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Dispersant-free Dyeing of Poly(lactic acid) Knitted Fabric with Temporarily Solubilized Azo Disperse Dyes

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Abstract: Poly(lactic acid) (PLA) is known for environmentally friendly material as it is derived from annually renewable crops and biodegradable. Dispersant-free dyeing of PLA fabric with three temporarily solubilized azo disperse dyes which contain β-sulfatoethylsulfonyl group was investigated and their dyeing and fastness properties were compared with those of commercial disperse dyes. The temporarily solubilized azo disperse dyes were successfully applied to PLA fabric without the use of dispersant. The color yield on PLA fabric was dependent on dyebath pH and dyeing temperature as well. The optimum results were obtained at pH 7-8 and 110 °C. The dyes showed markedly higher color yield on PLA fabric when compared to commercial disperse dyes. Wash fastness was very poor to poor but light fastness was good. The COD levels of the dyeing effluent from the temporarily solubilized disperse dyes were considerably lower than those from commercial disperse dyes.

Keywords: Temporarily solubilized disperse dye, Dispersant-free dyeing, PLA, Dyeing effluent, COD

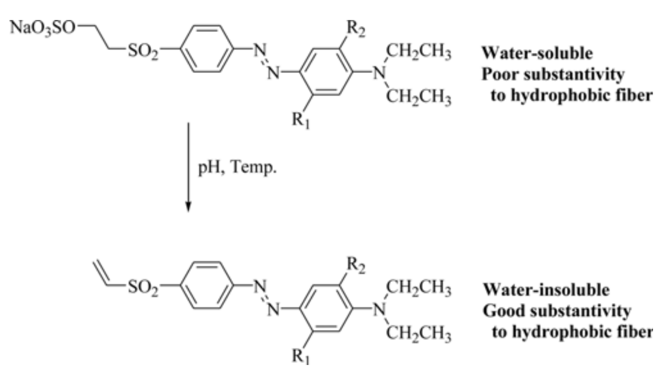
Introduction

Poly(lactic acid) (PLA) is a kind of aliphatic polyester and derived from annually renewable resources such as corn and sugar beet. Although aromatic polyesters, mainly poly(ethylene terephthalate) (PET), are predominantly used for apparel applications and their use is continuously increasing, they have a few problems; production of these polyesters consumes fossil fuel resources, they are non-biodegradable and recycle is not easy. Therefore, the use of PLA in fabric for apparel applications is beneficial to environment as PLA fiber is derived from annually renewable crops, it is 100 % compostable and its life cycle potentially reduces the earth's carbon dioxide level [1].

Since PLA is a hydrophobic polymer, disperse dyes show good substantivity to PLA fiber and many works reported dyeing and fastness properties of this fiber with disperse dyes [2-8]. Attempts of dyeing with some indigoid vat dyes were also reported [9,10]. Whereas PET fiber is conventionally dyed at about 130 °C to enable disperse dyes to diffuse into the fiber at an acceptable rate, PLA fiber is typically dyed at 110-115 °C for 30-40 min because of their lower T_g and greater hydrolytic sensitivity compared to PET fiber [11]. Severe processing conditions such as excessive dyeing temperature and/or extended dyeing time might lead to fiber degradation and reduced physical strength [12].

Disperse dyeing of hydrophobic fibers such as PET, PTT, and PLA is typically performed in the presence of dispersant. Dispersants are added to the dyebath in order to increase solubility of disperse dye and to maintain dispersion stability during dyeing procedure. However, they are not adsorbed onto fiber substrates. Instead, they are discharged as components in the residual dyeing liquor, which increases the COD and BOD values of the effluent [13]. In order to improve the water quality of dyeing effluent, dispersant-free PET dyeing was investigated using temporarily solubilized azo disperse dyes containing β-sulfatoethylsulfonyl group [14,15]. As the β-sulfatoethylsulfonyl group of the dye imparts good water solubility at room temperature, dispersants are not needed to prepare dyebath. During the dyeing procedure, the β-sulfatoethylsulfonyl group is hydrolyzed into vinyl sulfone group via β-elimination reaction (Scheme 1), which makes the soluble dye gradually convert to insoluble form. Then the insoluble dye having substantivity to hydrophobic fiber can be exhausted onto the fiber. As the extension of these works, we has reported several works about synthesis of the temporarily solubilized disperse dyes which have various color range and dyeing properties of the dyes on PET, PET/Cotton blend, and PTT fiber [16-22].

