0.9998	0.9997	0.9988	0.016
Cubic	0.017	0.9999	0.9997	0.9879	0.160

SD; Standard Deviation

$$Y_3 = 3.69+0.816A-0.0896B+3.378AB-0.0602A^2 \quad (5)$$

The R^2 values for Eq. 3-5 were 0.9998, 0.9962 and 0.9998 for complex modulus, phase angle and viscosity, respectively. The R^2 values obtained indicates that 99.9, 99.6 and 99.9% of the total variations in the responses were attributed due to the experimental variables. A high R^2-value approximately 1.0 indicates a reasonable and desirable agreement between experimental and predicted values (Fang *et al*., 2008). The three models equations have SD values of 0.045, 0.97 and 0.018 for Y_1, Y_2 and Y_3, 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.

Lack of fit test: The experimental responses were first subjected to Lack Of Fit test (LOF) for the model formulation and matching their residual errors together with their pure errors from replicated design points. If the value of the pure error is obtained to be high, it indicates that experimental conditions are not uniform and dependent variables investigated are not adequate.

Table 5: Lack of fit tests summary for different models

		Source of variation		
Response	Units	Residue	Pure error	Lack of fit error
Complex modulus	Pa	0.62	0.00035	0.01400
Phase angle	Deg	53.27	4.48000	2.0900
Viscosity	Pa.s	26.58	0.00010	0.0020

However, for the LOF error, it is generally associated with the model selected. If a model were selected properly, LOF error becomes small; otherwise, the values become very large (Anderson *et al*., 1994).

Table 5 presents LOF test for the models. It can be seen that all the residues are acceptable and the LOF errors are relatively low which shows that the LOF is not significant and the models selected are highly suitable. Values for pure error are significantly small, this indicates that the experimental conditions are found to be uniform and the dependent variables investigated are very adequate. LOF and pure error values indicate that the models selected are highly significant and they can be used to describe the relationship between the factors and the responses with a high degree of accuracy.

Table 6: Analysis of ANOVA for responses

Sources	S.S	df	Mean square	F-values	p-values	AP
Complex modulus						
Model	75.75	5	15.15	7356.16	<0.0001	286.6
A	6.46	1	6.46	3137.36	<0.0001	
B	68.59	1	68.59	33303.4	<0.0001	
AB	0.025	1	0.025	12.01	0.0105	
A^2	0.080	1	0.080	38.67	0.0004	
B^2	0.37	1	0.37	178.46	<0.0001	
Residual	0.014	7	0.0026			
Phase angle						
Model	1733.02	5	346.60	369.28	<0.0001	58.75
A	73.50	1	73.50	78.31	<0.0001	
B	1504.17	1	1504.17	1602.56	<0.0001	
AB	0.25	1	0.25	0.27	0.6217	
A^2	0.0073	1	0.0073	0.0073	0.9318	
B^2	133.34	1	133.34	142.06	<0.0001	
Residual	6.57	7	0.94			
Viscosity						
Model	13.53	5	2.71	8800.54	<0.0001	304.03
A	0.75	1	0.75	2432.69	<0.0001	
B	12.75	1	12.75	41472.49	<0.0001	
AB	0.018	1	0.018	59.39	0.0001	
A^2	0.0098	1	0.0098	32.16	0.0008	
B^2	0.00002	1	0.00002	0.00002	0.9246	
Residual	0.0022	7	0.00030			

SS is Sum of Squares, DF is Degree of Freedom and AP is Adequate Precision

ANOVA study for the models: ANOVA studies were used for assessing the selected model's suitability and evaluating significances of each variable factor. In ANOVA statistical outcomes are simply classified and cross classified and then tested by using identified classification variance, that was approved by Fisher's statistical test (F-test). F-value in ANOVA analysis is described as the proportion of Mean square of Regression (MRR) to Error (MRe) and the worthiness of the corresponding coefficients are related to lower F-values. ANOVA linear models that prove the adequacy of the models selected are presented in Table 6.

