PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

*Prog. Color Colorants Coat. 11 (2018), 165-172*

Ministry of Science, Research and Technology
Institute for Color Science and Technology

# Comparison of Dyeing of Polyester Fibers with Natural dye and Bio-Mordant

**A. Sen*, A. Bhowal , S. Datta**

Department of Chemical Engineering, Jadavpur University, 188, Raja S. C. Mallick Road, Kolkata- 700032, India.

ARTICLE INFO

Article history:
Received: 7 Jul 2018
Final Revised: 20 Sept 2018
Accepted: 22 Sept 2018
Available online: 25 Sept 2018

Keywords:
Poly-trimethylene terephthalate
Poly-lactic acid
Lac
Catechu
Response surface methodology.

## ABSTRACT

*In this study, dyeing of two regenerated polyester fibers, poly-trimethylene terephthalate (PTT) and poly-lactic acid (PLA), with natural dyes were compared with that of poly-ethylene terephthalate (PET) fiber. Lac was used as the primary natural colorant while Catechu was chosen as a natural color that can also act as a biomordant. The effects of temperature, initial pH of dye bath and dyeing time on color strength of the fibers were examined with Lac and Lac-Catechu combination. The results indicated the regenerated polyester fibers to have more number of functional groups and less compact structure than PET, favoring dyeing under milder conditions. PTT exhibited higher color uptake than the other fibers. Also, with Lac and Catechu in the same dye bath, the color strength was found to increase for all fibers, indicating that Catechu acted as a biomordant. Response Surface Methodology (RSM) based on $2^3$-Central Composite Design (CCD) was used for optimization of dyeing of PTT with Lac-Catechu combination. The optimal values for temperature, initial pH and dyeing time were found to be 127 °C, 6 and 26 min, respectively. The quadratic regression model developed was found to be statistically significant using ANOVA, with $R^2$-value and adjusted $R^2$-value of 0.9708 and 0.9271, respectively. Prog. Color Colorants Coat. 11 (2018), 165-172© Institute for Color Science and Technology.*

## 1. Introduction

The family of polyester fibers has been popular for high strength, stable dimensional properties, etc. Poly-ethylene terephthalate (PET) is traditionally the most common polyester fiber used, as its properties are more favorable than the others in the family. Its blends with natural fibers like cotton, wool, etc. have helped in developing newer textile products with unique properties. However, dyeing of PET has remained a problem. Not only the high temperatures has increased the carbon footprint for the process but also the use of carriers and other auxiliary chemicals have made the dye effluents excessively pollutant to the environment [1, 2].

Poly-trimethylene terephthalate (PTT) and poly-lactic acid (PLA) are polyester fibers obtained from renewable sources like corn [3, 4]. As both fibers are regenerated from natural resources, they can be classified as regenerated polyester fibers. Due to their natural sources, there is a possibility of presence of functional groups that may help bonding with dyes. Being regenerated fibers, the crystallinity of their polymer matrix may also be lower as compared to PET, leading to a more open and less compact

*Corresponding author: aabsens@gmail.com

structure. Both of these attributes may help in dyeing of PTT and PLA under milder conditions regarding temperature, pH, etc. leading to lower energy consumption and usage of milder chemical auxiliaries with lower extent of pollution.

Natural dyes have been extensively used for coloration of natural fibers like cotton, wool, silk, etc. They have also been tried on synthetic fibers like polyester, polyamide and poly-acrylonitrile fibers. Lac, a natural dye (C.I. Natural Red; C.I. 75450) obtained from an insect called *Coccus laccae (Laccifer lacca* Kerr*)*, has been reported to dye many natural fibers in strong hues of purple and red [5-7]. It is a polyphenolic anthraquinone based dye comprised of laccaic acids A and B as major components and laccaic acids C, D and E as the minor ones. The primary functional groups present are –OH, -COOH and $–NHCOCH_3$ [6-9]. Catechu is another commonly used natural dye obtained from the wood of *Acacia catechu*, which also exhibits the unique property as a biomordant owing to its high tannin content [10, 11]. Natural dyes like Lac often need a mordant to help in binding with the fibers. The commonly used synthetic mordants increase the pollution due to dye effluents [2, 11]. A biomordant may help in binding the natural dye with the fiber without the effluent being more pollutant.

