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An approach to the dyeing of polyester fiber using indigo and its extended wash fastness properties

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Abstract

Polyester fiber was dyed with indigo vat dye to examine the practical dyeing feasibilities and behaviors. Vat dyes, which commonly applied to the cellulosic fibers, could be considerable colorants to dye polyester substrate, especially focusing on fastness aspect in terms of washing test. In this work, the optimized dyeing conditions and behaviors were investigated. In addition, extended multiple washings of indigo dyeing, which were compared with the results of disperse dyeing, were carried out to determine the fastness properties. HPLC analysis showed that when dyeing time increased, structural changes of indigo components were attributed to the decreasing color strength of dyeings. From the comparison of indigo disperse system and leuco system, it was found that disperse system of indigo had little effect to achieve dye uptakes.

Keywords: Indigo; Polyester; Wash fastness; Leuco; Staining; Disperse dyes

1. Introduction

Dyeings of the most commonly used to the synthetic fibers, namely polyester and polyamide, have been carried out using disperse dyes and acid dyes. The application of these mentioned dye types, and indeed all dyes for substrates, relies on the reciprocal reaction characteristics between the substrates and dye molecules [1,2]. In this paper, an interest on dyeing using indigo vat dye to the polyester fibers was attended.

Although polyester fibers have been dyed dominantly using disperse dyes and over the years a number of studies have been carried out to examine the exhaustion properties, little attention has focused on the application of vat dyes on polyester fibers. In terms of fastness properties, especially to the washing, the satisfactory levels of wash fastness are not present in the results from disperse dyeings due to the dye reduction and migration behavior. In this context, the vat dyeing [3] leaves a potential possibility and is an alternative method to overcome the disadvantage in use.

In general, dyeings produced with vat dyes [4–8] impart overall higher wash fastness properties than results obtained by other classes of dyes. An insoluble characteristic of vat dyes is attributed to

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this superior wash fastness results. In this context, indigo, one of the most important vat dyes, was attempted to the polyester fibers and its fundamental dyeing properties were investigated.

Thus, this paper concerns the dyeing behaviors and properties using indigo. Besides, HPLC analysis of indigo moieties extracted from indigo dyed samples was investigated to determine the spectral adsorption changes. It is found that the deep shade of indigo dyeing was achieved and full indigo penetration within the substrates was confirmed from cross-sectional photographs of dyed polyester fibers. In this article, it is concerned that the effects of indigo dyeing conditions such as temperature, time and wash fastness to the polyester fibers are investigated and its corresponding results discussed.

2. Experimental

2.1. Materials

Polyester filament taffeta (warp 75 denier/yarn 107 yarns/in., weft 75 denier/yarn 97 yarns/in., 70 ± 5 g/m^2) was used in this experiment. Indigo employed in this work was purchased from Aldrich Chemical Company. Thiourea dioxide as a reducing agent was purchased from Aldrich Chemical Company. For reduction clearing a commercial sample of non-ionic surfactant *Sandopur MCL Liq.* was generally provided by Clariant. All other chemicals used were laboratory grade reagents.

2.2. Dyeing

Polyester fabric was dyed in sealed, stainless steel dye pots of 120 cm^3 capacity in a laboratory-scale dyeing machine (ACE-6000T). Samples were placed in a 40 °C dyebath of 20:1. After 10 min, the temperature was raised until reaching 70 °C. At this temperature the vatting of indigo was continued for 30 min. At the end of vatting, a polyester sample was added and temperature was then increased to the range of temperatures of 90–130 °C. At the end of dyeing, the dyed samples were removed, rinsed thoroughly in tap water and allowed to oxidize in the open air.

2.3. Reduction clearing of dyeing

At the end of oxidation, the samples were reduction cleared to remove the loosely fixed dye on the surface of dyed fibers. The dyed samples were washed off using 1 g/l of $Na_2S_2O_4$, 2 g/l of Na_2CO_3 and 2 g/l of a non-ionic surfactant at 60 °C for 20 min and were then rinsed in running tap water.

