Optimal Dyeing Systems for Resistance to the Physical Strength Loss of the PLA/cotton Blended Fabric

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ABSTRACT: In this study, optimization of disperse/reactive dyeing systems for resistance to the physical strength loss of Poly(lactic acid) (PLA)/cotton blended fabric was investigated. The blended fabric underwent a two-bath, two-stage dyeing process in which the PLA component of the blended fabric was dyed using two disperse dyes, followed by the cotton component being dyed with six reactive dyes containing different reactive groups—dichlorotriazine, monochlorotriazine, sulphatoethylsulphone, monofluorotriazine, monochlorotriazine/sulphatoethylsulphone, and monofluorotriazine/sulphatoethylsulphone groups. The optimal dyeing systems were established according to the fixation rate of the dyes, tear/tensile strength loss, and SEM micrographs of the fabric. To avoid the strength loss during the disperse/reactive dyeing process, the recommended disperse dyeing conditions were 110°C, pH 5 for 20 min, whereas the reactive dyeing conditions should be temperature $\leq$60°C and alkali concentration $\leq$3 g/L. In this regard, reactive dyes containing monofluorotriazine and monofluorotriazine/sulphatoethylsulphone groups were especially suitable for the reactive dyeing systems. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 886–895, 2011

Key words: poly(lactic acid)/cotton blends; reactive dyes; dyeing; strength

INTRODUCTION

Poly(lactic acid) (PLA) fiber was the first biodegradable synthetic fiber.[1] It has similar characteristics with polyester but much better moisture regain and crease resistance properties.[2] Now, this fiber is gradually incorporated into apparel systems. The blend of PLA fiber with cotton can not only shows the advantages of both fibers but also possesses many excellent performances such as good draping property and soft hand feel.[3]

However, dyeing process for PLA/cotton blended fabric has many critical problems caused by the conditions associated with dyeing of the cotton fabric component using reactive dyes. Most reactive dyes require high temperature and high alkali concentrations to form covalent bonds with cotton.[4] Under such conditions, PLA component may degrade significantly due to its sensitivity to temperature and alkali.[5,6] As the dyeing temperature and alkali concentration are determined by the reactivity of the reactive dyes, to protect the PLA fiber from degradation, study on the suitable reactive dyeing conditions and reactive dyes should be most important for dyeing of PLA/cotton blended fabric. In this article, we used six reactive dyes containing different reactive groups of dichlorotriazine (DCT), monochlorotriazine (MCT), sulphatoethylsulphone (SES), monofluorotriazine (MFT), MCT/SES, and MFT/SES to access the effects of their dyeing conditions on the strength loss properties of the PLA/cotton blended fabric and to develop optimal dyeing systems for reactive/disperse dyeing of this biodegradable blend.

It has been reported that significant strength loss of PLA/cotton blended fabric was caused by one-bath dyeing process, so a two-bath, two-stage dyeing process for the blends was recommended.[6] In this article, PLA component of the blends were first dyed in the disperse dying process with two disperse dyes, and then the cotton component were dyed in the reactive dyeing process with six reactive dyes. Among the reactive dyes, C.I. Reactive Yellow 1 and C.I. Reactive Yellow 17 were chosen, respectively, as typical DCT dye and SES dye. MCT and MFT dyes, which contained nearly the same chromogen as C.I. Reactive Yellow 1 and C.I. Reactive Yellow 17, were synthesized to get clear comparison among these monofunctional dyes. The bifunctional MCT/SES and MFT/SES reactive dyes, which had same orange chromogen, were also synthesized and used.

During the disperse dyeing process, C.I. Disperse Yellow 16 and C.I. Disperse Orange 30, due to their identical color to the selected reactive dyes, were

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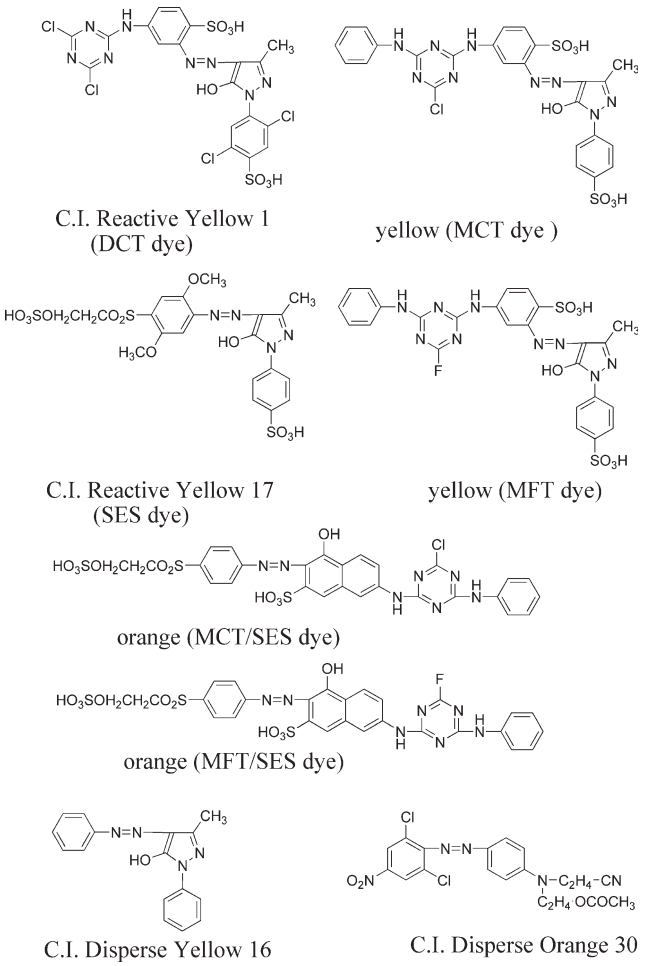

