Modified cotton fabrics for improved ultraviolet protection performance and reactive dyeing property

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Reactive quaternary ammonium cationic compound, [2,3-epoxypropyl-1-methy imidazole ammonium chloride (EPMI)] has been synthesized with 1-methylimidazole and epoxy chloropropane to improve the dyeing property of cotton fabrics and the cationic cotton fabrics combined Fe^{3+} to obtain UV protective property. The dye fixation (F%) of three reactive dyes is found to be 84.5-89.7% on modified cotton fabrics. Ultraviolet protection factor (UPF) value of modified cotton fabric is increased to 137.47 from 7.57 of untreated cotton fabric. The breaking strength of modified cotton fabrics is well retained. The hue (h) of dyed samples before and after modification shows a little change. The UPF of modified cotton fabric shows excellent durability. After 50 laundering cycles, the UPF values decrease to 12.47%. Scanning electron microscopy observations and XRD patterns show that the modified cotton fibres are left nearly undamaged by the modification. The FTIR spectra suggest that the EPMI and Fe^{3+} are combined on the cotton fibres.

Keywords: Cotton, Dyeing, Quaternary ammonium cationic compound, 1-Methylimidazole, UV protection property

1 Introduction

Though cotton is one of the oldest and most widely used textile materials[1], the ultraviolet (UV) – blocking properties of cotton fabrics are poor. In addition, the dye exhaustion of reactive dyes on cotton fabrics is relative low, and high-salinity waste water is produced in dyeing process to pollute environment. To improve these properties, cotton fabrics need to be modified to gain good anti-UV and dyeing properties.

To obtain cotton fabrics with good UV protective properties, organic and inorganic anti-UV finishing agents have been used to modify cotton fabrics[2-4]. The organic UV absorbers[5] mainly contain benzotriazole derivatives, anthraquinone derivatives[6], monochlorotriazine derivatives[7], dyes[8-11], and plant extract[12]. Inorganic UV-shield agents primarily contain ZnO^{13-16} and TiO_2^{17-18} that are deposited on the surface of cotton fabrics as multilayer films[19] via nano-sol technique[20]. Cationic modification[21-26] is a typical method for improving the dyeing properties of cotton fabrics. In general, dyeing does not require the use of salts and the dye exhaustion of cationic cotton fabrics is greatly improved.

In this study, 2, 3-epoxypropyl-1-methy imidazole ammonium chloride (EPMI) was synthesized with 1-methylimidazole and epoxy chloropropane. The EPMI was grafted on cotton fabrics to enrich the cotton fibres with cationic functional groups to improve the dyeing properties of the cotton fabrics. One of the N atoms in EPMI has a lone pair of electrons that can combine with Fe^{3+} to form complexes[27-28]. Cotton fabrics with Fe^{3+} have excellent UV-blocking properties. Cotton fabrics modified by EPMI and treated with Fe^{3+} compounds not only have good dyeing property, but also have excellent UV protective properties.

2 Materials and Methods

2.1 Materials

Desized, scoured, and bleached cotton fabric (weight 119.6 g/m^2, and warp & weft density of 539×291 and 13.71×13.25 tex) was purchased from a Chongqing supermarket (China). Epoxy chloropropane, sodium carbonate, sodium sulfate and peregal-O were purchased from the Ruijinte Chemicals Ltd. Co., Tianjin, China; 1-methylimidazole from Aladdin Industrial Corporation; and ferric trichloride hexahydrate from Kelong Chemical Reagent Factory, Chengdu China. Reactive dyes (C.I. Reactive Red 195, C.I. Reactive Yellow 145 and C.I. Reactive Blue 194) were supplied by the Zhejiang Wenling Dyeing Chemical Company, Zhejiang, China.

