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Preparation and UV-protective properties of functional cellulose fabrics based on reactive azobenzene Schiff base derivative

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ABSTRACT

Azobenzene Schiff base possesses excellent photochromic or thermochromic properties based on intermolecular proton transfer or cis-trans isomerization. The azobenzene Schiff base containing two reactive groups, N, N-bis{p-[(2′-sulphatoethyl)sulphonyl phenylazo] salicylidene}-1,2-ethylenediamine (BSPEA), was applied to modify cellulose materials. The functional cellulose fabrics containing azobenzene Schiff base groups were prepared. The chemical and morphological structures of functional cellulose fabrics were characterized by element analysis, FT-IR spectrum, and scanning electron microscopy (SEM). The UV-protection properties of the fabrics were investigated by the ultraviolet transmittance spectra and ultraviolet protection factor (UPF). The results show that the functional cellulose fabrics had excellent UV-protection properties with higher UPF value (UPF value reached 31.7) and lower ultraviolet transmittance (less than 5%). The modified cellulose fabrics had not significant influence on the physical properties. The functional cellulose fabrics based on reactive azobenzene Schiff base would have potential application in textile and functional materials.

1. Introduction

The ultraviolet radiation (UVR) is one of the major causes of degradation of polymer or textile materials due to photo oxidation. The ultraviolet (UV) protection of biomaterials against photodestruction is of high practical interest (Gouda and Keshk, 2010; Lu, Fei, Xin, Wang, & Li, 2006). On the other hand, UV radiation can penetrate into the top layer of the skin causing a range of negative health effects such as acceleration of skin ageing, photodermatosis, and even severe skin cancers. Although protecting the skin with clothing is a convenient and valid method, common clothing in summer is not effective for UVR protection because of the high UV ray transmittance of the fabrics. The use of UV-protecting fabrics can provide excellent protection against the harmful effects of sunlight (Czajkowski, Paluszkiewicz, Stolarski, Kazmierska, & Grzesiak, 2006; Feng, Zhang, Chen, & Zhang, 2007; Maged, Mamdouh, El-Naggar, Fathalla, & Nisreen, 2009). The investigation of the materials with UVR protection, such as nanofibers and functional biomaterials, is an important issue attracting increasing interest from fundamental and practical perspective (Yang, He, Xu, & Yu, 2009; Yung et al., 2010).

Surface modification of a substrate is an important method for making materials with enhanced performance in some specific areas (Hou, Yu, & Chen, 2010; Xie, Wang, & Xu, 2010). Cellulose fiber is one of the excellent natural materials that have wide application in different production. Much attention has been paid on the utilization of cellulose, due to its good biodegradability, biocompatibility and nontoxicity. A number of attempts have been made to modify cellulose fiber using the compounds containing the certain groups (Adamopoulos et al., 2007; Hou, Wang, & Yu, 2009a; Hou, Zhou, & Wang, 2009b; Xie, Liu, & Wang, 2009a). To date, many approaches have been investigated to modify cellulose surface for improving the UV protection function of cotton fabrics (Ibrahim, E-Zairy, & Eid, 2010; Wang and Hauser, 2010). For example, 2-(2-hydroxyaryl) benzotriazoles and 2-(2-hydroxyaryl)-1,3,5-trizines as UV absorbers have been applied for improving the UV radiation protection of fabrics and achieved good protection properties (Sun, Zhao, & Freeman, 2007; Tragoonwichian, O'Rear, & Yanumet, 2008). The important properties of these molecules are that they strongly absorb UV radiation and rapidly dissipate the energy via some suitable inter or intramolecular rearrangement. However, especially interesting from practical point of view is absorber containing reactive groups which could form covalent bonds with cellulose. Modified cellulose fabrics will be able to maintain their protecting properties for prolonged time.

