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Optimization of high performance styrenated alkyd resin for surface coating using response surface methodology

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Abstract: **The optimization of copolymerization process of high performance styrenated resin from non-drying palm kernel oil (PKO) was studied. During the process of copolymerization, response surface methodology (RSM) based on three-level, three-factorial central composite rotatable design with categorical factor of zero was employed to optimize the process. The effects of three variables, such as reaction temperature, reaction time, and the amount of styrene on the synthesis of styrenated alkyd resin were examined. The optimum conditions (reaction temperature of 150^{0}C, reaction time of 180min and styrene weight of 4.95g) were determined by the results of statistical analysis, under which experiment was carried out and the fractional conversion of 82.52% for PKO styrenated alkyd resin was obtained. The effect of reaction time, reaction temperature and amount of styrene were investigated. The predicted value of model (83.57%) was in excellent agreement with the experimental value (82.52%).**

Keywords: **Synthesis copolymerization, alkyd resin, modification, optimization, surface coating.**

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1. INTRODUCTION

Alkyd resins are the most versatile of coating binders, and they are used extensively in all major categories of coatings: architectural, industrial, and special purposes [14]. The popularity of alkyd as vehicles in coating are due to their film hardness, durability, gloss, and gloss retention, abrasion resistance and other characteristics imparted on them through modification of the drying oil [7].

Despite these advantages of alkyd resins, there are some draw-backs, for instance, its susceptibility to alkali as a result of splitting of the ester linkages by hydrolysis, this reaction is very typical of esters. In addition, compared to other synthetic resin,alkyd resin is relatively slow drying. However, it can be modified by several physical (blending) and chemical (copolymerization) processes which will lead to products that could meet up with wide range of applications. Therefore, this present study is intended to explore the most significant process variables which influence the overall efficiency of styrene modification on the properties of palm kernel oil alkyd resin as it is known that polystyrene is very resistant to the action of alkali both in alcoholic and non-aqueous media and optimize the major process parameters like reaction time, temperature, and percentage weight of styrene used during the copolymerization process.The characterization of these major contributing variables to the process response would be achieved through design of experiment (DOE) and analysis of variance (ANOVA) while the control and optimization tasks would be accomplished using response surface methodology (RSM).

Response surface methodology (RSM) refers to a collection of statistical and mathematical techniques that are used to create, improve, and optimize a given process [11].The main goal of RSM is the development of a mathematical model of a given system based on experimental results. When nonlinear interactions are foreseen, experiments at higher levels become a necessity to achieve good modeling, considering a minimum of three points is required to obtain a response curve [11].

In this study, central composite design was used to optimize the process conditions for the copolymerization of palm kernel oil-modified alkyd resin with styrene because it guarantees advantage of minimized number of distinct investigations.

2. EXPERIMENTAL

2.1. Materials:

Laboratory-grade phthalic anhydride with assay 99.7%, maleic anhydride with assay 99.0%, glycerol with assay 99.7%, styrene with assay 99.5%, xylene with assay 98%, benzoyl peroxide with assay 96%, and manganese (drier) from British Drug House (Poole, UK) were used in the preparation of the alkyds and styrenated alkyds. The palm kernel oil (PKO.) was purchased from Head Bridge Market, Onitsha, Anambra State, Nigeria.

2.2. Methods:

2.2.1. Refining procedure:

2.2.1.1. Crude palm kernel oil and distilled water:

At the start of the experiment, 50mls of CPKO was measured and poured into a beaker; the same quantity of water was added into the beaker. The mixture is heated for about 25 minutes in electric heater after which it is allowed to cool and settle and later decanted. The upper phase discharge is the washed oil with lesser impurities while the lower phase discharge is the water containing impurities.

2.2.1.2. CPKO and phosphoric acid:

The washed oil is treated with phosphoric acid of the same quantity. A reaction time of 20 minutes is allowed during which the gums (phosphatides) are precipitated.