Up to date, dyeing of PLA fabric with temporarily solubilized azo dyes has not been reported yet. In this study, dispersant-free dyeing of the temporarily solubilized azo disperse dyes on PLA fabric was investigated. Color fastness of the dyes have also been examined and compared with



Scheme 1. Conversion of β-sulfatoethylsulfonyl group into vinylsulfone group in the temporarily solubilized azo disperse dyes.

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those of commercial disperse dyes. For the evaluation of eco-friendliness, COD value of the dyeing effluent from the temporarily solubilized disperse dyes was compared with those from commercial disperse dyes.

Experimental

Materials

100 % PLA knitted fabric was obtained from Huvis Co. Three temporarily solubilized azo disperse dyes were prepared by previous method [20], and their structures are given in Table 1. Three commercial disperse dyes were supplied by Myung-Jin Co. as shown in Table 2. Inkanol AZ-100 (Poong Yeong Chem. Co. Ltd.) and Protesol DSL (PROTEX Korea) was used for scouring agent and dispersant, respectively. All the other reagents used were of laboratory grade.

Scouring of PLA

Scouring bath was prepared with 1 g/*l* scouring agent and then PLA fabric samples were scoured in an IR dyeing machine. Scouring was carried out at 60 °C for 20 min and the scoured samples were rinsed and dried.

Dispersant-free Dyeing of PLA

PLA fabrics were dyed in an IR dyeing machine at a liquor-to-goods ratio of 20:1. The dyebaths were prepared with temporarily solubilized disperse dyes 1-3 (0.2-3.0 % owf) and buffered as follows: at pH 4 and 5 with sodium acetate (0.05 M)/acetic acid; at pH 6, 7 and 8 with sodium dihydrogen phosphate (0.05 M)/disodium hydrogen phosphate; at pH 10 with sodium dihydrogen phosphate (0.05 M)/trisodium phosphate. No dispersant was added to the dyebath.

Dyeing was commenced at 60 °C. The dyebath temperature was raised at a rate of 1 °C/min to 90-110 °C maintained at these temperatures for 40 min and rapidly cooled to room temperature. The dyed samples were reduction-cleared with 2 g/*l* sodium hydroxide and 2 g/*l* sodium hydrosulfite at 60 °C for 20 min.

PLA fabric samples were also dyed with commercial disperse dyes (Cdyes 1-3) in a similar manner to the dyeing with temporarily solubilized disperse dyes except that 1 g/*l* dispersant was used, dyebath pH was adjusted to pH 5 using sodium acetate (0.05 M)/acetic acid buffer system and dyeing temperature was 110 °C. The dyed samples were also reduction-cleared under the same condition previously mentioned.

The color parameters of the dyed PLA fabrics were determined on a Macbeth coloreye 3100 spectrophotometer, under standard illuminant D65 using 10 ° standard observer with specular component excluded and UV component included. *K/S* values were measured at maximum wavelength of each dye.

Table 1. Temporarily solubilized azo disperse dyes used in this study

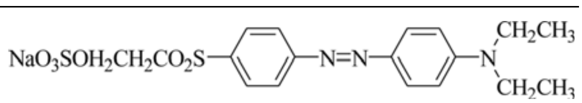
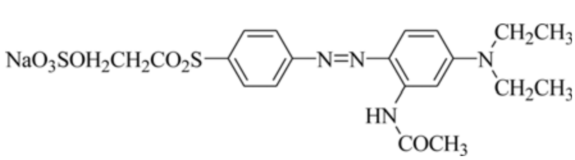
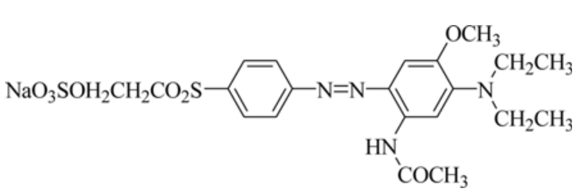
Dye	Structure
1	
2	
3	