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2.2 Synthesis of EPMI and Modification of Cotton Fabric

Epoxy chloropropane (4.5mL), 1-methylimidazole (4.5mL), and distilled water (40 mL) were added to a 150 mL conical flask. The flask with the ingredients was placed into a thermostatically controlled water bath at $50^{\circ}C$ and the mixture was magnetically stirred for 30 min. After the reaction completion, a clear and transparent solution was obtained. The synthesis reaction is given in Scheme 1(a).

Firstly, the cotton samples were immersed in 1, 2, 4, 6, 8, 10 and 12% (o.w.bath) 2,3-epoxypropyl-1-methy imidazole ammonium chloride(EPMI) solution for 20 min at $45\ ^{\circ}C$ using liquor-to-goods ratio 20:1. Then, the samples were padded to reach average wet pickup of 100%. The padded samples were continuously prebaked at $60\ ^{\circ}C$ for 10 min, cured at $110\ ^{\circ}C$ for 30 min, finally washed by rinsing several times with water at room temperature and dried at $100\ ^{\circ}C$. The optimal EPMI concentration was determined by the dye exhaustion (E %) of samples. Secondly, cotton samples were dipped in the optimal

concentration of EPMI solution and cured at 80, 90, 100, 110 and 120 $^{\circ}C$ to choose the optimal curing temperature. Finally, the cotton fabric samples treated with EPMI were immersed into 0.01, 0.03, 0.06 and 0.1% (o. w. bath) ferric chloride ($FeCl_3$) solution in 1:20 bath ratio at room temperature for 30 min and dried at 50 $^{\circ}C$. The UPF values and E% of cotton samples modified with different concentration of ferric chloride were analyzed to determinate optimal finishing process. The grafting reaction of EPMI and the complexation reaction are shown in Scheme 1(b).

2.3 Dyeing Procedures

Dyeing of the cotton fabrics modified with EPMI and $FeCl_3$ was carried out at 60 $^{\circ}C$ for 45 min using material-to-liquor 1:50 and dye concentration 2% (o w f). Then, sodium carbonate (10 g/L) was added to dye bath for fixation for 30 min. The dyeing of untreated cotton fabrics followed the same dyeing procedure using 60 g/L sodium sulphate.

After dyeing, all the cotton fabric samples were rinsed continuously with cold, warm and cold water. The dyed cotton fabrics were soaped in a solution including 2 g/L sodium carbonate and 1 g/L Peregal O at 90 $^{\circ}C$ for 20 min at liquor ratio 1:50 and finally rinsed. The fabrics were air dried.

2.4 Determination of Color Parameters, Color Fastness and Breaking Strength

The dye exhaustion (E %) was calculated using the following equation:

$$E\%=(C_0-C_1)/C_0\times100\% \qquad …(1)$$

where C_0 and C_1 are the concentrations of dye bath before and after dyeing respectively.

The dye fixation (F %) was calculated using the equation as shown below:

$$F\%=(C_0-C_1-C_2)/C_0\times100\% \qquad ... (2)$$

where C_2 is the dye concentration of the soaped solution.