2.2.1.3. CPKO and NaOH (Caustic Soda):

The acid treated oil is then continuously dosed with caustic soda. The concentration and amount of the alkali used varied with the free fatty acid (FFA) content of the oil. Intimate contact between the alkali and the oil is ensured by the choice of a well-designed mixer. The alkali results with the FFA forming precipitated soaps which are removed through centrifuge.

2.2.1.4. Neutralized palm kernel oil and distilled water:

The neutralized oil then undergoes washing. Here the oil is washed with water to remove the soap impurities present. The oil-water mixture passes through a centrifuge separator where the heavy phase discharge contains soapy water and the light phase discharge is water – washed oil with a soap content of less than 80ppm which is subsequently reduced at the next bleaching stage.

2.2.1.5. Dehydration of Palm Kernel Oil:

$50cm^3$ of the refined PKO was poured into a conical flask and mixed with $0.5gH_2SO_4$ as catalyst. The mixture was then heated to 250^{0C} and this temperature was maintained for an hour in an inert atmosphere of nitrogen. At the end of this period, the source of heat was removed and the dehydrated oil was allowed to cool.

2.3. Preparation of alkyd resin:

Three different alkyds were prepared with dehydrated palm kernel oil, glycerol, phthalic anhydride, maleic anhydride using lead (ii) oxide as catalyst using the formulations shown in Table 1. The reactions were carried out in a three necked round bottom flask titled with a motorized stirrer, a dean-stark trap titled with water-cooled condenser and nitrogen in let tube at a temperature of 230-250^0C. Xylene was also employed as the azeotropic solvent. Two stages were involved

State 1 (Alcoholysis): At this stage, the measured quantity of dehydrated palm kernel oil was poured into the flask and heated to about 120^0 to remove moisture. The heating was achieved with a heating mantle. Thereafter, the measured quantity of glycerol was added and the temperature was raised to 230^0C. After 30 minutes, a small quantity of the aliquot was taken to check for its solubility in methanol. Alcholysis was completed when the solubility test in methanol was positive. The reaction mixtures was cooled to about 140^0C

Stage 2 (Esterification process): At this stage, the measured quantity of phthalic anhydride, maleic anhydride and xylene was added into the flask and heated with a heating mantle. The temperature was gradually raised to about 230^0C and maintained at a range of about 230-250^0C for about 3hours. Aliquots were withdrawn from the reaction mixture at time intervals of 30minutes to check for drop in acid value. The reaction was then discontinued as soon as the acid value of the mixture attained the value of about 10mg K0H/g.

Table1. Recipe of the preparation of resins

Raw materials	Weight (g)	Weight (%)
Dehydrated oil	50	24.94
Phthalic anhydride	25	12.47
Maleic anhydride	25	12.47
Glycerol	100	49.88
Catalyst(LiOH)	0.5	0.25
Total	200.5	100

2.4. Preparation of styrenated alkyd resin:

The styrenated alkyds were prepared by post co-polymerization of the alkyd resin. The alkyds were with-draw into 100ml flask and heated in the presence of an initiator, benzoyl peroxide, under reflux at 120^0C for 3hrs.

2.5. Design of Experiment:

Table 2: Independence Factors and Corresponding Levels used for Optimization

Variables	Coded Levels/ Real Values		
	-1	0	+1
Temperature (^{0}C) (A)	100	125	150
Time (min)(B)	90	135	180
Styrene (g)(C)	3	4	5

