

# Transfer Printing with Disperse Dyes on Cotton Fabric Modified with an Aqueous Tolylene Diisocyanate Derivative

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**Abstract:** Transfer printing with disperse dyes on cotton fabric modified with an aqueous tolylene diisocyanate derivative (TDD) was discussed in this paper. The effect of the degree of substitution (*DS*) on color strength (*K/S* value) of the modified and transfer printed fabric was investigated. The *DS* of the cotton fabric increased with increases in TDD concentration and curing temperature and time, while the sample whiteness decreased with the increasing curing temperature and time. And the change of structure of the modified cotton fabric was characterized by FT-IR spectra, DSC curves, and SEM images. All of the factors, such as the concentration and molecular weight of poly(ethylene glycol), the *DS* of the modified fabric, the transfer printing temperature and time would affect the *K/S* value of the sample. After transfer printing with disperse dye, the *K/S* value and printing fastness of TDD-modified cotton fabric were higher than those of cotton control fabric, the change of chromatic difference was not obvious, but the tensile strength of the modified fabric was lower than that of original cotton.

**Keywords:** Cotton fabric, Tolylene diisocyanate derivative, Modification, Transfer printing, Disperse dye

## Introduction

Printing of fabric can be defined as local coloration of fabric using a set pattern [1]. Because cotton fabric is more comfortable than synthetic fabrics, printed cotton fabric has an important place in textile markets. The output of printed cotton fabric is rapidly increasing, because of the possibility of generating layers of color and elaborate designs. Increasing awareness of environmental protection is also driving the search for new textile printing techniques that are environmentally friendly.

Ink-jet printing of cotton fabric has become possible with the development of digital jets [2,3]. Ink-jet printing is an environmentally friendly technique with many advantages, such as clear images and low dye consumption. However, current ink-jet technology for cotton fabric printing still suffers from low efficiency and the fabric needs to be washed after printing.

Transfer printing at low temperature has also been investigated. A reactive dye was first printed onto paper. Cotton fabric was pretreated using an exhausting agent and a fixation auxiliary and the pattern on paper was transferred to pretreated samples [4]. However, both the printing quality and efficiency were not very good and the printed fabric needed to be washed after printing.

Lewis, Broadbent, and co-workers synthesized a benzoyl thioglycolic acid and used it to modify cotton fabric. Investigation of the effect of the degree of substitution (*DS*) of benzoyl thioglycolic acid on *K/S* values revealed that it was possible to dye the modified cotton fabric with disperse

dyes [5-10].

Wang modified cotton fabric using a non-polar resin to realize thermal transfer printing on the fabric [11-13]. However, the moisture absorption capacity of the cotton fabric was much lower after modification due to the strong hydrophobicity of the resin.

In the present study, an aqueous tolylene diisocyanate derivative (TDD) was used to modify cotton fabric before transfer printing with disperse dyes. The CIELAB color values, color strength (*K/S* value), printing fastness, and relative whiteness of the modified cotton fabric with different *DS* values were measured under the different transfer printing condition to evaluate the possibility of transfer printing on TDD-modified cotton fabric.

## Experimental

### Materials

Scoured and bleached woven cotton fabric (150 g/m<sup>2</sup>) free of fluorescent brightener was used in all experiment. Transfer printing paper supplied by Longda Transfer Print Ltd. (Wuxi, China) was printed with three disperse dyes (Table 1). Poly(ethylene glycol) (PEG, molecular weight 200, 400, and 1000), tolylene diisocyanate (TDI), alcohol, sodium bicarbonate, sodium sulfate, and sodium bisulfite were obtained as AR grade materials from Kelong Chemical Reagent Company (Chengdu, China). The anionic softener was prepared as previously reported [14].

