Modeling the effect of dammar additions on the mass loss response of soy wax/beeswax/dammar blends via response surface methodology

S I S Shaharuddin¹, N B A Aziz¹, N Bacho¹, N K M Khairussaleh¹, A Tumian², I A Zakaria³

¹Department of Manufacturing and Material Engineering International Islamic University Malaysia Gombak, Selangor
²Facilities of the Future, Petronas Research Sdn. Bhd., Putrajaya, Wilayah Persekutuan
³Faculty of Mechanical Engineering, Universiti Teknologi MARA, Selangor

Abstract. The wax used in the batik industry plays a significant role as its composition dictates the ease of wax rendering, dye layering, and wax removal process. This study aims to evaluate the effect of dammar additions on soy wax/beeswax blends based on the mass loss (%) of the wax-covered cotton fabric in 100°C water. Central composite design (CCD), a subset of response surface methodology (RSM) was used to develop a response model (Y: mass loss %) for three independent variables (X₁: beeswax, X₂: soy wax, X₃: dammar). The final quadratic response model obtained (F value =5.43, lack of fit F value = 4.70, adequate precision = 7.65) was proposed in this study. ANOVA analysis showed that the standard error of design was relatively small, ranging between 0.43 to 1.18 for the design space. It was deduced from the response model, that increasing the dammar content in the soy wax/beeswax blends increases the mass loss (%), possibly due to the compositional inhomogeneity of the blends. The result of this study shows great potentials in formulating new soy wax-based compositions that produce varying degrees of ease of wax removal for the batik industry.

1. Introduction
Batik is a process that applies resist-based materials such as wax to create batik motifs on fabrics. Once the batik motifs have been completely outlined using wax, the fabric is given soda ash (Na₂CO₃) pre-soak before being dyed. Alternatively, soda ash can also be mixed with the dye and immediately applied to the fabric. Soda ash increases the alkalinity of the solution and a pH reading in the range of 10 to 11.5 is desirable to encourage a stronger chemical reaction between the cellulosic fiber anion and the dye. This will result in batik cloth having better color vibrancy and steadfastness. Once the coloring phase has been completed, the final stage of batik production involves the removal of the batik waxes to reveal the batik motif outline via immersion in hot water. Traditional batik wax composition in Malaysia is composed of a blend of paraffin, microcrystalline wax, beeswax, dammar, and vegetable oil. The use of paraffin and microcrystalline wax has raised environmental concerns as these synthetically produced materials do not biodegrade easily in water. Recently, there is an overwhelming supply of vegetable-based oils, and soy wax, in particular, has been receiving great attention as a renewable and biodegradable replacement to paraffin wax [1].
Soy wax is derived from the hydrogenation process of soy oil by transforming full or partial unsaturated fatty acids into saturated form. Soy wax biodegrades better than paraffin and offers a cheaper option in comparison to beeswax [2]. Currently, the use of soy wax is not very popular amongst batik artisans. In comparison to the traditional batik wax blends, soy wax easily dissolves in water and therefore may not be suitable for multiple dye immersion techniques. In addition, soy wax is also hard and brittle or greasy [3]. To improve such shortcomings, Bowen [4] added beeswax to increase the water resistance and adhesive capacity of soy wax. Previously, dammar resin has also been added into the wax to impart stickiness or adhesive property [5]. The hydrophobic nature of soy wax, beeswax, and dammar has been studied to improve the hydrophilic properties of various materials [6–8].

Except for palm oil-based batik wax [9] and sago-based batik wax, it was realized that compositional study on naturally sourced batik wax alternatives has been quite limited [10]. Prior studies on dammar additions have mainly focused on chemical composition and properties [3,11,12] whilst their degradation reaction has been evaluated due to the aging effect from light and heat exposure. This study aims to investigate the effect of dammar additions on the mass loss response of soy wax/beeswax blends via response surface methodology (RSM). RSM is commonly adopted in physical and chemical experimental designs [13]. In this work, the RSM applies central composite design (CCD) to develop the design of the experiment (DOE) since it dictates a fewer number of tests and has been proven to effectively describe most steady-state process responses. CCD is also a useful approach to model various processes in comparison to the "one variable at a time" approach. The statistical analysis in this study was performed using ANOVA.

2. Methodology

2.1. Material preparation

The ratios of beeswax (Global Sdn Bhd, Malaysia), soy wax (Jargeous Sdn Bhd, Malaysia), and dammar resin (Rupert, Gibbon & Spider Inc.America) were weighed according to the weight ratios specified based on DOE using CCD in Figure 1. Each component of the batik wax compositions was then melted in a pan in the order of decreasing melting temperature as follows; dammar (melting point = 90°C), followed by beeswax (melting point = 70°C), and finally soy wax (melting point = 55°C). Upon complete melting, the blends were stirred and poured into metal pans covered with aluminum foil. The prepared batik wax blends were then left to solidify.

