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Effect of Direct Dyes on the UV Protection Property of 100 % Cotton Knitted Fabric

Chi-wai Kan* and Chui-ha Au

Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong
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Abstract: In this study, 100 % cotton knitted fabrics were dyed with direct dye with different colour depths. The colour properties such as CIE $L^*a^*b^*$ values as well as dyeing levelness of the dyed fabrics were measured. The relationship between colour properties and the ultraviolet (UV) protection property were investigated. Experimental results revealed that the colour depth and dye concentration are the most important factors influencing the UV protection property of cotton knitted fabrics. In addition, only CIE L^* values have a significant relationship with UV protection factor (UPF). The CIE a^* and CIE b^* values did not have significant correlation with UPF values but the dyeing levelness would affect the UV protection property of coloured 100 % cotton knitted fabric.

Keywords: Direct dye, Dyeing, UV protection, Cotton fabric, UV protection factor

Introduction

The prevention of ultraviolet (UV) radiation damage has become more important issue in recent years because UV radiation has detrimental effects on human skin [1-3]. Researches prove that ultraviolet radiation (UVR) from the sun could be one of the primary causes of skin cancer [4,5] including both non-melanoma and melanoma skin cancers [6]. Therefore, an adequate level of sun protection is required and clothing has long been considered as a valuable mean of protection against ultraviolet (UV) radiation [7]. UV protective property of clothing materials depends on many factors and factors which are most frequently cited are fibre composition, fabric construction, fabric cover factors, dye and finishes on fabrics [8-10]. However, most of the studies have concentrated on the fabric parameters with woven fabrics only, whereas there have been few studies concerning knitted fabrics. In this study, direct dye will be used with different dye concentrations for dyeing 100 % cotton knitted fabrics. After dyeing, the colour properties such as CIE $L^*a^*b^*$ as well as dyeing levelness will be measured. The main focus of this paper is to study the relationship between colour properties and the UPF of dyed cotton knitted fabrics will be investigated.

Experimental

Materials

Circular knitting machine (DXC Fukuhara) with gauge number 20 was used for making 100 % plain cotton knitted fabrics using yarns with yarn count Ne20 (yarns were provided by Central Textiles (H.K.) Ltd.). Fabric specifications were shown in Table 1. The major difference between Fabric 1 and Fabric 2 is the type of cotton fibre used.

Combined Scouring and Bleaching of Cotton Knitted Fabric

The fabrics were scoured and bleached by hydrogen peroxide 50 % (12 m*l*/*l*), detergent Sandopan DTC (0.5 g/*l*) (supplied by Clariant), sodium silicate (0.5 g/*l*), stabilizer AWN (0.5 g/*l*) (supplied by Clariant) and add sodium hydroxide (10 g/*l*) to the liquor until the pH reached 10. The fabrics were scoured and bleached in the bath at boil for 60 minutes. The liquor ratio was 50:1. After scouring and bleaching, the fabrics were rinsed thoroughly with hot water first then cold water. Finally, the fabrics were neutralized with cold dilute sulphuric acid solution (0.5 %). The samples were rinsed again with tap water, until they were free from acid and air dry. After scouring and bleaching, the fabrics were subjected to a standard conditioning environment (relative humidity: 65±2 % and 20±2 °C) for 24 hours prior to use.

Direct Dye Dyeing

Direct dyes (three primary colours, i.e. red, yellow and blue) were supplied by Clariant, Hong Kong. All dyes were used as received without further purification. In addition, mixture of dye was carried out to investigate their effect of UV protection. The dye specifications were listed in Table 2.

