Dyeing Processes of 100% Bio-based and Degradable PLA/PHBV Textiles

ZH Zhang, ZQ Xu, XX Huang and XM Tao

Abstract:

This paper reports an investigation of dyeing processes of textiles made from a novel 100% bio-based and fully degradable PLA/PHBV fiber. The dye exhaustion, depth of shade and fastness, as well as bursting strength of dyed PLA/PHBV fabrics have been evaluated in terms of types and concentration of dyestuff, dyeing bath temperature, duration, liquor ratio and pH value. Finally, the energy cost of the whole dyeing process of the proposed material are calculated and compared with that of PET. The experimental results show that excellent dyeing effect and bursting strength can be achieved by properly applied dyes (e.g. C.I. Disperse Orange 30, Red 74, and Blue 79) under optimal low-dyeing-temperature conditions (100℃, 10 min, pH 5, LR 30:1). Additionally considering the low energy cost during the whole process, PLA/PHBV fibers can be regarded as a promising and environment-friendly material for textile industry.

Keywords:

PLA/PHBV, bio-based fiber, dyeing, color fastness, low-dyeing-temperature process

1 Introduction

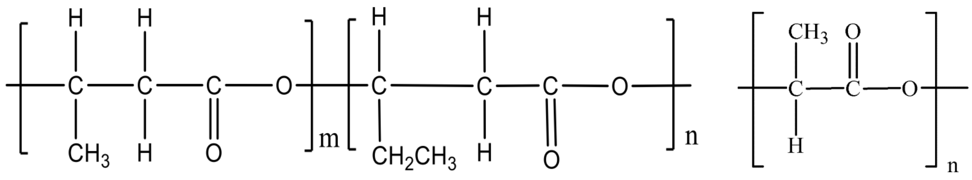
The low biodegradability of common synthetic fibers are becoming increasing concerns for sustainability, as most of them are derived from non-renewable petroleum although recycling programs can reduce the consumption of the natural resource. Accordingly, bio-based materials lately have attracted more and more attention, attributed to their eco-friendliness and recyclability, as well as independence of petroleum. Bio-degradability of the bio-based fibers is another desirable feature as landfill space is getting scarcer. Among various 100% bio-based and degradable materials,[1-3] polylactide (PLA) is one of the commercialized bio-based fibers.[4, 5] However, its low heat resistance, high rigidity and brittleness after long-term storage brought many difficulties into textile processing including yarn texturing, dyeing, finishing, etc.[6] These difficulties can be overcome by using copolymers from bio- or petroleum sources like Triexta (polytrimethylene terephthalate), e.g. Sorona@ of DuPont, where 37% of bio-based materials are used in the fiber composition while the rest of the copolymer is petroleum based. Both bio-based polyamides (nylon) and polyethylene terephthalate (PET) fibers have excellent properties and stability, however, their benefits are limited due to their high cost and chemical pollution during the production processes. Furthermore, bio-based PET fibers are even non-biodegradable.[7] Recently, 100% bio-based and biodegradable poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV, see Fig. 1) and PLA have been fused to make textile fibers which exhibit improved heat stability and softness from pure PLA fibers.[8] The structures of drawn PLA/PHBV fibers were relatively stable, which indicates that the properties of PLA/PHBV fibers would not change significantly even after being stored for a long time.[9]

Although the dyeing processes of PLA have been widely investigated,[10-13] the processes for PLA/PHBV have seldom been reported. This paper presents a systematic study on the low-dyeing-temperature processes of fabrics made from the newly developed PLA/PHBV fibers. The dye exhaustion, depth of shade and fastness, as well as mechanical properties of dyed PLA/PHBV fabrics were evaluated. Finally, the energy cost of the whole dyeing process of the proposed material was calculated and compared with that of PET.

2 Experimental

2.1 Materials

PLA/PHBV single jersey fabrics weighing 110g/cm^2 were knitted by using 80dtex/48f PLA/PHBV filament yarns in Wuxi Minerva Knitted Fashion Co., Ltd.. The PLA/PHBV filament yarns (Trade name Hesu^{TM}) were provided by Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Science and Ningbo Hesu Fibers Co. Ltd. Before dyeing, all fabrics were scoured in a bath with non-ionic surfactant (Diadavin EWN, 200%, Bayer, 2g/L) for 30 min at 40℃. Sodium carbonate (Na_2CO_3), sodium dithionite ($Na_2S_2O_4$) and acetic acid (CH_3COOH) were supplied by Hong Kong Labware Co. Ltd and disodium methylenebisnaphthalenesulphonate (Dispersant NNO) was bought from Suzhou Nuotenghuagong Co. Ltd.



(a) (b)

Fig. 1 Chemical structure of PHBV (a) and PLA (b)

Disperse dyes were selected since they have high affinity to PLA and PHBV which possess molecular structures of aliphatic polyesters. Ten commercial dyestuffs, including primary colors and black, were chosen to dye the PLA/PHBV fabrics. Most of these dyes have been used for dyeing PLA fabrics as reported by Yang, Scheyer, Choi etc.[12-14] Since PHBV has a similar chemical structure to PLA, these disperse dyestuffs may have similar dye exhaustions by PLA/PHBV fabrics. The details of these dyestuffs are shown in Table 1 and Table 2.

