

2015

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Xu, Suxin; Chen, Jiangang; Wang, Bijia; and Yang, Yiqi, "Sustainable and Hydrolysis-Free Dyeing Process for Polylactic Acid Using Nonaqueous Medium" (2015). *Biological Systems Engineering: Papers and Publications*. 548.

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Sustainable and Hydrolysis-Free Dyeing Process for Polylactic Acid Using Nonaqueous Medium

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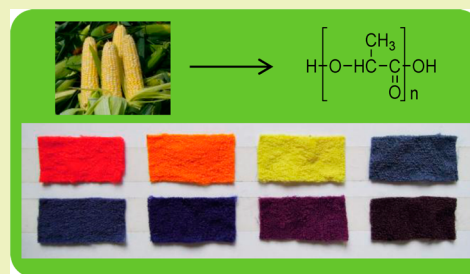
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S Supporting Information

ABSTRACT: A sustainable and hydrolysis-free dyeing process was developed for polylactic acid (PLA) fibers. PLA is a biobased alternative to petroleum based polyethylene terephthalate (PET), which is the most widely used textile fiber. However, the hydrolytic degradation of PLA fibers under the conventional aqueous dyeing conditions limited its applications in textile industry. A new solvent dyeing process was developed using liquid paraffin as a nonaqueous dyeing medium. High quality dyed PLA fabrics were obtained without consuming water and auxiliaries. Minimal strength loss of dyed fibers was achieved by postheat setting treatment. The 3R principle (reduce, reuse, and recycle) was implemented to ensure the environmental friendliness of solvent dyeing process. The result of a 9-cycle reuse sequence demonstrated excellent color consistency of dyed PLA fabrics. The sustainability of our new dyeing process was quantified in the framework of environmental-health-social impact. The dyeing process sustainability index indicated that the solvent dyeing process was preferred over the aqueous dyeing. The method developed in the present work enabled the practical applications of PLA as textile fibers. It represented an important step toward a sustainable textile industry.

KEYWORDS: Polylactic acid, Solvent dyeing, Disperse dye, Sustainability assessment, 3R (reduce, reuse, and recycle) principle



INTRODUCTION

Biobased polylactic acid (PLA) is a sustainable alternative to petroleum based polyethylene terephthalate (PET).^{1–6} PLA is derived from renewable crops, such as corn or sugarcane.^{7,8} The nonrenewable energy use and greenhouse gas emission values for the production of 1 metric ton of PLA are 42 gigajoules and 1.3 tons of CO₂ respectively, approximately 40% lower than those for petrochemical PET (69.4 gigajoules and 2.15 tons of CO₂).⁹ In addition, PLA is 100% compostable, whereas the disposal of PET results in environmental pollution.

PLA has been studied intensively with the aim of replacing PET. One major application for PET is as textile fibers. The worldwide production volume of PET textile fibers was 48 million metric tons in 2014.¹⁰ PLA has higher moisture regain, better elastic recovery, higher limiting oxygen index, and lower smoke generation than those of PET (Table S1 in the Supporting Information). These good performance properties make PLA position strongly in the textile sector. However, only 54 000 metric tons of PLA are used as textile fibers.^{11,12} PLA is, so far, primarily used in packaging industry. The potential of PLA as PET replacement has not been fully realized. One of main technical hurdles is the dyeing of PLA fibers.

PLA is prone to hydrolytic degradation.^{13–15} It is a double-edged sword. On one hand, it makes PLA environmentally friendly. On the other hand, it causes trouble for the coloration of PLA under aqueous dyeing conditions.^{16–18} PLA fibers had shown 35–40% loss of strength at pH 4–6 and 110 °C during dyeing and complete strength loss at 130 °C.¹⁹ It has been shown that the strength loss of PLA during dyeing process is primarily due to hydrolysis of the polymer.^{19–21} In principle, a water-free dyeing technique should be able to alleviate the degradation problem of PLA fabrics. One major goal of this work is to develop a nonaqueous dyeing process for PLA.