2.4. Preparation of acid leuco moiety

The vatting of indigo was commenced at 40 °C, with the addition of 2 g/l of Na_2CO_3 and 5 g/l of thiourea dioxide. After raising the temperature to 70 °C vatting was continued for 30 min. With completion of vatting confirmed by the color change of the bath solution (lemonish-yellow), the non-ionic dispersing agent with constant stirring was added to the solution and an addition of formic acid was given to bring acid pH conditions, which produced the acid leuco form of indigo and provided a stable dispersion of acid leuco dye.

2.5. Color measurement

Colorimetric data of indigo dyeings were determined using a *Datacolor SF 600 plus* spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10° standard observer. Each fabric was folded once so as to give two thickness and average of five readings was taken each time.

2.6. HPLC analysis

The HPLC (Hewlett Packard, series 1100) instrument was used to analyze the changes of indigo moieties within the dyed sample. In order to investigate the indigo moieties, an extraction using *N*,*N*-dimethylformamide (DMF) was carried out to strip indigo moieties from the dyed samples at 90 °C for 30 min. HP Eclipse® XDB-C18 (4.6×150 mm, 3.5 μm) column was employed using a mixed solution (water and methanol, 10:90) as a mobile phase. The flow rate was 0.5 ml/min.

2.7. Preparation of the disperse dyeing using color matching system

The disperse dyeing having the same color strength with indigo dyeing was prepared using color matching system (*Datacolor SF 600 plus*) to compare the wash fastness properties of the both dyed samples. Disperse dyeing was prepared with following chosen dyes: C. I. Disperse Yellow 54, C. I. Disperse Red 167 and C. I. Disperse Blue 79.

2.8. Color fastness

The wash fastness of the dyeings was tested using the method of ISO 105 C06 A1S [9]. SDC multifiber strip fabric as an adjacent material was used. The samples were sequentially washed five times.

3. Results and discussion

3.1. Effect of dyeing temperature

In order to examine the effect of temperature on the color strength, polyester fibers were dyed with indigo at various temperatures (90–130 °C). A 2 g/l of thiourea dioxide as a reducing agent, 5 g/l of Na_2CO_3 and 6% of indigo were used for this work. Employed dyeing method was mentioned above. Fig. 1 shows the color strength of indigo dyeings on polyester fibers. Generally, the color strength of the dyeings increased with increasing application temperature. The adsorption was more favorable at higher temperature than at lower temperature. Within the lower range of dyeing temperatures (90–100 °C), these conditions had little effect on the dye uptake to the substrates. Especially, satisfactory dyeing exhaustions were obtained in the range of temperatures of 110–130 °C. It is found that dyeing temperature of indigo is higher than that of method used to apply the vat dye to the cellulosic fibers, this having been attributed to the low diffusional power within the higher crystalline structure of polyester molecules. The observed results that the color strength of indigo dyeings increased with increasing application temperature was attributed to the higher kinetic energy of the indigo molecules, the greater diffusional power within the polymer substrates and the higher fiber swelling effect. In this context, it is thought that in terms of dyeing temperatures, the adsorption behavior of indigo on polyester fibers is following a similar dyeing mechanism for commercial disperse dyes, which involved a high-pressure and a high-temperature dyeing method. The effect of temperatures on the dye exhaustion can be also supported from the cross-sectional photographs of the dyed polyester fiber (Fig. 2). To verify the penetration evidence of indigo molecules within the substrate, the black shade of fibers were placed around indigo dyed fibers at a range of temperatures of 90 and 100 °C. On the contrary, in the case of 110 and 120 °C, the core fibers of indigo dyeings were embedded in the white shade of background. It is thought that this attempt was very useful to determine the dye penetration within the substrates with dyeing temperatures. Fig. 2 reveals that the photograph of indigo dyeing at 120 °C clearly shows the complete penetration of indigo molecules into the interior area of the substrates in full.