Figure 1 Structures of dyes used in this article.

applied to dye the PLA component of the blended fabric at the first dyeing stage. For investigation of the whole dyeing process, the dyeing conditions of the disperse dyes on PLA were also discussed. Structures of the dyes used in this study are shown in Figure 1.

EXPERIMENTAL

Materials

The scoured and bleached PLA/cotton blended fabric (PLA 30% by weight) was obtained from QiSai Textile Company. Shandong, China. C.I. Disperse Yellow 16, C.I. Disperse Orange 30, C.I. Reactive Yellow 1, C.I. Reactive Yellow 17, 2,4-diamino-benzenesulfonic acid, 3-methyl-1-(4-sulfophenyl)-5-pyrazolone, 2-amino-5-naphthol-7-sulfonic acid, and 4-(β-sulfatoethylsulfonyl) aniline were obtained from Shanghai Dyestuff Company. Cyanuric fluoride was obtained from Zhongxin Chemical Factory, Anhui, China. All other chemicals were analytical grade quality and purchased from Shenyang No. 1 Chemical Reagent Factory, Liaoning, China. Mass spectra were recorded at CID = 50–200 V with an HP 1100 HPLC/MS system from Hewlett Packard, USA. The scanning electron microscope photographs of the PLA/cotton blended fabric were taken using a JSM-5600LV SEM.

Synthesis of reactive dyes

MCT yellow dye

2,4-Diamino-benzenesulfonic acid (0.01 mol) dissolved in 20 mL water was added with stirring to 0.0103 mol cyanuric chloride in 20 mL water with some ice, maintaining the temperature at 0–5°C and pH 3.5–4. These conditions were held for 2 h, and the reaction was monitored by thin layer chromatography (TLC) using *n*-BuOH : *n*-PrOH : EtOAc : H_2O (2 : 4 : 1: 3) as eluent and silica gel TLC plates as the stationary phase (R_f = 0.8). After filtration, 2.5 mL of concentrated hydrochloric acid and 0.0105 mol of $NaNO_2$ were added to the filtrate and this solution was stirred at 0–5°C for 30 min until no reaction to the Erich reagent was detectable, then sulfamic acid was added to destroy excess nitrous acid (starch–iodide paper no longer turns blue). The resultant diazo compound was added to a solution of 0.01 mol 3-methyl-1-(4-sulfophenyl)-5-pyrazolone in 25 mL water at 0−5°C and pH 6.5–7 (stirring was continued for 1.5 h, TLC: R_f = 0.73). Then, 0.01 mol aniline was added, and the temperature was increased to 20–25°C at pH 6–6.5 and held for 1 h. The synthesized dye was isolated by adding 10% KOAc, collected by filtration, washed with ethanol for several times after filtration to remove KOAc, and dried in vacuum to give 6.36 g (Yield: 97%). R_f = 0.75, λ_{max} (H_2O) = 398 nm. The atmospheric pressure chemical ionization mass spectrometer (APCI-MS) gave peaks at 327.5 for $[M\text{-}2H]^{2-}/2$ and 656 for $[M\text{-}H]^-$.

MFT yellow dye

The synthesis of the MFT dye was essentially the same as that of the MCT dye except that the temperature of the condensation reaction between 2, 4-diamino-benzenesulfonic acid and cyanuric fluoride was reduced to −5–0°C, and the temperature of second condensation with aniline was adjusted to 0–5°C. The MFT dye was also isolated by the same method of the MCT dye. Yield 93%, one product spot of R_f = 0.75, λ_{max} (H_2O) = 398 nm. The APCI-MS spectrum of the MFT dye gave peaks at 319.5 for $[M\text{-}2H]^{2-}/2$ and 640.0 for $[M\text{-}H]^-$.

MCT/SES orange dye

The solution of 0.01 mol 2-amino-5-naphthol-7-sulfonic acid dissolved in 25 mL water was added with stirring to 0.0105 mol cyanuric chloride at 0–5°C, maintaining at pH 3 for 2 h (TLC control and same eluent and stationary phase as in the synthesis of the MCT dye, R_f of this condensation product was

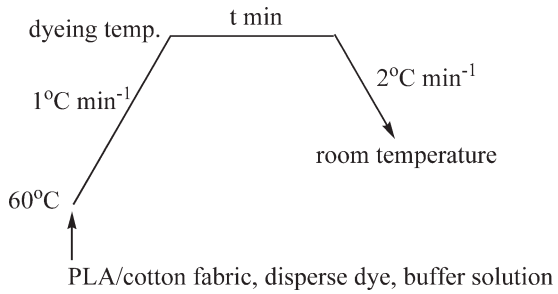

Figure 2 Dyeing profile for disperse dyeing.