2.2. Response surface methodology

The RSM via CCD was represented by mass loss (Y, %) for three independent variables (k-3) consisting of beeswax (X1, g) soy wax (X2, g), and dammar (X3, g). These independent variables were considered at two levels: low (30g) and high (100g). The total number of proposed experiments, used in this study was N= 2^k + 2k + n0 = 20 where 2^k = 2^3 = 8 factorial points, 2k = points located at “±\sqrt{k}” from the centre points = 6 axial points and n0 = replicates = 6 central points. The experimental design in coded and uncoded values is listed and schematically shown in Table 1. Figure 1 shows the wax compositions (in gram) that represent the factorial points, axial points, and center points in a 3D design space. The ANOVA analysis and statistical values were determined using Design-Expert software (version 6.0.8). To evaluate how close the selected response model fits with the experimental values obtained, the parameters F-value, R^2, P-value, and lack of fit are used [13]. Insignificant lower-order terms in the initial response models were removed. Only insignificant lower-order terms that are included in significant higher-order terms were considered to form the final response model. ANOVA analysis was performed for the second time.
Table 1. CCD coded and uncoded values of the input variables for the experimental design.

| Variables          | Codes levels | Lowest -\sqrt{2} | Low -1 | Centre 0 | High 1 | Highest \sqrt{2} |
|--------------------|--------------|------------------|--------|----------|--------|------------------|
| (X_1) Beeswax (gram) | 6            | 30               | 65     | 100      | 124    |
| (X_2) Soy wax (gram)  | 6            | 30               | 65     | 100      | 124    |
| (X_3) Dammar (gram)   | 6            | 30               | 65     | 100      | 124    |

Figure 1. The $2^3$ factorial design spaces representing the proportion of the independent variables.\(^{(X_1 \text{ g } \text{beeswax}, \ X_2 \text{ g } \text{soy wax}, \ X_3 \text{ g } \text{dammar})\)} used in this study.

2.3. Mass loss protocol
The wax blends were re-melted, and a small brush was used to apply the wax according to the sketched 8 x 8 cm guideline on the 10cm x10cm cotton fabric. The mass of the fabric with wax was initially weighed (M_i). Each waxed fabric sample was immersed in an alkaline solution for 1 hour. An alkaline solution of pH 10-11.5 was prepared by dissolving 0.62 grams of soda ash or sodium bicarbonate (Na_2CO_3) in 200 ml of water to increase the water’s pH. After drying for 24 hours, each fabric was boiled in 100°C water for 1 hour. The sample fabric was then removed, dried and the final mass (M_f) was measured. The mass loss (%) was calculated according to Equation (1).

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\text{Mass loss (\%)} = \frac{M_i - M_f}{M_i} \times 100\% \tag{1}
\]

3. Results and Discussions
In this study, CCD was used to develop a polynomial model for the response (Y: mass loss %) based on a set of independent variables (X_1: beeswax (g), X_2: soy wax (g), X_3: dammar (g)). A quadratic response model was then selected since the cubic model was aliased. An aliased model indicates the lack of insufficient unique design points and will result in unstable coefficient values and inaccurate graphs [13]. The standard error of design contour shown in Figure 2 at the central point of the DOE shows that the root means the square error is relatively small, ranging between 0.43 to 0.50. At the axial points of the DOE, the standard design error estimation only increases slightly in the range of 0.86 to 1.18 for the studied design space. It was concluded that near-uniform precision designs have been achieved since the error gradient is nearly uniform. Therefore, it was deduced that the response model (Y: mass loss %) will be able to deliver accurate predictions for the mass loss error for the intended range of batik waxes used in this study.
Figure 2. Standard design error estimation for the response based at (a) central points and (b) axial points for the design space.

The resulting mass loss (%) due to alkaline exposure and boiling water is presented in Table 2.

Table 2. Response (mass loss, %) for three-factor, two-level CCD matrices used in RSM in uncoded and coded values.

| Run No. | Independent variables in uncoded value | Response (Mass loss, %) |
|---------|---------------------------------------|------------------------|
|         | $X_1$ (A) Beeswax (g) | $X_2$ (B) Soy wax (g) | $X_3$ (C) Dammar (g) | Y |
| 1       | 65 | 65 | 6 | 8.93 |
| 2       | 65 | 65 | 65 | 8.91 |
| 3       | 30 | 100 | 30 | 11.16 |
| 4       | 65 | 65 | 65 | 7.89 |
| 5       | 30 | 30 | 100 | 11.56 |
| 6       | 65 | 65 | 65 | 11.16 |
| 7       | 100 | 30 | 30 | 22.11 |
| 8       | 30 | 100 | 100 | 25.03 |
| 9       | 30 | 30 | 30 | 14.71 |
| 10      | 6 | 65 | 65 | 24.33 |
| 11      | 65 | 65 | 65 | 11.81 |
| 12      | 65 | 124 | 65 | 26.17 |
| 13      | 65 | 65 | 124 | 19.61 |
| 14      | 65 | 6 | 65 | 19.68 |
| 15      | 100 | 30 | 100 | 23.77 |
| 16      | 100 | 100 | 100 | 23.18 |
| 17      | 65 | 65 | 65 | 13.65 |
| 18      | 65 | 65 | 65 | 14.01 |
| 19      | 124 | 65 | 65 | 18.03 |
| 20      | 100 | 100 | 30 | 20.18 |