In the present study, PET, PTT and PLA fibers have been subjected to dyeing with Lac. The effects of various parameters like temperature, initial pH of dye bath and dyeing time have been evaluated. The fibers were also dyed with Lac and Catechu in the same dye bath to find out if Catechu helped in achieving higher color strength by acting as a biomordant. With the fiber and dye combination showing the best color strength, optimization was done for the affecting parameters using Response Surface Methodology (RSM) based on $2^3$-Central Composite Design (CCD). A quadratic regression model was developed to predict the optimal levels of the parameters, the adequacy of which was checked using ANOVA.

## 2. Experimental

### 2.1. Materials and chemicals

Poly-ethylene terephthalate (PET) and poly-trimethylene terephthalate (PTT) fibers were obtained from the DuPont Knowledge Centre, Hyderabad, India, while poly-lactic acid (PLA) fiber was obtained from the University of Leeds, U.K. The natural dyes, Lac and Catechu, were obtained as commercial varieties in powdered form from Sky Morn Exports Ltd., NOIDA, India. Acetic acid (laboratory grade) and distilled water were used for dyeing.

### 2.2. Methods

#### 2.2.1. Dyeing

Dyeing of loose fibers was carried out in Superlab high temperature and high pressure (HTHP) dyeing machine (Supertech Textile Instruments Pvt. Ltd., New Delhi, India). Stock solutions (1%) of the natural dyes, Lac and Catechu, were prepared and 1 mL mixed with distilled water of total volume 40 mL in the dye bath (material to liquor ratio of 1:40). Acetic acid solution (10%) was used to maintain the desired level of initial pH.

After addition of dye and acetic acid, the loose fibers were introduced in the dye bath at room temperature. The temperature was raised to the desired level at a gradient of 1 °C/min. Experiments were carried out at different temperatures (90-130 °C), different initial pH values of dye bath (3-7) and dyeing time (15-75 min). After dyeing, the fibers were washed, treated with acetic acid solution (10% v/v) and finally washed with distilled water at room temperatures. The dyed fibers were dried in air and the color strength (K/S value) was evaluated. Five experiments were carried for each set of conditions and the average value is reported.

#### 2.2.2. Assessment of color parameters

In order to assess the color strength of dyed fibers, the K/S value was measured using XRite Color i5 spectrophotometer and was computed according to the Kubelka-Monk equation (Eq. 1)[12, 13]

$$K/S = (1 - R^2) / 2R \qquad (1)$$

where $k$ is the absorption coefficient measured as the fractional absorption loss of radiant flux per unit basis weight; $S$ is scattering coefficient measured as the fractional scattering loss of radiant flux per unit basis weight; $R$ is surface reflectance value at a particular wavelength where maximum absorption occurs.

The K/S value was found to be maximum at wavelength of 530 nm with the selected dyes. The L*, a*, b*, C* and h° values of the dyed fibers were also measured using the same spectrophotometer [12, 13].

### 2.2.3. Experimental design and statistical analyses

To identify the relationship of color strength ($y$) of the dyed fiber with the three process variables, viz. dyeing temperature, initial pH of dye bath and dyeing time, Response Surface Methodology (RSM) based on $2^3$-Central Composite Design (CCD) was used. The response function can be expressed as a function of the independent process variables according to the following response surface quadratic model (Eq. 2) [16].

$$y = \beta_0 + \beta_i x_i + \beta_j x_j + \beta_{ij} x_i x_j + \beta_{ii} x_{ij} + \beta_{jj} x_{jj} + \varepsilon \quad (2)$$

where $y$ is the response function, $\beta_0$ is constant, $\beta_i$, $\beta_j$ are coefficients of linear effects, $\beta_{ii}$, $\beta_{jj}$ are coefficients of quadratic effects, $\beta_{ij}$ is coefficient of interaction effect, $x_i$ and $x_j$ are independent variables, and $\varepsilon$ is error.

A total of 20 experiments ($2^3$= 8 factorial points, 6 axial points and 6 centre points) were performed in duplicate according to the Central Composite Design and the average values reported for experimental study. For regression and graphical analyses, Statistica 12 software of Statsoft Inc., USA, was used. The optimum values of the selected process variables were generated for the response function by solving the regression model equation and analyses of the response surface contour plots.