0.79). Then, 0.01 mol aniline was added, and the temperature was increased to 20–25°C at pH 6–6.5 for 2 h (TLC control, R_f of the second condensation product was 0.82). After the temperature of the solution decreased to 0–5°C, 0.01 mol fresh diazo 4-(β-sulfatoethylsulfonyl) aniline solution, which was made by traditional method, was added, and the pH was kept at 6.5–7 for another 2 h (TLC control). All the pH in this process was controlled by 15% Na_2CO_3 solution. The synthesized dye was also isolated by adding 10% KOAc, then the dye was washed with ethanol for several times after filtration to remove KOAc, and dried in vacuum to give 7.13 g (Yield: 95%). TLC analysis showed one product spot ($R_f = 0.7$), λ_{max} (H_2O) = 477 nm. The APCI-MS spectrum of the MCT/SES dye gave peaks at 366.5 for $[M\text{-}2H]^{2-}/2$ and 734.1 for $[M\text{-}H]^{-}$.

MFT/SES orange dye

The MFT/SES dye was synthesized as nearly the same process as the MCT/SES dye except that the temperature of the cyanuric fluoride condensation reaction with 2-amino-5-naphthol-7-sulfonic acid decreased to −5–0°C and the second condensation reaction with aniline also needed a low temperature 0–5°C for 2 h. Yield 96.5%, one product spot of R_f = 0.7, λ_{max} (H_2O) = 477 nm. The APCI-MS spectrum of the MFT/SES dye gave peaks at 358.5 for $[M\text{-}2H]^{2-}/2$ and 718.1 for $[M\text{-}H]^{-}$.

Dyeing process

Dyeing of the PLA

The first dyeing stage involved the disperse dyeing of the PLA component using C.I. Disperse Yellow 16 and C.I. Disperse Orange 30 was carried out at a liquor ratio of 20 : 1 and 1% (owf) dye, and the dyeing profile is shown in Figure 2. The PLA/cotton fabric was first immerged into dye-bath at 60°C, the pH (3, 4, 5, 6, and 7) of the bath was adjusted by the buffer solution of HOAc/NaOAc. Then, the temperature was raised to 80, 90, 100, 110, and 120°C, dyeing was continued at these conditions for 0–100 min. After dyeing, the fabric was rinsed with water. The

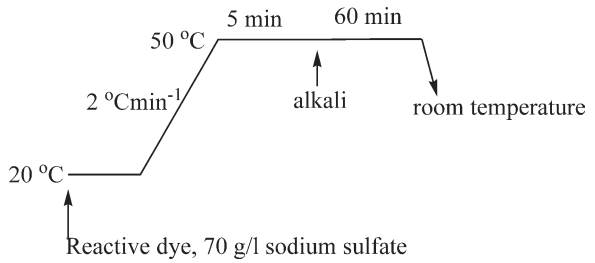

Figure 3 Dyeing profile for reactive dyeing using C.I. Reactive Yellow 1.

reduction clearing was carried out in a bath containing 1.5 g/L Na_2CO_3 and 1.5 g/L $Na_2S_2O_4$ at 60°C for 15 min. Then, the blended fabric was air dried and used in the reactive dyeing process.

Dyeing of the cotton

The cotton component of the blended fabric was dyed after PLA had been dyed with disperse dyes. The reactive dyes were all used at a liquor ratio of 20 : 1, 1% (owf) dye, and 70 g/L Na_2SO_4. The dyeing profile for C.I. Reactive Yellow 1 application is shown in Figure 3. The fabric was immerged into dye-bath at 20°C in the presence of 70 g/L Na_2SO_4 for 10 min, then the temperature was raised to 50°C at a rate of 2°C/min. Dye exhaustion was continued for 5 min before alkali was added, and then dyeing was continued for 60 min. The fabric was removed and washed with water until neutral, then dried at air. The dyeing profile for the MCT dye is shown in Figure 4, and dyeing process was similar to that used for C.I. Reactive Yellow 1 except that the temperature was raised to 90°C. Profiles for C.I. Reactive Yellow 17, MFT dye, MCT/SES dye, and MFT/SES dye are shown in Figure 5. Different alkali concentrations (0, 1, 3, 5, and 10 g/L) were used for the dyeing processes of six reactive dyes. The alkali used in this article was Na_2CO_3. Finally, the PLA/cotton blended fabric after dyeing was soaped in 2 g/L nonionic detergent at 95°C for 10 min, then washed and dried.

Color measurement

Adsorption% of disperse dye on PLA

Aliquots from residual and the initial dye-baths were diluted using 50/50 (v/v) water/acetone. The

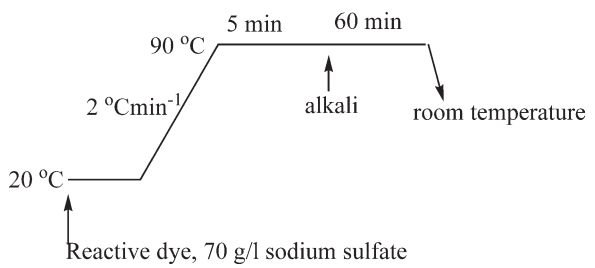

Figure 4 Dyeing profile for reactive dyeing using MCT dye.