The most active fields in water-free dyeing are supercritical carbon dioxide (ScCO₂) dyeing technology and solvent dyeing technology. ScCO₂ dyeing is a water-free dyeing process that exploits the unique properties of supercritical fluids. Two research groups had dyed PLA fibers in ScCO₂. Dai et al. reported 9.22% loss of breaking strength in PLA fibers at 120 °C and 200 bar (1 h).²² Bach et al. reported 12–18% loss of tensile strength in PLA fibers at 90 °C and 280 bar (1 h).²³

Received: November 28, 2014

Revised: January 25, 2015

Published: April 30, 2015

ScCO₂ dyeing technique appears to be attractive. However, the cost of high pressure dyeing machines is a clear hindrance to commercial adoption of the technology.²⁴

Recently, a solvent dyeing process for PET fabrics was developed in our lab. Liquid paraffin was selected as the dyeing medium using an environmental, health, and safety profile based computational screening protocol. The new dyeing method produced high quality dyed goods without using water and auxiliaries. Most importantly, solvent dyeing could be carried out using aqueous dyeing machine with minor modifications. PET is an aromatic polyester and PLA is an aliphatic polyester. Both fibers are dyeable using disperse dyes.²⁵ It was expected that solvent dyeing method developed for PET could be also applied to PLA.

Another design goal of the new dyeing process for PLA is sustainability: waste minimization, reduction of material and energy consumption. The current aqueous dyeing process is not sustainable. It leaves one of the largest water footprints on the planet and utilizes a large amount of chemicals and energies.^{26–30} The discharged wastewater also contains various kinds of hard-to-destroy surfactants and unused dyes. The new dyeing process for PLA was designed basing on the 3R principle (reduce, reuse, and recycle) to ensure the environmental friendliness. In past decades, there were numerous works on developing new processes for PLA-fibers based end products.^{31–35} However, few efforts were made to analyze the sustainability of those processes. Previous studies have been exclusively devoted to Cradle-to-Factory gate analysis for the production of PLA fibers.^{7,36,37} Ideally, the sustainability of a newly developed process for end products should be also evaluated.

A variety of measurements have been proposed to quantify the sustainability of process technologies and manufacturing operations.^{38–42} It is generally acknowledged that the metrics should represent all three aspects of sustainability: economic, environmental, and societal.^{43,44} Recently, Martins et al. reported a new framework for sustainability metrics.⁴⁵ It had been shown that the framework was very effective in selecting the most sustainable process among alternatives. In the present work, the sustainability of new dyeing process was quantified based on a modified framework originally developed by Martins and co-workers. Six metrics were calculated, including material intensity, energy intensity, potential chemical risk, potential eco-risk, COD/BOD₅ ratio, and capital cost. Six calculated metrics were further aggregated into one index, the dyeing process sustainability index (DPSI). The DPSI allows for the easy comparison between different dyeing processes.

In the present work, a hydrolysis free and sustainable dyeing process for PLA fibers was developed. Disperse Blue 56 and Disperse Blue 79 were chosen as the representative low and high energy dyes for anthraquinone and azo classes, respectively. A hydrolysis-free dyeing method for PLA fibers had been developed using nonaqueous medium. The influence of dyeing conditions on the mechanical properties of PLA fibers was elucidated. The sustainability performance was evaluated using six metrics. The results were compared with the traditional aqueous dyeing process.

MATERIALS AND METHODS

Materials. Acetone and *n*-hexane were analytical grade. Liquid paraffin was chemically pure grade. These chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Pure dyes

were purchased from Longsheng Co. (Zhejiang, China). Chemicals were used as received.

The PLA fabrics investigated were supplied by NatureWorks (USA) containing 2% of D-LA, with a weight-average molecular weight (M_w) of 58 kDa and polydispersity of 1.415 determined by gel permeation chromatography (GPC). The glass transition temperature and melting point were determined to be 59 and 168 °C, respectively, by differential scanning calorimetry (DSC). The fabrics used for the studies were woven fabrics (160 g/m², 6 denier). PLA fabrics were scoured in a solution containing 2.0 g/L of anionic surfactants at 25 °C for 20 min. The chemical structures of Disperse Blue 56, Disperse Blue 79, and PLA are shown in Figure 1.

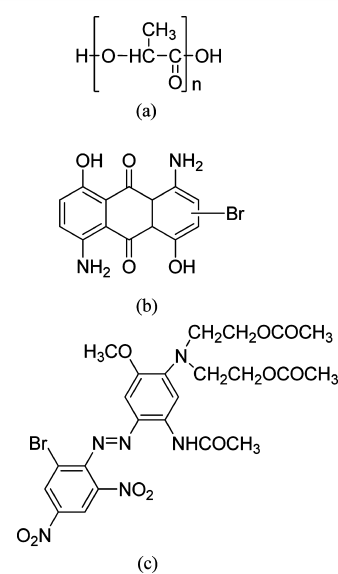


Figure 1. Chemical structures of PLA (a), Disperse Blue 56 (b), and Disperse Blue 79 (c).