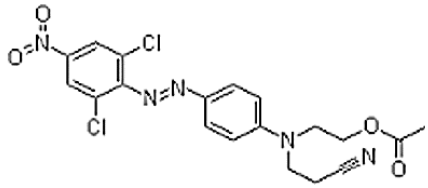
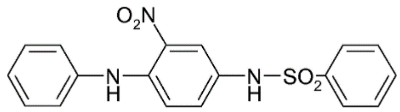
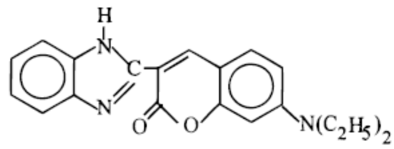
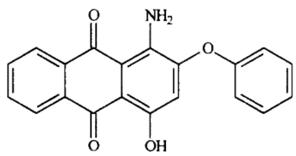
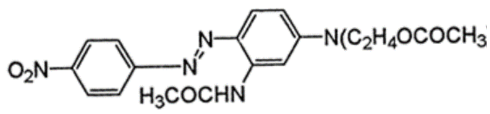
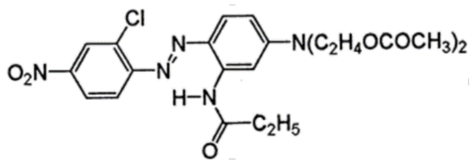
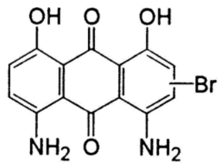
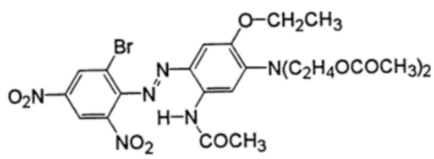
Table 1 Details of dyestuffs

No.	Dyestuff	Commercial name	Manufacturer
1	Disperse Orange 30	Terasil brown 2RFL 200%	Huntsman
2	Disperse Yellow 42	Dianix yellow AM-42	Dystar
3	Disperse Yellow 82	Disperse yellow 8GFF	RunTu, China
4	Disperse Red 60	Terasil red FBN conc	Huntsman
5	Disperse Red 74	Disperse scarlet H-BGL 150%	RunTu, China
6	Disperse Red 167	Terasil rubine 2GFL	Huntsman
7	Disperse Blue 56	Terasil blue 3RL-02 150%	Huntsman

8	Disperse Blue 79	Terasil navy GRL-C 200%	Huntsman
9	Disperse Blue 277	Dianix blue XF	Dystar
10	O30/R54/B79*	Disperse black ECO	RunTu, China

* Disperse black ECO is a mixture of C.I. Disperse Orange 30, Red 54 and Blue 79.

Table 2 Chemical structures of applied disperse dyes

Disperse Dyes	Energy level	Chemical structure
Disperse Orange 30	High	
Disperse Yellow 42	Medium	
Disperse Yellow 82	Medium	
Disperse Red 60	Low	
Disperse Red 74	High	
Disperse Red 167	High	
Disperse Blue 56	Low	
Disperse Blue 79	High	

2.2 Dyeing procedure

AHIBA IR dyeing machine (Datacolor, Switzerland) was used for disperse dyeing experiments of PLA/PHBV fabrics. Three levels of liquor-to-goods ratios of 20:1, 30:1 and 40:1were used in this paper for comparison, and the mass of each piece of fabric sample was 4.0g. Before dyeing, the pH value of dye bath was adjusted to 3.5～6.3 by using acetic acid solution. The glass transition and melting temperature of PLA/PHBV fibers is 50~70℃ and 150~170℃,[9] respectively. Based on this data, dyeing processes were properly designed. The processes started at a temperature of 20℃, and then ascended to the maximal dyeing temperatures (see Table 2) with a rate of 2℃/min. After maintaining the maximal temperatures for 10~40 min, the dye baths were gradually cooled down to 50℃ at a rate of 3℃/min. Fabrics were then taken out of the dyeing liquor and rinsed with cold water. The dyeing profiles and the main parameters which could influence the dye exhaustion, including dyeing temperature, dyeing time and dye dosage, and their corresponding designed values are presented in Fig. 2 and Table 3, respectively.

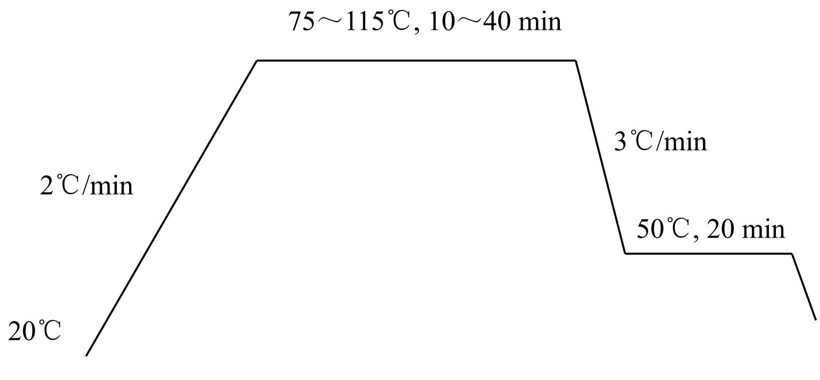


Fig. 2 Profile of the dyeing process

Table 3 Main influencing factors of PLA/PHBV dyeing

Influencing factors	Set value
Dyeing temperature (℃)	75, 85, 95, 100, 105, 110, 115

