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Evaluation of Indigo Dyeing on Poly(lactic acid) by Response Surface Methodology

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Poly(lactic acid) fabric is dyed with natural indigo dye from *Indigofera tinctoria*. The dyeing conditions were evaluated from the relationship between colour strength (K/S) of dyed poly(lactic acid) fabrics and three independent variables (dyeing temperature, dyeing time and indigo dye concentration) using response surface methodology. The 5-level-3-factor central composite design was applied in order to study the effect of different factors on the colour strength. Regression analysis generated the second-order polynomial equation for the prediction of colour strength. The model adequate check was confirmed by ANOVA parameters and validation test. The effect from the combination of variables on colour strength was considered by the surface plots. The optimum conditions obtained from response surface methodology were at 85.5 °C for dyeing temperature, 56 min for dyeing time and 12.9 % owf for indigo dye concentration. Applying with the optimum dyeing conditions, dyed poly(lactic acid) fabrics gave a good result on colour strength and fastness properties.

Keywords: Poly(lactic acid), Indigo, *Indigofera tinctoria*, Response surface methodology, Central composite design.

INTRODUCTION

Indigo is a well known natural blue dye that is used *hitherto* even though synthetic ones are commercially available. The source of the indigoid pigments are leaves of indigo plants such as *Indigofera tinctoria*, *Strobilanthes flaccidifolius* and *Marsdenis tinctoria*. Indigo is predominantly applied on cellulosic fibers *via* the vat dyeing process. In principle, a water-insoluble indigoid pigment is first reduced to a water-soluble leuco form and then penetrates into cellulose to which the colourless leuco compound is substantive. The permeated fiber is subsequently exposed to oxygen in the air in order to reoxidize the leuco dye back to the original pigment form and hence trapping it inside the fiber [1]. Natural indigo dyes can provide high levels of wet fastness and light fastness on cellulosic fibers [2,3]. The attempts to apply indigo dyes on synthetic fibers such as polyester especially poly(ethylene terephthalate) (PET) and poly(lactic acid) (PLA), nylons, acrylics and polyurethanes, have been reported [4-10]. Although natural indigo dyes have a low substantivity for synthetic fibers, the investigation of vat dyeing on synthetic fibers has been motivated by the environmental benefit of using natural dyes.

Poly(lactic acid) is an aliphatic polyester fiber material that has potential to be an alternative replacement of poly(ethylene terephthalate). Besides the similar properties to poly(ethylene terephthalate), poly(lactic acid) is favourable because it is synthesized from corn starch or sugar which are renewable starting materials. Therefore, poly(lactic acid) can be biodegraded by particular fungi into carbon dioxide and water once it is left in the environment [11]. Disperse dyes are typically applied on poly(lactic acid) at the recommended pH of 4.5-5 and dyeing temperature of 110-115 °C for 15-30 min [12]. Poly(lactic acid) dyeing with natural indigo dyes is possible by either disperse or leuco methods [13-15].

In this work, the dyeing conditions of natural indigo dyes on poly(lactic acid) were optimized by response surface methodology (RSM) using central composite design (CCD) for the experimental design. The study was based on three independent numerical factors (dyeing temperature, dyeing time and dye concentration) and the response (dependent variable) is the colour strength (K/S values) of dyed fabrics. The quantitative data from the dyeing experiment is used to generate the mathematic equation and also presented graphically in surface plots. Indigo dyes were then applied on poly(lactic acid) using the optimum conditions from response surface methodology to evaluate the colour strength and fastness properties.

EXPERIMENTAL

Indigo dyes extracted from *Indigofera tinctoria* were purchased in a paste form. The paste was washed in repetition using distilled water in order to adjust the pH to be 7 and then vacuum filtered. Fine indigo powder was obtained by drying the filter cake at 100 °C overnight and grinding with a mortar.

Poly(lactic acid) fabric: Knitted poly(lactic acid) fabric used was 40 Ne interlock from Hebei Tianlun Textile Co. Ltd, China. The fabric was scoured in a solution containing 2 g/L sodium carbonate and 1 g/L Sera Wash using a liquor ratio of 10:1. The scouring process was carried out at 60 °C for 20 min. The scoured fabric was then rinsed with water and dried at room temperature.

Dyeing process: Dyeing poly(lactic acid) fabric with indigo dyes was conducted in a DaeLim Starlet II Infrared dyeing machine. The dyebath contained 10 g/L sodium dithionite, 0.1 g/L sodium hydroxide and indigo dye which was varied from 6-14 % owf. The liquor ratio used was 100:1. The dyeing profile is shown in Fig. 1. Indigo dyes were reduced at 30 °C for 20 min before immersing poly(lactic acid) fabrics into the dyebath. The dyeing experiments were carried out under the designated temperatures and times. After the dyeing process, the dyed poly(lactic acid) fabrics were rinsed in water and air-dried to oxidize the leuco dyes to the pigment form.