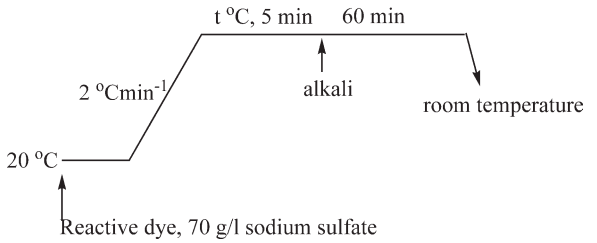

Figure 5 Dyeing profile for reactive dyeing using C.I. Reactive Yellow 17, MFT dye, MCT/SES dye and MFT/SES dye.

absorbance of the resultant solutions were then measured using an HP 8453 UV-visible spectrophotometer at λ_{max}. Then, dye adsorption values (%) were calculated using eq. (1), where C_0 is the absorbance of the initial dye-bath, and C_1 is the absorbance of the dye-bath after the dyeing.

$$\text{Adsorption}\% = (C_0 - C_1)/C_0 \times 100 \quad (1)$$

Fixation studies on cotton

For all the reactive dyes, the total fixation rate (T%), which refers to the percentage of the dye originally applied to the cotton of the blends forming covalent bond, was calculated from eq. (2).

$$\text{T}\% = (A_0 - A_1 - A_2)/A_0 \times 100 \quad (2)$$

where A_0 is the absorbance of the initial dye-bath, A_1 is the absorbance of the dye-bath after the dyeing, and A_2 is the absorbance of the soap bath. All the absorbances are measured at λ_{max} of the dyes.

Physical strength test

The tensile strength of the dyed and undyed PLA/cotton fabrics was assessed with YG (B) 026H weave force-machine (Wenzhou, China) according to ISO 13934-1-1999. The tear strength of the dyed and undyed PLA/cotton was assessed with YG (B) 033A tearing instrument (Wenzhou, China) according to ASTM D 5734-1995. The decrease rate (Decr.%) in physical strength was calculated from eq. (3):

$$\text{Decr.}\% = (N_0 - N_1)/N_0 \times 100 \quad (3)$$

where the N_0 is the strength before dyeing, and N_1 is the strength after dyeing.

RESULTS AND DISCUSSION

Investigation on disperse dyeing

Effect of dyeing parameters on disperse dye adsorption% and fabric strength

For 100% PLA fabric, a high-temperature and high-pressure dyeing process is recommended and pH, temperature, and time are the main factors influence on the dyeing and strength properties of the fabric.[4–6] These parameters were used as reference of dyeing of this PLA/cotton blended fabric with C.I. Disperse Yellow 16 and C.I. Disperse Orange 30, and their influences on the tear strength of the blends and dye adsorption% were studied. The results were summarized in Figure 6. Symbols of ■ and ● in the figures were used to show the weft/warp tear strength (6.8/8.5 N) of the blended fabric before dyeing.

According to Figure 6(a,a′), remarkable loss of weft/warp tear strength of the blends were observed as the pH was higher or lower than 4–5, which indicated that PLA component degraded under strong acidic or neutral conditions. Thus, a weak acidic dyeing bath was suitable to the dyeing of PLA although higher adsorption% of the disperse dyes could be achieved under neutral condition. From results in Figure 6(b,b′), when pH 5 and 60 min were used for dyeing of PLA, it was clear that the weft/warp tear strength of the blended fabric had small reduction (6.5/8.0 N) at 110°C, whereas decreased obviously at 120°C (to 4.8/5.9 N). This stated that much higher temperature was also harmful to the strength of the blended fabric even if the dye adsorption% uptake increased. The results shown in Figure 6(c,c′) depicted that extending dyeing time over 20 min led to an evident loss in the tear strength of the fabric when pH 5 and 110°C were used for dyeing, while this had no effect on the adsorption% of both disperse dyes used. It can be seen that a long dyeing time should be avoided to insure the PLA integrity, making dyeing at 110°C and pH 5 for 20 min optimum.

Investigation on reactive dyeing

Six reactive dyes as typical examples of six types of reactive dyes containing different reactive groups were applied to dyeing of cotton component of the PLA/cotton blends in the second stage of the dyeing process. Dyeing parameters including temperature and addition concentration of alkali (Na_2CO_3) were investigated to show their influence on both the strength properties of the fabric and total dye fixation.

Investigation of DCT and MCT dyes, effect of dyeing parameters on the strength of the PLA/cotton blended fabric and T%

Reactive dyes containing the highest reactivity group (DCT) and the lowest reactivity group (MCT) were first selected to discuss their dyeing results on the PLA/cotton blended fabric. In this study, C.I. Reactive Yellow 1, a typical DCT reactive dye, was applied to the blends. Table I showed the effect of the alkali concentrations on the strength properties of the blends and T%. It could be seen from the table