3.2. Effect of dyeing time

Having ascertained that dyeing was optimally achieved at a temperature of around 120 °C, a further set of experiments examined the effect of dyeing time on the color strength of indigo dyeings. The result displayed in Fig. 3 shows that the color strength (K/S value at 610 nm) of dyeings gradually decreased with increasing dyeing time. It is proposed that the structural changes of indigo molecules within the dyed substrates were responsible for the observed decreasing color strength. To confirm this understanding HPLC analysis was followed. In order to investigate the indigo moieties, an extraction using *N*,*N*-dimethylformamide (DMF) was conducted to strip indigo moieties from the dyed samples. Typical HPLC chromatograms of indigo and its moieties are shown in Fig. 4. The corresponding chemical structures of indigo moieties with retention times (4.4 min at 506 nm and 5.9 min at 478 nm) have not been determined yet. However, these changes resulted in arising other adsorption peaks such as 506 and

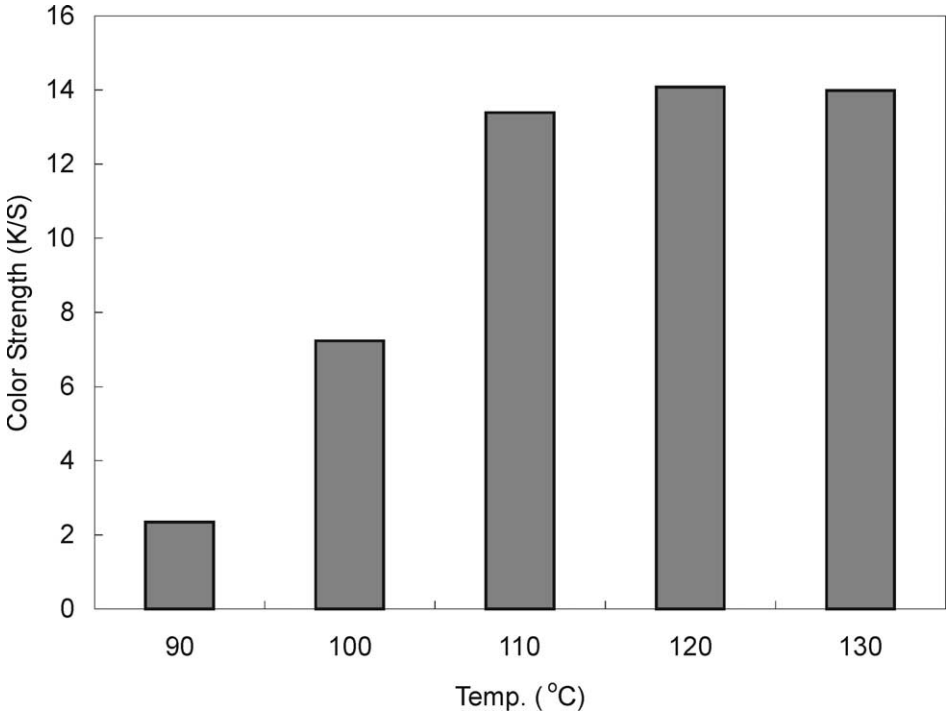

Fig. 1. Effect of dyeing temperatures on color strength of dyeings.