The dyeing process was carried out in an oscillating sampling machine (Tung Shing Dyeing Machines Factory Ltd., Hong Kong, China). Dyebath was prepared based on liquor-to-goods ratio of 100:1 and 1 g cotton knitted fabric was used for dyeing. Auxiliaries that used for dyeing different direct dye colour depths (represented by dye concentration of 0.1 %, 1.0 % and 5.0 % on-weight of fabric (owf)) and the dyeing condition were illustrated in Table 3 and Figure 1 respectively. Initially, the temperature of dyebath was kept at a temperature of 40 °C for 10 minutes after the addition of fabric and sodium sulphate. The direct dye was then added to the dyebath which was maintained at 40 °C for further

*Corresponding author: tccwk@polyu.edu.hk

Table 1. Specifications of the fabrics

Sample code	Fibre type	Yarn count	Weight (g/m^2)	Thickness (mm)	Courses per inch (CPI)	Wales per inch (WPI)
Fabric 1	Combed cotton	Ne20	180.0	0.82	35	30
Fabric 2	Combed supima cotton		157.5	0.94	33	28

Table 2. Dye specifications

Colour	Dye used	Ratio	Sample code
Red	Indosol Rubinole SF-RGN	1	D-R
Yellow	Indosol Yellow SF-2RL	1	D-Y
Blue	Indosol Blue SF-2G 400	1	D-B
Green	Indosol Blue SF-2G 400 + Indosol Yellow SF-2RL	1:1	D-G
Orange	Indosol Yellow SF-2RL + Indosol Rubinole SF-RGN	1:1	D-O
Purple	Indosol Blue SF-2G 400 + Indosol Rubinole SF-RGN	1:1	D-P
Black	Indosol Blue SF-2G 400 + Indosol Yellow SF-2RL + Indosol Rubinole SF-RGN	1:1:1	D-Bk

Table 3. Auxiliaries that used for dyeing different direct dye concentrations

Dye concentration (%)	Sodium sulphate (g/*l*)	
	1st addition	2nd addition
0.1	2.5	2.5
1	7.5	7.5
5	15	15

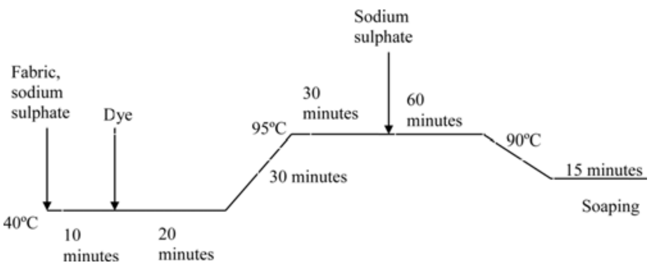

Figure 1. Dyeing condition of direct dye.

20 minutes. Afterward, the dyebath temperature was increased to 95 °C within 30 minutes. Sodium sulphate was added after 30 minutes when the dyebath temperature reached 95 °C. After adding the sodium sulphate, the dyebath was run for further 60 minutes and then washed off with running water. Finally, soaping with detergent (Sandopan DTC, 2 g/*l*) was conducted for 15 minutes at 90 °C. Samples were dried by air. All samples were subjected to a standard conditioning environment (relative humidity: 65±2 % and 20±2 °C) for 24 hours prior to further evaluation. In addition, a blank dyeing without dye was carried out for comparison purpose.

UPF Measurement

UV properties of fabrics were evaluated by the Australian/New Zealand standard (AS/NZS 4399) with a Varian Cary 300 Conc UV-visible spectrometer. The UV protection properties in terms of UV protection factor (UPF) and UV ray transmittance were measured by the spectrophotometer. Fabrics (size: 22×34 mm) were cut out from the middle of each piece of fabric. These fabrics were then mounted, without tension, on the slide frames for measurement. The UV spectrophotometer recorded the transmittance between 290 nm and 400 nm at every 5 nm. For each fabric sample, four measurements were taken and the mean UPF was calculated according to equation (1) [11]. Table 4 shows the classification system of good sun protection according to AS/NZS 4399.

Table 4. AS/NZS 4399 UPF classification system

UPF range	UVR protection category	Effective UVR transmission (%)
15-24	Good protection	6.7-4.2
25-39	Very good protection	4.1-2.6
40-50, 50+	Excellent protection	<2.5

$$UPF = \frac{\sum_{290}^{400} E_\lambda \cdot S_\lambda \cdot \Delta_\lambda}{\sum_{290}^{400} E_\lambda \cdot S_\lambda \cdot T_\lambda \cdot \Delta_\lambda} \quad (1)$$

where

S_λ is the solar spectral irradiance (in $Wm^{-2}Nm^{-1}$),
E_λ is the erythemal spectral effectiveness from CIE 1987,
T_λ is the spectral transmission through the textile,
Δ_λ is the bandwidth (in nm),
λ is the wavelength (in nm).