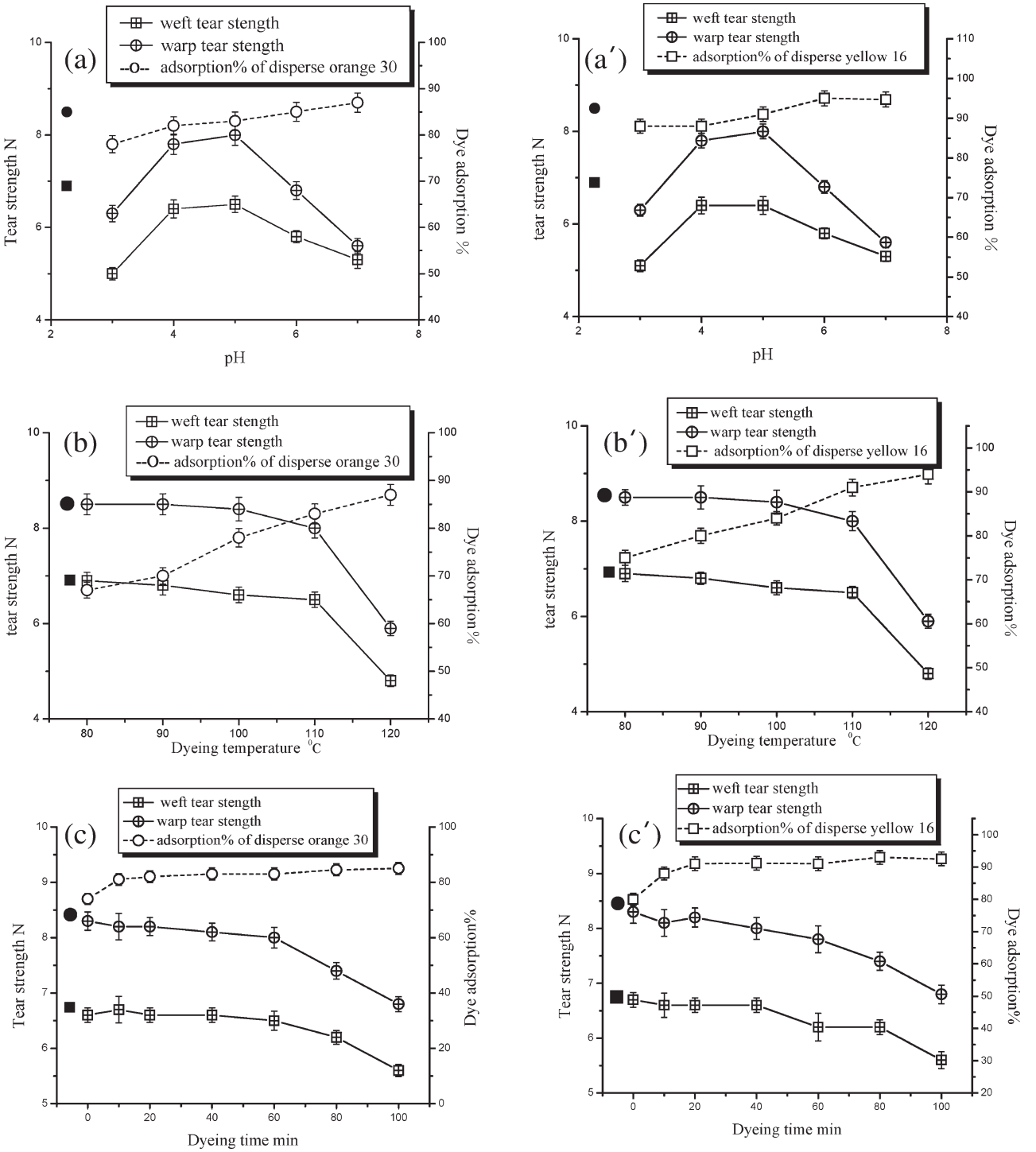

Figure 6 Effect of the dyeing pH (a, a′, 110°C, 60 min), temperature (b, b′, pH 5, 60 min) and time (c, c′, 110°C, pH 5) on the adsorption% of the disperse dyes and strength properties of the PLA/cotton blended fabric (●: warp tear strength before dyeing, ■: weft tear strength before dyeing).

that both the tear and tensile strength of the fabric had no decrease when the alkali concentration was no more than 3 g/L. With the alkali concentration increasing to 5 g/L, the strength of the fabric only exhibited slight loss. Analysis of the simulated dyeing sample arising from 3 g/L alkali without dye indicated that temperature and alkali concentration, not dye structure contributed to the mechanical strength of the fabric blend. These suggested that alkali concentration of no more than 3 g/L at 50°C did not cause strength loss of the blended fabric. In addition, according to the T% showed from Table I, the DCT dye can reach the highest T% (65.3%) at 3 g/L alkali.

TABLE I
Results from Applying C.I. Reactive Yellow 1 to PLA/Cotton at Different Alkali Concentrations[a,b]

	Tear strength				Tensile strength (N)				
	Warp		Weft		Warp		Weft		
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	T%
[c]	8.2	–	6.6	–	537.8	–	336.0	–	–
0	8.2	0	6.6	0	538.0	0	335.8	0	56.8
1	8.2	0	6.6	0	537.5	0	336.0	0	65.0
3	8.2	0	6.6	0	537.0	0	336.2	0	65.3
3[d]	8.2	0	6.6	0	536.8	0	336.3	0	–
5	8.1	1.3	6.6	0	537.2	0	334.8	0.4	64.3
10	7.9	3.7	6.5	1.6	535.0	0.6	329.0	2.0	62.8

[a] Dyeing profile in Figure 3, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4 at 50°C.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.
[d] Without reactive dye (blank test sample).