Table 2. Commercial disperse dyes used in this study

Dye	Commercial name	Type
Cdye 1	Esperse Yellow PLA	
Cdye 2	Esperse Red PLA	Mixed type
Cdye 3	Esperse Blue PLA	

Fastness Test

After dyeing with temporarily solubilized disperse dyes or commercial disperse dyes, the dyed PLA samples (dye concentration: 1 % o.w.f.) were heat-set at 130 °C for 60 s and subjected to wash (ISO 105-C06/C1S:1994) and light (ISO 105-B02:1994) fastness tests. The shade change, together with the staining of adjacent fabrics, was rated according to appropriate ISO grey scale.

COD Analysis of Dyeing Effluent

PLA fabrics were dyed with temporarily solubilized disperse dyes 1-3 (dye concentration: 1 % o.w.f.) without using dispersant and also dyed with commercial disperse dyes (Cdyes 1-3, dye concentration: 1 % o.w.f.) using dispersant. Before and after dyeing, dyeing liquor of 300 m*l* was collected and then COD_{cr} values were measured according to the test method in ISO 6060:1989 (Determination of the chemical oxygen demand).

Results and Discussion

Dyeing Properties

In the application of temporarily solubilized disperse dyes containing β-sulfatoethylsulfonyl group on hydrophobic fibers, dyebath pH and dyeing temperature are important factors [14-16,20], which can affect the conversion rate of the dye from soluble form into insoluble vinylsulfone form.

Figure 1 shows the color yield of dye 2 on PLA fabric at

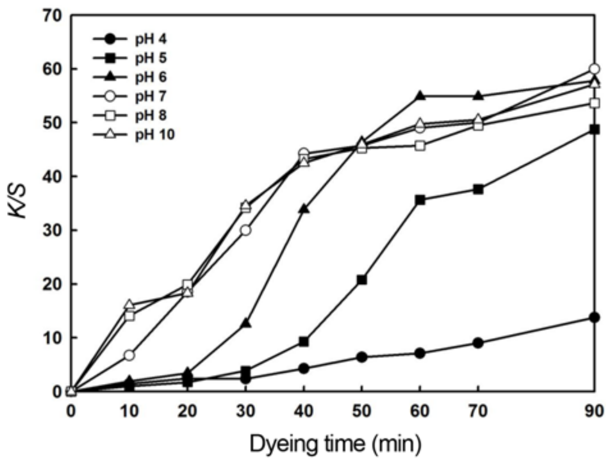


Figure 1. Effect of pH on the color yield of Dye 2 on PLA fabric (dyeing concentration: 2 % o.w.f., dyeing temperature: 110 ^{o}C).

various pH values while dyeing temperature and dye concentration were fixed to 110 ^{o}C and 2 % o.w.f., respectively. Color yield was highly affected by dyebath pH. At pH 4, relatively low color yield was obtained, which is due to the low conversion rate of the soluble dye into the insoluble vinylsulfone form. Although dyeing rate at pH 4 was low, the color yield increased continuously throughout the whole dyeing procedure, which suggested that the conversion of dye occurred steadily. When dyebath pH increased to pH 5 and 6, overall dyeing rate and final *K/S* value was also increased, which can be explained by the increased conversion rate of the dye compared to pH 4. As dyebath pH further increased to pH 7, 8, and 10, initial dyeing rate was also increased but no more increase of dyeing rate was observed after 20 min and dyeing rates at pH 7, 8, and 10 became similar to one another. Thus, final *K/S* values at pH 6, 7, 8, and 10 were similar while the maximum final *K/S* value was obtained at pH 7. In the previous reports about dispersant-free dyeing of PET fiber with temporarily solubilized disperse dyes [16,18,20], maximum final *K/S* value was obtained at pH 5. The difference in optimum pH value could be explained by considering that PLA in this study was dyed at 110 ^{o}C while PET in the previous study was done at 130 ^{o}C. The conversion reaction in Scheme 1 would occur faster as dyeing temperature or dyebath pH would increase. As dyeing temperature of PLA is lower that of PET, the optimum conversion would be obtained at higher pH values.