Dyeing Procedures. For the solvent dyeing, PLA fabrics weighing 1.0 g were dyed in liquid paraffin with 5.0% owf (on the weight of fabric) of disperse dyes and a fixed liquor-to-goods ratio of 30:1. Dyeing started at ambient temperature. Temperature was raised to the dyeing temperature at a rate of 2 °C/min and held at the dyeing temperature for a fixed time. After dyeing, the fabrics were washed using a mixture of *n*-hexane and acetone at ambient temperature.

Dyebath Reuse. At the completion of the dyeing cycle, a sample from the dyebath was analyzed for residual dye concentration. The dyebath was reconstituted to the concentration required for the following dyeing. A second batch of fabrics was placed in the dyebath for a second dyeing cycle. The sequence was repeated for eight times. *K/S* values and color difference (ΔE) were used to assess the color reproducibility of dyed fabrics.

Measurements. The detailed procedures for dye uptake, color yield, colorfastness, and breaking strength test are provided in the Supporting Information.

Wide-Angle X-ray Diffraction (WAXD). The WAXD analysis was performed on a Rigaku D/max 2550 PC X-ray diffractometer with a Cu X-ray tube operated at 40 kV and 250 mA. The scan was done with a step of 0.02°. For the orientation studies, the fiber bundle was fixed at 16.5° in a plane perpendicular to the direction of the X-ray beam. The azimuthal intensity distribution of equatorial peaks was taken by rotating the fiber bundle.

Gel Permeation Chromatography (GPC). The weight-average molecular weight (M_w) and molecular weight distribution of PLA fabrics were determined using GPC (Malvern, UK) equipped with a 270 dual detector at 40 °C. The columns used were CLM1013 (I-MBHMW-3078) and CLM1014 (I-OLIGO-3078). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min and poly(methyl methacrylate) was used as the standard.

Biodegradation. Biodegradation of the aqueous dyeing effluents was determined in terms of COD and BOD₅. The COD tests were conducted according to the ISO 6060:1989. In present work, the potassium dichromate reflux method was replaced by a microwave digestion method. The samples were digested for 5 min with the microwave power of 600 W. The 5 day BOD test was performed according to the ISO 5815-1:2003. The oxygen levels in the water before and after treatment were measured using a dissolved oxygen probe (YSI58, USA). The samples were appropriately seeded. The water used for the test confirmed to the standard and had an oxygen depletion of less than 0.2 mg/L in 5 days.

Sustainability Assessment. There are four steps to be considered when applying the metric based sustainability assessment: (1) metrics identification, (2) data processing, (3) weighting of metrics, and (4) their aggregation.⁴⁶ For the first step, six metrics were identified: material intensity, energy intensity, potential chemical risk, potential eco-risk, COD/BOD₅ ratio, and capital cost. The data processing step followed the procedure described by Martins and co-workers.⁴⁵ The detailed data processing of the aqueous dyeing and solvent dyeing are provided in the Supporting Information. It is important to note that the quantity class of chemicals used to evaluate the potential chemical risk is different from Martins's original definition. The solvent dyeing process was designed as a closed loop system. There is no chemical released into environment. Thus, the quantity class for solvent dyeing was set to the lowest level (class 1). For the weighting step, the potential eco-risk score for solvent dyeing was multiplied by a factor of 0.1 to account for the closed system nature. At the last step, six calculated metrics were aggregated into dyeing process sustainability index (DPSI) based on the following equation:

$$DPSI = \left(\prod_i^n [c_i (y_i/x_i)] \right)^{1/n} \quad (1)$$

where c_i is a weighting factor for metric i , and y_i and x_i are the values of metric i between the processes Y and X (X being the reference), and n is the number of metrics used.⁴⁷ The threshold values are introduced for (y_i/x_i) to prevent the values of DPSI being artificially low/high:

$$y_i/x_i = \begin{cases} 0.1 & y_i/x_i \leq 0.1 \\ 10 & y_i/x_i \geq 10 \end{cases} \quad (2)$$

RESULTS AND DISCUSSION

Solvent Dyeing of PLA Fabrics. The first objective is to explore the dyeability of PLA fibers in liquid paraffin. To this end, the dyeing behavior of disperse dyes on PLA fibers was investigated with respect to temperature and time. The quality of dyed products was also evaluated.