CIE L*, a*, b*, c* and h of the dyed cotton fabrics were tested using a Datacolor 650 spectrophotometer (Datacolor Co., USA). Each sample was tested with ten different points and the average values were used. Wash fastness and rub fastness of dyed cotton fabrics were tested according to AATCC 8-2013 and AATCC 61-2013 A1 standard test methods, respectively. The breaking strength of cotton fabrics before and after modification was tested according to ISO 13934-1-1999. All cotton fabric samples were tested 5 times and the average values were obtained.
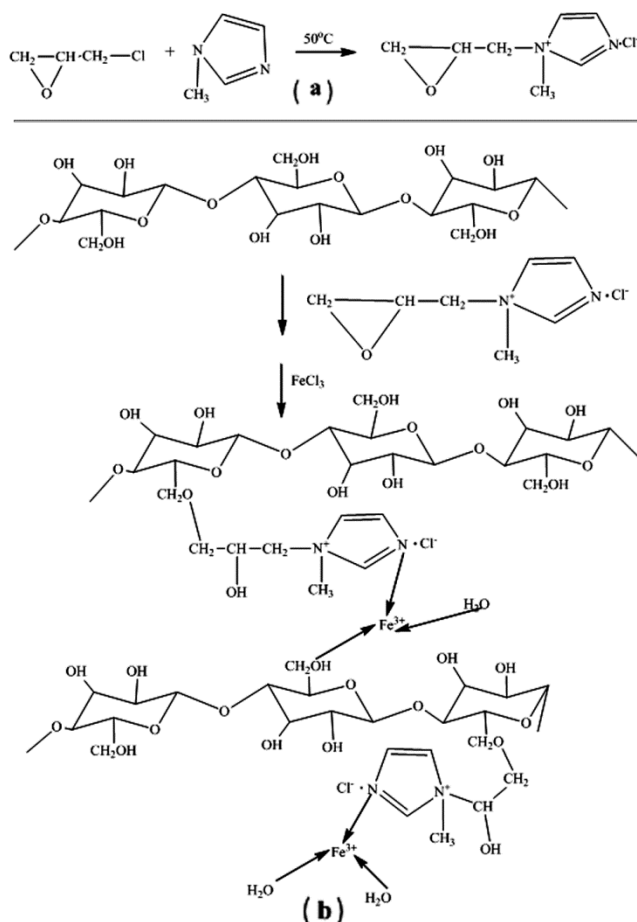
Scheme 1

2.5 Characterisation of Cotton Fibres Before and After Modification

The surface morphologies of the cotton fibres before and after modification were observed with a JEOL JSM6610 scanning electron microscope using 20 kV accelerated voltage. To obtain clear images of the surfaces, all cotton fibres were sputter-coated with gold. The crystalline structure of the cotton fibres was analyzed using a Shimadzu 6100 X-ray powder diffractometer with Cu Kα radiation at 36 kV and 20 mA. The 2θ range was 5° - 50° in scanning steps of 0.02°. The FTIR spectra were obtained with a Spectrum GX spectrometer (PE Co., USA) using a KBr disk, resolution of 1.0 cm^{-1} and 15 scans. The data were collected at 20 °C and 65% RH.

2.6 UV Protective Properties and Washing Resistance of Modified Cotton Fabrics

The UV protective property of the cotton fabric samples before and after modification was determined using a textile UV transmittance prevention tester (UV-1000, Labsphere USA). The spectral transmittance (T %) and UV protection factor (UPF) of the samples were tested at 280–320 nm and 320–400 nm ranges.

The wash resistance of the modified cotton fabric samples was assessed based on the UPF values and %T of samples after washing multiple times. The AATCC 61-2003 A1 standard test method was employed to evaluate the durability of modified cotton fabrics.

3 Results and Discussion

3.1 Optimum Conditions to Prepare Modified Cotton Fabrics

To optimize the preparation conditions, the concentration of EPMI, baking temperature and concentration of $FeCl_3$ are investigated. The optimum conditions are determined based on the percentage of dye exhaustion (E %) and UPF values of modified cotton fabrics. The dye C.I. Reactive Red 195 is chosen to dye the cotton fabrics modified at different preparation conditions.