### Preparation of Tolylene Diisocyanate Derivative (TDD)

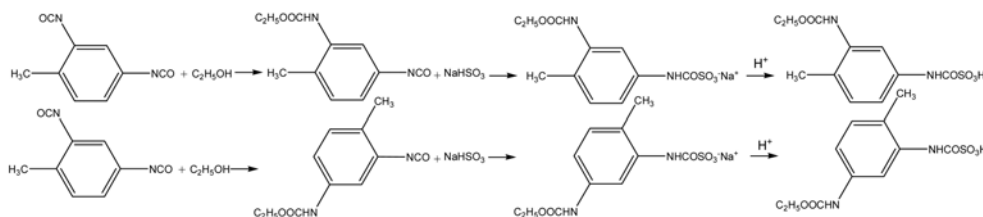
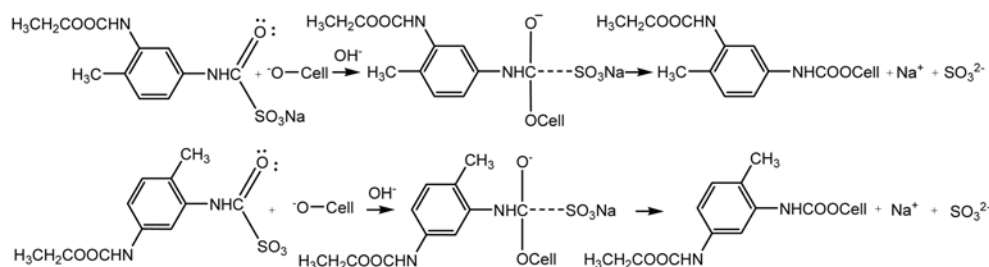
The water-soluble TDD was prepared by the reaction of tolylene diisocyanate (TDI), absolute alcohol, and sodium

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**Table 1.** Structure of the dyes used

Commercial name	CI generic name	Structure
Disperse Red E-4B	CI Disperse Red 60	
Disperse Yellow SE-3GE	CI Disperse Yellow 54	
Disperse Blue GL	CI Disperse Blue 60	

bisulfite at  $-5$ – $5$  °C [14,15] (Scheme 1). Toluene diisocyanate (0.2 mol) was added to cold absolute alcohol below  $0$  °C for 2 h. Ethyl acetate (0.2 ml) and the solution of water and isopropanol ( $V_{\text{H}_2\text{O}}/V_{\text{C}_3\text{H}_7\text{OH}}=1/1.5$ ) containing sodium sulfate (0.04 mol) and sodium bisulfite (0.22 mol) in water was rapidly added in the above reaction vessel with thorough stirring at former temperature for 20 min. And then, the reaction was allowed to proceed until a constant pH between 7 and 8 was obtained. Concentrated HCl (1 mol) was then gradually added to the solution to precipitate the TDD which were mixed 3-(ethoxycarbonylamino)-4-methylphenylamino formylsulfonic acid and 3-(ethoxycarbonylamino)-6-methylphenylamino formylsulfonic acid. The precipitate was collected, washed with water, dried, and then purified by recrystallization from

**Scheme 1.** Preparation of toluene diisocyanate derivative.**Scheme 2.** Reactions of TDD with cellulose.

toluene. The TDD yield was 71.6 % under optimum conditions.

### Modification of Cotton Fabric and Transfer Printing

The modifying reaction is presented in Scheme 2. The cotton fabric was padded with modifier solution using a laboratory pad mangle under the following conditions: room temperature, 80 % pickup, TDD concentration 50–300 g/l, sodium bicarbonate 2.5 g/l, and softener concentration 1.0 g/l. Then the padded fabric was pre-dried at  $80$  °C for 180 s, followed by curing at  $160$  °C for 100 s. The cotton was finally washed with 2 g/l non-ionic detergent (liquid ratio 20:1) at  $95$  °C for 15 min, then thoroughly rinsed and dried.

The modified cotton fabric was padded with PEG solution using a laboratory pad mangle under the following conditions: room temperature, liquid ratio 30:1, 80 % pickup, and PEG concentration 20 %. The fabric was then dried at  $80$  °C for 180 s. Transfer printing of the modified cotton fabric was carried out at  $220$  °C and 1.2 atm for 26 s. The printed fabric was then washed and in 2 g/l non-ionic detergent (liquid ratio 20:1) solution at  $95$  °C for 15 min, and finally thoroughly rinsed and dried.

### Degree of Substitution (DS) of Modified Cotton

Every glucose ring of cotton fiber contains three hydroxyl groups to be able to react with toluene diisocyanate derivative. So, the degree of substitution of modified cotton was used to denote the degree of modification of the three hydroxyl groups in glucose ring by TDD [9]. The weight gain for modified cotton fabric was measured and DS was calculated according to:

$$DS = \frac{3 \times \text{actual weight gain}}{\left(\frac{832}{172} \times \text{fabric weight}\right) - \text{fabric weight}} \quad (1)$$

where 832 is the molecular weight of the tri-modified anhydroglucoside residue and 172 is the molecular weight of the original anhydroglucose residue.