Figure 2a presents the dye uptakes versus temperatures for Disperse Blue 56 and Disperse Blue 79. PLA fabrics were dyed at 80, 90, 100, 110, 120, 130, and 140 °C. As shown, the dye uptakes for both dyes increase with increasing dyeing temperatures. This is due to the enhanced chain mobility at elevated temperatures which created more free volume and facilitated the dye sorption.¹⁹ The dye uptakes reach saturation when temperature reached 130 °C. To investigate any possible shade change of disperse dyes in solvent at high dyeing temperature, UV-vis analysis was performed (Figure S1 and S2 of the Supporting Information). The adsorptions of both dyes in the visible region were unchanged after 60 min at 140 °C. The dyeing temperature had a negligible effect on the shades of Disperse Blue 56 and Disperse Blue 79.

To obtain the optimal dyeing condition, the dye uptakes of Disperse Blue 56 and Disperse Blue 79 were plotted as a function of temperature and time in Figure 2b. Figure 2b shows there is almost no dye sorption below 90 °C. A holding time of 10 min at 130 °C should be sufficient based on the equilibrium

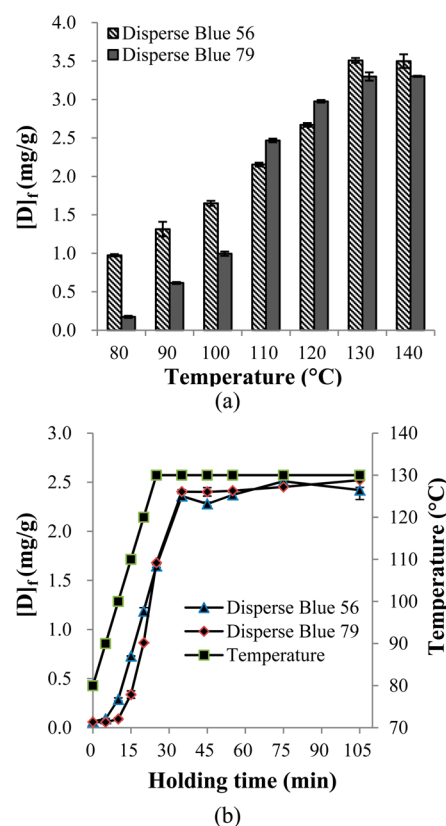


Figure 2. (a) Effect of temperature on dye uptakes of Disperse Blue 56 and Disperse Blue 79 on PLA fabrics. Dyeing was performed for 2 h with 5.0% owf and liquor-to-goods ratio of 30:1. (b) Dye uptakes of Disperse Blue 56 and Disperse Blue 79 on PLA fabrics as a function of temperature and time. Dyeing was performed with 3.0% owf and liquor-to-goods ratio of 30:1.

points for the dyes examined. The exhaustions of both dyes are below 10%. The low dye exhaustions are caused by favorable chemical potential of hydrophobic disperse dyes in hydrophobic solvent and lack of interacting functional groups on PLA. However, the low dye exhaustion is not a limitation for solvent dyeing. Figure S3 of the Supporting Information illustrated that the dark shades could be achieved for PLA. PLA fabrics are known to have high color yield due to the low refractive index.¹⁶ Higher color yield means a smaller amount of dye uptake is needed for the same shade depth.

Colorfastness to crocking of dyed PLA is shown in Table S2 of the Supporting Information. The dry and wet crockfastness of fabrics dyed in liquid paraffin were the same as those of fabrics dyed in water. Colorfastness to light of dyed PLA is also listed in Table S2 of the Supporting Information. The light fastness of PLA dyed in water and solvent are comparable. Colorfastness to washing and staining of PLA is listed in Table S3 of the Supporting Information. The solvent dyed PLA had acceptable wash fastness for apparel applications. The gray scales for staining of fabrics dyed in solvent were comparable to those of aqueously dyed fabrics.

The results indicated that PLA fibers could be successfully dyed with disperse dyes in liquid paraffin. Compared to aqueous dyeing,⁴⁸ the solvent dyeing method produced high quality dyed goods without using water and auxiliaries. This is very important because the use of auxiliaries would result in hard-to-destroy chemicals. Compared to ScCO₂ dyeing, the

solvent dyeing method does not require the high pressure dyeing equipment.