The three-level, three-factorial central composite rotatable design (CCRD) with categorical factors of 0 was employed to optimize the treatment process based on the conversion of styrene. The design was composed of three levels (low, medium and high, being coded as -1, 0 and +1) and a total of 20 runs were carried out in duplicate to optimize the level of chosen variables such as temperature, time and styrene. For the purpose of statistical computations, the three independent variables were denoted as x_1, x_2 and x_3, respectively. According to the preliminary experiments, the range and levels used in the experiments are selected and listed in Table 2. The experimental design matrix by CCRD is tabulated in Table 3 and corresponding experiments were performed. The results were analysed by applying the coefficients of determination (R^2), response plots and analysis of variance (ANOVA). For Response Surface Methodology (RSM), the most commonly used second- order polynomial equation developed to fit the experimental data and determine the relevant model terms can be written as:

$$Y_{\text{predicted}} = \beta_0 + \sum \beta i x i + \sum \beta i i x i^2 + \sum \beta i j x i x j + \varepsilon \text{............ (1)}$$

Where $Y_{\text{predicted}}$ represents the predicted response, i.e. the fall in iodine value as the reaction progresses, β_0 the constant coefficient,β_i, the ith linear coefficient of the input factors xi, β_{ii}, the ith quadratic coefficient of the input factors xi, β_{ij}, the different interaction coefficients between input factors xi and x_{ij} (i = 1 – 3, j = 1 -3 and i ± j) and ε , the error of the model. The equation expresses the relationship between the predicted response and the independent variable in coded values according to Tables 2 and 3.

Table 3: Design matrix for the manufacturing of styrenated resins

Std	Run	Temp(A)	Time(B)	styrene(C)	Conversion(%)
11	1	0	-1	0	30.8
7	2	-1	+1	+1	81.6
12	3	0	+1	0	93.7
19	4	0	0	0	96.6
6	5	+1	-1	+1	59.7
4	6	+1	+1	-1	91.8
5	7	-1	-1	+1	61.7
15	8	0	0	0	96.3
8	9	+1	+1	0	95.54
20	11	0	0	0	96.1
3	12	-1	+1	-1	53.1
10	13	+1	0	0	81.9
14	14	0	0	-1	83.1
16	15	0	0	0	96.7
9	16	-1	0	0	48.5
1	17	-1	-1	-1	35.7
18	18	0	0	0	50.3
13	20	0	0	-1	33.11

3. RESULTS AND DISCUSSION

3.1. Optimization study:

The optimization study on the styrenated alkyd resin production is conducted according to the design matrix and corresponding results are listed in Table 3. The experiments were carried out at twenty runs and the fractional conversion of the manufactured palm PKO styrenated alkyd resin designated with Y was estimated in terms of the measured reduction in iodine value (IV) over the reaction periods. The response (Y) recorded for the different runs shows that the factors have significant effects. The deductions from the characterization, control and optimization protocol implemented for the manufacturing processes are discussed as follows.

3.1.1. Statistical process analysis:

The effect of temperature, time and the weight of styrene were investigated in order to serve as a tool for predicting final film performance of styrenated alkyd resins with different loadings of the individual's components. The quadratic equation for predicting the optimum point was obtained according to the Central Composite Design (CCD) and input variable, and then the empirical relationship between the response and the independent variable in the coded units was presented on the basis of the experimental results as follows:

$$Y_{\text{predicted}} = 95.95 + 7.04 + 14.29B + 9.26C + 1.85AB - 8.33AC - 3.55BC - 10.22A^2 - 11.27B^2 - 12.73C^2 \ldots. (2)$$

Table 4: ANOVA for response surface quadratic model analysis of variance table [partial sum of squares - type iii]

Source	F-val	P-value
Model	14.99	0.0001
A-TEMP	9.08	0.0131
B-TIME	37.38	0.0001
C-STYRENE	15.69	0.0027
AC	7.43	0.0213
A^2	20.19	0.0012
B^2	24.51	0.0006
C^2		0.0002

Std. Dev.	**8.64**	**R-Squared**	**0.9310**
Mean	72.58	Adj R-Squared	0.8689
C.V. %	11.90	Pred R-Squared	0.7566
PRESS	5874.94	Adeq Precision	12.252