3.1.1 Optimization of EPMI Concentration

Figure 1(a) shows the relationship between the concentration of EPMI and E% of C.I. Reactive Red 195. The baking temperature is kept 110 °C and baking time 30 min. It is observed that the E%
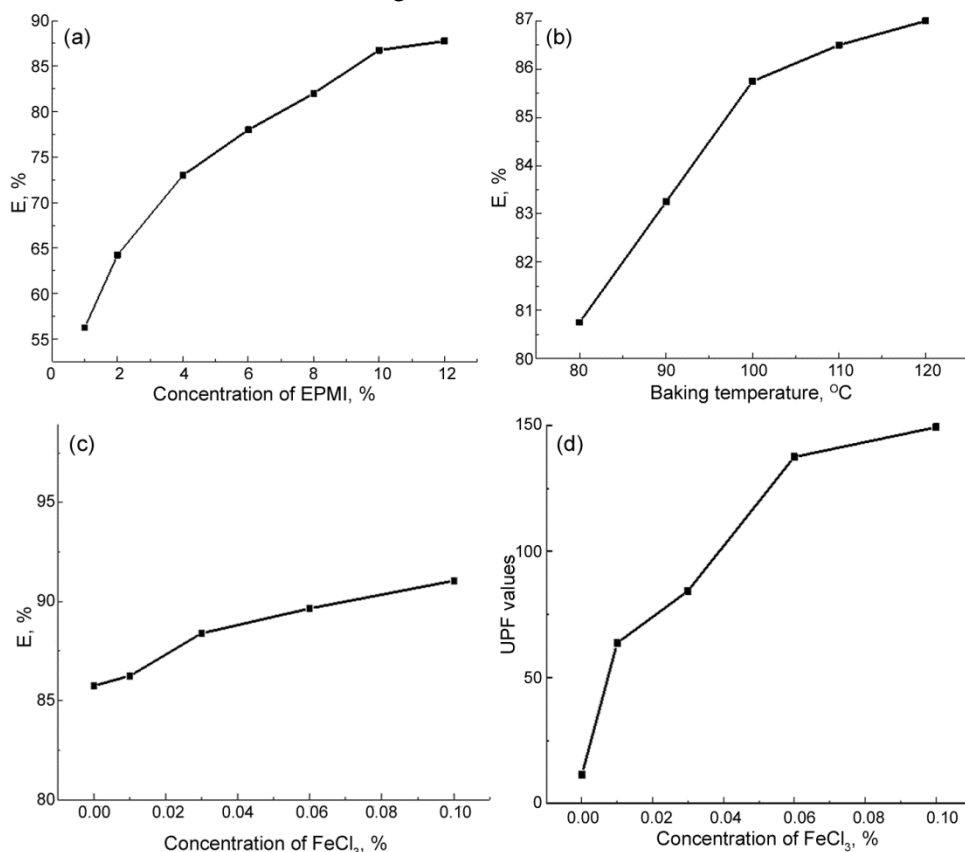

Fig. 1 — Effect of (a) EPMI concentration, (b) baking temperature, (c) $FeCl_3$ concentration on the dye exhaustion (E %), and (d) effect of $FeCl_3$ concentration on UPF values

gradually increases with the increase of EPMI concentration. However, when EPMI concentration increases from 10% to 12%, the E% does not increase obviously. This may be because of the fact that most of the reactive sites on cotton fabrics react at 10% EPMI, then continuously increasing EPMI concentration dose not increase E%. Therefore, 10% of EPMI is used in the further experiments.

3.1.2 Optimization of Baking Temperature

Figure 1(b) presents the relationship between baking temperature and E%. The EPMI concentration is kept 10% and the baking time 30 min. With the increase in baking temperature upto $100^{\circ}C$, E% is improved. However, when temperature is above $100^{\circ}C$, the E% only increases a little with the increase in temperature. It is inferred that the higher finishing temperature not only needs more energy sources, but also damages the cotton fibres mechanical properties. Hence, 100 $^{\circ}C$ is selected as the optimum baking temperature in the following investigation.

3.1.3 Optimization of FeCl₃ Concentration

Figures 1(c) and 1(d) show the effect of $FeCl_3$ concentration on the E% and UPF values of cotton fabrics modified with EPMI and $FeCl_3$ respectively. The concentration of EPMI is kept 10% and the baking temperature 100 $^{\circ}C$. It can be seen from Fig. 1(c) that the E% increases from 85.75% to 91.05% with the increase in $FeCl_3$ concentration. It is obvious that absorbing Fe^{3+} increases the positive charges, and then the E% of samples increases slightly. From Fig. 1(d), when the cotton fabric is only treated with EPMI, the UPF value of cotton fabrics is 11.62; the UPF value of untreated cotton fabric is 7.57. Thus, the EPMI only has little effect on improving the UV protective property of cotton fabrics. After the cotton fabrics are treated with $FeCl_3$, the UV protective properties of samples are improved