## 3. Results and Discussion

The effects of temperature, initial pH and time on the color strength of the dyed fibers were observed, both in cases of dyeing with Lac alone and in combination with Catechu. The L*, a*, b*, C* and h° values of the fibers dyed with both Lac and Lac-Catechu at 120 °C and initial pH of 6 for 30 min are listed in Table 1.

### 3.1. Effect of temperature

The three fibers were dyed with 10% (w/w) of Lac at five different temperatures (90-130 °C) with initial pH of 6 for 30 min. They were also dyed with 10% (w/w) each of Lac and Catechu in the same dye bath at these five temperatures, keeping other conditions constant. The effects of dyeing temperature on the color strength of the fibers are shown in Figure 1(a) with Lac, and in Figure 1(b) with Lac-Catechu combination.

In both cases, the color strength increased considerably with temperature for PTT and PLA. For PET, the rise with temperature was very little. PTT and PLA are polyester fibers regenerated from natural sources. As a result, the functional groups that can bond with Lac and Catechu are present in higher numbers in them than PET. By increasing the temperature, a greater proportion of them are activated, thereby bonding with natural dyes and hence showing a rise in color uptake, the values being higher for PTT. Opening up of the polymer matrix with temperature increase also contribute to the easy entrance of dyes, but a lower dye uptake for PET indicates its more compact nature and higher crystallinity in comparison with the other fibers.

### 3.2. Effect of initial pH

In order to evaluate the effects of initial pH on color strength, the fibers were dyed at five different values of initial pH (3-7) at 120 °C for 30 min. The results with Lac and Lac-Catechu are shown in Figures 2(a) and 2(b) respectively..

**Table 1:** Coding of dyed PTT samples and values of their color coordinates.

| Fiber | Dye | Color coordinates | | | | |
|---|---|---|---|---|---|---|
| | | L* | a* | b* | C* | h° |
| PET | Lac | 89.56 | 7.18 | 7.92 | 10.69 | 47.80 |
| PET | Lac-Catechu | 73.42 | 10.49 | 7.41 | 12.84 | 35.23 |
| PLA | Lac | 65.62 | 8.04 | 5.78 | 9.90 | 35.72 |
| PLA | Lac-Catechu | 57.44 | 8.88 | 4.79 | 10.09 | 28.36 |
| PTT | Lac | 55.10 | 12.31 | 3.00 | 12.67 | 13.69 |
| PTT | Lac-Catechu | 48.49 | 13.25 | 5.74 | 14.44 | 23.41 |