### Measurements

IR spectra of modified and untreated cotton were obtained on a Perkin-Elmer 1725 FTIR spectrophotometer using a diffuse reflectance DRIFTS attachment with KBr discs.

The thermal stability of modified cotton was measured in air by differential scanning calorimetry (DSC) using a CDR-4P Caloric Analysis instrument (Cary Precision Instruments). The following conditions were used: temperature range, 0-500 °C; scan rate, 10 °C/min; differential thermal compensation range, 120 mW; and sampling temperature, 0-475 °C [16].

An S-2150 scanning electron microscope (Hitachi, Ltd., Tokyo, Japan) was used for morphology observation of modified cotton fiber surface. Before scanning electron microscopy observation, the test specimens of modified cotton fiber surface were first cold-fractured in liquid nitrogen, and then the fractured surface of these specimens were coated with a thin layer of gold [17].

The reflectance of printed samples was measured by reflectance spectrophotometry (Spectra Flash SF600, Data Colour Co.) under a  $D_{65}$  illuminant using 10° standard observation. The color strength of printed samples was expressed as a  $K/S$  value calculated from the Kubelka-Munk equation. And CIELAB color difference between printed modified cotton fabric and original sample was also compared [18].

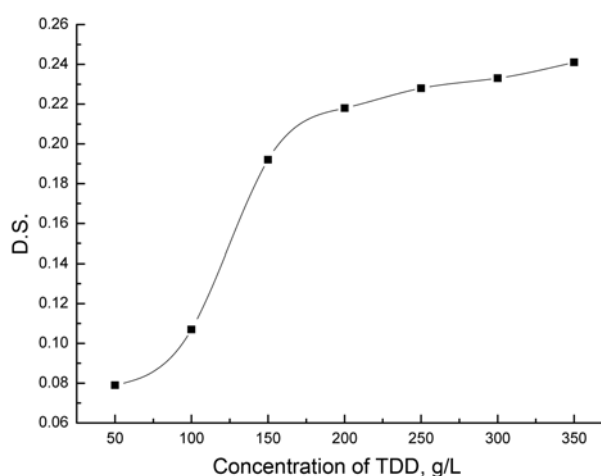
The relative whiteness of samples was tested according to ISO 105-J12 (1993). The tensile strength of modified and printed samples was tested according to ISO/DIS 13934.1-94. The rubbing fastness, washing fastness, and light fastness of printed samples were tested according to ISO 105-X12 (1993), ISO 150-C02 (1989), and ISO 150-B02 (1994), respectively [18].

## Results and Discussion

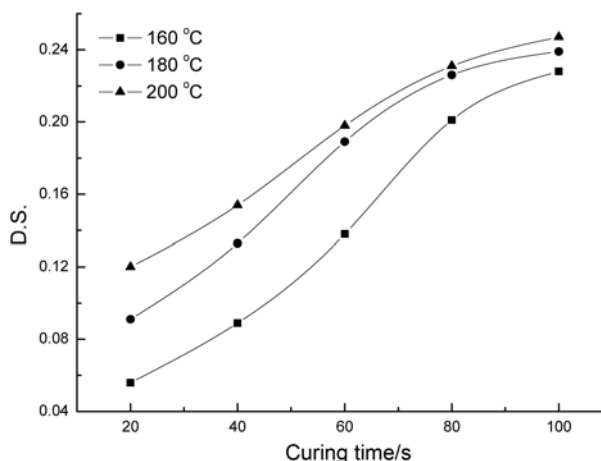
### Effect of TDD Concentration, Curing Temperature and Time on $DS$

Figure 1 showed that the  $DS$  of modified cotton fabric increased with the TDD concentration increasing in the pad liquor under the condition of curing temperature of 160 °C for 100 s. When TDD concentrations was over 200 g/l, the  $DS$  of modified cotton increased slowly with the TDD concentration. The  $DS$  curve indicated that TDD was a remarkably efficient modifying agent for cotton fabric under the treatment conditions used. The reaction between TDD and cellulose molecules took place less in the crystalline area of cellulose fiber. Thus, it was difficult to promote the  $DS$  furthermore after the TDD concentrations over 200 g/l.