greatly. When the $FeCl_3$ concentration is increased from 0.01% to 0.1%, the UPF values of modified cotton fabrics increases from 63.66 to 149.25. This shows that Fe^{3+} could endow the cotton fabrics with excellent UV protective property. Figure 1(d) shows that when the $FeCl_3$ concentration is increased from 0.06% to 0.1%, the UPF values of treated samples increases a little. Hence, 0.06% is selected as the optimum $FeCl_3$ concentration.

Depending on the above determination, the optimum conditions of preparing the modified cotton fabrics are the EPMI concentration 10%, the baking temperature 100 $^{\circ}C$ and the $FeCl_3$ concentration 0.06%.

3.2 SEM of Unmodified and Modified Cotton Fabrics

Figure 2 shows SEM images of the unmodified cotton fibres, cotton fibres modified with 10% EPMI, and cotton fibres modified with 10% EPMI and 0.06% ferric chloride. The surfaces of the cotton fibres before and after grafted with EPMI show a smooth texture. This suggests that the EPMI grafting does not affect the surface, and the EPMI mainly enters the interior of the cotton fibres. However, parts of the surfaces of cotton fibres modified with EPMI and $FeCl_3$ show a little crystals, possibly a little hydrolyzed Fe^{3+} formed the crystals.

3.3 X-ray Diffraction of Cotton Fibers

Figure 3(a) shows the X-ray diffraction spectra of the unmodified and modified cotton fibres. The main diffraction peaks of the unmodified cotton fibres are at 14.87°, 16.52°, and 22.76°; for the cotton fibres modified with EPMI, these are at 15.08°, 16.63°, and 22.76°; and for the cotton fibres modified with EPMI and $FeCl_3$, the peaks are at 14.87°, 16.62°, and 22.76°. They are nearly the same with no new crystalline structures present. Presumably, EPMI and $FeCl_3$ enter the amorphous parts of the cotton fibres and do not affect the crystalline parts.
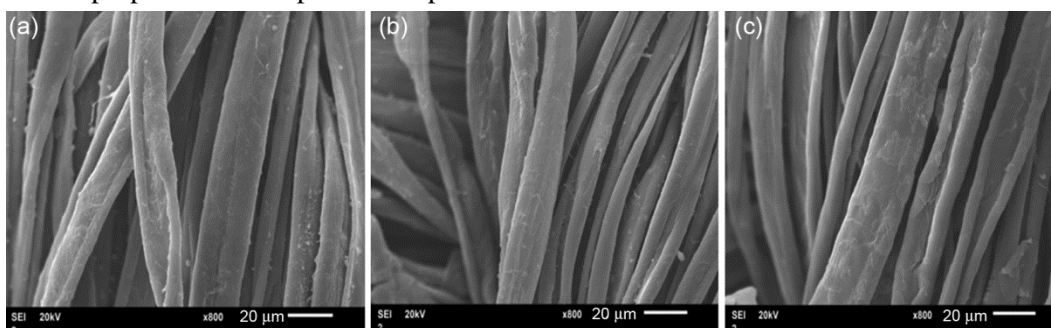

Fig. 2 — SEM images of (a) unmodified cotton fibres, (b) cotton fibres modified with 10% EPMI, and (c) cotton fibres modified with 10% EPMI and 0.06% ferric chloride

3.4 FTIR Spectra of Cotton Fibres

Figure 3(b) shows the infrared spectra of cotton fibres before and after modification. The unmodified cotton fibres are characterized by the stretching peak of –OH at 3440 cm^{-1} and the peak of the C–O–C group at 1090 cm^{-1}. Besides these peaks, the cotton fibres modified with EPMI show peaks of C–H in –CH$_3$ at 2905 cm^{-1}, and C–N in =CH–N– at 1158 cm^{-1} and 1028 cm^{-1}. Clearly, the – CH$_3$ and =CH–N– groups are from EPMI. Nevertheless, the FTIR spectrum of the cotton fibres modified with EMPI and ferric chloride show a peak at 556 cm^{-1}, contributed by ferric iron[29, 30], and the peak of –OH shifted from 3440 cm^{-1} to 3377 cm^{-1}.