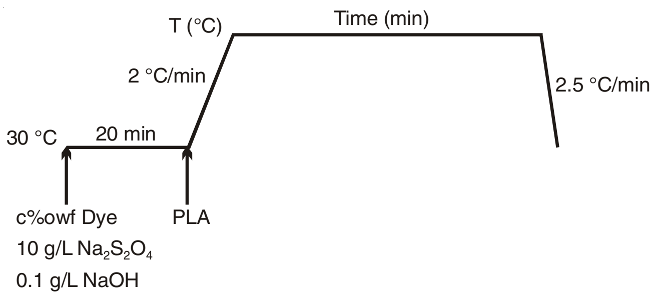

Fig. 1. Dyeing profile of natural indigo on poly(lactic acid) fabric

Colour strength measurement: The reflectance values of dyed poly(lactic acid) were evaluated using a Macbeth Color-Eye 7000 Spectrophotometer at a maximum absorption wavelength (λ_{max}). The colour strength (K/S values) was calculated according to Kubelka-Munk Equation as shown in eqn. 1.

$$\frac{K}{S}=\frac{(1-R)^2}{2R} \quad (1)$$

where K is the absorption coefficient, S is the scattering coefficient and R is the observed reflectance at the λ_{max} = 600 nm.

Colour fastness test: The fastness properties of the dyed poly(lactic acid) were evaluated based on the International Organization for Standardization (ISO). Fastness to washing was determined using the ISO 105-C10:2006 test method and fastness to dry and wet rubbing was performed according to the ISO 105-X12:2001 test method.

Experimental design: The experiment point was designed by five-level-three-factor CCD using Design Expert software package version 8.0.4. Three independent variables were dyeing temperature, dyeing time and concentration of the indigo dye while the dependent variable was the colour strength of the dyed poly(lactic acid). The range of each variable was selected in accordance with the previous work [16]. The coded and uncoded (actual) levels of the independent variables are given in Table-1. A total of twenty experiments from the design consist of 8 factorial points, 6 axial points and 6 central points as shown in Table-2. The dyeing experiments for each condition were carried out in three replications.

Statistical analysis: The effect of each independent variable was analyzed by analysis of variance (ANOVA) and regression analysis. A second-order polynomial regression equation was established from the experimental data that can be used to generate a quadratic response surface. The equation includes response Y which depends on the independent variables and their interactions as given in eqn. 2.

$$Y=b_0+\sum_{i=1}^{3}b_ix_i+\sum_{i=1}^{3}b_{ii}x_i^2+\sum^{2}\sum_{i<j=1}^{3}b_{ij}x_ix_j+\varepsilon \quad (2)$$

where Y is the response, x_i and x_j are the uncoded independent variables (when i ≠ j), b_0, b_i, b_{ii} and b_{ij} are intercept, linear, quadratic and interaction coefficients, respectively. The statistical significance was determined by p- and F-values. The validation of the equation was confirmed by the experiments that were carried out with the combinations of independent variables, which were not part of the original experimental trials but were within the studied range.

RESULTS AND DISCUSSION

Statistical analysis: The observed and predicted colour strength values of the dyed poly(lactic acid) fabrics, obtained from the actual dyeing experiment and the equation prediction, were compared at the designed point as presented in Table-2. The coded and uncoded levels of the independent variables are also shown for all twenty experiments. The results of the analysis based on the response surface methodology method are shown in Tables 3 and 4. The quadratic response surface model is suggested by the p-value which is the probability that the value can be obtained by the statistic test [17]. The smaller the p-value is, the more significant is the model. At the 95 % confident level, if the p-value is less than 0.05 implies that the model is significant. According to Table-3, the quadratic model is significant since the p-value < 0.0001 and the F-value (36.27) is greater than the F table value ($F_{8,5}$ = 4.82).

Regression coefficients of analysis: Using the experimental data from Table-2, the second-order polynomial model

TABLE-1
INDEPENDENT VARIABLES AND CODED VALUES USED FOR CCD IN THE DYEING PROCESS

Variable	Symbols	Coded level				
		-2 (-α)	-1	0	1	+2 (+α)
Dyeing temperature (°C)	A	60	70	80	90	100
Dyeing time (min)	B	40	50	60	70	80
Indigo dye concentration (% owf)	C	6	8	10	12	14

Transformation from coded (X) to uncoded variable levels could be obtained as: A = 80 + 10X, B = 60 + 10X and C = 10 + 2X.