TABLE II
Results from Applying MCT Dye to PLA/Cotton at Different Alkali Concentrations[a,b]

	Tear strength				Tensile strength (N)				
	Warp		Weft		Warp		Weft		
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	T%
[c]	8.2	–	6.6	–	537.8	–	336.0	–	–
0	7.8	4.8	6.5	1.5	535.7	0	331.3	0	49.8
0[d]	7.8	4.8	6.5	1.5	535.7	0	331.3	0	–
1	7.5	8.5	6.1	7.5	530.1	1.4	329.7	0	57.3
3	7.1	13.4	5.6	15.2	521.1	3.0	325.6	3.3	61.7
5	6.8	17.0	5.6	15.2	515.3	4.2	317.0	5.7	62.0
10	6.8	17.0	5.5	16.7	510.0	5.2	310.0	7.7	66.0

[a] Dyeing profile in Figure 4, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4 at 90°C.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.
[d] Without reactive dye (blank test sample).

TABLE III
Results from Applying C.I. Reactive Yellow 17 to PLA/Cotton at Different Alkali Concentrations[a,b]

	Wear strength				Tensile strength (N)				
	Warp		Weft		Warp		Weft		
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	T%
[c]	8.2	–	6.6	–	537.8	–	336.0	–	–
0	8.2	0	6.6	0	537.5	0	336.0	0	34.0
1	8.2	0	6.6	0	538.0	0	335.3	0	65.0
3	8.2	0	6.6	0	537.4	0	332.6	0	67.1
3[d]	8.2	0	6.6	0	537.7	0	334.3	0	–
5	8.1	1.2	6.4	4.5	532.0	0	332.7	1.0	67.0
10	7.7	6.1	6.0	9.1	529.0	1.6	330.0	1.8	64.7

[a] Dyeing profile in Figure 5, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4 at 60°C.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.
[d] Without reactive dye (blank test sample).

TABLE IV
Effects of Fixation Conditions on PLA/Cotton Tear Strength Following the Application of Synthesized MCT/SES Dye[a,b]

	Tear strength (weft/warp)							
	60°C		70°C		80°C		90°C	
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%
[c]	6.6/8.2	–	6.6/8.2	–	6.6/8.2	–	6.6/8.2	–
0	6.6/8.2	0	6.6/8.2	0	6.5/8.1	1.5/1.2	6.5/7.7	1.5/6.1
1	6.6/8.2	0	6.6/8.1	0	6.3/8.0	4.5/2.4	6.0/7.3	9.1/11.0
3	6.6/8.2	0	6.5/8.1	1.5/0	6.0/7.8	9.1/4.8	5.6/7.1	15.1/13.4
5	6.4/8.1	4.7/1.2	6.2/8.0	6.1/2.4	5.7/7.0	13.6/14.6	5.6/6.8	15.1/17.0
10	6.1/7.7	7.6/6.1	6.0/7.7	9.1/6.1	5.6/6.7	15.1/18.3	5.5/6.8	16.7/17.0

[a] Dyeing profile in Figure 5, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.

Because of the low reactivity of MCT group, dyeing temperature as high as 90°C is required for the reactive dyes containing MCT group. The dyeing results of the synthesized MCT dye were summarized in Table II. It was indicated that at 90°C, even in the absence of alkali, the weft/warp tear strength of the blended fabric had already lost 4.8/1.5% with or without dye addition. With increase of the alkali concentration, more distinct strength loss was observed. Although investigation on disperse dyeing showed 110°C could be used, the dyeing conditions must be weak acidic (pH 4–5) to protect the PLA component. As alkali conditions are necessary for reactive dyeing process, relatively low temperature should be selected. Therefore, it can be concluded that the dyeing conditions of the reactive dyes containing MCT group are not logical colorants for PLA/cotton blended fabric.

Investigation of SES and MCT/SES dyes, effect of dyeing parameters on the strength of the PLA/cotton blended fabric and T%

According to the reactive dyeing results mentioned above, the SES group whose reactivity is between that of the DCT and MCT one were selected to investigate whether it was suitable for the blended fabric.

Dyes containing SES group is also very popular for dyeing cotton, its recommended dyeing temperature is 60°C. Results from applying SES dye C.I. reactive yellow 17 to PLA/cotton were shown in Table III. It could be observed that the strength of the blended fabric had nearly no loss at $\leq$3 g/L of alkali concentration, and this SES dye reached the highest T% (67.1%) when 3 g/L Na_2CO_3 was added. PLA/cotton fabric processing in the absence of dye indicated that the temperature and alkali were the influencing factors on fabric strength, adding support to the use of SES-based reactive dyes for this type fabric.