Final color yields of dyes 1 and 3 on PLA fabric after dispersant-free dyeing at various pH values are shown in Figure 2. The effect of pH on the final color yield of dye 1 or 3 was generally similar to that of dye 2. Thus, very small *K/S* value was obtained at pH 4, *K/S* values increased as pH increased up to pH 8, and then *K/S* value decreased slightly at pH 10. When the dyebath pH is higher than the optimum pH level, the conversion rate would become fast so that the insoluble dyes could make unwanted aggregations in the

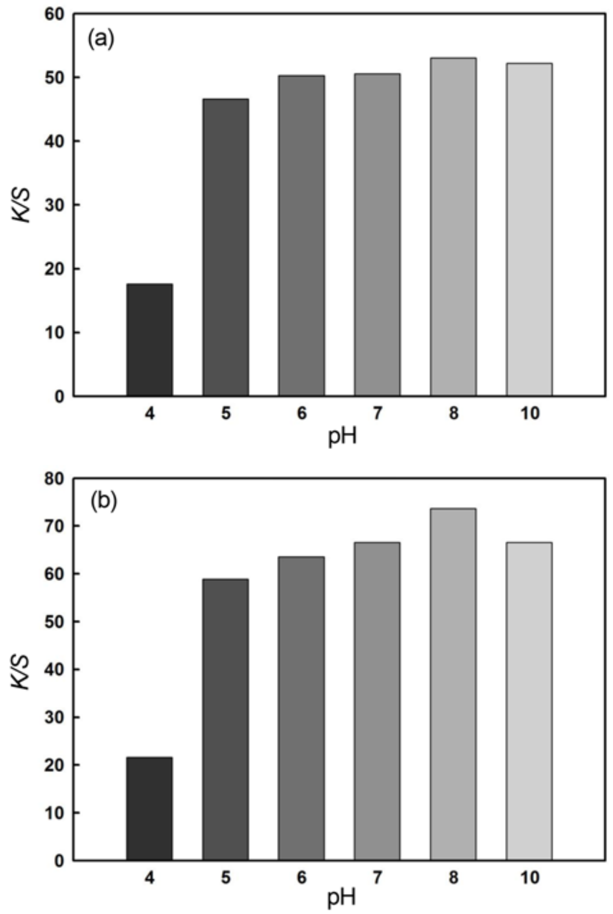


Figure 2. Effect of pH on the color yields of Dye 1 and 3 on PLA fabric (dyeing concentration: 2 % owf, dyeing temperature: 110 ^{o}C), dyeing time: 40 min; (a) Dye 1 and (b) Dye 3.

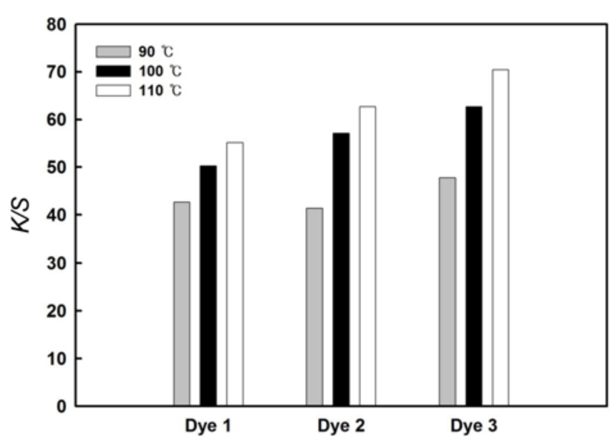


Figure 3. Effect of dyeing temperature on the color yields of temporarily solubilized disperse dyes on PLA fabric (dyeing concentration : 2 % owf, dyeing pH : Dye 1, 3 - pH 8, Dye 2 - pH 7).