TABLE-2
EXPERIMENTAL DESIGN WITH THE OBSERVED AND PREDICTED RESPONSE VALUES USED FIVE-LEVEL-THREE-FACTOR CCD FOR RESPONSE SURFACE METHODOLOGY

Run No.	Point type	Temperature (°C)	Time (min)	Dye concentration (% owf)	Colour strength (K/S)	
					Observed	Predicted
1	Factorial	(–1)70	(–1)50	(–1)8	1.421	1.386
2	Factorial	(+1)90	(–1)50	(–1)8	2.286	2.406
3	Factorial	(–1)70	(+1)70	(–1)8	1.573	1.653
4	Factorial	(+1)90	(+1)70	(–1)8	2.391	2.378
5	Factorial	(–1)70	(–1)50	(+1)12	1.989	2.178
6	Factorial	(+1)90	(–1)50	(+1)12	2.973	3.069
7	Factorial	(–1)70	(+1)70	(+1)12	2.498	2.554
8	Factorial	(+1)90	(+1)70	(+1)12	2.939	3.150
9	Axial	(–α)60	(0)60	(0)10	0.833	0.775
10	Axial	(+α)100	(0)60	(0)10	2.509	2.390
11	Axial	(0)80	(–α)40	(0)10	2.681	2.584
12	Axial	(0)80	(+α)80	(0)10	3.012	2.932
13	Axial	(0)80	(0)60	(–α)6	1.643	1.655
14	Axial	(0)80	(0)60	(+α)14	3.408	3.219
15	Center	(0)80	(0)60	(0)10	2.556	2.610
16	Center	(0)80	(0)60	(0)10	2.649	2.610
17	Center	(0)80	(0)60	(0)10	2.717	2.610
18	Center	(0)80	(0)60	(0)10	2.537	2.610
19	Center	(0)80	(0)60	(0)10	2.703	2.610
20	Center	(0)80	(0)60	(0)10	2.674	2.610

TABLE-3
ANALYSIS OF VARIANCE (ANOVA) FOR QUADRATIC MODEL

Source	Sum of squares	df	Mean square	F-value	p-value
Model	7.120	9	0.790	36.27	< 0.0001
Residual	0.220	10	0.022	–	–
Lack of fit	0.190	5	0.038	6.57	0.0297
Pure error	0.029	5	5.759E–003	–	–
Total	7.340	19	–	–	–

TABLE-4
RESULTS OF REGRESSION ANALYSIS OF SECOND ORDER POLYNOMIAL MODEL

Source	Regression coefficients*	Standard error	F Value	p-value**	Significant at 95 % confidence
Intercept	–23.29027	0.059	–	–	–
A†	0.51162	0.037	119.61	< 0.0001	Yes
B††	9.59205E–003	0.037	5.57	0.0400	Yes
C†††	0.45866	0.037	112.25	< 0.0001	Yes
AB	–7.37500E–004	0.052	2.00	0.1881	No
AC	–1.61250E–003	0.052	0.38	0.5506	No
BC	1.36250E–003	0.052	0.27	0.6131	No
A^2	–2.56795E–003	0.029	76.03	< 0.0001	Yes
B^2	3.70795E–004	0.029	1.59	0.2366	No
C^2	–0.010793	0.029	2.15	0.1734	No

*R^2 = 0.9703, %CV = 6.15, Adeq prediction = 23.408
**The p-value more than 0.05 is not significantly different at 95 % confidence level
†A is dyeing temperature; ††B is dyeing time; †††C is indigo dye concentration

for K/S based on three dyeing parameters was generated as expressed in eqn. 3.

$$Y = -(23.29) + (0.512*A) + (9.592 \times 10^{-3}*B) + (0.459*C) - (2.568 \times 10^{-3}*A^2) + (3.708 \times 10^{-4}*B^2) - (0.0108*C^2) - (7.375 \times 10^{-4}*AB) - (1.613 \times 10^{-3}*AC) + (1.363 \times 10^{-3}*BC) \quad (3)$$

where Y is the response (K/S), A is the dyeing temperature, B is the dyeing time and C is indigo dye concentration.