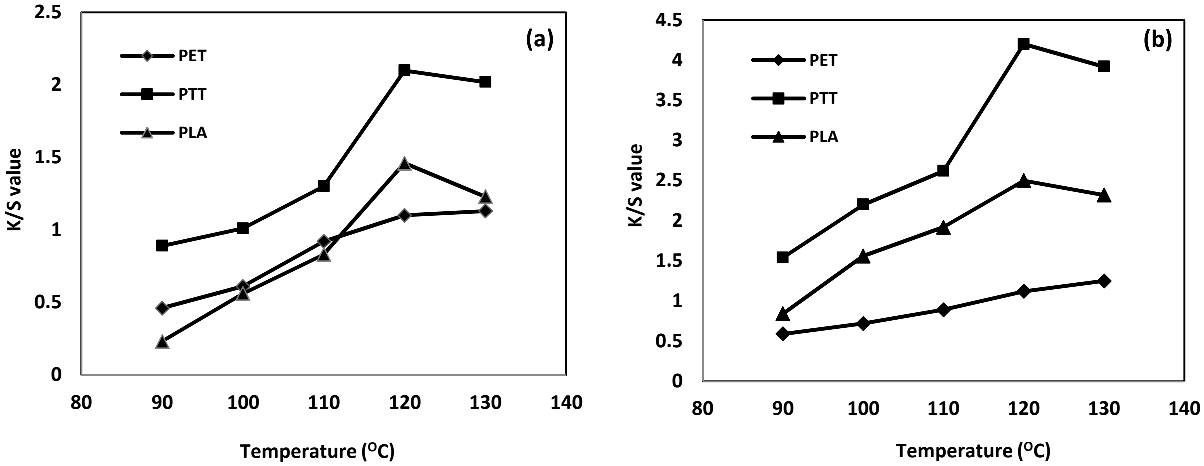


**Figure 1:** Effect of temperature on color strength (K/S value) of fibers dyed with (a) Lac and (b) Lac-Catechu.

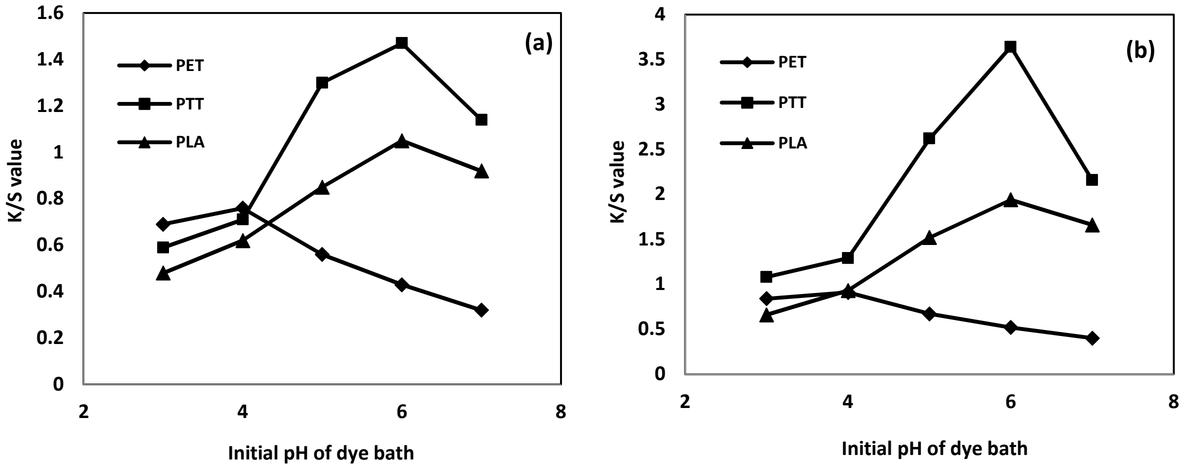


**Figure 2:** Effect of initial pH of dye bath on color strength (K/S value) of fibers dyed with (a) Lac and (b) Lac-Catechu.

It could be observed that at pH of 6, the color strength of PTT and PLA were highest but the highest values were obtained for PET at pH of 4. It indicated that the functional groups in PTT and PLA could be activated comparatively easily at pH values near to neutral than in PET. It also indicated a more compact structure in case of PET that caused hindrance to entry of dyes, thereby needing a lower and more acidic level of pH. The results also suggested the presence of functional groups in more number in PTT and PLA, requiring a milder pH to be activated as compared to PET. It could thus be inferred that dyeing of PTT and PLA required a milder pH, thereby reducing the environmental pollution due to lesser presence of stronger chemicals in the dye effluent.

### 3.3. Effect of time

The effect of time on the color strength was evaluated by dyeing the three fibers at five different dyeing times (15-75 min) at 120 °C and initial pH of 6. The results are depicted in Figure 3(a) for Lac and 3(b) for Lac-Catechu. It could be seen that for all fibers, the highest color strength was obtained at 30 min. At longer dyeing times, the color strength started to fall, indicating the possibility of degradation of dyes due to prolonged exposure to such elevated temperatures.