Dyeing time (min)	10, 20, 30, 40
pH values of dye bath	3.5～6.3
Liquor ratio	20:1, 30:1, 40:1
Dye dosage (%o.m.f.)	0.5, 1, 2, 4

The reduction clearing was performed in a bath containing Na_2CO_3 (1g/L), $Na_2S_2O_4$ (2g/L), and non-ionic surfactant Diadavin EWN (2g/L) at 50℃ and pH 9～9.5 for 20 min, prior to rinse at 20℃ for 5 min. Drying was carried out at 80℃ for 20 min in a dryer. Final heat-setting was then implemented at 95℃ for 60 sec.

2.3 Measurements

To evaluate the effects of various disperse dyes and dyeing parameters, several properties of dyed fabrics including depth of shade, dye exhaustion, dye uptake, color fastness and bursting strength were measured and compared.

Depth of shade (K/S value) of the dyed samples were obtained at the wavelength of maximal absorbance (λ_{max})，by means of Macbeth Color-Eye 7000A spectrophotometer (X-Rite, Hong Kong, China), with D_{65} illuminant while UV was excluded. The depths of shade of dyed fabrics were measured at four different points and the averaged results were recorded.

Dye exhaustion was determined by measuring the absorbance of diluted dye bath samples (diluted with 1:1 acetone-water solution) at a wavelength of the maximum absorption (λ_{max}) of the dye, with Lambda 18 UV/VIS spectrometer (Perkin Elmer, Hong Kong, China). The percentage of dye exhaustion was calculated from equation (1):

$$\%E = \frac{A_0 - A_1}{A_0} \times 100 \tag{1}$$

where A_0 and A_1 are the absorbencies at λ_{max} of the dye bath before and after dyeing respectively.

Dye uptake was calculated by the following equation:

$$\%D = \frac{K_1}{K_0} \times \%E \tag{2}$$

where K_0 and K_1 are the K/S values of fabrics before and after reduction clearing, %E is the value of dye exhaustion.

Color fastness to laundering and color fastness to rubbing of the dyed fabrics were evaluated according to Standard ISO 105-C06 and ISO 105-X12, respectively.

Bursting strength of fabrics in the dry state was measured before and after dyeing based on Standard ISO 13938-2.

3 Results and Discussions

3.1 Factors influencing dye exhaustion

As PHBV/PLA has the molecular structure of polyester type, the distribution of dye molecules in dye bath (including fabrics and dye liquor) is like the distribution of solute in different solvents, obeying the Nernst distribution law.[15] Thus,

$$[D]_f = K[D]_s \tag{3}$$

Here, K is constant, $[D]_f$ and $[D]_s$ are the concentrations of dye in fiber and dye liquor, respectively. If activity coefficient equals to 1, then the dyeing standard affinity is:

$$-\Delta\mu^{\circ} = RT\ln[D]_f/[D]_s \tag{4}$$

Disperse dye molecules are absorbed with a procedure of dispersion in bath, dissolution, dispersion on fiber, absorption and diffusion inside, following a solid solution theory.[16] During these procedures, dyeing standard affinity and dyeing performance can be influenced by many factors, which are analyzed as follows.