CIE $L^*a^*b^*$ Measurement

Colour appearance in terms of CIE $L^*a^*b^*$ values were measured by Macbeth CE-7000A spectrophotometer. Colours are represented by L^*, a^* and b^* coordinates where L^* represents

Table 5. Suggested interpretations of RUI values [12]

RUI	Visual appearance of levelness
<0.2	Excellent levelness
0.2-0.49	Good levelness
0.5-1.0	Poor levelness
>1.0	Bad levelness

lightness (from 0 (black) to 100 (white)), a^* represents red-green (positive a^*=red, negative a^*=green) and b^* yellow-blue (positive b^*=yellow, negative b^*=blue). The a^* and b^* coordinates are close to zero for neutral colours such as white, black or grey while more saturated colors have higher a^* and b^* coordinates.

Dyeing Levelness

Relative unevenness index (RUI) [12] was found by measuring colour reflectance values at 8 random locations on the sample by reflectance spectrophotometer (Macbeth Color-Eye 7000A) with illuminant D65 and 10 ^{o} standard observer spectrophotometer with D65 Illuminant and 10 ^{o} standard observer from 400 nm to 700 nm with 20 nm interval. RUI of the colored sample was calculated by equations (2) and (3).

$$S_\lambda = \sqrt{\frac{\sum_{i=1}^{n}(R_i - R_m)^2}{n-1}} \tag{2}$$

where S_λ is standard deviation of reflectance values, R_i is reflectance value of the ith measurement for each wavelength and R_m is mean of reflectance values of n measurements for each wavelength.

$$RUI = \sum_{400}^{700} C_\lambda V_\lambda = \sum_{400}^{700} \frac{S_\lambda}{R} V_\lambda \tag{3}$$

where C_λ is the coefficient of variation of reflectance values measured for each wavelength for 400-700 nm and V_λ is photopic relative luminous efficiency function.

The degree of evenness is described according to the RUI value obtained; suggested interpretations of RUI values are shown in Table 5 [12].

Air Permeability Measurement

The air permeability was evaluated by KES-F8-AP1 air permeability tester. The testing result, expressed as air resistance (R), was recorded in kPa-s/m, in which a greater value of R indicates a poorer air permeability of the fabrics. The sample size used in this test was 10 cm×10 cm. 10 specimens were tested and the average values were reported.

Results and Discussion

Relationship between Colour Depth and UPF

All dyes have the ability to absorb visible light but some of them could even absorb UV rays in the near ultraviolet region. The structure of dye molecules play an important role regarding to the UV blocking ability. Moreover, the type of dyes, present of absorptive groups, depth of dyeing and the uniformity are also affecting the UV blocking ability of the dyes [13,14]. Therefore, previous research [15] confirmed that direct dye could substantially increase UPF of bleach woven fabrics but there is limited research on the UV properties of direct dyed cotton knitted fabrics. Therefore, this study is continuously investigating the influence of direct dyed fabrics on UPF values.