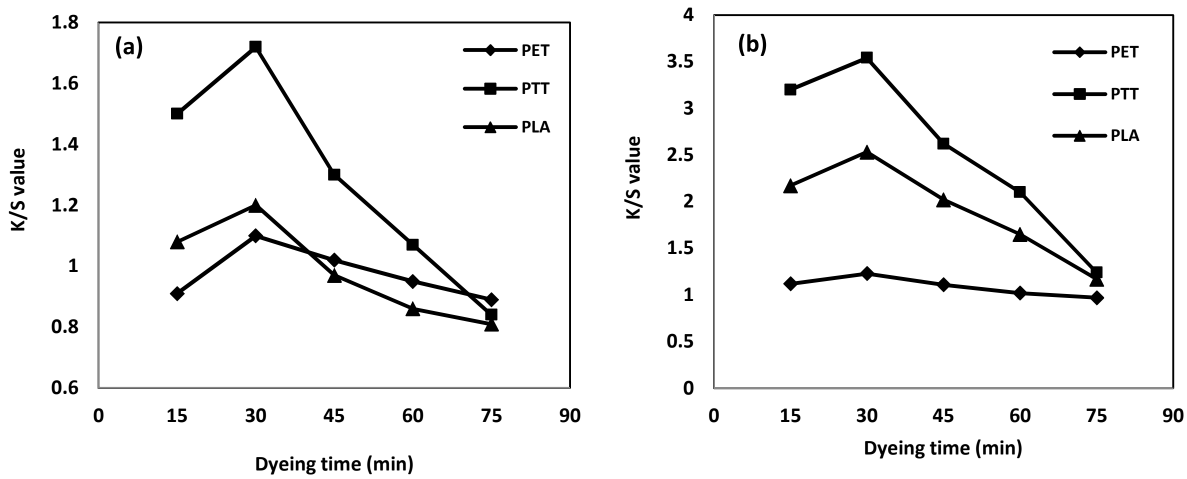


**Figure 3:** Effect of dyeing time on color strength (K/S value) of fibers dyed with (a) Lac and (b) Lac-Catechu.

In all above cases, it was observed that the color strength was higher with Lac-Catechu than Lac alone for each fiber. This indicated that Catechu, being rich in tannin content, may act as a biomordant, facilitating the bonding of Lac with the functional groups present in the fibers. This also removed the need for synthetic mordant in dyeing of the fibers with Lac, thereby making the process eco-friendly.

### 3.4. Optimization of dyeing conditions

It was observed that PTT exhibited the highest color strength among other tested fibers. Besides, the values were higher when dyeing was performed with Lac-Catechu. Thus, dyeing of PTT with Lac-Catechu was considered for optimization. The average experimental values in Table 3 were used to optimize using Response Surface Methodology (RSM) based on $2^3$-Central Composite Design (CCD). The empirical model equation obtained with coded variables is as follows (Eq. 3).

$$y = 4.02 + 0.39A - 0.30A^2 - 0.004B - 0.26B^2 - 0.20C - 0.38C^2 - 0.04AB - 0.04AC - 0.05BC \quad (3)$$

The statistical significance of these factors was evaluated using the analysis of variance (ANOVA) as given in Table 4. It was observed that the linear terms A and C, and the quadratic terms $A^2$, $B^2$ and $C^2$, are the significant terms because of their high F values and corresponding p-values lesser than 0.05 [14]. Although A has a positive influence on color strength (y), $A^2$ affects it negatively. It signifies that although the color strength increases with temperature, it falls down on both sides of the optimum temperature. $B^2$ also has an antagonistic influence, indicating that the color strength decreases on both sides of the optimum initial pH value. C and $C^2$ also affect color strength negatively, indicating that it decreases with increase in dyeing time. The results confirmed the inferences that could be drawn from the effects of these factors on color strength.

The adequacy of equation (3) was verified using the analysis of variance (ANOVA) for the quadratic regression model, as shown in Table 5. At 95% level of confidence, the model F value (36.97) was much higher than the lack of fit F value (7.74).

**Table 2:** Real variables and corresponding coded values of central composite design (CCD).

| Factors | Notations | Coded values | | | | |
|---|---|---|---|---|---|---|
| | | -α (-1.68) | -1 | 0 | 1 | +α (+1.68) |
| | | Real values | | | | |
| Temperature (°C) | A | 103 | 110 | 120 | 130 | 137 |
| Initial pH | B | 4 | 5 | 6 | 7 | 8 |
| Dyeing time (min) | C | 5 | 15 | 30 | 45 | 55 |

It suggested that the regression model is statistically significant. It was also confirmed by the correlation coefficient, $R^2$ value, of 0.9708. It also indicated that 97.08% of the total variations observed could be explained and only 2.92% of variations were left unexplained by the regression model. The adjusted $R^2$ value of 0.9271 was reasonably close to the $R^2$ value, suggesting a high goodness of fit for the model [14-16].