dyebath before approaching the surface of the PLA fiber, which might cause low color yield. Maximum final *K/S*

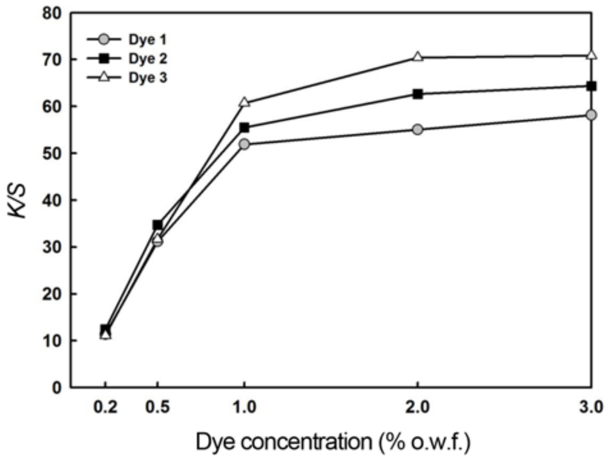


Figure 4. Effect of dye concentration on the color yields of temporarily solubilized disperse dyes on PLA fabric (dyeing temperature: 110 °C, dyeing time: 40 min, dyeing pH: Dye 1, 3 - pH 8, Dye 2 - pH 7).

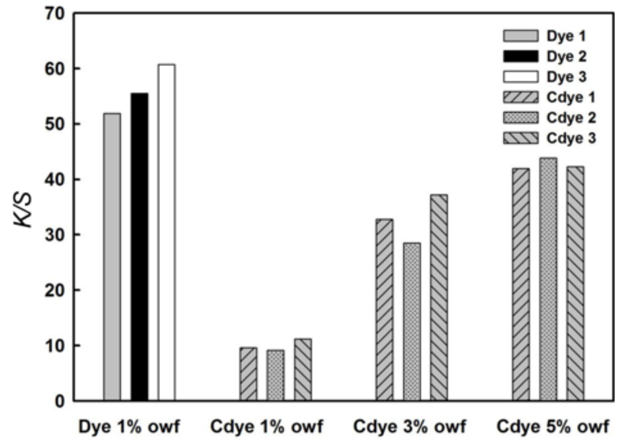


Figure 5. *K/S* values of PLA fabrics dyed with temporarily solubilized disperse dyes and commercial disperse dyes (dyeing temperature: 110 °C, dyeing pH: Dye 1, 3 - pH 8, Dye 2 - pH 7, Cdyes - pH 5).

values was obtained at pH 8 for both dyes 1 and 3.

Figure 3 shows the effect of dyeing temperature on *K/S* values of temporarily solubilized disperse dyes on PLA knitted fabric when dyed at optimum dyebath pH. As dyeing temperature increased from 90 to 110 °C, *K/S* value as a color yield also increased. Thus, maximum color yield was obtained at 110 °C. It is well known that dye molecule would diffuse into PLA fiber more easily at higher dyeing temperature. Another explanation is the low conversion rate of soluble dye into insoluble form at lower temperature than 110 °C which would result in low color yield.

Figure 4 shows the build-up of the dyes 1-3 on PLA fabric. The *K/S* values of dyes 1-3 markedly increased as concentration of dye increased up to 1 % o.w.f. and then they slightly increased and reached saturation level at 2 or 3 % o.w.f. However, when the amount of dye applied was over 1 % o.w.f., *K/S* values of all the dyes reached to very high level (51.9-58.2 for dye 1, 55.5-64.6 for dye 2, and 60.7-70.8 for dye 3) which suggested good color build-up on PLA fabric.