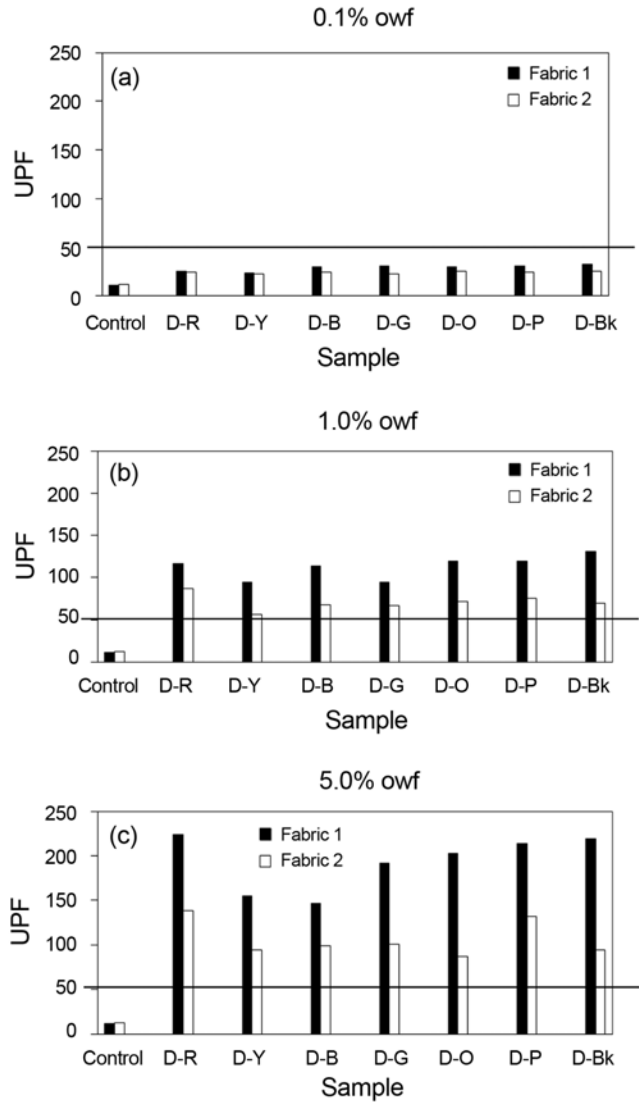

Figure 2. UPF results of direct dyed fabrics.

The results of UPF measurements of direct dyed colour fabrics with three colour depths are shown in Figure 2. The UPF result of direct dyed colour fabrics also shows that colour has significant effect on UV protection. The UPF values of the control samples are around 11-13 (<15) which mean undyed fabrics do not posses any UV protection ability. Once colouration of the same fabrics carried out with the use of direct dye, there is a remarkable increase in UPF values. The result shows that the application of any colour of dye at any one of the concentration produces an improvement of the UPF of the cotton knitted fabrics. Thus, the colouration is an efficient way to increase the ultraviolet protection of fabric. The coloured fabrics demonstrates that they could offer good (≥15) at 0.1 % owf dye concentration, shows in Figure 2(a) and excellent (≥50+) UV protection at 1 % and 5 % owf dye concentration, which shows in Figures 2(b) and 2(c). There is a noticeable increase in the UPF values and nearly all the fabric samples could obtained UPF values of 50+ which means excellent protection category. The extent of improvement in the UPF value is due good penetration and higher diffusion ability of direct dye contributes to the high UPF results. During dyeing process, direct dye aggregates and then broken down progressively to single molecules. Thus, those single molecules could penetrate into the microspores of the cellulose fibres [16]. The excellent dye affinity and uptake enable dye absorb ultraviolet radiation in the visible and UV radiation band. Dye reacts like additives to the fabric and improve UV protection abilities as they blocks UV transmission through a fabric to skin [15].

Figure 3 shows the spectra of diffuse transmittance in the UV region for the seven studied direct dyes. D-R and D-Bk get the lowest transmission in the UVB and UVA region where mean these two dyes got higher light absorption ability in UV region, as the result D-R and D-Bk get the high UPF value (50+). D-B and D-Y got the highest transmission in UVB and UVA region respectively, which means weak UV blocking properties. The results in this study confirmed Srinivasan and Gatewood study [7]. Their results showed that colour is not a reliable indicator of the UV protection of the dyed fabrics. They reported that direct dye black does not necessarily provide the best UV protection. Nevertheless, other dyes such as direct dye red, blue, green and brown may increase the UV protection depending on their absorption