In all the models, the temperature was found as the most influencing and significant factor among the two independent variables after showing the highest F-values of 33303.4, 1602.56 and 41472.6 for complex modulus, phase angle and viscosity respectively, together with the required Prob>F of< 0.05 in all the models. The model F-values of 7356.16, 369.28 and 8800.54 for the responses together with Prob>F of 0.0001 for all responses proves the significances of the model. Generally, a P>F values of <a 0.05 signifies that terms in the model are very significant (Bas and Boyaci, 2007), from this results, both A and B are found to be significant. For values larger than 0.1, it signifies that terms in the model are not significant, based on this B is not significant in the case of phase angle model.

An adequate correlation coefficient (R^2) of 0.9998, 0.9962 and 0.9968 were obtained for the experimental responses. This high correlation coefficient indicates that an excellent correlation exists between the predicted and experimental results. In all the models, the difference between adjusted and predicted R^2 are found to be less than 0.2. This further justified that, the models are significant and the quadratic models selected fit more to the experimental data.

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 is acceptable. In this investigation, high AP ratios of 286.6, 58.75 and 304.03 were obtained for all the responses variables. These values indicate adequate signal and confirm that the models selected can satisfactorily navigate the design space using CCD to provide parameters for optimum mix design.

Normal probability plots are used to check whether the residual follows a normal distribution, residual indicates the difference between experimental response measurement observed value and the value fitted in the model. Figure 1a presents a plot of the normal probability of studentized residuals for complex modulus. It can be seen that there is very less scattered along the straight line, this shows that the data is normally distributed and almost the overall variations were credited to the variable factors studied.

For checking of model suitability, a predicted against actual values plots are used. The plot of predicted against actual indicates whether an acceptable agreement exists

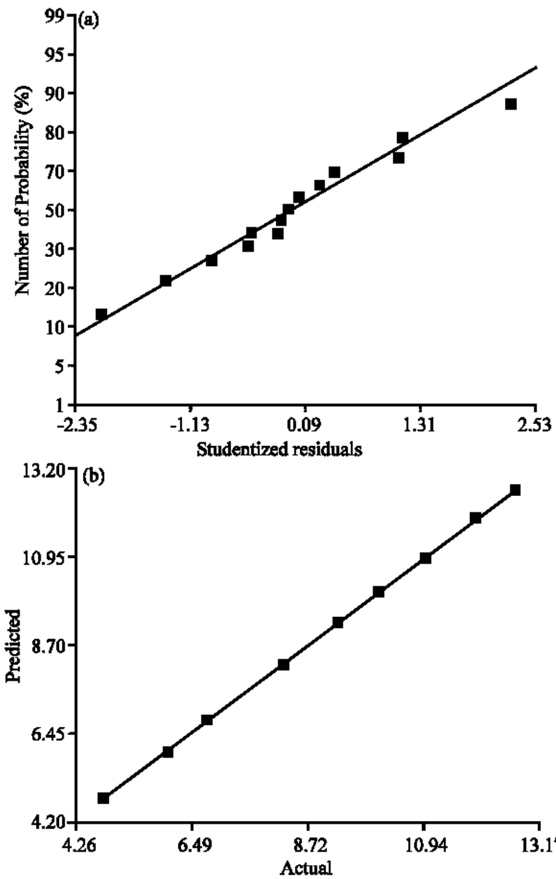

Fig. 1: Diagnostic plots for complex modulus: a and b normal probability versus Studentized residuals Predicted versus actual