Mechanical Properties of Solvent Dyed PLA Fabrics.

The second objective is to obtain dyed PLA fabrics with minimal strength loss. Breaking strength testing was performed to examine the effect of dyeing conditions on the mechanical properties of dyed PLA fibers. Figure 3 shows the time

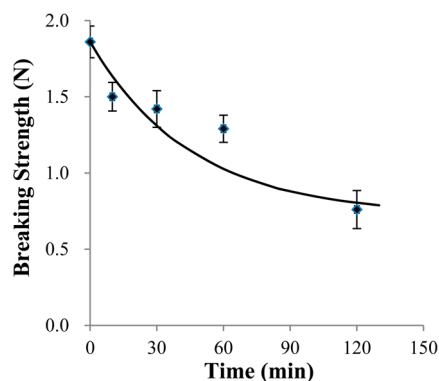


Figure 3. Effect of treating time on breaking strength of PLA filament yarns raveled from PLA fabrics dyed with Disperse Blue 79 at 130 °C and 5.0% owf. The solid line is added to guide the eyes.

dependence of breaking strength for dyed PLA fibers at dyeing temperature of 130 °C. As shown, breaking strength decreased with increased dyeing time. It changed from 1.86 to 0.76 N in 120 min. The loss of breaking strength in dyed fibers could be attributed to three possible mechanisms: solvolysis, thermal degradation and thermal induced structure change.

Solvolysis is the most unlikely mechanism since liquid paraffin is non-nucleophilic, chemically inert solvent. Figures S6–S8 of the Supporting Information show the DSC, thermogravimetric analysis (TGA), and fourier transform infrared (FTIR) spectra results for PLA fibers with and without solvent treatment. There is no detectable difference between two sets of samples. Therefore, the loss of strength is not caused by solvolysis.

Thermal degradation mechanism was tested by examining the changes in molecular weight of PLA fibers from thermal treatment. The weight-average molecular weights (M_w) and polydispersity indexes (PDI) were determined by GPC. Figure 4 shows the dependence of M_w of PLA on the dyeing

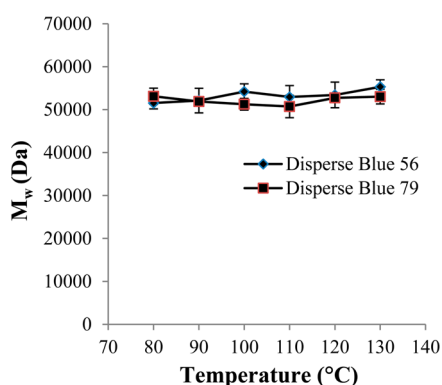


Figure 4. Effect of dyeing temperature on the weight-average molecular weights of PLA fibers raveled from PLA fabrics dyed with Disperse Blue 56 and Disperse Blue 79 for 2 h with 5.0% owf and liquor-to-goods ratio of 30:1.

temperature. The molecular weights are obtained over three independent measurements. Anova analysis indicates that the differences between the measured molecular weights at different temperatures are statistically insignificant (P values > 0.05). Table S4 of the Supporting Information lists the representative M_w and PDI of PLA from GPC measurements. Thermal treatment at different temperatures resulted in little change in the molecular weight distributions. This is expected because TGA of PLA fibers (Figure S7 of the Supporting Information) indicates the onset decomposition temperature is around 300 °C,⁴⁹ much higher than the dyeing temperature (130 °C).

The third mechanism is thermal induced structure change. If PLA fibers were thermally treated in a tensionless state, the fibers would shrink and cause the decrease in preferred orientation.⁵⁰ WXRd experiments were performed to determine the changes in the degree of orientation. The degree of orientation versus dyeing time is presented in Figure S9 of the Supporting Information. The degree of orientation decreases with increasing dyeing time. This is consistent with the time dependence of breaking strength loss. A linear relationship is indeed found between the degree of orientation and breaking strength with high degree of confidence ($R^2 = 0.97$) (Figure 5).

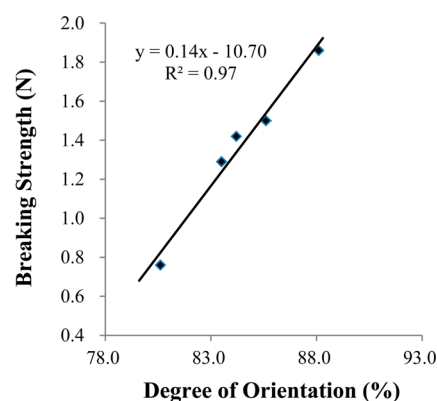


Figure 5. Correlation between breaking strength and degree of orientation of PLA filament yarns raveled from PLA fabrics dyed with Disperse Blue 79 at 130 °C and 5.0% owf. The solid line represents the linear fitting.