**Table 3:** Central composite rotatable (CCR) design and experimental response values.

| Runs | Temperature | Initial pH | Dyeing time | Experimental values |
|---|---|---|---|---|
| | A | B | C | K/S |
| 1 | -1 | -1 | -1 | 2.76 |
| 2 | -1 | -1 | 1 | 2.62 |
| 3 | -1 | 1 | -1 | 3.01 |
| 4 | -1 | 1 | 1 | 2.34 |
| 5 | 1 | -1 | -1 | 3.84 |
| 6 | 1 | -1 | 1 | 3.22 |
| 7 | 1 | 1 | -1 | 3.62 |
| 8 | 1 | 1 | 1 | 3.11 |
| 9 | -1.68 | 0 | 0 | 2.54 |
| 10 | 1.68 | 0 | 0 | 3.85 |
| 11 | 0 | -1.68 | 0 | 3.23 |
| 12 | 0 | 1.68 | 0 | 3.41 |
| 13 | 0 | 0 | -1.68 | 3.22 |
| 14 | 0 | 0 | 1.68 | 2.74 |
| 15 | 0 | 0 | 0 | 3.98 |
| 16 | 0 | 0 | 0 | 4.06 |
| 17 | 0 | 0 | 0 | 4.02 |
| 18 | 0 | 0 | 0 | 3.92 |
| 19 | 0 | 0 | 0 | 4.08 |
| 20 | 0 | 0 | 0 | 3.96 |

**Table 4:** Variance analysis (ANOVA) of factors on response.

| Factors | Sum of Squares | Degrees of Freedom | Mean Square | F Value | p-Value Prob>F |
|---|---|---|---|---|---|
| $A$ | 2.03 | 1 | 2.03 | 95.76 | 0.00 |
| $A^2$ | 0.85 | 1 | 0.85 | 40.13 | 0.00 |
| $B$ | 0.00 | 1 | 0.00 | 0.01 | 0.92 |
| $B^2$ | 0.62 | 1 | 0.62 | 29.27 | 0.00 |
| $C$ | 0.55 | 1 | 0.55 | 26.09 | 0.00 |
| $C^2$ | 1.33 | 1 | 1.33 | 62.79 | 0.00 |
| $AxB$ | 0.01 | 1 | 0.01 | 0.53 | 0.49 |
| $AxC$ | 0.01 | 1 | 0.01 | 0.60 | 0.47 |
| $BxC$ | 0.02 | 1 | 0.02 | 1.04 | 0.35 |

**Table 5:** Variance analysis (ANOVA) of quadratic regression model.

| Source | Sum of squares | Degree of freedom | Mean square | F-value | Probability>F |
|---|---|---|---|---|---|
| Model | 4.228551 | 9 | 0.4698 | 36.9681 | 0.0000 |
| Residual | 0.127093 | 10 | 0.0127 | - | - |
| Lack of fit | 0.123893 | 5 | 0.0248 | 7.7433 | 0.2660 |
| Pure error | 0.003200 | 1 | 0.0032 | - | - |
| Total | 4.355644 | 15 | - | - | - |