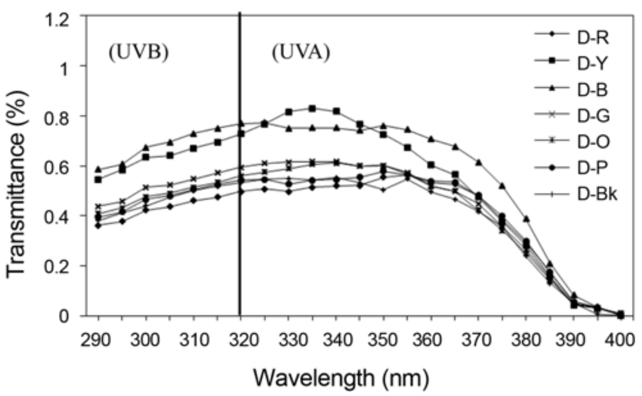

Figure 3. The spectra of diffuse transmittance in the UV region for the direct dyes at 5 % owf.

characteristics in the UV region. Therefore, a more professional coloristic parameters (CIE $L^*a^*b^*$) were used to describe the colour of fabric and their correlation with UPF in the next section.

When the fibre type is taken into consideration, generally speaking, if the UPF is compared in dry and undyed state, combed supima cotton yarn provides a better UPF rating than combed cotton yarn when using the same spinning method [17]. However, in this study, after dyeing, the UPF of dyed knitted fabrics made from combed supima cotton is generally worse than the combed cotton and the results are opposite to undyed knitted fabrics as shown in Figure 2. Since combed cotton is short staple fibre while combed supima cotton is long and fine staple fibre, during dyeing, the short staple fibre will migrate easier than the long staple fibre to the yarn surface. As a result, knitted fabrics made from combed cotton fibre (short staple fibre) will have more short fibres in the fabric surface which may block or absorb the UV radiation so that a better UV protection property could be achieved.

Relationship of Colour Values and UPF

The influence of colour values CIE $L^*a^*b^*$ on UPF values of direct dyed fabric was investigated and illustrates in Table 6. The correlation coefficients Rxy shows the relationship of UPF values and the individual values of CIE L^*, CIE $a^*$and CIE b^* values. The CIE L^* value has a better mathematical relationship with UPF than CIE $a^*$and CIE b^* values. The CIE L^* value and the UPF is a highly negative correlation. The correlation coefficients Rxy of Fabric 1 is -0.80 and Rxy of Fabric 2 -0.78. Moreover, Table 6 also shows that is a correlation of CIE a^* value and the UPF value but the correlation relationship is not as strong as CIE L^* value. The correlation coefficients of CIE a^* value and the UPF are positively correlated, Rxy of Fabric 1 is 0.21 and Rxy of Fabric 2 is 0.25. However, the correlation of CIE b^* and the UPF value is obviously very week and on the average is 0.0 (Fabric 2) to -0.05 (Fabric 2). In this study for both reactive and direct dyed fabric samples, only CIE L^* value can be direct mathematically related with UV protection factor. Moreover, CIE a^* and CIE b^* values do not have significant correlation with UPF values. It is because colour itself is not a reliable indicator of the UV protection of the dyed fabrics but colour depth is the most important variable affecting transmittance [18]. Generally speaking, people believe that blue was more effective block to orange. However, Gorensek and Sluga found that pale blue was shown to be less protective than pale orange which was in turn less protective than dark blue [19]. From this case, colour/hue is not a reliable indicator of UV blocking properties of a dyestuff but colour depth do, thus CIE L^* value has a high correlation with UPF but CIE a^* and CIE b^* do not have a significant correlation with UPF.