Alternatively, cold crystallization during the dyeing process might increase the crystallinity of PLA and change the mechanical properties. The crystallinities were determined using DSC. A linear regression had been performed to relate the breaking strength with crystallinity ($R^2 = 0.647$) (Figure S10 of the Supporting Information). The correlation between the breaking strength with crystallinity is weak. Therefore, the loss of breaking strength could be attributed to thermal induced deorientation.

Postheat setting in a tension state was performed to recover the loss of breaking strength. The effect of heat setting temperature and time on breaking strength was investigated. During the heat setting, the samples were stretched to the original length to restore the shrink caused by dyeing. The results are presented in Figures S12 and S13 of the Supporting Information. The optimal heat-setting condition is determined as 45 s at 90 °C. The degree of orientation of dyed PLA fibers (130 °C, 120 min) increased from 80.6% to 85.6% after heat setting. The corresponding loss of breaking strength decreased from 59.14% to 16.67%.

The microstructures of the PLA before and after the heat setting treatment were investigated. DSC, scanning electron microscopy (SEM), FTIR spectra of the PLA before and after the heat setting treatment are shown in Figures S14, S15, and S16 of the Supporting Information, respectively. There was no drastic changes in crystallinities, morphologies, and chemical structures of PLA after heat setting treatment. Therefore, heat setting treatment primarily modulates the degree of orientation of PLA. The changes in crystallinities, morphologies and chemical structures are negligible.

In summary, a hydrolysis free dyeing method was developed by using liquid paraffin as dyeing medium. The results indicated the dyed PLA fabrics had good colorfastness and minimal strength loss. The solvent dyeing is a promising technique enabling widespread textile applications for PLA fibers.

Reuse of Dyebath. Another major goal of present work is to develop a sustainable dyeing process for PLA fibers. To this end, the dyeing process was designed based on the 3R (reduce, reuse, and recycle) principle. Figure 6 illustrates the flowcharts

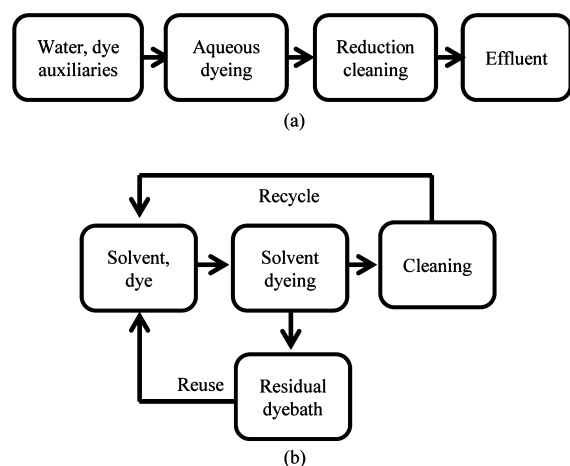


Figure 6. Flowcharts of dyeing process: aqueous dyeing (a) and solvent dyeing (b).

of traditional aqueous dyeing and new solvent dyeing processes. Traditional dyeing consumes a large amount of water and auxiliaries, which is eliminated by solvent dyeing. Dyebath reuse and rinse solvent recycling are implemented to ensure the environmental friendliness. Rinse solvent recycling was carried out using reduced pressure distillation.

To examine the effectiveness of dyebath reuse, repeated dyeing with replenished spent dyebath was carried out for nine times. Table 1 presents the K/S values and color difference ΔE of PLA fabrics dyed in each recycling. The fabrics dyed with spent dye liquors in each recycling exhibited good shade consistence. The K/S values were consistently high. The average K/S value was around 15.4. The color differences were all smaller than 1.0. Thus, the color differences were within acceptable limit for commercial applications. The results demonstrated that dyebath reuse were feasible for the solvent dyeing procedure developed in this work. As shown before, the exhaustions for disperse dyes in solvent dyeing were generally low. Large amounts of dyes were left in spent dye liquors. The dyebath reuse eliminated the problem of effluent control associated with low dye exhaustions.