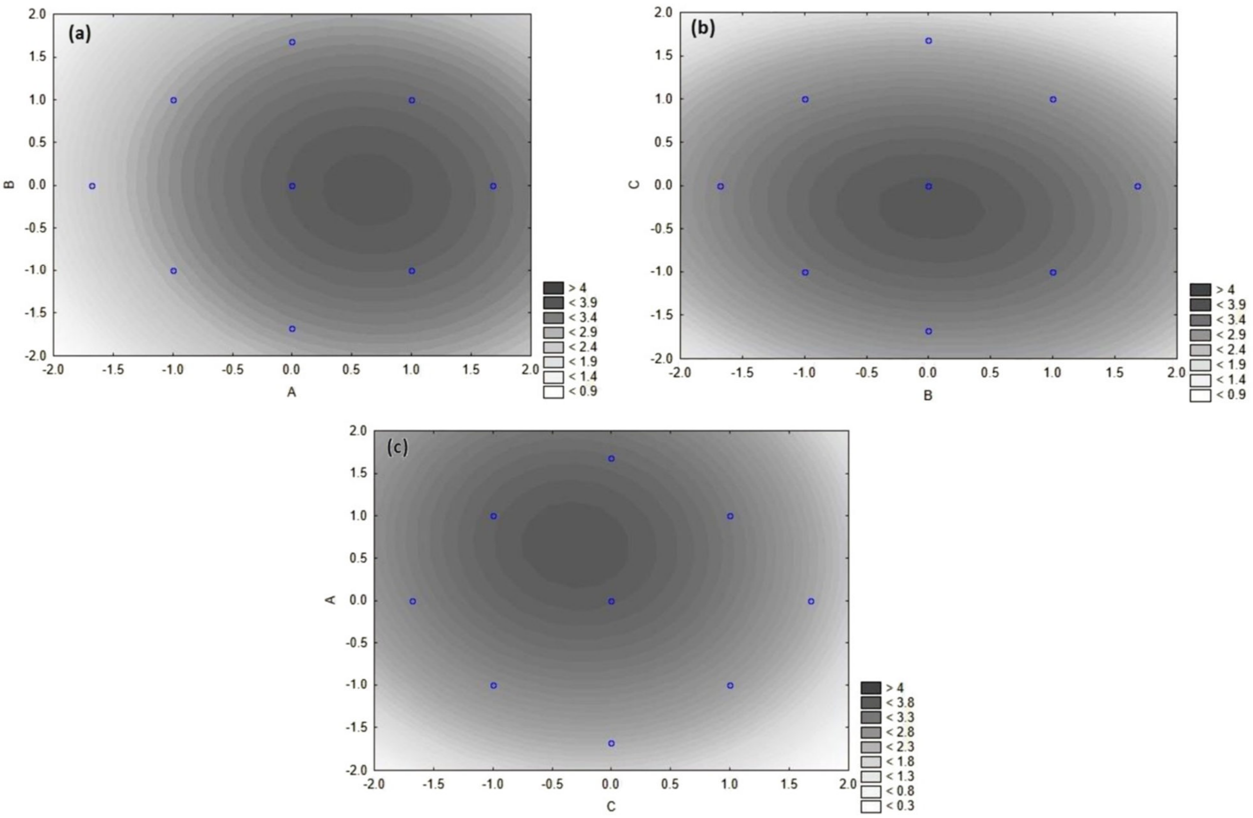


**Figure 4:** Contour plots of K/S value (*y*) for PTT fiber dyed with Lac-Catechu for (a) temperature (A) and initial pH (B); (b) initial pH (B) and dyeing time (C); (c) dyeing time (C) and temperature (A).

The contours were plotted by considering two factors while keeping the third factor at the middle level, as shown in Figures 4(a)-(c). The predicted optimized value for color strength was 4.18, occurring at 127 °C, initial pH of 6 and dyeing time of 26 min.

## 4. Conclusion

In this study, dyeing of two regenerated polyester fibers, PTT and PLA, with Lac and Catechu, were compared with that of conventional polyester fiber, PET. The regenerated polyester fibers exhibited higher dye uptake owing to the presence of functional groups capable of bonding with natural dyes in higher proportion due to their natural sources. The results also indicated a less compact structure and lower crystallinity % of PTT and PLA than PET, enabling easy entry of dyes.

Temperature, initial pH and dyeing time affected the color strength of PTT dyed with Lac and Catechu in the same dye bath in quadratic manners, which decreased on both sides of the optimum levels for these parameters. The optimal levels were obtained for dyeing at 127 °C, for 26 min at pH of 6. The regression model equation developed predicted a K/S value of 4.18 at these conditions. The $R^2$-value of 0.9708 and adjusted $R^2$-value of 0.9271 indicated that the model was statistically significant with a high level of goodness of fit.

The optimal temperature predicted for PTT was lower than standard dyeing temperature of PET (130 °C). The initial pH level was also milder at 6, as compared to pH of 3-4 for PET. The dyeing time was less than half of that of PET (60 min). These indicated that less power and energy is needed for dyeing PTT due to lower required temperature and a considerably shorter dyeing time. The dye effluent was also less polluting owing to milder chemicals used for obtaining the desired pH value. The synergistic contribution of using Catechu with Lac as a biomordant also removed the need for use of synthetic mordants that will add to environmental pollution. As a result, dyeing of PTT with natural dyes is much more eco-friendly than that of PET.