Table-4 shows that A, B, C and A^2 were significant at 95 % confidence level because their p-values are less than 0.05. Dyeing temperature (A) has the most effect on the K/S value because of its high F-value (F = 119.61) and the corresponding small p-value. The interactions of independent variables in terms of AB, AC and BC are insignificant because their F-values are relatively low and p-values are also greater than 0.05 at 95 % confidence. The determination coefficient (R^2) of the model in this study is 0.9703, justifying an excellent correlation between the independent variables and response. Coefficient of variation (CV) is 6.15 denotes that the experiments are reliable, precise and well-fitting with the model. Adequate precision is calculated using the comparison between the ranges of predicted values at design points to prediction error. In this case, the adequate precision is 23.408 indicating the adequacy of the model for prediction [17]. Moreover, the accuracy of model is described by the plot between observed values and predicted values in Fig. 2. The result reveals a strong relationship between the model's prediction and the observed values.

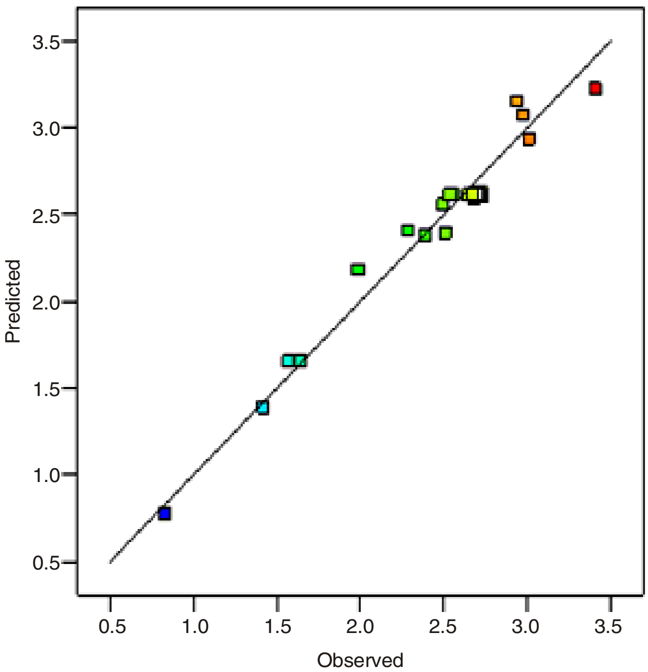

Fig. 2. Plot of predicted *versus* observed colour strengths

Validation test: Ten validation points were investigated using the same range of each independent variable but were not exactly the same conditions as the main twenty experiments. The observed K/S was assessed and reported as the average of three repeating measurements. The differences between observed and predicted K/S values were less than 5 % (Table-5).

Effect of independent variables: Response surface plots (3D) of regression were generated as shown in Fig. 3. The values of K/S increased as dyeing temperatures increased until around 85 °C (Fig. 3a) which could be contributed to the higher kinetic energy of indigo molecules at the high temperature,

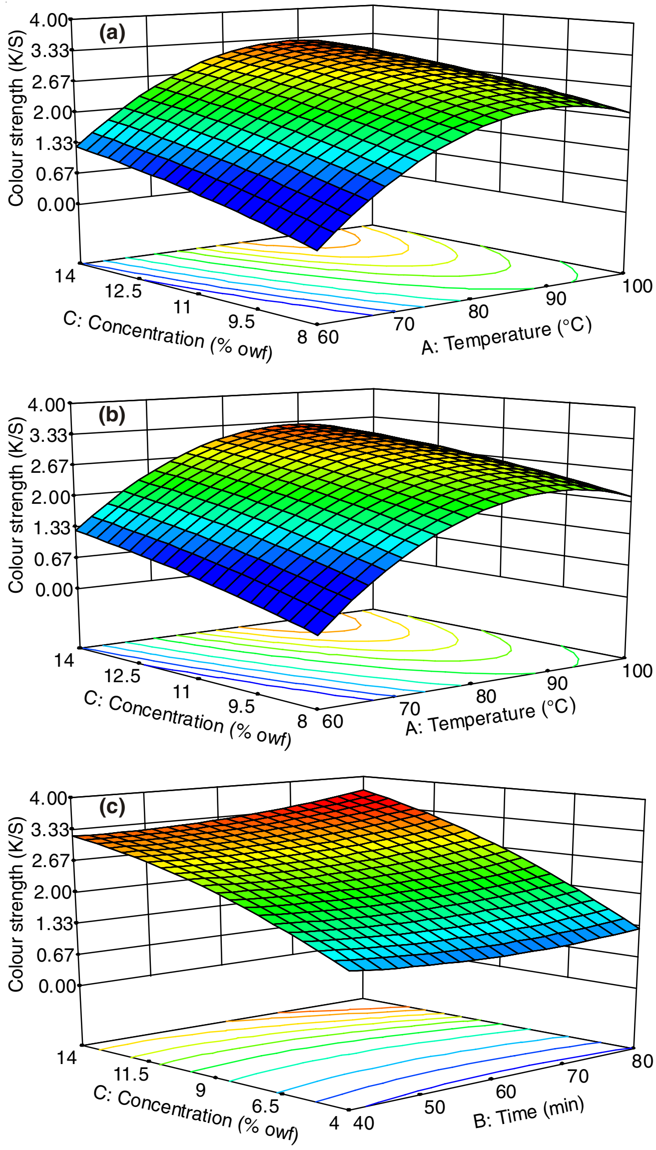

Fig. 3. Response surface plot of independent variables combination; a) combination of dyeing temperature and dyeing time; b) combination of dyeing temperature and indigo dye concentration; c) combination of dyeing time and indigo dye concentration