Sustainability Metrics of Dyeing Process. The sustainability metrics were assessed to evaluate the societal-environmental-economic impact of solvent dyeing process versus

Table 1. Color Value Data of Dyed Fabrics in 9-Cycle Reuse Sequence

| run in reuse sequence | K/S | L^* | a^* | b^* | ΔE^a |
|-----------------------|--------------|-------|-------|--------|--------------|
| 1 | 15.64 ± 0.40 | 32.04 | 8.04 | −40.01 | |
| 2 | 15.25 ± 0.16 | 32.63 | 7.94 | −40.46 | 0.34 |
| 3 | 15.23 ± 0.35 | 32.88 | 8.16 | −41.09 | 0.58 |
| 4 | 16.31 ± 0.21 | 31.86 | 8.65 | −40.90 | 0.53 |
| 5 | 15.62 ± 0.14 | 32.44 | 8.78 | −41.29 | 0.71 |
| 6 | 14.97 ± 0.49 | 32.87 | 8.49 | −41.01 | 0.60 |
| 7 | 15.08 ± 0.39 | 32.21 | 8.22 | −40.65 | 0.29 |
| 8 | 15.11 ± 0.02 | 32.83 | 8.38 | −41.04 | 0.57 |
| 9 | 14.68 ± 0.22 | 33.09 | 8.08 | −40.74 | 0.55 |

^a ΔE is the overall color difference between cycle 1 and the cycles studied.

aqueous dyeing process. Six metrics were used in the present work, including material intensity, energy intensity, potential chemical risk, potential eco-risk, COD/BOD₅ ratio, and capital cost.

Table 2 summarizes the calculated values of six metrics for both processes. The calculated metrics were aggregated into a

Table 2. Sustainability Analysis of Solvent Dyeing and Aqueous Dyeing Processes

| metrics | dyeing processes | |
|-------------------------------------|------------------|----------------|
| | aqueous dyeing | solvent dyeing |
| energy intensity (GJ) | 10.97 | 19.47 |
| material intensity (t) ^a | 70.12 | 0.26 |
| potential chemical risk | 63.00 | 33.00 |
| potential eco-risk ^b | 119.28 | 11.08 |
| COD/BOD ₅ ratio | 5.14 | 1.00 |
| capital cost (\$) | 1039.94 | 1725.63 |
| DPSI | 1.00 | 0.38 |

^aThe ratio of material intensity of solvent dyeing and aqueous dyeing was less than 0.1. Therefore, the threshold value (0.1) was used in the calculation of DPSI. ^bThe ratio of potential eco-risk of solvent dyeing and aqueous dyeing was less than 0.1. Therefore, the threshold value (0.1) was used in the calculation of DPSI.

single indicator (DPSI) using eq 1. The aggregate metric DPSI is determined as 1.0 and 0.38 for aqueous dyeing and solvent dyeing, respectively. The result clearly shows that solvent dyeing process is a better option.

The material intensity of solvent dyeing is 0.26 t, much smaller than that of aqueous dyeing (70.12 t). The major contribution of material intensity for aqueous dyeing comes from water usage (70 t). In fact, textile industry leaves one of the largest water footprints on the earth. Given the increasingly scarce water resource, the large amount of water consumption represents a major problem for textile industry. Solvent dyeing lowered the material intensity by implementing the 3R (reduce, reuse, and recycle) principle. The chemical consumption was reduced since the solvent dyeing did not require auxiliary chemicals, as in aqueous dyeing. The dyebath and cleaning solvents could be reused and recycled using a closed-loop system design.

The potential chemical risk score for solvent dyeing process is 33, approximately 48% lower than that for aqueous dyeing (63). Chemical risk is a function of exposure and hazard. The reduced chemical risk could be accomplished by either reducing

the chemical exposure or eliminating the hazardous chemicals. The major contribution of potential chemical risk for aqueous dyeing comes from auxiliaries. In contrast, the solvent dyeing eliminates the usage of auxiliaries. In addition, solvent dyeing process is designed as a closed loop system. There is no chemical released into environment. Therefore, solvent dyeing process imposes less chemical risk than aqueous dyeing.