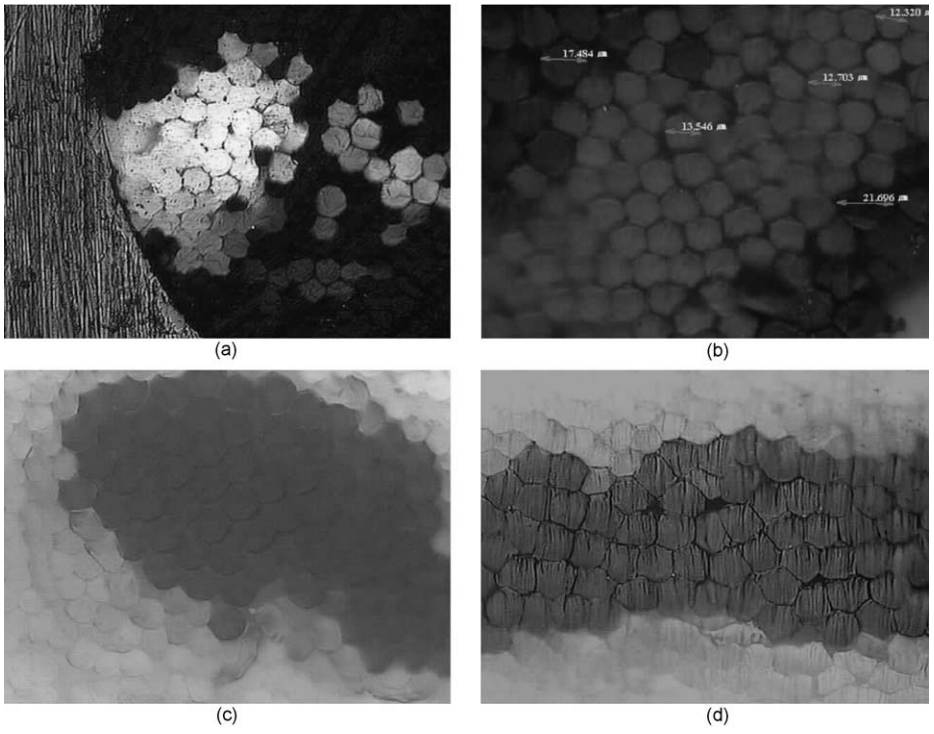

Fig. 2. Cross-sectional photographs of dyed polyester fibers: (a) 90 °C; (b) 100 °C; (c) 110 °C; (d) 120 °C.

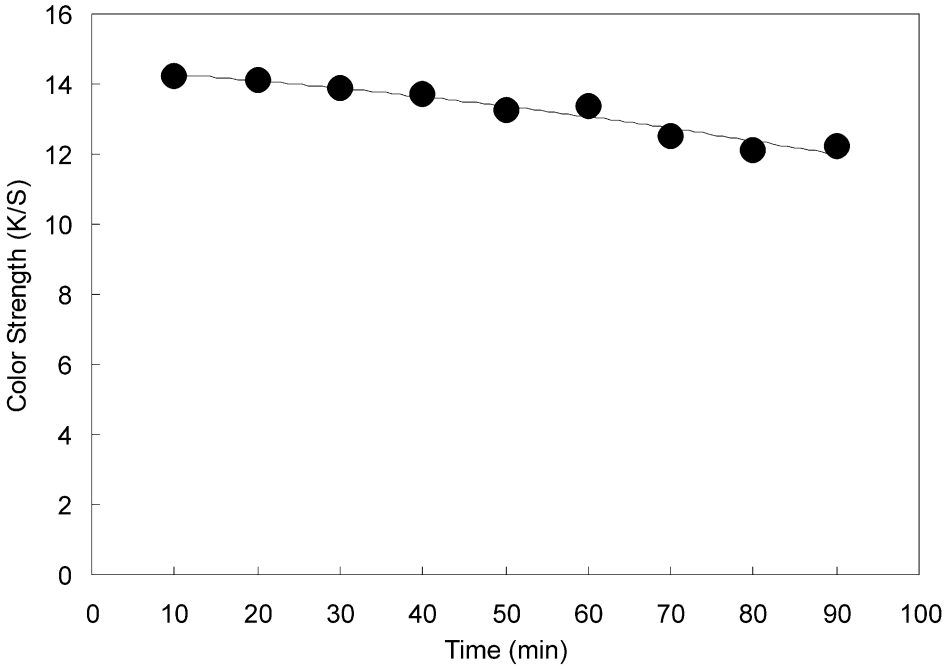

Fig. 3. Effect of dyeing time on color strength (K/S at 610 nm) of dyeings.