Figure 2 demonstrated that higher curing temperature and longer curing time yielded higher  $DS$  value. A maximum  $DS$



**Figure 1.** Effect of TDD concentration on the degree of substitution of cotton fabric.



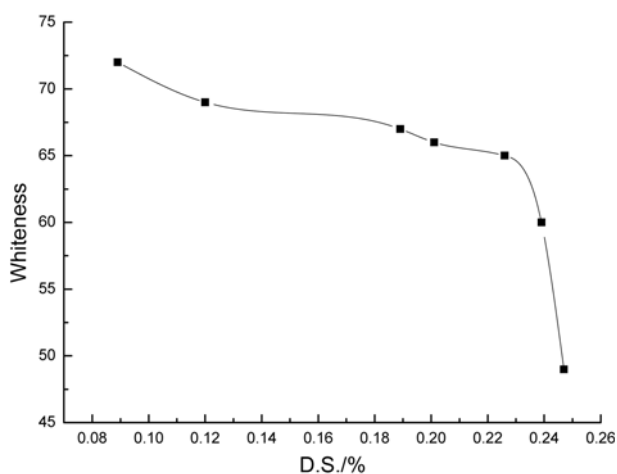
**Figure 2.** Effect of the curing time and temperature on the TDD degree of substitution (200 g/l TDD, 1 g/l softener) of cotton cellulose.

value of 0.241 % could be obtained in the experimental range.

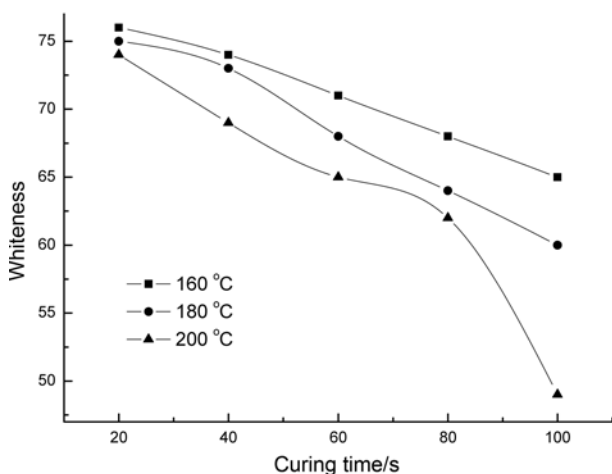
### The Characterization of the Modified Cotton Fabrics

The curve in Figure 3 showed that the whiteness of modified cotton decreased with the  $DS$  increasing. The data in Figure 4 indicated that the whiteness of modified fabric decreased with the increasing curing time and temperature. Higher curing temperature would accelerate the oxidation of cellulose fiber and result in the decreased whiteness of modified fabric.

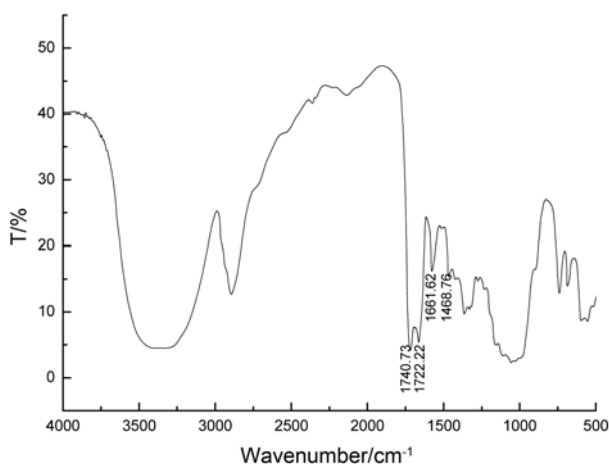
Two strong adsorption peaks at 1740.73 and 1722.22  $\text{cm}^{-1}$  appearing on the FT-IR spectrum of TDD-modified cotton in Figure 5 should be attributed to the stretching adsorption of carbonyl group in  $-\text{NHCOOCH}_3$  and  $-\text{NHCOO-Cell}$ , respectively. The adsorption peaks at 1661.62 and 1468.76  $\text{cm}^{-1}$  corresponded to the stretching vibration of carbon-