The results of the analysis of variance (ANOVA) for the quadratic equation are tabulate in Table 4. The ANOVA indicates the equation and actual relationship between the response and significant variable represented by the equation are accurate. The significant of the coefficient term is determined by the values F and P, and the larger the value of F and the smaller the value of P, the more significant is. The P is lower than 0.05, suggesting the model is considered to be statistically significant. The ANOVA results derived from the predictive model show that the main linear effects due to individual control factors such as temperature (x_1), time (x_2) and styrene weight (x_3) coded as A, B, and C are all significant process variable indicated with the observed p- values <0.05 in the numerical analysis. The linear effect between temperature and weight of styrene (AC) is significant while linear effect between temperature and time (AB) and time and weight of styrene (BC) are not significant. The quadratic effects of temperature (A^2), time (B^2) and weight of styrene (C^2) are significant. The data obtained for specific investigation were refitted with a modified mode obtained by excluding the non-significant variables from the general predictive equation as shown in the equation below:

$$Y = 95.95 + 7.04A + 14.29B + 9.26C - 8.33AC - 10.22A^2 - 11.27B^2 - 12.73C^2 \ldots\ldots\ldots. (3)$$

As indicated by the ANOVA results, the F- value for the model was 14.99 suggesting that only a 0.01% chance of a “model F – value” so large could occur due to noise and the most of the variation in the response could be explained by the regression equation and that the model is significant. On checking the R² value, the “predicted R^2” of 0.7566 is in reasonable agreement with the “Adjusted R^2” of 0.8689 as one might normally expect. “Adequacy precision” measures the signal to noise ratio. It is reported that a ratio greater than 4 is desirable. The ratio of 12.252 indicates an adequate signal. As analysed above, this model can be used to navigate the design space.

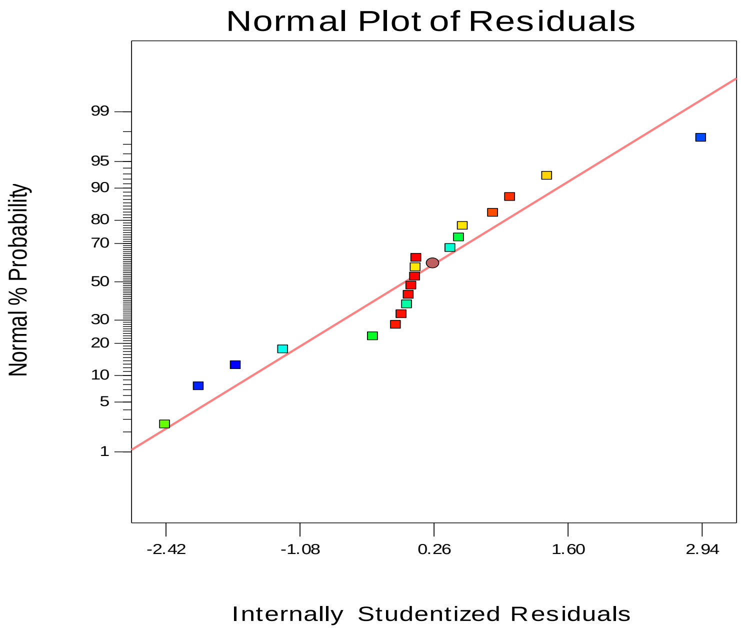
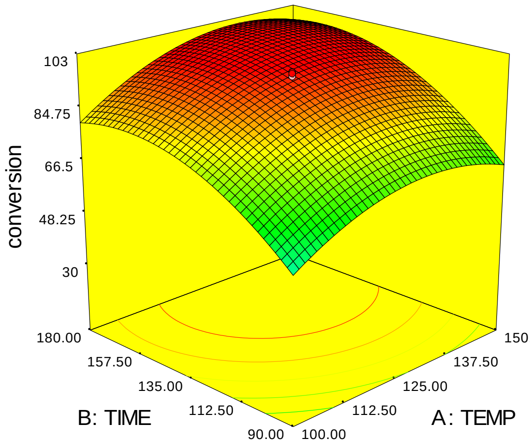


Fig.1: Normal Probability Plots obtained from Styrenated Resinanalysis

The diagnostics analyses were given in Figure 1. A clear look of the plot shows that the residuals follow a normal distribution. A picture of points which interlock a straight line with some moderate scatter is expected with normal data. The results equally show that the data points were well distributed which suggested an excellent relationship between the experimental and predicted values of the response, and the underlying assumptions of the above analysis were appropriate. Also, it indicated that the selected quadratic model was adequate in assuming the response variable for the experimental data.