Types of Dyes

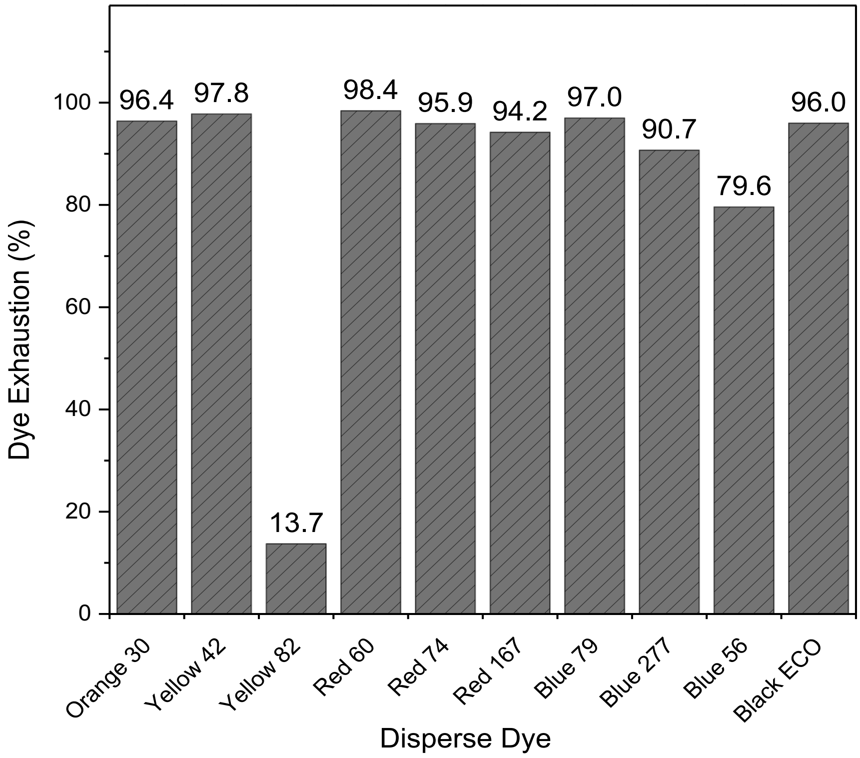


Fig. 3 Percentage exhaustion of applied disperse dyes (1% o.m.f.)

In order to understand the dyeing properties of various dyes for PLA/PHBV fabrics, dyeing trials were carried out at a maximum temperature of 110℃ for 10 min (maintained time at maximum temperature). A dye dosage of 1% o.m.f. , a liquor ratio of 30:1 and pH 5 were employed. As shown in Fig. 3, all of the dyes for PLA/PHBV fabrics have exhaustion values above 90%, except C.I. Disperse Yellow 82 and Blue 56

(13.7% and 79.6% respectively).

The percentage exhaustion values were generally much higher than that of previously reported data for PLA fabric dyeing[10] as lower dye dosages (only 1% o.m.f.) were used in the trials. For example, C.I. Disperse Yellow 42, Orange 30, Red 74 and Blue 79 can all achieve exhaustion values of over 95%, while the exhaustion percentages of the same dyestuff only reached about 80% when dyeing PLA fabrics (4% o.m.f.,10:1 LR at 110℃)[10], and the exhaustion value of 73% for Blue 79 for PLA fabrics was even lower (2% o.m.f.,15:1 LR at 110℃)[12]. The dye exhaustions of C.I. Disperse Yellow 82 and Blue 56 are relatively low, probably due to the lack of strong polarity groups, such as $–NO_2$, $–SO_2–$ and so on[17]. However, some earlier studies revealed that C.I. Disperse Yellow 82, Red 167, Blue 56 could reach higher exhaustion values for PLA fabrics, even higher than that of PLA/PHBV fabrics presented in this paper, with either higher dye dosages (2% or 4% o.m.f.) or lower dyeing temperature (100℃).[10, 12, 13] C.I. Disperse Red 54 was inferred to get an excellent dye exhaustion because of the high exhaustion value of Disperse Black ECO which contains it.

Thus, abundant colors can be obtained for PLA/PHBV fabrics based on the high exhaustion values of disperse dyes of various hues.

Dyeing temperature

Fig. 4 shows that the percentage dye exhaustion is closely correlated with the dyeing temperature. The trials were carried out for 30 min at pH 5.0. It can be seen that both C.I. Disperse Orange 30 and Red 74 can reach their maximum dye exhaustion at 85℃, while C.I. Disperse Blue 79 and Red 60 can get almost the highest dye exhaustion at

95℃ and 115℃, respectively. It seems that high-energy dyes (C.I. Disperse Orange 30, Red 74 and Blue 79) have stronger affinities to PHBV/PLA fibers than low-energy dye (C.I. Disperse Red 60), possibly owing to stronger van der Waals forces between fiber and higher molecular mass dyes. To avoid hydrolysis and shrinkage of PLA/PHBV fabrics during dyeing, lower dye bath temperatures were preferred[18]. C.I. Disperse Orange 30, Red 74 and Blue 79 could be matched with each other for combination dyeing, so that dye bath temperature of 95℃～100℃ would be enough to obtain excellent dye exhaustion. In the studies of PLA dyeing, most dyes could reach the highest dye exhaustion at 100℃～115℃[11, 13, 14] except for some novel synthesized dyes (at 90℃) ,[19] furthermore, the usual temperature of disperse dyeing for PET is 130℃.[20] Thus, PLA/PHBV fabric dyeing can be considered as a relatively lower energy-consuming process.