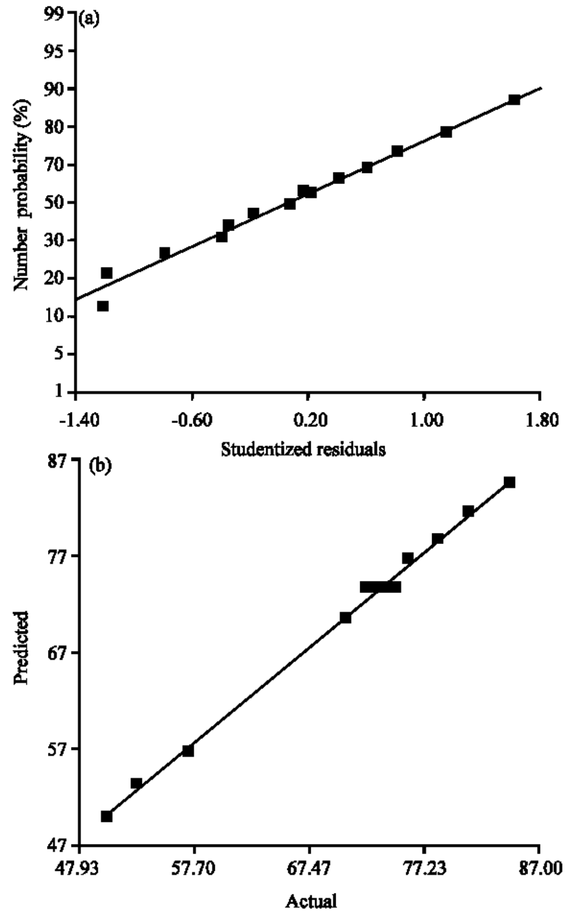

Fig. 2: Diagnostic plots for phase angle: a and b normal probability versus studentized residuals Predicted versus actual

between real experimental results and the results found from developed models. Figure 1b presents plots of predicted versus actual complex modulus, it can be realized that all the observed points are relatively on the straight line, this justified that adequate agreement exists between real results and those obtained from the model and the model selected could be used to navigate the design space with a reasonable accuracy.

Figure 2a presents normal probability plot of studentized residuals for phase angle. It can be observed that only a few points are scattered along the straight line, this indicates that the data is normally distributed almost the overall variations were credited to the variable factors studied. Figure 2b presents plots of predicted versus actual complex modulus, it can be seen that most of the observed points are relatively on the straight line, this indicates that adequate agreement exists between real results and those obtained from the model and the model can be used to navigate the design space.

Figure 3a presents normal probability plot of studentized residuals for complex viscosity. It can be seen that the data is normally distributed since most of the points lie along the straight line. Figure 3b presents plots of predicted versus actual complex modulus, it can be realized that most of the observed points relatively lies along the straight line, this indicates that there is an adequate agreement between real results and those obtained from the model and the model can be used to navigate the design space.

Surface plots for responses: Response surface plots are employed for a detailed analysis of interactions between independent variables and responses. Three-dimensional surface views (3D surface plots) shows detail behavior of the experimental mix design parameters within the experiment, moreover, surface plots allows for checking variable factors influence on the experimentation responses and the contour between the variable factors

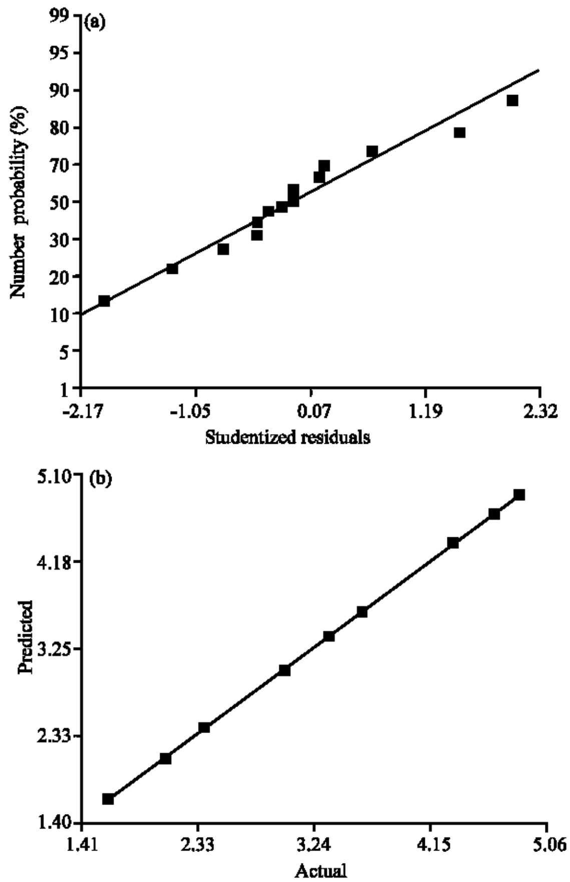

Fig. 3: Diagnostic plots for viscosity: a and b normal probability versus studentized residuals predicted versus actual