3.5 Total Dye Fixation, Color Fastness and Breaking Strength of Dyed Cotton Fabrics

Table 1 shows dye fixation (F%), color fastness and breaking strength of dyed cotton fabrics. The unmodified cotton fabrics are treated with 60g/L Na$_2$SO$_4$ as accelerant before dyeing, and the modified cotton fabrics are dyed without any accelerant. It is obvious from Table 1 that compared to untreated cotton fabrics, F% of modified cotton fabrics increases greatly even without accelerant. After treated with EPMI, the cotton fabrics are endowed with lots of cationic groups which could absorb the negative charge reactive dyes molecules. Table 1 also shows that the wash and rub fastness values of dyed cotton fabrics modified with EPMI and FeCl$_3$ are same but higher than that of untreated cotton fabrics. These are attributed to the cationic groups on modified cotton fabrics. From Table 1, it can be seen that the warp and weft breaking strength of modified cotton fabrics decreases 4-6%. This shows that the modifying process almost does not damage the cotton fabrics.

3.6 Colorimetric Data of Dyed Cotton Fabrics

The colorimetric data of both dyed cotton fabrics before and after modification have been examined and the results are presented in Table 2. Table 2 shows that the L* values of the modified cotton fabrics are lower than that of untreated cotton fabrics. This is because the F% of modified cotton fabrics is higher than that of untreated cotton fabrics. The redness-greenness (a*), yellowness-blueness (b*), chroma (C*) and hue (h) show a little change. This may be
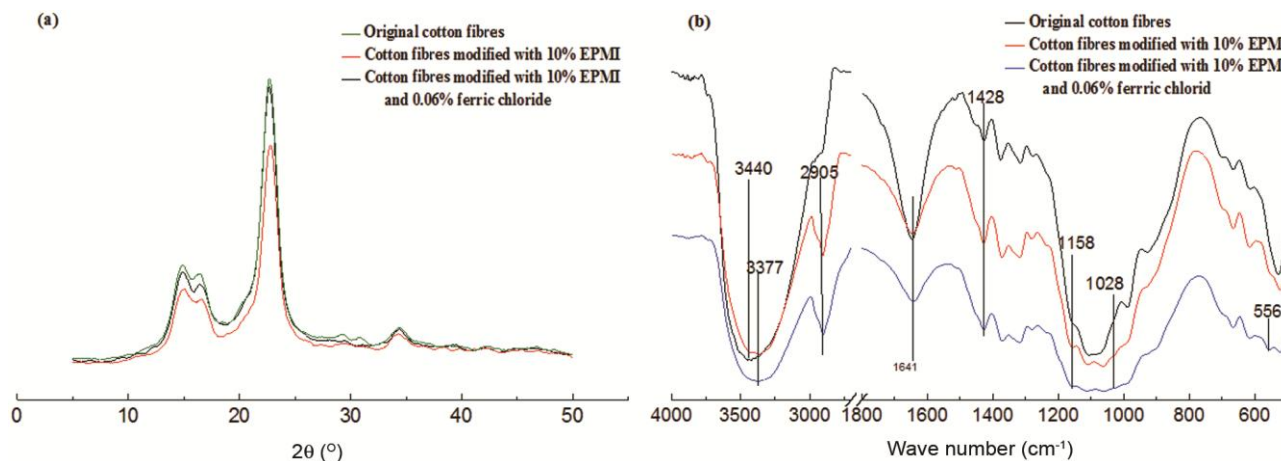

Fig. 3 — (a) XRD patterns, and (b) FTIR spectra of cotton fibers before and after modification