478 nm. In addition, Fig. 5 shows the area of peaks obtained HPLC analysis that with regards dyeing time, the original component of indigo at 610 nm gradually decreased with increasing dyeing time. At the same time, other two peaks were gradually observed at 506 and 478 nm. The area of these two peaks increased with increasing time. In this context, it is proposed that as dyeing was proceeded, two components, namely the moieties of red color at 506 nm and orange color at 478 nm, were converted from original indigo molecules and the corresponding these structural changes were attributed to the reduction in color strength (K/S value at 610 nm) of dyed samples.

3.3. A comparison of the leuco dyeing method and the indigo dispersion method

A comparison of the indigo dyeing properties using leuco dyeing method and indigo dispersion method was examined. Leuco dyeing was followed by the method described above. In the case of indigo dispersion method, the dyeing system using a commercial sample of indigo was conducted by the way used in the similar manner of disperse dyes to dye polyester fiber. Furthermore, to improve dispersibility of the indigo particles the milling process was carried out to decrease the particle size distribution of indigo. Fig. 6 shows the density distribution of indigo particle size, where it is confirmed that the particle size of indigo was decreased by milling process. It could be expected from Fig. 6 that a smaller particle size of indigo could provide the improved dispersibility, compared to the initial size of a commercial indigo as received. Table 1 represents that although the reduction in particle size of indigo could improve dispersibility, both dispersion methods of the indigo had little influence on increasing the color strength of dyeings whereas the leuco method was able to impart a satisfactory color yield to the polyester fibers.

3.4. Effect of acid leuco dyeing

Another aspect was considered that vat dyes could be applied to the substrates using the acid leuco technique. It has been reported [3] that the