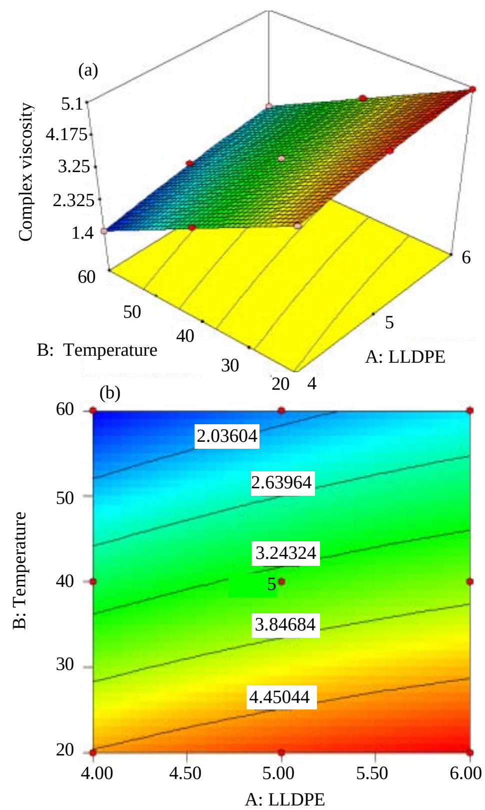

Fig. 4: Effect of temperature and LLDPE content on complex modulus: a) 3D and b) 2D

(Sangita *et al.*, 2011). Contour plot of the response function is used to describe the interaction effects between the independent variables.

Complex modulus modulus: Figure 4a present the 3D response surfaces plots for complex modulus based on the effects of the interactive variables, polymer content and temperature, the 3D surface plot curvature shows that both temperatures as well as LLDPE have a significant interaction effect on complex modulus. It can be observed that as temperature increases, complex modulus decreases with the addition of more LLDPE content up to 3%, the complex modulus increases significantly. This can be attributed to an increase in binder's viscosity due to LLDPE polymer content, also observed from 3D surface plot curvature is that complex modulus is influenced strongly by temperature than LLDPE content. Figure 4b present contour plot for complex modulus in 2D. From the plot, the complex modulus values tend to increase remarkably with an increase in both temperature and LLDPE content which indicates there is good interaction between the independent variables.

Phase angle: Figure 5a presents 3D response surfaces for phase angle, the 3D plot curvature indicates that the only temperature has a significant interaction effect on phase angle. It can be seen that as temperature increases, phase angle increases from 50 to almost 85° but with the addition of more LLDPE content up to 3%, only slight reduction in phase angle were observed. This can be attributed to the viscoelastic properties of bituminous binders which are highly controlled by temperature. Bituminous binders are brittle and rigid under low temperatures, flexible at room temperature and under high temperatures it flows (Noordin *et al.*, 2004). Also, it is observed that phase angle is highly influenced by temperature than LLDPE content. Figure 5b presents 2D contour plot for phase angle, based on the contours, it can be seen that there is less interaction between the independent variables (Panesar, 2008).

Viscosity: Figure 6a present the 3D response surfaces plots for viscosity, the 3D surface plot indicates that both