**Figure 3.** Effect of the degree of substitution on the whiteness of modified cotton fabric.



**Figure 4.** Effect of the curing time and temperature on the whiteness of modified cotton fabric.



**Figure 5.** IR spectrum of TDD-modified cotton.

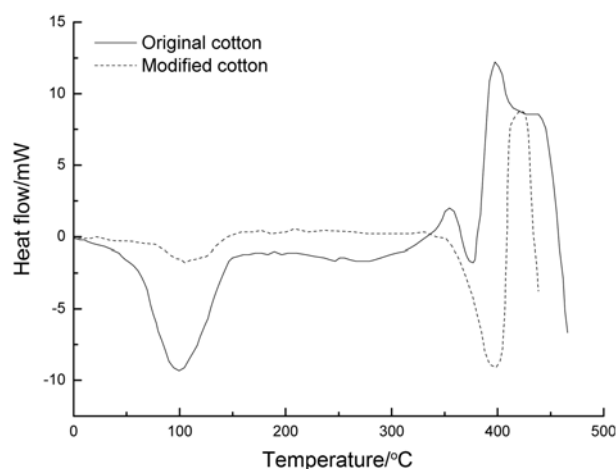
carbon double bond in benzene ring of TDD-modified cotton.

The endothermic peaks near 100 °C on the DSC curves of untreated and TDD-modified cotton fabric were associated with the removal of water from cellulose fiber. But the area of the endothermic peak near 100 °C on the DSC curve of TDD-modified cotton was smaller than that on the DSC curve of untreated cotton fabric, which indicated that the hydroxyl group on cellulose fiber was converted into -NHCOO-Cell by the reaction between TDD and cellulose and the hydrophobicity of the fabric increased after modification.

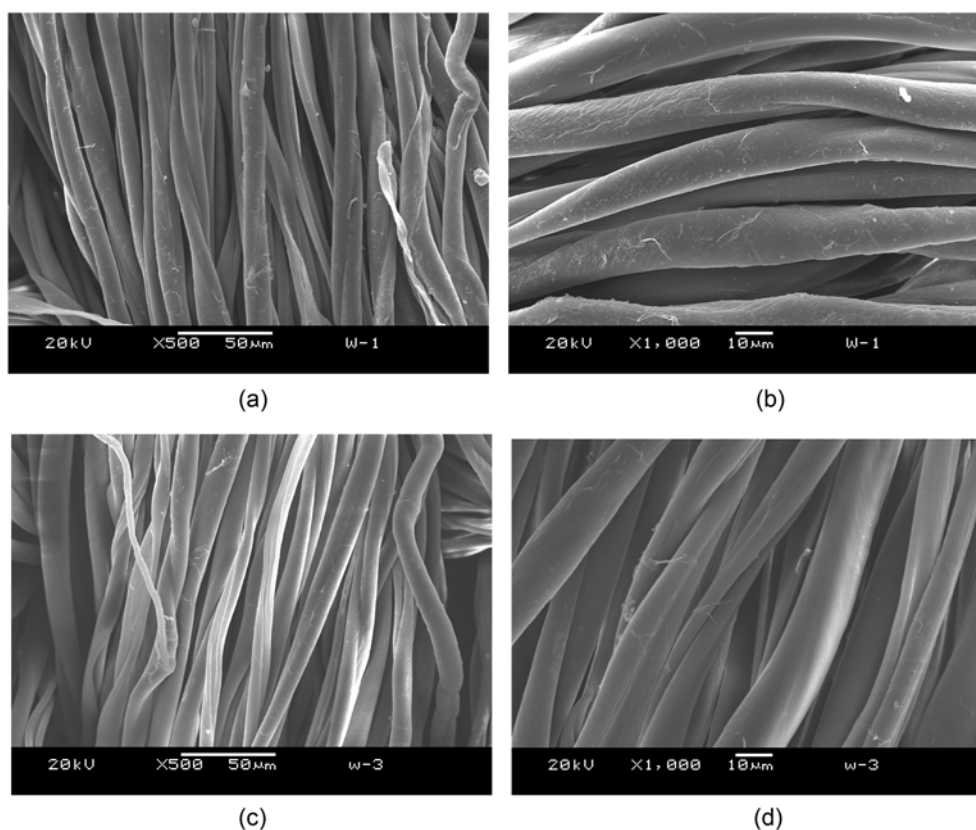
The DSC plot for untreated cotton contained exothermic peaks at 354 and 397 °C and an endothermic peak at 376 °C. And the corresponding DSC plot for TDD-modified cotton contained an endothermic peak at 398 °C and an exothermic peak at 432 °C (Figure 6).