To get high T% values, the SES-based dyes usually contain an MCT group in same dye molecule.[7] Therefore, we synthesized an MCT/SES dye to examine its effects on PLA/cotton. According to the different reactivity of MCT and SES groups, various dyeing temperatures (60, 70, 80, 90 °C) were selected. Results from fabric strength assessment in Tables IV and V showed that at a given alkali

TABLE V
Effects of Fixation Conditions on PLA/Cotton Tensile Strength Following the Application of Synthesized MCT/SES Dye[a,b]

	Tensile strength(weft/warp)							
	60°C		70°C		80°C		90°C	
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%
[c]	336.0/537.8	–	336.0/537.8	–	336.0/537.8	–	336.0/537.8	–
0	336.0/537.8	0	336.1/537.8	0	332.3/535.4	0	331.7/535.0	1.5/0
1	336.3/537.4	0	335.7/538.0	0	333.0/531.7	1.1/0	331.2/533.0	1.5/0
3	335.1/535.8	0	336.0/534.1	0	329.1/526.4	2.1/2.7	327.6/524.1	2.5/2.6
5	330.0/535.2	1.8/0	331.1/535.0	1.5/0	319.2/520.0	5.1/3.3	317.8/516.3	5.4/4.0
10	328.5/530.0	2.2/1.5	326.8/531.1	2.7/1.2	311.0/513.1	7.4/4.6	310.3/511.0	7.6/5.0

[a] Dyeing profile in Figure 5, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.

TABLE VI
T% of Synthesized MCT/SES Dye on the PLA/Cotton Blended Fabric at Different Dyeing Conditions[a]

	T%			
Alkali conc. (g/L)	60°C	70°C	80°C	90°C
0	50.7	51.3	53.4	52.0
1	60.2	62.1	65.0	68.1
3	66.1	65.4	69.5	75.0
5	70.5	70.7	73.7	74.0
10	72.5	73.2	73.4	73.1

[a] Dyeing profile in Figure 5, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4.

concentration, the strength loss of the fabric increased with temperature increasing; and the fabric had no strength reduction only at conditions of 60°C with alkali concentration $\leq$3 g/L and 70°C with alkali $\leq$1 g/L. On the other hand, the data in Table VI indicated that the highest T% obtained at 60°C (72.5%) required 10 g/L alkali and that T% could be increased to 75.0% by increasing the dyeing temperature to 90°C and decreasing the alkali level to 3 g/L. These results are consistent with the previously reported inverse relationship between dyeing temperature and alkali concentration.[8] But bearing in mind the strength losses, the optimal conditions should be 60°C and 3 g/L alkali, while under those conditions, the T% was only 66.1% (Table VI).

Investigation of MFT and MFT/SES reactive dyes, effect of dyeing parameters on the strength of the PLA/cotton blended fabric and T%

Because of the higher electronegativity of the F atom than the Cl atom, the replacement of an MCT group by an MFT group increases dye reactivity.[7] Accordingly, the application of MFT reactive dyes should involve lower temperatures and alkali levels. The above study suggested that the reactive dyeing temperature should not be more than 60–70°C, so the synthesized MFT dye was applied at 60°C initially. The effect of reactive dyeing on the tear strength and tensile strength and T% of the dye was examined (see Table VII). It showed that both the strength results of the PLA/cotton blended fabric had no reduction at 3 g/L alkali concentration, while this dye also gave T% of 71.0%. These results make the MFT reactive dye more suitable than the corresponding MCT dye for application on PLA/cotton fabric.

As the reactivity of the MFT group more closely matches that of the SES group than the case involving the MCT group, the MFT/SES reactive dyes may give higher T% compared with the MCT/SES reactive dyes. With this point in mind, the synthesized MFT/SES dye was applied on the PLA/cotton blended fabric. From the results in Table VIII, it is clear that 3 g/L alkali concentration was suitable for applying this MFT/SES dye, and that dye application was accompanied by fabric strength retention. When the MCT/SES dye containing the same chromophore dyed at the same dyeing conditions, the T% obtained was only 66.1%; however, this value of the MFT/SES dye was 84.8%, illustrating the advantage of the MFT/SES dye to the PLA/cotton blended fabric.

SEM micrographs of PLA/cotton blended fabric

The surface erosion of PLA/cotton blended fabric, caused by disperse/reactive dyeing, was detected by SEM (Fig. 7). It was clear that the integrity of the blended fabric was maintained very well after disperse dyeing [Fig. 7(b), pH 5, 110°C and 20 min]. The micrographs of samples dyed at 60°C, 10 g/L alkali [Fig. 7(d)] and 90°C, 3 g/L alkali [Fig. 7(e)] exhibited surface damage compared with the fabric

TABLE VII
Results from Applying the MFT Dye to PLA/Cotton Fabric at Different Alkali Concentrations[a,b]

	Tear strength				Tensile strength (N)				
	Warp		Weft		Warp		Weft		
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	T%
[c]	8.2	–	6.6	–	537.8	–	336.0	–	–
0	8.2	0	6.6	0	538.0	0	335.8	0	50.0
1	8.2	0	6.6	0	537.5	0	335.3	0	62.0
3	8.2	0	6.6	0	537.3	0	335.6	0	71.0
5	8.1	1.2	6.3	4.5	534.3	0	334.1	0	71.2
10	7.8	4.9	6.1	7.6	530.9	1.3	329.3	2.0	70.5

[a] Dyeing profile in Figure 5, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4 at 60°C.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.