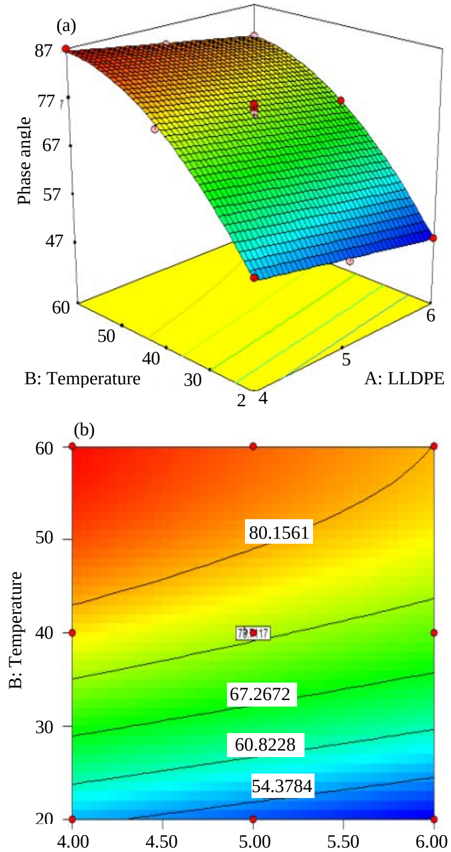

Fig. 5: Effect of temperature and LLDPE content on phase angle: a) 3D and b) 2D

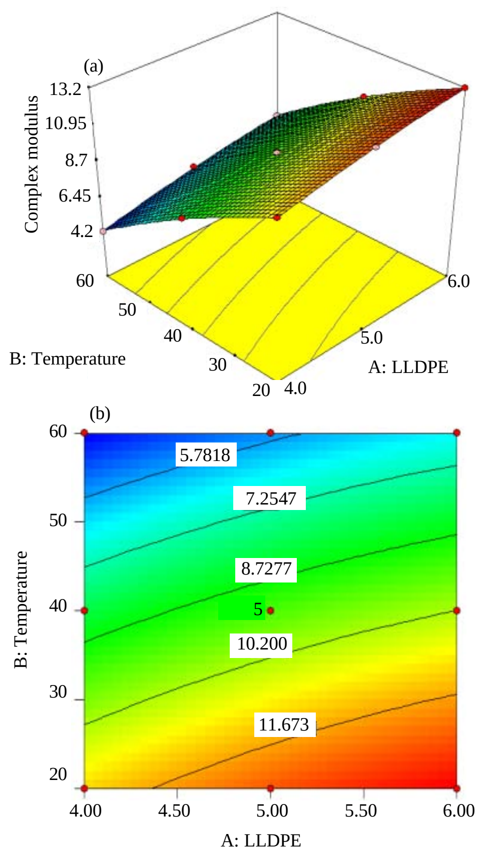

Fig. 6: Effect of temperature and LLDPE content on viscosity (a) 3D and (b) 2D

temperature and LLDPE have a significant interaction effect on viscosity. It can be observed that as temperature increases, viscosity decreases but with the addition of more LLDPE content up to 3%, the viscosity increases significantly. This indicates that viscosity is influenced remarkably by temperature than LLDE content. Figure 6b presents 2D contour plot of viscosity, from the 2D contours it can be observed that viscosity values tend to increase progressively with increase in both temperature and LLDE content which indicates a good interaction between the two factors.

Numerical optimization and validation of experiment: A Numerical conditions optimization process was conducted to estimate the optimum value of LLDPE under different temperature conditions using the design-expert software. The desired goal was chosen within the ranges presented in Table 7. The LLDPE content was set to be minimum to reduce the quantity of the polymer, the temperature was set in range and the desirable phase angle response was set to be in range to obtain high viscoelasticity for achieving good performance. To validate the reliability and accuracy of the predicted model, a further laboratory experiment was performed based on optimum mix design combinations obtained from proposed RSM Model. Table 8 summarizes the results with absolute relative deviation, ARD (%), calculated as a measure of predictability based on Eq. 6:

Table 7: Numerical optimization criteria

Criteria	Desired goal	Lower limit	Upper limit
LLDPE content	Minimize	4	6
Temperature	In range	20	60
Phase angle	In range	30	70

Table 8: Verification of experiment at optimum conditions

Response	LLDEP (%)	Temperature (°C)	Predicted	Observed	ARD (%)	De
Phase angle	4.0	25	62.16	63.8	2.57	1.00

SD; Standard Deviation, De; Desirability

$$\text{ARD} = \frac{\text{Eperimental-Model}}{\text{Experimental}}\times 100\% \quad (6)$$

It can be observed that the ARD value obtained is quite small, being <5%, this indicates that the predicted values of the proposed models are in good agreement with the experimental values.

CONCLUSION

The study was conducted for investigation on the effect of LLDPE polymer concentration and temperature on modified bitumen viscoelastic parameters (complex modulus, phase angle and viscosity) using a response surface method. The results obtained showed that the experimental data were interpreted accurately by proposed quadratic models. Also, the RSM result offers a fully comprehensive view of the effect of the variation of LLDPE polymer and temperature on the viscoelastic responses of the modified binder as all parameters is investigated at one time. The experimental data obtained are in real agreement with the suggested quadratic models applied, having correlation coefficients (R^2) of 0.9998, 0.9962 and 0.9998 for complex modulus, phase angle and viscosity.

SUGGESTIONS

The results suggested that, among the variable factors, temperature proves to be the most significant parameter that determines the viscoelastic properties of the binder having the highest positive coefficient in the model equation when compared to LLDPE content which has less coefficient value. Additional test conducted for validation showed a good agreement with the numerical optimization result and statistical analysis with a mean error of 2.57%.

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