Table 3 shows the analysis of variance (ANOVA) for the final quadratic response model (Equation 2). The model has an F-value of 5.43. The $p$-value of 0.0055 of the response model indicates that there is only a 0.55% chance that the model F-value this large could occur due to noise. This implies the quadratic model is significant. The F value for Lack of Fit (4.70) has a corresponding $p$-value of 0.0516 which indicates that the lack of fit is not significant in comparison to the actual pure error. "Adequate Precision" measures the signal-to-noise ratio. A ratio value greater than 4 is highly desirable. The ratio value of 7.649 obtained in this study indicates an adequate signal, hence the final model can be used to
navigate the design space. The $R^2$ value of 0.66 shows that there is a slightly high variability (mass loss (%) values) around the mean regression line. It is postulated that the $R^2$ value is affected by the method of wax deposition on the fabric. The manual brush stroke may have produced a slight inconsistent in the wax thickness layer. Wax that was spread thinly across the fabric can be easily degraded in high-temperature water compared to areas covered with a thicker layer of wax. However, important conclusions can still be drawn for the independent variables since the overall model is still statistically significant.

Table 3. Analysis of variance (ANOVA) for response surface quadratic model for mass loss (%).

| Independent variables | F-value | P-value |
|-----------------------|---------|---------|
| Model                 | 5.43    | 0.0055  |
| Beeswax: $X_1$        | 1.15    | 0.3008  |
| Soy wax: $X_2$        | 1.48    | 0.2442  |
| Dammar: $X_3$         | 4.91    | 0.0437  |
| $X_1^2$               | 8.80    | 0.0102  |
| $X_2^2$               | 12.56   | 0.0032  |
| Lack of fit           | 4.70    | 0.0516  |

Adequate precision (ratio >4) = 7.649
$R^2$=0.6599

The proposed final regression model in coded value is shown in Equation (2).

$$Y = 12.09 + 1.19X_1 + 1.34X_2 + 2.45X_3 + 3.17X_1^2 + 3.79X_2^2 \quad (2)$$

The positive sign before each polynomial factor indicates that the response increases with the factor, while a negative sign indicates a reciprocal interaction [14]. As the P-value gets smaller, the significance of the coefficient increases [15]. Thus, the ranking of the first-order main effect that influences the response model is as follows: $X_3$ (dammar) > $X_2$ (soy wax) > $X_1$ (beeswax).

Figure 3 shows the normal probability and studentized residual plot for the mass loss (%) which indicates that the error terms were distributed normally and there are no extreme outliers. The interactions between RSM CCD design variables in 3D surface forms are shown in Figure 4. It was observed that further additions of dammar of more than 30g into the soy wax/beeswax increases the mass loss % of the blends. It was postulated that the increase in mass loss with the increase in dammar (wt%) was attributed to the loss in barrier efficiency. Soy wax is formed from partial or fully hydrogenated soybean oil [3] and is very sensitive to high temperatures. As the soy wax and beeswax were melt-blended approximately at 90 °C, the natural oil phase in soy wax may form and become separated from the wax. This explains the slightly greasy nature of the solidified blends. Yao et al.’s [2] study revealed that the addition of dammar into fully hydrogenated vegetable oil resulted in decreased compositional homogeneity. In general, the uniformity of hydrophobic multicomponent blends affects its barrier efficiency [16]. Therefore, it was postulated that the decrease in inhomogeneity due to higher dammar content (wt%) may have reduced the barrier efficiency of the blends.
Figure 3. Normal residual plot for the batik waxes via ANOVA.

Figure 4. 3D surface interaction effect of $X_1$ (beeswax) and $X_2$ (soy wax) and response, $Y$ (mass loss%) at fixed values of (a) $X_3$ (dammar) = 30 g, (b) $X_3$ (dammar) = 65 g, (c) $X_3$ (dammar) = 100 g.

4. Conclusion
In this study, RSM via CCD was used to evaluate the effect of dammar additions based on mass loss % of the waxed covered fabric in 100°C water. The statistical ANOVA analysis for the obtained quadratic model is as follows; F-value of 5.43 with a corresponding p-value of 0.0055, ‘lack of fit’ at 4.70 with a corresponding p-value of 0.0516, ‘adequate precision ratio value of 7.649 and $R^2$ value of 0.66. A statistically significant quadratic response model was then proposed in this study. The response model predicted that the addition of dammar increases the mass loss percentage attributed to the increase in inhomogeneity of the blend. The results of this study can be used to formulate new batik wax compositions with varying degrees of ease in wax removal during batik production. In addition, these
compositions have the potentials to be used as an environmentally friendly batik wax composition for the batik industry.

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