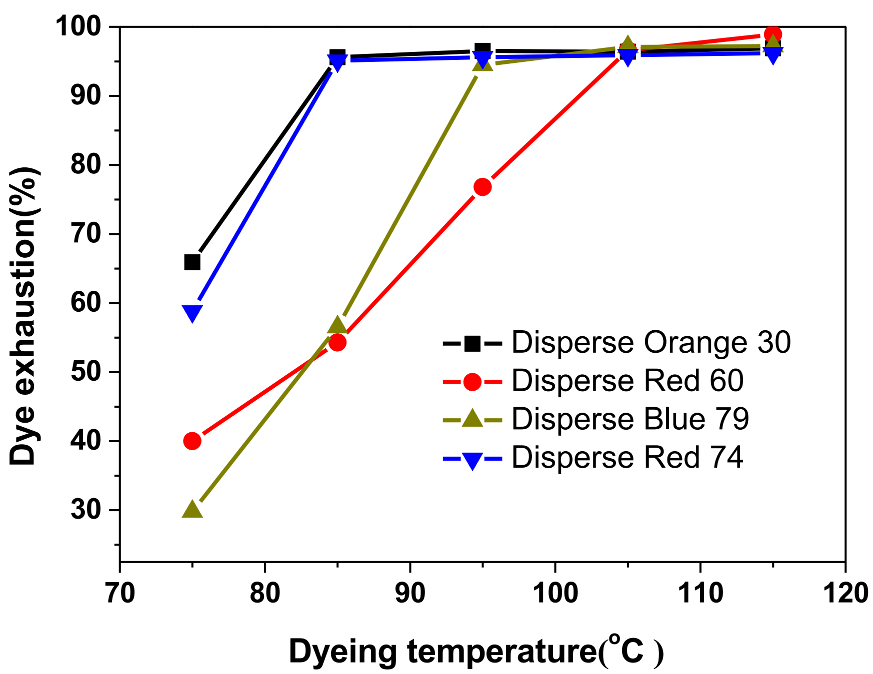


Fig. 4 The effect of dyeing temperature on the dye exhaustion

(Dyeing time: 30 min, pH=5.0, 1% o.m.f., LR: 30:1)

Dyeing time

As showed in Fig. 5, C.I. Disperse Orange 30, Red 74, Blue 79 and Red 167 can all get an exhaustion of over 90% in only 10 min (maintained time at maximum temperature of 100℃, not including the time of heating phase), and no further obvious increase even with prolonged dyeing time. However, C.I. Disperse Red 60 only reaches less than 80% in 10 min, gradually advances with increasing dyeing time. The exhaustion is still less than 85% after dyeing for 40 min. Therefore, it can be concluded that longer dyeing process can promote the exhaustion of dyes, but not significantly when the dyes approach their exhaustion limits, especially when the dyes are prone to be absorbed by the fabrics in short dyeing time at maximal dyeing temperatures. Similar results have been reported for PLA dyeing, when the dyeing temperature was less than 90℃.[19, 21] The positive effect of dyeing time on exhaustion was greater at 110℃ when dyeing PLA fabrics.[14]

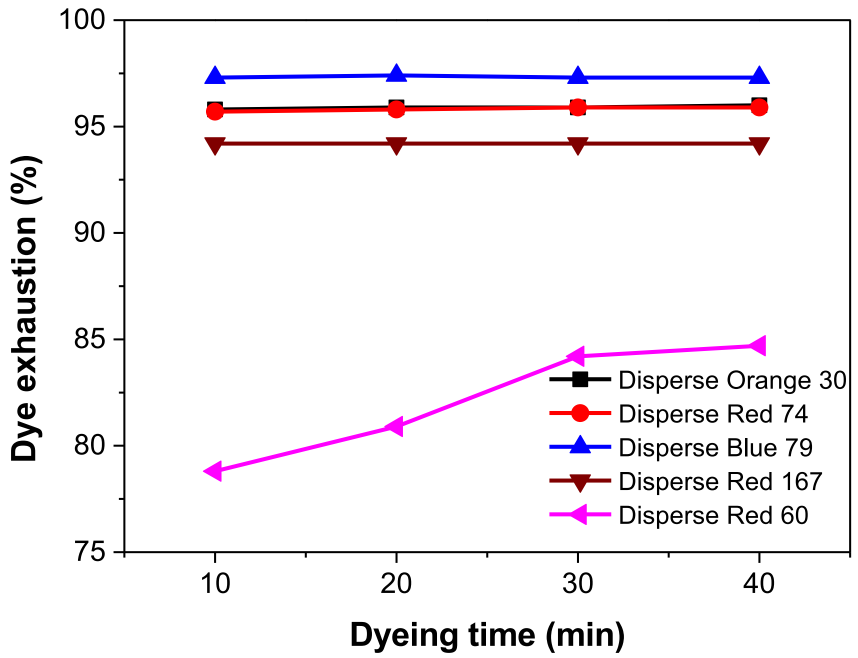


Fig. 5 The effect of dyeing time on dye exhaustion

(Dyeing temperature:100℃, pH=5.0, 1% o.m.f., LR: 30:1)

pH value of dye bath

In order to understand the effect of pH value of dye bath on dye exhaustion, 1% o.m.f. C.I. Disperse Red 60 was applied to the fabrics at 110℃ for 30 min with a liquor ratio of 40:1 and 1g/L Dispersant NNO. Acetic acid was used to adjust the pH of the dye bath. Table 4 indicates that there is no obvious change in dye exhaustion when the pH value before dyeing increases from 3.47 to 6.30. In other words, pH value is not a critical factor for dye exhaustion. This differs from PLA fabrics. A previous study shows that the dye exhaustion of PLA dyeing first increased with increasing pH values before the pH values reached 5, then decreased with further increasing pH of dye bath.[19]

Table 4 Dye exhaustions under various pH values of dye bath

Quantities of CH_3COOH (g/L)	pH value before dyeing	pH value after dyeing	pH value change	Dye exhaustion of R60 (%)
0.4	3.47	3.43	0.04	89.4
0.2	3.75	3.68	0.07	89.5
0.1	4.11	3.97	0.14	88.6
0.04	5.21	4.38	0.83	88.8
0.02	6.30	4.80	1.50	89.0