Table 1 — Dye fixation (F%), color fastness and breaking strength of dyed cotton fabrics

C.I. Reactive dye	Cotton fabric [a]	F%	Wash fastness			Rub fastness		Breaking strength, N	
			Change	Staining		Dry	Wet	Warp	Weft
				Cotton	Wool				
Red 195	Modified	84.50	4-5	4-5	4	4-5	4	678.3	412.5
	Control	63.25	4	4	4	4	3	712.5	437.9
Yellow145	Modified	86.25	4-5	4-5	4-5	4-5	4	673.6	409.7
	Control	70.10	4-5	4-5	4-5	4-5	4	706.7	432.5
Blue194	Modified	89.70	4-5	4-5	4	4-5	4	670.2	406.1
	Control	71.35	4	4	4	4	3-4	698.4	428.8

[a] Control samples were dyed with 60g/L Na$_2$SO$_4$ as the accelerant; and the modified samples were dyed without accelerant.

Table 2 — Colorimetric data of dyed cotton fabrics before and after modification

C.I. Reactive dye	Cotton fabric [a]	L*	a*	b*	c*	h
Red 195	Modified	42.8	55.3	-2.2	55.3	353.5
	Control	49.1	57.7	-4.0	57.9	356.0
Yellow 145	Modified	68.3	27.7	69.0	74.3	68.1
	Control	74.7	24.3	71.1	75.1	71.2
Blue 194	Modified	29.2	-5.2	-16.6	17.5	252.5
	Control	32.4	-5.4	-20.2	20.9	255.0

[a] Control samples were dyed with 60g/L Na_2SO_4 as the accelerant; and the modified samples were dyed without accelerant.

Table 3 — UV protection property and durability of modified cotton fabrics [a]

Laundering cycles (LCs)	T%		UPF values
	UVA (320–400 nm)	UVB (280–320 nm)	
0	2.8	0.53	137.47
5	2.9	0.54	134.25
10	3.1	0.55	130.62
15	3.1	0.57	128.30
20	3.2	0.57	126.52
25	3.2	0.58	124.63
30	3.2	0.58	124.63
40	3.2	0.59	122.41
50	3.3	0.59	120.32

[a] Cotton samples were treated with 10g/L EPMI and 0.06% $FeCl_3$.

due to the fact that after modification, the cationic groups on the cotton fabrics could form electrostatic interaction with the reactive dye molecules to influence the colorimetric data. But from Table 2, it can be seen that the modification only has little influence on the colorimetric data.

3.7 UPF Durability of Modified Cotton Fabrics

Table 3 shows the UV transmittance (T %) and UPF values of modified cotton fabrics after different laundering cycles (LC). After 50 LCs, the UVA transmittance (T %) changes from 2.8% to 3.3%, the UVB transmittance (T %) from 0.53% to 0.59%, and UPF values decrease to 12.47% from 137.47 to 120.32. These results suggest that the EPMI is firmly grafted on the cotton fabrics via covalent bonds and Fe^{3+} well combined with =N– and –OH groups. Clearly, the modified cotton fabrics have excellent UPF durability.

4 Conclusion

Grafting EPMI on cotton fabrics improves the dyeing properties of the cotton fabrics greatly. The modified cotton fabrics are dyed without using salts, and the dye fixation (F%) of C.I. Reactive Red 195, C.I. Reactive Yellow 145 and C.I. Reactive blue

194 on the modified cotton fabrics reach 84.50%, 86.25% and 89.70% respectively. The wash fastness of both the modified cotton fabric is found same but higher than that of untreated cotton fabric. The cotton fabrics modified with EPMI and $FeCl_3$ show excellent UV protection property, and the UPF values could reach 137.47. The modified cotton fabrics show good durability. The SEM and X-ray diffraction data suggest that the structure of the modified cotton fibres is unaffected by the modification process, and the FTIR spectra suggest that EPMI and Fe^{3+} are well combined on the cotton fibres.

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