## 5. References


1. M. Ahani, M. Khatibzadeh, M. Mohseni, Studying the thermodynamic parameters of disperse dyeing of modified polyethylene terephthalate sheets using hyperbranched polymeric additive as a nanomaterial, *J. Ind. Eng. Chem.*, 19(2013), 1956-1962.
2. R. G. Ovejero, J. R. Sanchez, J. B. Ovejero, J. Valldeperas, M. J. Lis, Kinetic and diffusional approach to the dyeing behavior of the polyester PTT, *Text. Res. J.*, 77(2007), 804-809.
3. J. V. Kurian, A new polymer platform for the future-Sorona from corn derived 1,3-propanediol, *J. Polym. Environ.*, 13(2005), 159-167.
4. O. Avinc, A. Khoddami, Overview of Poly(Lactic Acid) (PLA) fiber, *Fib. Chem.*, 42(2010), 68-78.
5. D. Cardon, Natural Dyes Sources, Tradition, Technology and Science, Archetype Publications, London, 2007, 469-472 & 656-667.
6. P. Kongkachuichay, A. Shitangkoon, N. Chinwongamorn, Thermodynamics of adsorption of laccaic acid on silk, *Dyes. Pigm.*, 53(2002), 179-185.
7. R. Mongkholrattanasit, C. Saiwan, N. Rungruangkitkrai, N. Punrattanasin, K. Sriharuksa, C. Klaichoi, M. Nakpathom, Ecological dyeing of silk fabric with lac dye by using padding techniques, *J. Text. I.*, 106(2015), 1106-1114.
8. L. Liu, J. Zhang, R.-C. Tang, Adsorption and functional properties of natural lac dye on chitosan fiber, *React. Funct. Polym.*, 73(2013), 1559-1566.
9. Y. Nishizaki, K. Ishizuki, H. Akiyama, A. Tada, N. Sugimoto, K. Sato, Preparation of a ammonia-treated lac dye and structure elucidation of its main components, *Food. Hyg. Safe. Sci.*, 57(2016), 193-200.
10. S. Jose, H. G. Prabu, L. Ammayappan, Eco-friendly dyeing of silk and cotton textiles using combination of three natural colorants, *J. Nat. Fiber.*, 14(2016), 40-49.
11. M. Yusuf, F. Mohammad, M. Shabbir, M. A. Khan, Eco-dyeing of wool with *Rubia cordifolia* root extract: assessment of the effect of *Acacia catechu* as biomordant on color and fastness properties, *Text. Cloth. Sustain.*, 2(2016), 17-22.
12. M. Hosseinnezhad, K. Gharanjig, S. Belbasi, S. H. S. Saadati, green Dyeing of Silk Fabrics in the Presence of Pomegranate Extract as Natural Mordant, *Prog. Color. Colorants. Coat.*, 10(2017), 129-133.
13. N. Ashrafi, K. Gharanjig, M. Hosseinnezhad, M. K. Mehrizi, H. Imani, N. Razani, Dyeing Properties and Color Fabrics Using Natural Dye and Mordant, *Prog. Color. Colorants. Coat.*, 11(2018), 79-83.
14. K. C. Bedin, S. P. de Azevedo, P. K. T. Leandro, A. L. Cazetta, Bone char prepared by $CO_2$ atmosphere: Preparation optimization and adsorption studies of Remazol Brilliant Blue R., *J. Clean. Prod.*, 161(2017), 288-298.
15. S. Ali, S. Jabeen, T. Hussain, S. Noor, U. H. Siddiqua, Optimization of extraction condition of natural dye from pomegranate peels using response surface methodology, *Intl. J. Engg. Sc. Res. Technol.*, 5(2016), 542-548.
16. K. Sinha, S. Chowdhury, P. D. Saha, S. Datta, Modeling of microwave-assisted -extraction of natural dye from seeds of *Bixa Orellana* (Annatto) using response surface methodology (RSM) and artificial neural network (ANN), *Ind. Crop. Prod.*, 41(2013), 165-171.


How to cite this article:
A. Sen, A. Bhowal , S. Datta, Comparison of Dyeing of Polyester Fibers with Natural dye and Bio-Mordant. Prog. Color Colorants Coat., 11 (2018), 165-172.