Nevertheless, for keeping the pH value of dye bath as stable as possible during dyeing process (the variation of pH value is not more than 1), and saving acetic acid, the optimal pH value for dyeing PLA/PHBV fabrics should be controlled at about 5.0, which is also an optimal pH for dyeing PLA.[22]

Liquor ratio

Table 5 Dyeing exhaustion of Disperse Blue 79 at different liquor ratios

Liquor ratio	Dye exhaustion (%)
20: 1	97.4
30: 1	96.7
40: 1	96.1

For assessing the impact of liquor ratio on dye exhaustion, three levels of liquor ratios were designed, as shown in Table 5. Besides, 1% o.m.f. C.I. Disperse Blue 79 was applied at a dyeing temperature of 110℃ for 30 min. It can be seen that the dye exhaustion decreased slightly with increase of liquor ratio. Since more liquor can dissolve more dye, less dye could be absorbed on the fibers, leading to relatively lower dye exhaustion. Furthermore, considering higher liquor ratio would waste more water and energy, low liquor ratio would also affect the levelness of the color of the dyed fabrics, a liquor ratio of 30:1 could be the best choice during dyeing of PLA/PHBV fabrics.

Build-up

The build-up of three disperse dyes on PLA/PHBV fabrics were studied at a dyeing temperature of 100℃ for 10 min (maintained time at maximum temperature), pH value of 5.0, and liquor ratio of 30:1. As shown in Fig. 6, the depths of shade (K/S value) of the fabrics advance with the increased dosages of dyes. When the dye dosage does not exceed 1%, depths of shade of three primary color dyes are sharply increased; whereas the further increase of dye dosage only slightly improve depths of shade. Similar tendencies have also been found in other reports.[17, 23] Therefore, 1% o.m.f. is an adequate dosage for these three dyes to obtain sufficient depths of shade to meet the generally commercial requirement (no less than K/S value of 20), higher dosage can give limited promotion to the shade.

C.I. Disperse Blue 79 can obtain higher depth of shade at 1% o.m.f. than Disperse Orange 30 and Disperse Red 74, probably attributing to higher purity in the commercial dyestuff or more strong polarity groups, e.g. $-NO_2$, $-N(C_2H_4OCOCH_3)_2$ etc, which can facilitate the strong interaction between dye molecules and PLA/PHBV.[17]

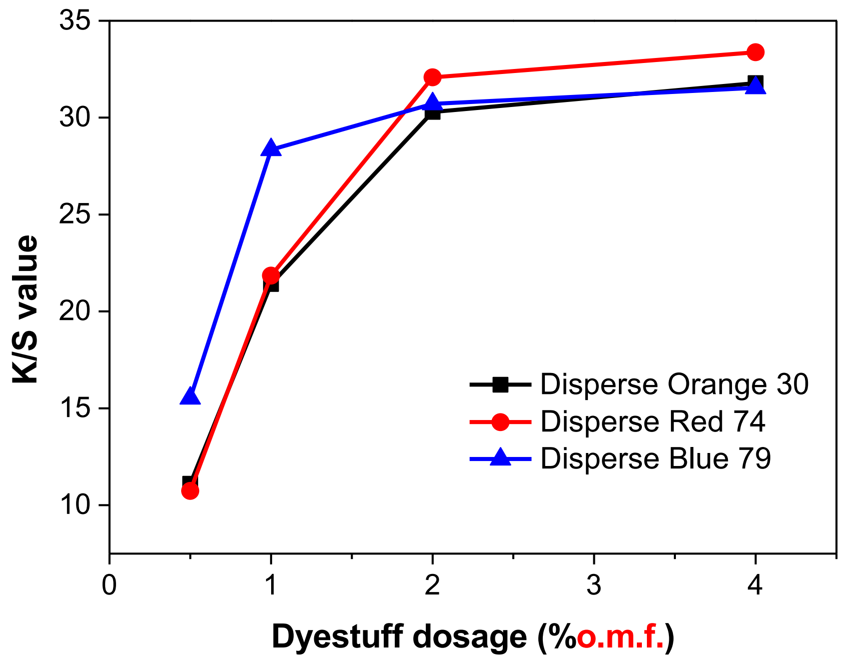


Fig. 6 Build-up curves of three primary color dyestuffs

3.2 Color fastness

Using the optimized dyeing process (maximum temperature of 100℃, maintained for 10 min, 1% o.m.f., pH 5, LR 30:1), PLA/PHBV fabrics were dyed and their color fastnesses were evaluated. As presented in Table 6, the color fastness to laundering of all PLA/PHBV fabric samples dyed with the three chosen dyestuffs were at or above Grade 4. Similarly, excellent color fastness to laundering of dyed PLA fabrics was reported by others, where proper experimental parameters were chosen, including types of dyes,[24] reduction agents,[25] air ratio in reduction clearing[26] etc.