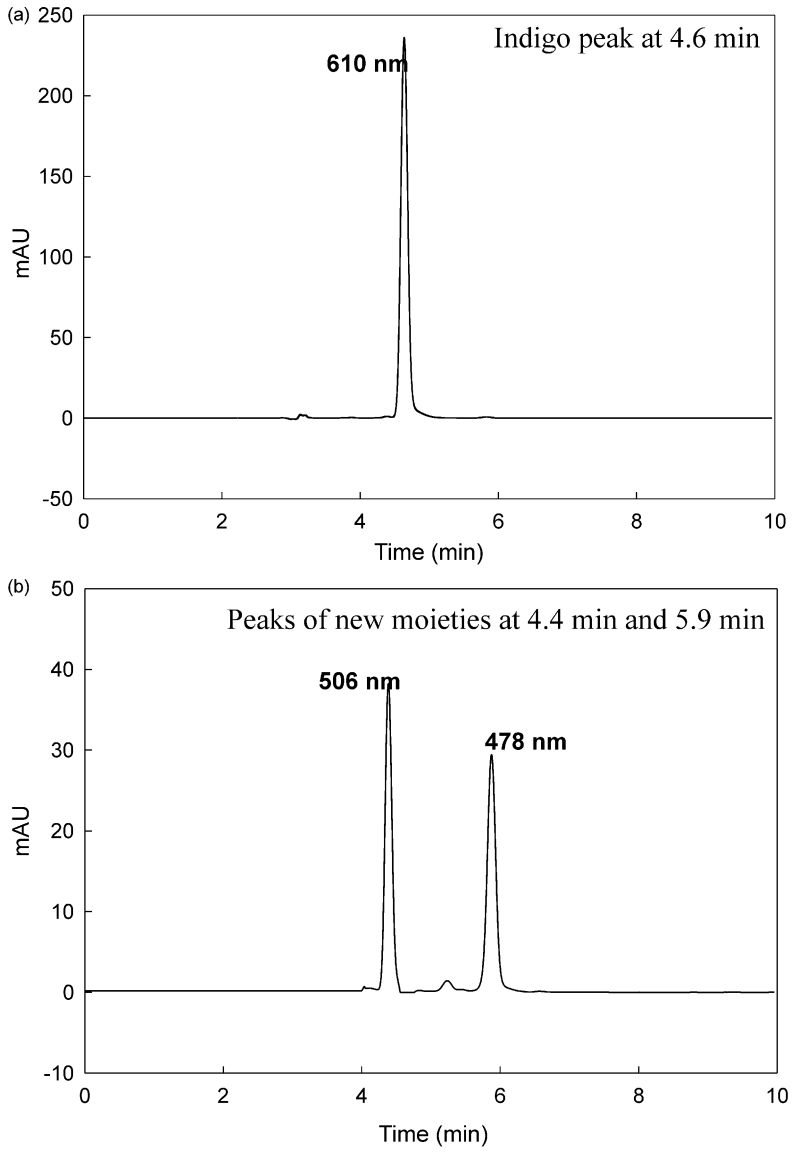

Fig. 4. HPLC chromatograms of indigo and its moieties.

acid leuco compound of vat dyes have considerable affinity for cellulose acetate and may be similarly applied to the synthetic fibers as disperse dye. This acid leuco moiety shows a sparingly soluble characteristic. In this context, the acid leuco form of indigo was applied to polyester fiber and its build-up effect was investigated. Table 2 shows that when compared with alkali leuco dyeing, satisfactory color strengths of the dyeings were obtained by acid leuco form except for a pH of 2.85, which was a similar result from the leuco dyeing in the normal manner. As a result of this behavior, it is proposed that the both leuco forms of indigo, namely alkali and acid leuco, could exist a monomolecular form in the dye bath and easily diffuse into the substrates. In other words, the intermolecular hydrogen bondings of indigo molecules in the oxidized pigment form were

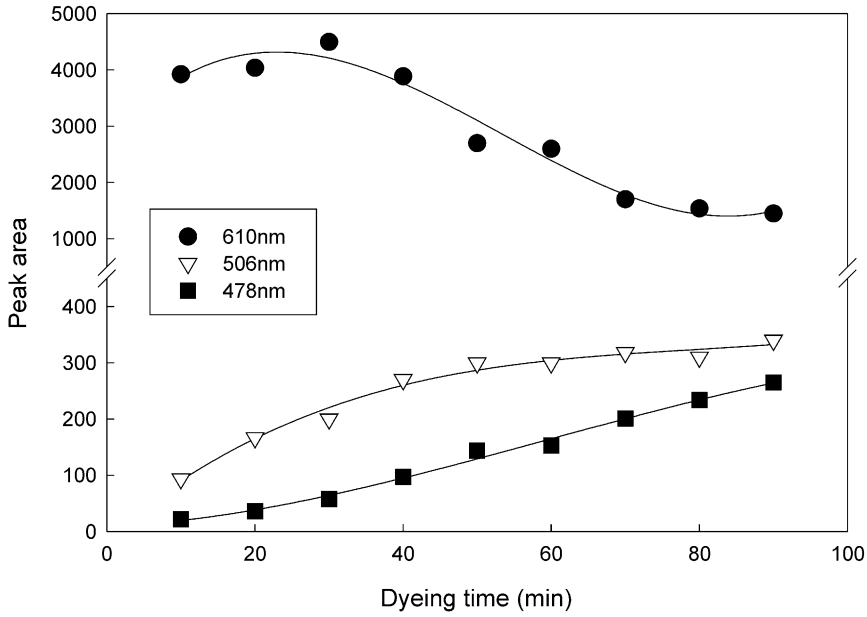

Fig. 5. Peak areas of indigo moieties extracted from dyed polyester fibers.