Comparison with Commercial Disperse Dyes

Three commercial disperse dyes (Cdyes 1-3), which were being used for PLA dyeing, were selected and their dyeing properties on PLA fabric were compared to those of the temporarily solubilized disperse dyes (dyes 1-3). Figure 5 shows the *K/S* values of dyes 1-3 (1 % o.w.f) and Cdyes 1-3 (1, 3, and 5 % o.w.f) on PLA fabric when dyed at their optimum dyebath pH. During dyeing procedure, dispersant were only used for Cdyes 1-3 and not for dyes 1-3. When the amount of dye was 1 % o.w.f., *K/S* values of dyes 1-3 (51.9-60.7) showed so much higher than those of Cdyes 1-3 (9.1-11.2). When the amount of Cdye increased to 5 % o.w.f., *K/S* values increased to 41.9 to 43.8 but they were still lower than those of dyes 1-3 with 1 % o.w.f. This can be probably explained by considering that the commercial dyes themselves contain large amounts of dispersant during the dye manufacturing process while the temporarily solubilized disperse dye is 100 % synthesized dye. Table 3 show CIE$L^*a^*b^*$ values and ISCC-NBS color name of the dyes 1-3 and Cdyes 1-3 on PLA fabric. Dyes 1-3 exhibited orange, reddish orange, and red shade on PLA and Cdyes showed yellow, purplish red, and blue shade.

Table 3. The color data of temporarily solubilized disperse dyes or commercial disperse dyes on PLA fabrics

Dyes	CIE $L^*a^*b^*$ values			ISCC-NBS color name
	L^*	a^*	b^*	
Dye 1	58.34	43.43	84.71	Vivid orange
Dye 2	52.74	50.93	65.29	Vivid reddish orange
Dye 3	34.30	55.75	29.66	Vivid red
Cdye 1	81.05	-7.08	72.50	Strong yellow
Cdye 2	51.50	55.54	12.40	Strong purplish red
Cdye 3	34.33	5.89	-35.17	Moderate blue

Table 4 shows the wash and light fastness results for the dyes 1-3 and Cdyes 1-3. The wash fastness of dyes 1-3 was very poor to poor and that of Cdyes were poor to fair. These results were attributed to the very high *K/S* values of the PLA samples dyed with dyes 1-3 as shown in Figure 5. Considering that less amount of dyes 1-3 could be needed for obtaining the same depth of shade, it is expected that the difference of wash fastness between dyes 1-3 and Cdyes 1-3 would be marginal if dyed samples of similar depth were tested. The light fastness ratings of the samples for all the dyes were identical, showing good light fastness. The wash and light fastness results demonstrate that dyes 1-3 can be

Table 4. Wash and light fastness of PLA fabrics dyed with Dyes 1-3 or commercial disperse dyes (Cdyes 1-3)

Dyes	Wash fastness							Light fastness
	Change	Staining						
		Acetate	Cotton	Nylon	Polyester	Acryl	Wool	
Dye 1	4-5	1	3	1	2-3	3-4	1	5
Dye 2	4-5	1-2	3	1-2	2-3	3-4	1	5
Dye 3	4-5	1	2-3	1	2-3	3	1	5
Cdye 1	4-5	2-3	4	2-3	3-4	4	3	5
Cdye 2	4-5	2-3	3-4	2	2-3	3-4	2-3	5
Cdye 3	4-5	1	3	1-2	2	3-4	2	5

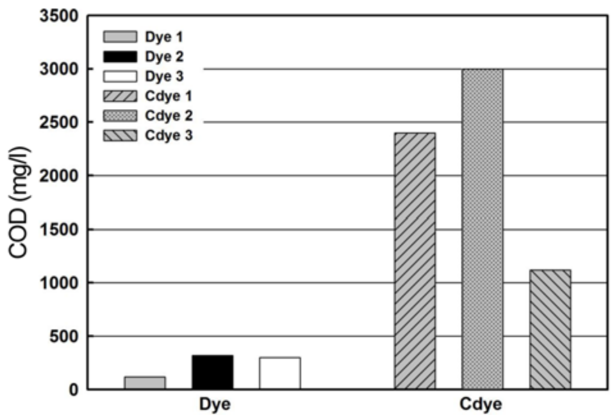


Figure 6. COD levels of PLA dyeing liquor before dyeing for temporarily solubilized dyes (Dyes 1-3) and commercial disperse dyes (Cdyes 1-3).