The exothermic changes observed for cotton were associated with several decomposition processes within the fabric during heating. The exothermic peak at 354 °C on the DSC curve of untreated cotton was caused by cellulose macromolecules decomposed into laevoglucose at that temperature, then the laevoglucose decomposed into coke and smaller molecules such as CO<sub>2</sub>, while the exothermic peak at 397 °C on the DSC curve of untreated cotton showed that the coke was oxidized further into CO<sub>2</sub> or secondary coke under the high temperature. The endothermic peaks for both untreated and TDD-modified cotton fabric are possibly due to local changes in the crystalline regions of natural cotton or breakdown of hydrophobic interactions in TDD-modified cotton on heating. The endothermic peak of modified cotton shifted to 398 °C, it seemed that the hydroxyl group on cellulose fiber was converted into urethane group by TDD through a linkage reaction and the heat resistance of the fabric increased after modification [10].

The scanning electron micrographs of the surface of the original and modified cotton fibers were shown in Figure 7.



**Figure 6.** DSC plots for untreated and TDD-modified cotton.



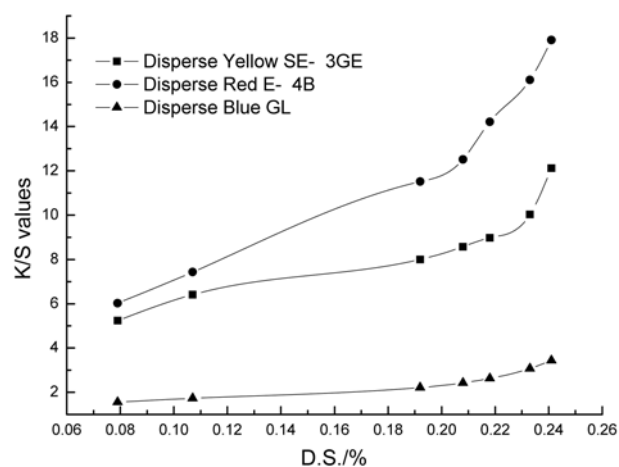
**Figure 7.** Scanning electron microscopy photographs of the surfaces of cotton fabrics; (a) original cotton ( $\times 500$ ), (b) original cotton ( $\times 1000$ ), (c) modified cotton ( $\times 500$ ), and (d) modified cotton ( $\times 1000$ ).

The surface of modified sample was smoother than that of original cotton fiber. This phenomenon may be at the pit of the surface of cotton fiber was filled up with the modification agent after modification.

#### Effect of DS and Printing Condition on the Printing Qualities

The  $K/S$  values of modified cotton fabric printed with different disperse dyes increased with the increasing DS, as shown in Figure 8. The corresponding  $K/S$  values of untreated cotton fabric were 3.179, 3.875, and 1.212 under the same transfer printing conditions. Higher color strength could be obtained after modification by TDD. The results suggested that the aromatic structure of TDD on the modified cotton fabric facilitated disperse dye molecule binding with cellulose fiber. As the modified cotton fabric contained more phenyl groups, the interaction between disperse dye molecule and cellulose fiber was stronger and the  $K/S$  value of the sample was higher after transfer printing with disperse dye [19-21].

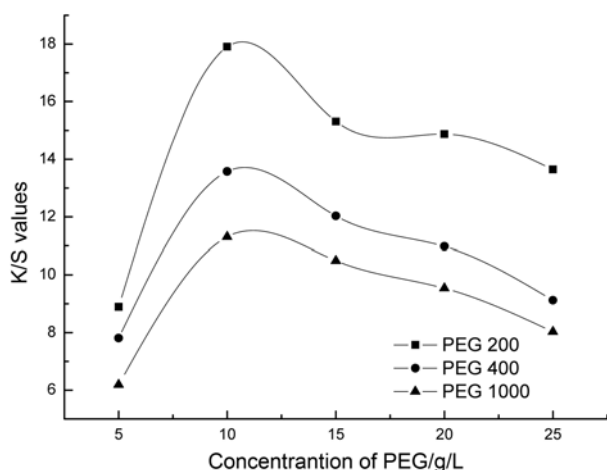
The data in Figure 9 showed that  $K/S$  values of sample the pretreated with low-molecular-weight PEG were higher than that of pretreated with high-molecular-weight PEG. The  $K/S$  values also increased with PEG concentration increasing up