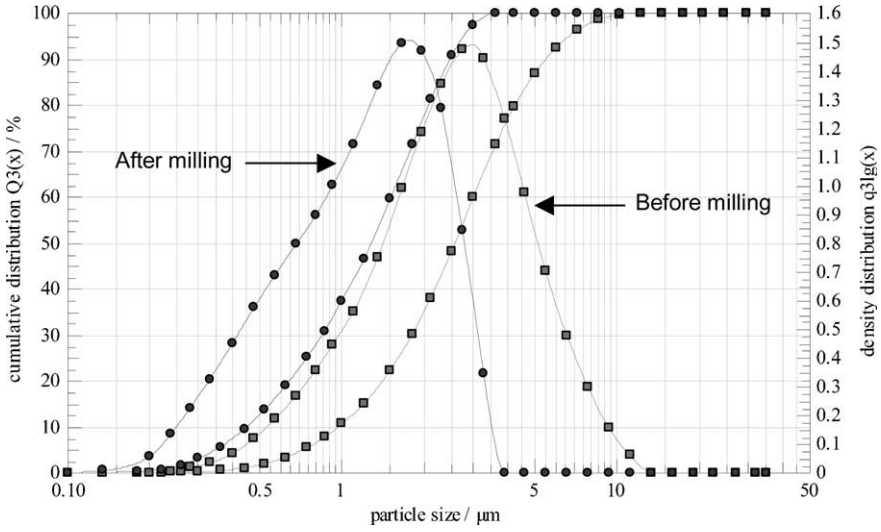

Fig. 6. Effect of milling process for particle size distribution of indigo.

greatly diminished due to being reduced and solubilized during the vatting procedure. The dependency of the dyeability can be explained by the structural form and size of indigo molecule in the dye bath and its corresponding diffusional power into the substrates.

3.5. Wash fastness

The wash fastness test of dyed samples with the indigo and the disperse dyes, having a similar color depth of shade, was carried out. The sample of disperse dyeing was prepared using color

Table 1
Comparison of colorimetric data of leuco dyeing and indigo dispersion dyeing

Dyeing methods	L^*	a^*	b^*	C	h°	fk
Disperse method						
Before milling	73.14	−0.40	−22.57	22.57	268.98	7.69
After milling	75.58	−3.25	−20.85	21.11	261.15	6.38
Leuco method	24.79	0.51	−12.58	12.59	272.33	265.29

Table 2
Colorimetric data for alkali leuco and acid leuco dyeings

pH of acid leuco	L^*	a^*	b^*	C	h°	K/S
2.85	40.52	−1.51	−12.95	13.04	263.34	6.07
4	25.2	−0.23	−11.27	11.27	268.84	13.59
5	25.44	0.09	−12.73	12.73	270.42	13.72
6	26.84	−0.85	−15.03	15.06	266.77	13.59
Alkali leuco	25.03	0.81	−13.51	13.54	273.42	13.94

Table 3
Colorimetric data of dyeings with indigo and disperse dyes

	L^*	a^*	b^*	C	H	fk
Indigo dyeing	26.44	5.03	−13.73	14.63	290.13	237.15
Disperse dyeing	26.23	2.86	−14.47	14.75	281.20	236.75

matching system to achieve a similar depth of shade with indigo dyed sample. Table 3 displays the colorimetric data of both dyeings using indigo and disperse dyes. It is evident that when compared to the colorimetric data of both samples, virtually a similar color strength value (fk) was obtained by the dyeing of disperse dyes. Thus, these two samples are appropriate for the comparison of wash tests. After wash tests, extraction of the samples with each washing using DMF was conducted and then the absorbance measurements were undertaken to determine the extent of the reduction of dyes in the substrates (unwashed and washed samples). The result was shown in Fig. 7 that in the case of disperse dyeing the extent of the reduction percentage of dyes increased with increasing number of washes, which showing that dye loss occurred in a progressive manner during wash tests. Due to an insoluble characteristic of indigo, clearly dyeing prepared by indigo was more effective in the reduction of dye loss than that of disperse dyeing. The corresponding assessments of the extent of staining to the adjacent mulifiber strip after five wash tests (Table 4) support the findings displayed in Fig. 7. Table 4 shows that the indigo dyeing displayed very good fastness properties to the five multiple washes in term of shade change and that very little staining to the adjacent multifiber strip occurred. This result can be also attributed to the insolubility of the indigo characteristics.