The fabrics dyed with C.I. Disperse Blue 79 have lower grades in both color change and color staining comparing to fabrics dyed by other dyes. This was probably due to the higher depth of shade of this dye (K/S value > 25 at λ max, as shown in Fig. 5), which makes the dyed fabric samples more liable to color fading. Besides, the molecule of C.I. Disperse Blue 79 contains more long branch groups, which may result in difficulty for molecules to diffuse into the core of PHBV/PLA fibers.

Moreover, the grey scale ratings for the color staining between dyed PLA/PHBV fabric and acetate, polyamide as well as polyester are relatively lower than other types of measured standard specimens, probably because of similar chemical structures of PLA/PHBV and acetate, polyamide and polyester, so that the dye molecules which are exhausted well on PLA/PHBV fabrics could also be easily combined with acetate, polyamide and polyester molecules via Van der Waals forces.

Table 6 Colorfastness to laundering of PLA/PHBV fabrics dyed with different dyes

Dyes	Color change	Color staining					
		Acetate	Cotton	Polyamide	Polyester	Acrylic	Wool
O30	5	4/5	5	5	4/5	5	5
R74	4/5	4/5	5	4/5	4/5	5	5
B79	4/5	4/5	5	4	4	5	5

Note: O30, R74 and B79 means Disperse Orange 30, Disperse Red 74 and Disperse Blue 79, respectively.

Table 7 exhibits that the color fastness to rubbing of dyed PLA/PHBV fabrics is also satisfactory as all the results are at or above grade 4.0. Nevertheless, it can be clearly seen that dyed fabrics with higher depths of shade, no matter whether dyed with dosage of 2% o.m.f. or 1%, e.g. C.I. Disperse Blue 79, have lower rubbing fastnesses. Similar results were found for dyed PLA fabrics.[27] Additionally, it is also shown that wet rubbing fastnesses of the dyed fabrics are lower than their dry rubbing fastnesses, probably because the wet condition promotes the transfer of dye molecules between fabrics.

Table 7 Colorfastness to rubbing of fabrics dyed with different dyes

Dyestuff	1% o.m.f.		2% o.m.f.	
	Dry	Wet	Dry	Wet
O30	5	5	5	4/5
R74	5	4/5	5	4
B79	4/5	4/5	4/5	4

3.3 Mechanical property

PLA/PHBV fabrics were dyed by the same process as Sec. 3.2 and their mechanical properties were determined. Table 8 shows that both greige fabrics and dyed fabrics have bursting strengths of over 370kPa. In addition, the dyed fabrics have slightly higher strengths than the non-dyed ones, which illustrates that the strengths of fabrics haven't been reduced by the dyeing process. With regard to the bursting height, dyed fabrics show a bit higher value than greige fabrics, which may be attributed to slippage of molecular chains in PLA/PHBV fibers which lead to more uniform molecular arrangement and improved fabric elasticity after dyeing (According to BS EN 14704-1:2005, the recovered elongation has been improved from 94.3% to 97.7% after dyeing, which is considered as a relatively high value for non-elastomeric fabric.).

Table 8 Bursting strength of PLA/PHBV fabrics before and after dyeing

	Greige		Dyed fabrics	
Dyestuff	Bursting strength (kPa) Mean [CV%]	Bursting height (mm) Mean [CV%]	Bursting strength (kPa) Mean [CV%]	Bursting height (mm) Mean [CV%]
/	375.76 [0.53]	12.0 [0.82]	/	/
O30	/	/	397.14 [0.34]	13.5 [1.75]
R74	/	/	390.24 [2.91]	13.1 [2.36]
B79	/	/	395.07 [0.70]	13.1 [2.40]

3.4 Energy required for the dyeing process

As illustrated above, PLA/PHBV fabrics can be dyed at dyeing temperatures of not more than 100℃ by using proper disperse dyes in short time. Besides, the ultimate dye uptakes after reduction clearing can regularly reach about 97% of the dye exhaustions, denoting the fully penetration of dye molecular. Therefore, significant energy is expected to be saved comparing with the normal disperse dyeing process of fabrics made by other chemical fibers such as polyester. Assumed that a batch of 100kg polyester and PLA/PHBV fabrics is dyed by means of a common dyeing machine, respectively, which has a superficial area of $38m^2$ and an actual dyeing volume of $3m^3$ with liquor ratio of 1:30. Common dyeing process of PET is carried out at a temperature of 130℃ for 40 min, while PHBV/PLA dyeing process is carried out at a temperature of 100℃ for 10 min, both the temperature of initial dyeing liquor and ambient temperature being 20℃, as shown in Fig.7.