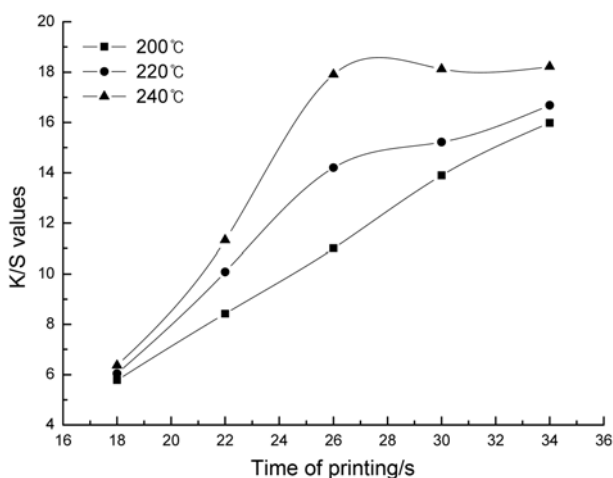
**Figure 8.** Effect of the degree of substitution of modified cotton fabric (printed at  $220^{\circ}\text{C}$  and 1.2 atm for 26 s) on  $K/S$ .

to a certain value and then decreased with PEG concentration further increasing.

Because hydroxyl groups locate at the end of PEG chains, the higher the molecular weight of PEG is, the lower the amount of hydroxyl group of PEG is. The hydrophilicity of hydroxyl group is much higher than that of ether group, so



**Figure 9.** Effect of poly(ethylene glycol) molecular weight and concentration on  $K/S$  for a modified cotton sample ( $DS$  0.226 %) transfer-printed at 220 °C and 1.2 atm for 26 s using Disperse Red E-4B.



**Figure 10.** Effect of printing time and temperature on  $K/S$ .

low-molecular-weight PEG can carry more water molecules into cotton fiber, which would benefit the swelling of cellulose fibers. In the dry dip-pad process, when high-molecular-weight PEG was employed as a swelling agent or

a high PEG concentration solution was used, the PEG macromolecule and water molecule would difficultly penetrate into cotton fiber due to the high solution viscosity and the swelling degree of cotton fiber was low after drying. Therefore, the aqueous PEG 200 of 10 g/l was used to pretreat the modified cotton fabric before transfer printing.

Figure 10 showed that  $K/S$  values of printed cotton fabric increased with the printing time increasing at three different temperatures. Moreover,  $K/S$  values of the samples printed at higher temperatures were higher than those printed at lower temperatures. The results indicated that with the printing time and temperature increasing, the amount of disperse dye transferred from printing paper to the modified cellulose fiber increased.

The CIELAB color,  $K/S$ , and whiteness values of different cotton samples were presented in Table 2. The whiteness and  $L^*$  of modified cotton fabric were lower than those of original one, but the  $b^*$  value was higher that of original one. In modifying process, the high temperature would accelerate the oxidation of cellulose fibers under alkaline condition, which resulted in the modified cotton fabric yellowing. The concentration of the dye increasing on the printed modified samples could also lead the  $L^*$  of the fabric value to decrease. For yellow and red samples, the values of  $a^*$  and  $b^*$  of the printed modified samples were approximately same as those of the printed original samples, whereas the  $a^*$  value was obviously observed to decrease on the modified blue sample. The results suggested that the modification of cotton fabric by the TDD exhibited a little effect on the chromic difference of printed fabrics.

The data in Table 3 revealed that the fabric strength decreasing was greater in the warp direction than that in the weft direction. The reason may be that no tension was exerted on the weft direction of the cotton fabric during modification process, while the warp direction suffered a tension, which caused the weft direction of swollen cotton fabric to shrink after curing. It also indicated that cross-linkage between TDD and cellulose molecules would affected the tensile strength of the cotton fabric.