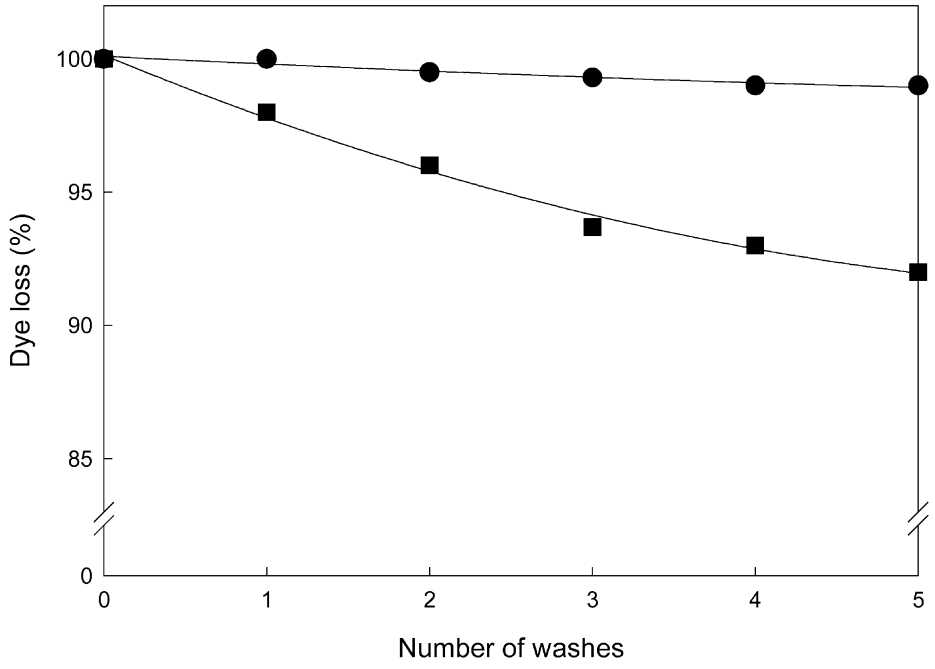

Fig. 7. Effect of repeated wash tests on dye loss of dyeings: ● Indigo; ■ disperse dyes.

Table 4
Staining assessments for indigo and disperse dyeing on polyester fiber

	Washes	Change in color	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Indigo dyeing								
	1	–	5	5	4–5	5	5	5
	2	–	5	5	4–5	5	5	5
	3	–	5	5	4–5	5	5	5
	4	–	5	5	5	5	5	5
	5	4–5	5	5	5	5	5	5
Disperse dyeing								
	1	–	3–4	4–5	3–4	3–4	4–5	4
	2	–	4	4–5	4	4	4–5	4–5
	3	–	4–5	5	4	4	5	4–5
	4	–	4–5	5	4	4	5	4–5
	5	4–5	5	5	5	5	5	5

4. Conclusions

For the indigo used, the color strength of the dyeings generally increased with increasing application temperatures. The observation that the color strength of indigo dyeing increased with increasing application temperatures could be attributed to the higher kinetic energy of the indigo molecules, the greater diffusional power within the polymer substrates and the higher fiber swelling effect. In the case of the effect of dyeing time, the color strength (K/S value at 610 nm) of

dyeing gradually decreased with increasing dyeing time. It is proposed that the structural changes of indigo molecules within the dyed substrates were responsible for the observed decreasing color strength. Dispersion methods of the indigo had little influence on increasing the color strength of dyeings whereas the leuco method was able to impart a satisfactory color yield to the polyester fibers. When compared with alkali leuco dyeing, satisfactory color strengths of the dyeings were obtained by acid leuco form. For wash fastness tests, indigo dyeings displayed very good fastness properties to the five multiple washes in term of shade change and very little staining to the adjacent multifiber strip occurred.

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