3.1.2. Three-dimensional response surface plot:



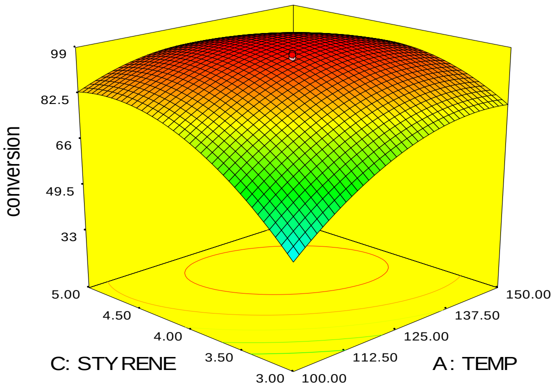


Fig.2. Response surface contour for interaction on Styrenated Resin production between time and temperature

Fig.3. Response surface contour for interaction on Styrenated Resin production between Styrene and temperature

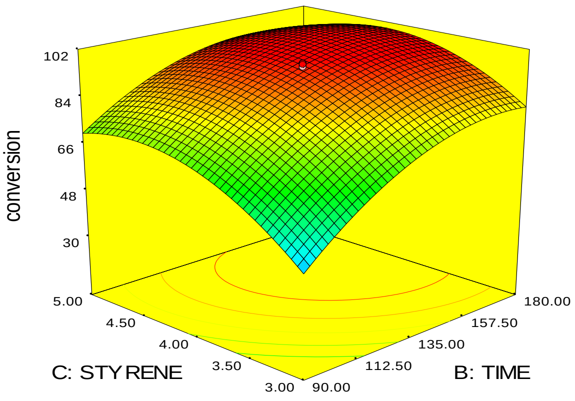


Fig.4. Response surface contour for interaction on Styrenated Resin production between Styrene and time

The interaction plots are representative of a slice of three-dimensional (3D) response surface plots at the low and high levels of one factor while another is held constant. The trend of these two factors over the range of the third variable at the specified condition is displayed in Figures 2 – 4.

The interaction effects on the process response between temperature (x_1) and time (x_2) in their natural units associated with the styrenated resin produced are depicted in Figure 2 at a constant weight of styrene of 4.0g. The percentage conversion ofstyrenated resins increased from 30 to 94.28% and then decreased to 78.56% at a reaction temperature of 100^0C when time of the reaction increased from 90min to 180min. The percentage conversion also increased from 30 to 70.698% at time of 90min as the temperature of reaction increased from 100^0C to 150^0C. The smooth curves on the reference surface contour are also a confirmation that the model equation is quadratic. This sharp increase in the conversion of styrenated resin at 135min and 125^0C follows the first order reaction kinetics in the copolymerization reaction while towards the completion of the reactions the responses assume a second order reaction. The decrease in the conversion at the above 150^0C and 180min is associated with the styrene structure [5].

The observed interaction effects on the responses between temperature (x_1) and the weight of styrene are depicted in Figure 3. The quadratic effect of temperature and weight of styrene is identified with smooth curves on the reference surface contour. This is in conformity with the model equation (3). The effects of reaction temperature and styrene weight were such that the conversion increased to 89.7979% and then decreased to 82.5% indicated that the production of styrenated alkyd resin is favoured at high temperature and styrene weight of 125^{0}C and 4g after which the production of styrenated resin begins to decrease. This is because at high temperature above 150^{0}C and at high weight styrene above 5g, the styrenated resin will become more thermoplastic, too brittle and detracts from the solvent resistance of the film. Also at low temperature and low weight of styrene, the product does not impart the desirable properties to the resin [3].