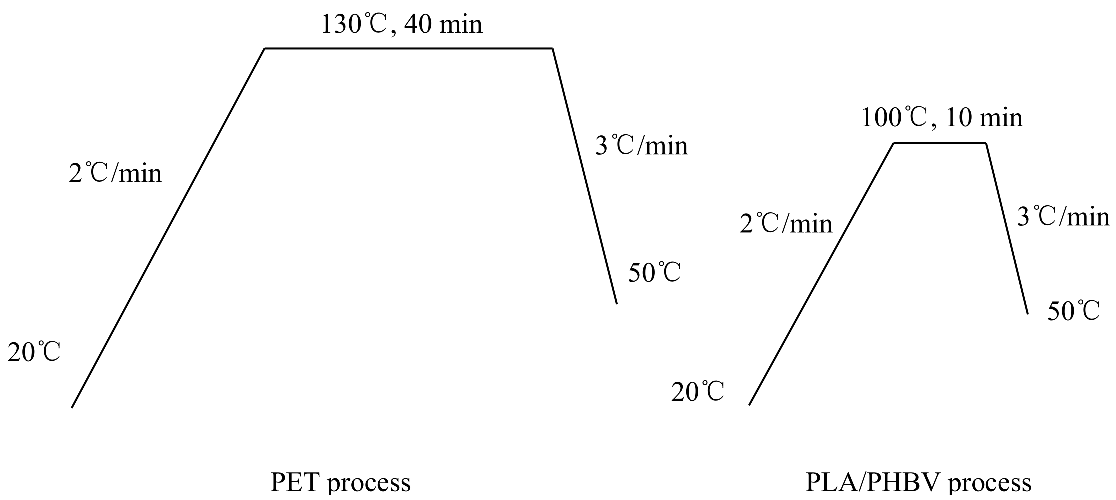


Fig. 7 Comparison between the PET and PLA/PHBV dyeing process

The main differences lie in the first and second step of the dyeing process, i.e. the temperature-rising and temperature-holding step. Therefore, consumed energy for dyeing each kind of fabrics in these two steps is calculated, respectively. For PET dyeing, during the first step, the energy used to heat the dyeing liquor can be calculated from the following equation,

$$E_1 = Cm(t_{w1} - t_{b1}) = 1.386 \times 10^9 J \tag{5}$$

where C is the specific heat of water, J /(kg·℃); m is the weight of water, kg; t_{w1} and t_{b1} represent the maximum and initial temperature of PET dyeing liquor, respectively.

During the second step, heat transfer coefficient (α_T) of convection and radiation can be calculated as followed:[28]

$$\alpha_T = 9.4 + 0.052 \times (t_{w1} - t_{b1}) = 15.12 \tag{6}$$

thus, the steady state heat is,[29]

$$Q_1 = \alpha_T A(t_{w1} - t_{b1}) = 63201.6W \tag{7}$$

where, A is the superficial area of the dyeing machine.

Then, the consumed energy in the second step of PET dyeing gives,

$$E_2 = Q_1 t = 1.517 \times 10^8 J \tag{8}$$

where t is the temperature-holding time.

For the energy used to heat the dyeing liquor is:

$$E_3 = Cm(t_{w2} - t_{b2}) = 1.008 \times 10^9 J \tag{9}$$

where t_{w2} and t_{b2} represent the maximum and initial temperature of PLA/PHBV dyeing liquor, respectively, ℃.

The heat transfer coefficient of convection and radiation during the temperature-holding period is given as:

$$\alpha_T = 9.4 + 0.052 \times (t_{w2} - t_{b2}) = 13.56 \quad (10)$$

thus the steady state heat is:

$$Q_2 = \alpha_T A(t_{w2} - t_{b2}) = 41222.4W \quad (2)$$

Then, the consumed energy in the second step of PLA/PHBV dyeing is

$$E_4 = Q_2 t = 2.473 \times 10^7 J \quad (3)$$

At last, the saved energy for each batch of 100kg fabrics can be obtained:

$$\Delta E = (E_1 + E_2) - (E_3 + E_4) = 5.050 \times 10^8 J \quad (4)$$

As one kilowatt-hour of electricity is equal to $3.6 \times 10^6 J$, and one ton of steam is equal to $2.51 \times 10^9 J$,[30] 140.3 kilowatt hours of electricity or 0.2012 tons of steam can be saved when every 100kg polyester fabrics are dyed. Common medium-sized and small enterprises can produce 1000 tons of fabrics every year, thus, totally 1.403×10^6 kilowatt hours of electricity or 2012 tons of steam can be saved every year for a typical company.

4 Conclusion

This study has experimentally identified the effects of different dyes, dyeing temperature, dyeing time, pH, and liquor ratio on the dye exhaustion in the dyeing process of PLA/PHBV fabrics, finding that C.I. Disperse Orange 30, Red 74, and Blue 79 have excellent dyeing properties on PLA/PHBV fabrics, especially under the optimal condition (maximum temperature of 100℃, maintained for 10 min, pH 5, LR 30:1). Besides, the build-up properties of these dyes have been revealed that the dye dosage of about 1% o.m.f. is a reasonable choice to obtain satisfactory shades.

Color fastness to laundering, color fastness to rubbing, and bursting strength of the dyed PLA/PHBV fabrics have all reached commercially acceptable levels, confirming the feasibility of the designed dyeing process.

Equally importantly, a large amount of energy ($5.050 \times 10^{12} J$ or 1.403×10^{6} kWh of electricity or 2012 ton of steam) can be saved each year for a typical medium-sized company, compared with the normal dyeing process of PET fabrics. Therefore, PLA/PHBV fiber is a kind of promising and environment-friendly material for textile industry, owing to its high dyeing quality and low energy cost.

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