Potential eco-risk and COD/BOD₅ ratio are used to assess the impacts of dyeing process on the environment. The potential eco-risk for solvent dyeing process is 11.08, approximately 9% of that for aqueous dyeing (119.28). The better score was also due to the closed system nature of solvent dyeing. The COD and BOD₅ for aqueous dyeing of 1 t of PLA fabrics were calculated as 632 and 123 t, respectively. Thus, the COD/BOD₅ ratio is 5.14. For solvent dyeing, there is no chemical discharged into water. Therefore, COD/BOD₅ ratio for solvent dyeing was set to be the lowest value (1). The COD/BOD₅ ratio indicates the relative biodegradability of dyeing effluents. The higher the ratio, the lower is biodegradability. A COD/BOD₅ ratio of 5.14 implies the moderate biodegradability.⁵¹

The data in Table 2 indicates that the energy intensity and capital cost for solvent dyeing are 1.8 and 1.6 times greater than those for aqueous dyeing, respectively. Further component analysis provides important insights into the source of higher energy intensity and capital cost. The higher energy intensity for the solvent dyeing could be attributed to the recycling of cleaning solvent, which accounted for nearly 93% of total energy consumption. The higher capital cost for solvent dyeing could be attributed to high price of the solvents and higher energy consumption, which accounted for 50.2% and 49.8% of total cost, respectively. Identifying the source of problems provides the guidance for future improvements. Selecting a cheap, effective cleaning solvent and improving the efficiency of energy usage would be the major focus for future work.

Overall, the analysis of material intensity, energy intensity, potential chemical risk, potential eco-risk, COD/BOD₅ index, and capital cost indicated that solvent dyeing, as a water-free and effluent-free process, was a more sustainable approach than traditional aqueous dyeing.

CONCLUSIONS

The present work developed a hydrolysis-free and sustainable dyeing process for PLA fibers. Hydrolysis-free dyeing was accomplished by using non-nucleophilic solvent (liquid paraffin) as dyeing medium. The dyeing time and temperature were optimized for PLA fabrics. High quality dyed PLA fabrics were obtained. The colorfastness of solvent dyed fabrics was found to be comparable to that of aqueously dyed fabrics. There was a loss of mechanical strength for dyed PLA fibers due to thermal induced deorientation. A linear relationship was found between the degree of orientation and the breaking strength. Minimal strength loss of dyed fibers was achieved by postheat setting treatment. Postheat setting after dyeing at 130 °C for 120 min decreased the breaking strength loss from 59.1% to 16.7%. The new solvent dyeing method developed in present work enables the practical textile applications for PLA fibers.

The new dyeing process was designed as a sustainable process based on the 3R (reduce, reuse, and recycle) principle. Traditional dyeing consumes a large amount of water and auxiliaries, which were eliminated by solvent dyeing. Dye bath reuse and solvent recycling were implemented to ensure the

environmental friendliness of dyeing process. The result of a 9-cycle reuse sequence also demonstrated excellent color consistency of dyed PLA fabrics. The sustainability of dyeing process was further quantified in the framework of environmental-health-social impact. Six metrics were evaluated and aggregated into the dyeing process sustainability index (DPSI). The DPSI indicated the solvent dyeing is more sustainable than aqueous dyeing. The better scores on material intensity, potential chemical risk, potential eco-risk, and COD/BOD₅ ratio reflected the advantage of 3R design principle for solvent dyeing. Quantitative analysis also provided important hints for the future research priorities. The result suggested that selecting a cheap, effective cleaning solvent and improving the techniques for solvent recycling would be the focus for future work. Overall, the combination of 3R design principle and quantitative analysis is a general approach to select and optimize a sustainable process. The method developed in this work represents an important step toward a sustainable textile industry.

ASSOCIATED CONTENT

Supporting Information

Characterization of liquid paraffin treated PLA fibers and untreated control; measurements for dye uptake, color yield and breaking strength test; sustainability analysis of solvent dyeing and aqueous dyeing processes; characterizations of the dyes and the dyed PLA fabrics; characterizations of the effect of liquid paraffin on PLA; correlation between breaking strength and crystallinity; effect of dyeing time on degree of orientation and crystallinity of PLA fibers; effect of heat setting temperature and time on breaking strength of PLA fibers; effect of heat setting on microstructures of PLA; comparison of fiber properties between PLA and PET; colorfastness to crocking, light and laundering; M_w and PDI of the PLA from GPC measurements; sustainability evaluation of the chemicals used in different dyeing processes. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/sc500767w.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Chinese National High Technology Research and Development Program 863 Project (2013AA06A307) and Agricultural Research Division, USDA NIFA Multi-State Project S-1054 (NEB 37-037), USDA Hatch Act at the University of Nebraska-Lincoln.

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