Table 6. The CIE $L^*a^*b^*$ values and UPF of direct dyed fabrics

Fibre type	Combed cotton - Fabric 1					Combed supima cotton - Fabric 2				
Code	Colour depth (%)	UPF	L^*	a^*	b^*	Code	UPF	L^*	a^*	b^*
Control	Undyed	11.24	90.50	-0.48	2.16	White	12.27	91.02	-0.47	2.27
D-R	0.1	25.03	65.80	31.16	-8.15	D-R	24.63	67.10	30.13	-8.25
	1.0	116.79	40.20	38.47	-7.32		87.14	40.80	38.56	-7.43
	5.0	223.98	27.30	32.08	-5.24		138.61	28.80	32.98	-5.26
D-Y	0.1	23.71	85.30	-1.78	41.67	D-Y	22.46	85.90	-1.96	41.32
	1.0	94.42	78.20	11.42	72.44		56.58	79.70	10.24	71.35
	5.0	154.90	72.80	23.27	82.91		94.02	73.80	22.17	82.46
D-B	0.1	29.95	62.80	-12.12	-16.95	D-B	24.18	64.00	-11.75	-16.55
	1.0	113.46	36.80	-9.58	-18.09		68.13	36.80	-10.15	-19.15
	5.0	146.56	25.30	-6.45	-14.92		99.09	26.10	-6.41	-14.88
D-G	0.1	30.48	68.70	-16.94	6.09	D-G	23.02	69.00	-16.16	5.66
	1.0	94.58	44.20	-19.71	6.00		66.65	45.40	-19.71	6.05
	5.0	191.82	31.20	-15.70	8.95		100.89	31.20	-15.48	8.90
D-O	0.1	29.98	72.30	19.24	12.80	D-O	25.35	72.70	19.30	12.80
	1.0	119.16	47.20	32.73	16.08		71.62	48.70	32.68	16.14
	5.0	202.29	34.40	32.46	20.04		87.19	35.10	32.84	19.94
D-P	0.1	30.77	61.90	4.30	-16.75	D-P	24.08	62.70	4.31	-16.82
	1.0	119.80	33.40	9.19	-20.30		75.14	34.70	9.31	-20.44
	5.0	213.37	22.10	6.46	-15.56		131.87	22.90	6.45	-15.32
D-Bk	0.1	32.88	66.50	-1.24	-1.73	D-Bk	25.45	68.10	-1.17	-1.67
	1.0	131.20	38.90	1.93	-4.17		69.73	40.60	0.66	-3.51
	5.0	219.25	25.40	1.01	-0.84		93.84	27.40	-0.65	-0.73
		Rxy	-0.80	0.21	0.00		Rxy	-0.78	0.25	-0.05

Relationship between Dyeing Levelness and UPF

Fabric with RUI value between 0.2-0.49 can be classified as good dyeing levelness [12], which means there is some noticeable unlevelness only under close examination. According to the suggested interpretation of RUI values [12], both Fabric 1 and Fabric 2 achieve good dyeing levelness. However, with the increase of colour depth, the dyeing levelness decreases because of the usual problem of dyeing, i.e. high risk of unlevel dyeing in high concentration of dye. It is noted that for colour produced by one dye, i.e. D-R, D-Y and D-B, the dyeing levelness is better than colour produced by two (D-G, D-O and D-P) and three (D-Bk) dyes. This is because with the use of more than one dye in dyeing, the rate of exhaustion of individual dye may be different which would lead to unlevel dyeing. Moreover, from Table 7, the mean RUI of Fabric 1 and Fabric 2 which dyed with reactive dye are maintaining at good dyeing levelness. From Table 7, the mean RUI of Fabric 1 and Fabric 2 which dyed with direct dye are 0.32 and 0.26 respectively which .

There is an interesting phenomenon was observed. The levelness of Fabric 2 is slightly better than Fabric 1. This can be explained by the nature of different cotton fibre used by Fabric 1 and Fabric 2. Fabric 1 is made of combed cotton and Fabric 2 is made of combed supima cotton respectively. The combed supima cotton yarn can absorb dye much better than combed cotton yarn due to its fineness as more fibres can be spun into a yarn of a given count which may enhance the dyeability of the fabric [20].

From Figure 4, when compared with Fabric 1 and Fabric 2, there was a positive correlation between the RUI and the UPF value for direct dyed samples as the R^2 values for Fabric 1 and Fabric 2 are 0.8028 and 0.6118 respectively [21]. This means the UPF values of direct dye coloured fabrics could be affected not only by dyes and dye concentration but also dyeing levelness.