improving the diffusion power of the dye molecules into fiber. Fiber swelling was also influenced by the increased temperature [14]. At low temperatures, increasing dye concentration (Fig. 3b) had a slight effect on the K/S values because the plots are almost parallel to the axis. However, at higher temperatures, K/S seemed to increase with dye concentration applied. From

TABLE-5
VALIDATION POINTS

Run No.	A	B	C	Observed K/S	Predicted K/S	Error (%)
1	100	80	7	1.748	1.765	0.92
2	70	60	10	1.949	2.044	4.64
3	82	65	9	2.515	2.532	0.65
4	75	55	11	2.593	2.477	4.68
5	85	70	10	2.834	2.857	0.78
6	76	58	9	2.175	2.265	3.97
7	92	70	12	3.216	3.119	3.11
8	80	45	14	3.090	3.004	2.87
9	65	50	14	1.917	1.884	1.76
10	63	66	11	1.542	1.474	4.63

TABLE-6
WASH FASTNESS AND RUB FASTNESS OF NATURAL INDIGO ON POLY(LACTIC ACID) FABRICS

Fabric	Wash fastness							Rub fastness	
	Shade change	Staining on the multifiber						Dry	Wet
		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate		
Dyed poly(lactic acid)	5	5	4/5	5	5	5	5	5	5

Fig. 3c, dyeing time did not show significant effect on the K/S values despite the complete reduction and higher exhaustion of leuco form was expected. The reduction of K/S after the optimum points occurred which could be explained by 3 main reasons. First, the stability of the leuco form of indigo dye is lower when dyeing time is longer [5]. Secondly, high temperatures with long dyeing time increase the rate of poly(lactic acid) hydrolysis, causing the damage of poly(lactic acid) fiber [8]. The other reason is dye aggregation from a large quantity of dyes applied in dyebath [5].

Optimization of dyeing condition: The Design Expert software was used to optimize the dyeing conditions. The optimum dyeing conditions calculated for K/S of 3.187 were at 85.5 °C for dyeing temperature, 56 min for dyeing time and 12.9 % owf for indigo dye concentration. Dyeing indigo on poly(lactic acid) fabrics with the optimum dyeing conditions gave the average K/S of 3.050. The difference between K/S values from the experiment and the prediction was 0.137 (3.187 – 3.050 = 0.137) which is less than 5 % error.

Fastness properties: Poly(lactic acid) fabrics dyed under the optimum conditions gave the results of fastness test as shown in Table-6. It revealed that the indigo dyeing on poly(lactic acid) has very good fastness properties both from staining on the multifiber and a colour change of a specimen. The unfixed dye on poly(lactic acid) surface transferred during washing to deposit only on acrylic (gray scale rating = 4/5). The shade of dyed poly(lactic acid) was unchanged because of the insolubility characteristic of the indigo that was trapped inside the fabric [14]. Rubbing fastness both dry and wet conditions were excellent. The results emphasized that indigo dye molecules were firmly trapped inside the poly(lactic acid) fiber structure.

Conclusion

Natural indigo dyes obtained from *Indigofera tinctoria* can be successfully applied on poly(lactic acid) fabrics by a vat dye method. Response surface methodology was applied with the 5-level-3-factor central composite design in order to optimize the dyeing conditions and examine the interaction effect among independent variables on the K/S values of the dyed poly(lactic acid) fabric. A quadratic model was suggested for the colour strength prediction with high R^2 (0.9703). The statistical results were conformed to surface plots to give the information of the effect from the combination of independent variables instead of only one factor consideration at a time in the conventional method. The dyeing temperature and indigo dye concentration have greater effects on the K/S than dyeing time. The optimum conditions obtained was at 85.5 °C for dyeing temperature, 56 min for dyeing time and 12.9 % owf for indigo dye concentration. This condition gave the predicted and observed K/S at 3.187 and 3.050, respectively. The fastness properties of the dyed poly(lactic acid) fabrics were excellent.

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