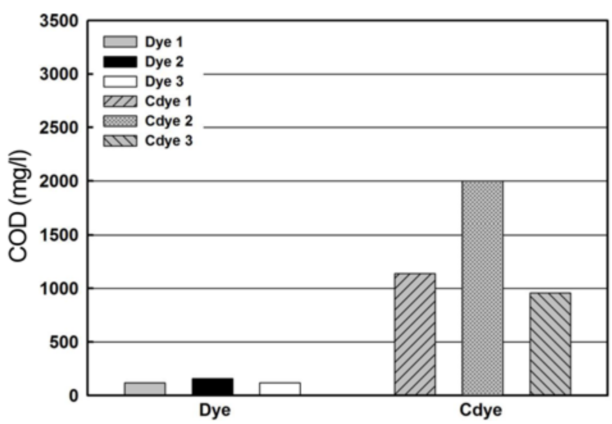


Figure 7. COD levels of PLA dyeing liquor after dyeing for temporarily solubilized dyes (Dyes 1-3) and commercial dyes (Cdyes 1-3).

applied and replace commercial dyes for the PLA fabric.

Figure 6 and 7 show COD_{Cr} levels of PLA dyeing liquor before and after dyeing for temporarily solubilized disperse dyes 1-3 and Cdyes 1-3. COD levels of initial dyeing liquor for Cdyes 1-3 (more than 1100 mg/*l*) were higher than those for dyes 1-3 (less than 320 mg/*l*). In case of dyeing effluent, COD levels of dyeing liquor after dyeing for Cdyes 1-3 (more than 960 mg/*l*) decreased when compared to initial COD levels but they were still high. Similarly, COD levels after dyeing for dyes 1-3 (120 to 160 mg/*l*) also decreased and were much lower than those of Cdyes. Low COD levels of dyeing effluents for the temporarily solubilzed disperse dyes are definitely due to the fact that no dispersant was used when applying dyes 1-3 to PLA. Dyeing effluents of dyes 1-3 would contain unexhausted dye and small amount of electrolyte which was added to adjust pH of dyeing liquors. On the other hand, dyeing liquor of commercial dye exhibited high COD levels at both initial and final stage of dyeing. In commercial dyeing of PLA, dispersants are already contained in commercial dye itself to some extent and added separately to the dyebath in order to stabilize dye dispersion. Most of these dispersants, not being adsorbed to the fiber, would remain in the dyeing liquor after dyeing and would increase the COD level.

Conclusion

Dispersant-free PLA dyeing of the temporarily solubilized azo disperse dyes from aminoazobenzene derivatives containing a β-sulfatoethylsulfonyl group was investigated and color fastness as well as environmental aspects of the dyes were compared with commercial disperse dye.

PLA knitted fabric was successfully dyed with the temporarily solubilized azo disperse dyes without using any dispersant. The color yield on PLA fabric was highly dependent on the dyeing pH and also dependent on dyeing temperature. The optimum result was obtained at pH 7-8 and 110 ^{o}C. Dyes 1-3 showed moderate build-up on PLA fabric.

The wash fastness of dyed fabrics with dyes 1-3 was very poor to poor and that of Cdyes 1-3 was poor to fair. But if dyed samples of similar depth were tested, it is estimated that the difference of wash fastness between dyes 1-3 and Cdyes 1-3 would be marginal. The light fastness was very good for all the dyes.

The COD levels of the PLA dyeing effluent from the temporarily solubilized disperse dyes were considerably lower than those from a commercial disperse dyes. This result is attributed to no usage of dispersant for the temporarily solubilized disperse dyes.

From these results, temporarily solubilized azo disperse dyes would be a good alternative for dyeing of PLA fabrics instead of commercial disperse dyes. Dispersant-free dyeing with temporarily solubilized disperse dyes could also extend the environmental friendliness.

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