Relationship between Air Permeability and UPF

Generally speaking, during dyeing, fabric may shrink which would cause reducing size of fabric voids and increasing in fabric cover factor. However, due to limited specimen size,

Table 7. Dyeing levelness of direct dyed samples

Fibre type	Combed cotton - Fabric 1		Combed supima cotton - Fabric 2	
Code	Depth of colour (%)	RUI	Code	RUI
D-R	0.1	0.17	D-R	0.12
	1.0	0.27		0.23
	5.0	0.36		0.30
D-Y	0.1	0.22	D-Y	0.16
	1.0	0.32		0.25
	5.0	0.39		0.30
D-B	0.1	0.20	D-B	0.14
	1.0	0.24		0.21
	5.0	0.39		0.30
D-G	0.1	0.25	D-G	0.20
	1.0	0.33		0.28
	5.0	0.41		0.35
D-O	0.1	0.25	D-O	0.21
	1.0	0.35		0.30
	5.0	0.41		0.36
D-P	0.1	0.24	D-P	0.22
	1.0	0.34		0.30
	5.0	0.42		0.36
D-Bk	0.1	0.27	D-Bk	0.24
	1.0	0.36		0.32
	5.0	0.45		0.40
	Mean RUI	0.32		0.26

air permeability is used as a measurement to the change in fabric structure. If poorer air permeability was obtained, a closely pack structure was obtained and this would imply that the UV transmission would be lowered. The air permeability between the undyed and blank dyed Fabric 1 are 0.19 and 0.20 respectively. In case of Fabric 2, the air permeability between the undyed and blank dyed Fabric 2 are 0.19 and 0.20 respectively. There is no significantly difference between the undyed and blank dyed fabrics in air permeability and it can reveal that the fabric structure changes are not serious.

In addition, the correlation between air permeability and UPF for Fabric 1 and Fabric 2 are 0.01 and 0.03 respectively. This relationship reveals that in case of direct dyes in this study, the fabric structure does not show strong correlation in affecting the UPF.

Conclusion

Colour is an important factor affecting in UPF rating. In this study, the relationship of knitted fabric colour shades and CIE $L^*a^*b^*$ values on UPF rating of direct dyestuffs were studied. The result shows that the colour depth and dye concentration are the most important factors for affecting the UV protection property of cotton knitted fabrics. In addition, only CIE L^* values have direct mathematical relationship with UV protection factor. The CIE a^* and CIE b^* values did not have significant relationship with UPF values. However, in case of direct dyes dyeing, the dyeing levelness of cotton knitted would have influence on the UV protection property.

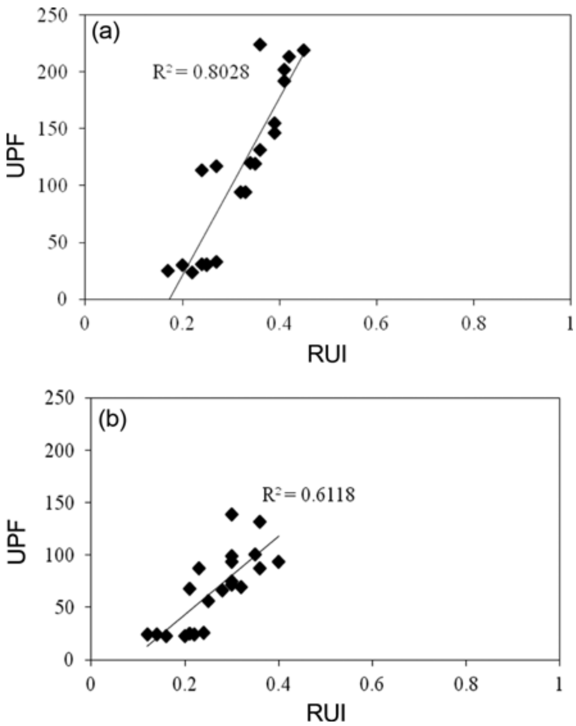

Figure 4. Correlation between dyeing levelness and UPF of direct dyed samples; (a) fabric 1 and (b) fabric 2.

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