As shown in Table 4, all fastness results of the printed modified cotton fabric were lower than those of the printed

**Table 2.** CIELAB color values,  $K/S$  values, and whiteness of original and modified cotton fabrics

Sample	$L^*$	$a^*$	$b^*$	$K/S$ value	Whiteness
Original cotton fabric	97.25	0.12	4.43	N/A	76.0
Modified cotton fabric	87.76	0.27	14.58	N/A	65.1
Printed original cotton (yellow)	78.59	9.12	53.27	3.179	N/A
Printed modified cotton (yellow)	65.32	9.43	54.03	12.122	N/A
Printed original cotton (red)	65.31	42.56	15.35	3.875	N/A
Printed modified cotton (red)	51.89	44.01	15.18	17.905	N/A
Printed original cotton (blue)	54.25	21.22	-35.89	1.212	N/A
Printed modified cotton (blue)	46.58	15.37	-37.10	3.438	N/A

Cotton fabric samples were modified at 160 °C for 100 s and printed at 220 °C and 1.2 atm for 24 s.

**Table 3.** Tensile strength of cotton fabrics printed with disperse dyes

Sample	Tensile strength (N)		Elongation (%)		Loss of strength (%)	
	Warp	Weft	Warp	Weft	Warp	Weft
Original cotton fabric	664	201	7.9	16.0	N/A	N/A
Modified cotton fabric	621	199	8.8	11.8	6.0	1.0
Printed modified cotton (yellow)	614	213	9.8	13.0	7.5	-6.0
Printed modified cotton (red)	586	200	8.8	12.2	11.7	0.5
Printed modified cotton (blue)	575	217	9.6	13.2	13.4	-8.0

Negative values denote an increase in tensile strength. Cotton fabric samples were modified at 160 °C for 100 s and printed at 220 °C and 1.2 atm for 24 s.

**Table 4.** Fastness properties of fabrics printed with disperse dyes

Sample	Light		Washing		Rubbing							
					Weft direction				Warp direction			
	20 h	50 h	A	C	A <sub>W</sub>	A <sub>D</sub>	C <sub>W</sub>	C <sub>D</sub>	A <sub>W</sub>	A <sub>D</sub>	C <sub>W</sub>	C <sub>D</sub>
Printed polyester (yellow)	7	6-7	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5
Printed polyester (red)	7	7	4-5	4-5	4	4-5	4-5	4	4	4-5	4-5	4
Printed polyester (blue)	6-7	7	4-5	4-5	4	4	4	4	4	4	4	4
Printed original cotton (yellow)	3-4	2	2	2	3	3	2	2	3	3	2	2
Printed original cotton (red)	4	2-3	2	2	2-3	3	3	2	2-3	3	3	2
Printed original cotton (blue)	4	2-3	2	2	2-3	3	3	2	2-3	3	3	2
Printed modified cotton (yellow)	6-7	5-6	3	3	3-4	4-5	3	3	3-4	4-5	3	3-4
Printed modified cotton (red)	6	5	3-4	3-4	4	4-5	3	3	4	4	3-4	3
Printed modified cotton (blue)	6	5	3-4	3-4	4	4-5	3-4	3-4	3-4	4-5	3-4	3-4

A: fading fastness, C: staining fastness, W: wet, D: dry. Cotton fabric samples were modified at 160 °C for 100 s and printed at 220 °C and 1.2 atm for 24 s. Polyester fabric samples were transfer-printed at 130 °C and 1.2 atm for 20 s with disperse dye paper.

polyester fabric. This demonstrated that Van der Waals' forces played a major role in the fixation of disperse dye on the modified cotton fabric. The phenyl group in polyester macromolecules was richer than that of modified cotton fiber. The affinity of disperse dye with modified cotton fiber was much lower than that of disperse dye with polyester fiber. It was different from polyester fiber that disperse dye was piled on the surface of modified fiber and seldom diffused into the cellulose fiber after transfer printing. These factors would affect the printing fastness of the modified cotton fabric. Disperse dye molecules were easy to rub or wash off from the modified cotton fibers. However, compared to a normal cotton sample, the modified sample showed high printing fastness after transfer printing with a disperse dye.

### Conclusion

Transfer printing with a disperse dye was possible on cotton fabric modified with an aqueous TDD derivative. The results demonstrated that the concentration of the modifying agent and the curing temperature and time would affect the *DS* and whiteness.

Compared to normal cotton, modified cotton sample exhibited high printing fastness after transfer printing with a

disperse dye and the printing fastness satisfied the requirements of wearability. Suitable conditions were 160 °C for 100 s for modification and 220 °C and 1.2 atm for 24 s for transfer printing.

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