TABLE VIII
Results from Applying the MFT/SES Dye to PLA/Cotton Fabric at Different Alkali Concentrations[a,b]

	Tear strength				Tensile strength (N)				
	Warp		Weft		Warp		Weft		
Alkali conc. (g/L)	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	(N)	Decr.%	T%
[c]	8.2	–	6.6	–	537.8	–	336.0	–	–
0	8.2	0	6.6	0	538.0	0	335.8	0	51.8
1	8.2	0	6.6	0	537.5	0	335.3	0	79.6
3	8.2	0	6.6	0	541.3	0	338.6	0	84.8
5	8.1	1.2	6.3	4.5	534.3	0	334.1	0	84.7
10	7.8	4.9	6.0	9.1	530.9	1.3	328.5	2.2	85.0

[a] Dyeing profile in Figure 5, liquor ratio of 20 : 1, 1% owf and 70 g/L Na_2SO_4 at 60°C.
[b] The standard deviation of all data were within 3%.
[c] Before reactive dyeing.

dyed at 60°C, 3 g/L alkali [Fig. 7(c)]. Because cotton always shows very good thermal and alkali stability,[9] the results of SEM micrographs suggested that the PLA fiber degraded at high temperature and alkali concentration. Referring to the dyeing results mentioned above, the reactive dyeing conditions should be temperature ≤60°C and alkali concentration ≤3 g/L alkali.

CONCLUSIONS

To avoid the strength loss of the PLA/cotton blended fabric during the dyeing process, especially the reactive dyeing process, the optimal disperse/reactive dyeing systems for the PLA/cotton blended fabric were established. For disperse dyeing process, recommended dyeing conditions were 110°C at pH 5 for 20 min. For reactive dyeing process, dyeing temperature and alkali concentration are the main factors affecting strength loss/retention of the blends. The reactive dyeing results suggested that optimal dyeing conditions should be temperature ≤60°C and alkali concentration ≤3 g/L alkali. And SEM micrographs of the PLA/cotton blended fabric before/after dyeing also confirmed that elevated temperatures or high alkali concentrations

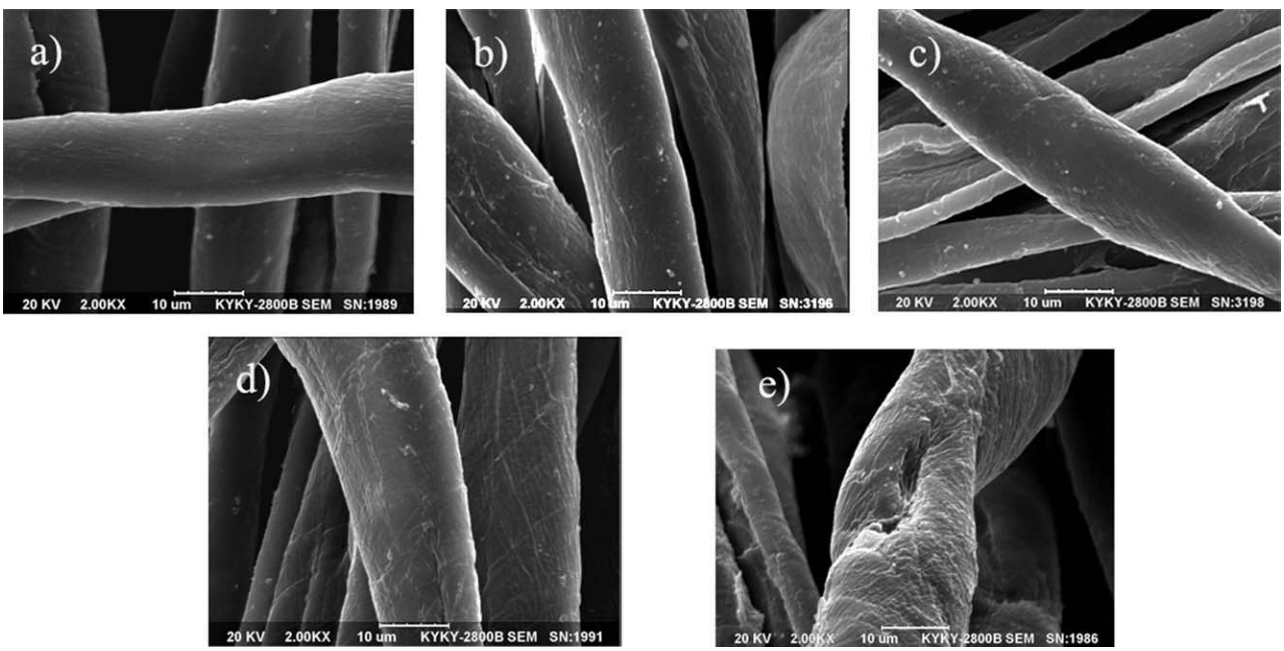

Figure 7 SEM micrographs of PLA/cotton blended fabric: (a) undyed; (b) after disperse dyeing; (c) after reactive dyeing at 60°C, 3 g/L; (d) after reactive dyeing at 60°C, 10 g/L; and (e) after reacitive dyeing at 90°C, 3 g/L (all the samples were treated without dyes).

significantly reduced fabric physical strength. In this regard, especially effective are the reactive dyes containing monofluorotriazine and monofluorotriazine/sulphatoethylsulphone groups in which they were applied without strength loss and gave higher total fixation rate than conventional monochlorotriazine and monochlorotrizaine/sulphatoethylsulphone groups-based dyes.

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