The response surface plot of Figure 4 reveals that the interactive effects between time and styrene are very important in the manufacturing of sturenated alkyd resin and there are need to be controlled. The percentage conversion of styrenated resin increased from 30 to 92.0284% and then decreased to 73.1568% at reaction time of 90 min when the weight of styrene increased from 3 to 5g. The percentage conversion also increased from 30 to 82.09% at styrene weight of 3g as the reaction time increased from 90 min to 180min. The smooth curve on the reference surface contour is also in agreement that the model equation (3) is quadratic.

3.1.3. Optimization process:

Almost any problem in manufacturing plants can be reduced to the problem of finding the largest or smallest value for a function of several variables. Optimization is a process of finding the set of conditions required to achieve the best results from a given situation. The situation here is the manufacturing of styrenated resin that will provide some obvious advantages like short drying time, high resistance in alkali and other chemical media, reduced material cost, improve film properties and weight. Another process of optimization is through reduction in reaction time and temperature which in effect minimize the overall cost of manufacturing [13]. Optimization problem may be compounded when the process (es) pose a multiple desired targets which may be a combination of two or more of above stated conditions [13]. A standard approach to this problem is to formulate global optimization criteria through which the necessary trade-off may be affected so as to achieve what may be considered as the best combination to the desired result.

The optimization exercise for the manufacturing of palm kernel oil styrenated alkyd resin was carried separately utilizing the flexibility of the design expert optimization tool function. Equation (3) was solved for the best solution such that the responses (Y) are maximized within the design space. Although no unique solutions were possible, yet a usual approach which involves selecting the best solution based on economic consideration is adopted and the chosen optimal solutions were presented in Table 5. The chosen optimal solution obtained by optimization exercise was then used to carry out experiment and the fractional conversion of 82.52% for PKO styrenated alkyd resin was obtained. This is in reasonable agreement with that of statistical model of design experts.

Efforts was made to compare these solution with previous works found in the literature but it does not provide desired results. This is because production of styrenated alkyd resin via copolymerization process of non-drying palm kernel oil modified alkyd resins have not receive adequate research attention. However, it has been shown that a lot of similarities exist between the result of current research and that reported by U.S.A patent 2986543 [6] and U.S.A patent 2647092 [3] where about 85% and above of styrene was converted to styrenated alkyd resin within 3hours of reaction at temperature maintain between 135 and 150^{0}C.

Table 5: Optimization values of process parameters for maximum responses palm kernel oil based styrenated resin

Process parameters	Optimum values
Fractional conversion (Y_n) (%)	83.57
Temperature (^{0}C) (x_1)	150
Time (min) (x_2)	180
Styrene weight (g) (x_3)	4.95
Desirability	0.940

4. CONCLUSION

Oil modified alkyd resin remains the work – horse of many coating system, especially in the automotive industry. This is due to some of its short comings such as poor adhesion, poor abrasion resistance and low viscosity. The accomplished study on optimisation of high performance styrenated alkyd resin shows that all the identified process parameters which include; reaction temperature, reaction time, and styrene weight have significant interactive effect on the overall efficiency on the copolymerisation of styrene and palm kernel oil based alkyd resin. The response surface methodology (RSM) based on central composite rotatable design employed for the analysis and optimization of the copolymerization process of the palm kernel oil modified resin with styrene predicts optimum fractional conversion of 83.57% at reaction temperature of 150^0C, time of 180 min, and styrene weight of 4.95g (approximately 49.5 %wt styrene). Fractional conversion of 83.57% predicted by statistical analysis shows close agreement with the 82.52% fractional conversion obtained with the validating experiment performed at the predicted optimum conditions.

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