Schiff base is an important sort of light sensitive materials and has got wide application in biological, clinical, analytical and industrial fields (Bibhesh, Hament, Anant, & Narendar, 2010; Xie, Zhang, & Yu, 2011). Azobenzene Schiff base can absorb UV radiation to convert it to less harmful energy by change of cis–trans

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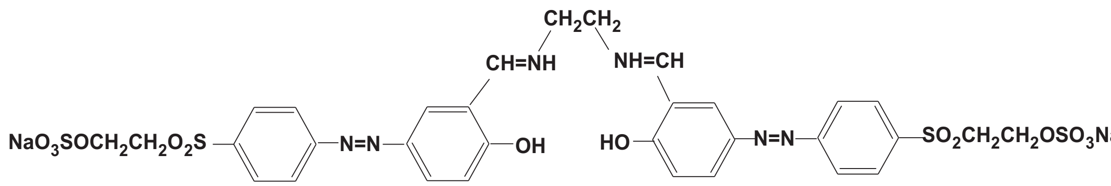


Scheme 1. Chemical structure of BSPEA.

isomerization or intermolecular proton transfer. There are some reports on the photochromic, thermochromic and other properties of azobenzene Schiff base compounds in the functional materials (Hadjoudis, Vitiorakis, & Moustakali, 1987; Shen and Tang, 1995). Few researchers so far, however, have focused on functional protection textile using azobenzene Schiff base compounds.

In this paper, cellulose fabrics were modified with the azobenzene Schiff base containing reactive groups, N,N-bis{p-[(2′-sulphatoethyl)sulphonyl phenylazo] salicylidene}-1,2-ethylenediamine (BSPEA). The chemical and morphological structures of the modified cellulose were investigated with FT-IR spectra, the nitrogen and carbon contents and SEM. UV protective properties of the functional cellulose fabrics were also discussed.

2. Experimental

2.1. Materials

Desized, scoured and bleached cellulose fabrics were obtained from Jinqiu Textile and Finishing Company, Shaoxing, China. The BSPEA Schiff base was obtained from Modern Textile Institute, Donghua University, Shanghai, China. The chemical structure of BSPEA is shown in Scheme 1.

Other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Modification of cellulose fabrics with BSPEA Schiff base

The cellulose fabrics were grafted in PYROTEC-2000 dyeing machine (Roaches International Ltd., UK), with BSPEA at a liquor ratio of 1:10. The sodium carbonate (10 g/l) as catalyst was used in the grafting process. Fabrics were immersed in the BSPEA solution at room temperature and the temperature was increased to 60 °C at a rate of 1 °C/min. Grafting was carried out at this temperature for 50 min. The modified samples were rinsed in hot water and soaped in a solution of a nonionic surfactant (OP-10, 1 g/l) at 85 °C for 15 min at liquor ratio 1:15. The fabrics were removed, rinsed thoroughly in hot tap water. Then the fabrics were dried at ambient conditions. Two functional cellulose samples with azobenzene Schiff base were obtained according to two concentrations, 2 g/l, and 5 g/l and named as FC-1 and FC-2, respectively.

2.3. Element analysis and FT-IR spectra

The nitrogen and carbon contents were determined by Elementar Vario(III) (Germany). The samples were dried under vacuum at the temperature of 50 °C before measuring. FT-IR spectrum of the sample was measured by an OMNI Sampler of the Nexus-670 FTIR-Raman Spectrometer (Nicolet Analytical Instruments, Madison WI), using a single ART reflecting method.

2.4. SEM

For SEM analysis, the samples were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

2.5. UV protection properties and physical property measurements

Ultraviolet protection factor (UPF), T (UVA), and T (UVB) were measured by UV Transmittance Analyzer, UV-1000F (Labsphere Co. USA). The UPF was calculated by using Eq. (1).

$$\mathrm{UPF} = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \times d\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times d\lambda} \quad (1)$$

where S_λ is erythema action spectrum, E_λ is solar irradiance, $d\lambda$ is wavelength interval in nm, and T_λ is spectral transmittance of the specimen.

A-range ultraviolet (UVA) transmittance and the B-range ultraviolet (UVB) transmittance can be calculated by using Eqs. (2) and (3), respectively.

$$\mathrm{T(UVA)} = \frac{\sum_{315}^{400} T_\lambda \times d\lambda}{\sum_{315}^{400} d\lambda} \quad (2)$$

$$\mathrm{T(UVB)} = \frac{\sum_{280}^{315} T_\lambda \times d\lambda}{\sum_{280}^{315} d\lambda} \quad (3)$$

Fabric tensile strength was determined by using a H10KS Tensile Testing Machine (Hounsfield SDL Co.). Six specimens (three for warp and three for weft) were tested at a gauge length of 200 mm with a stain rate of 30 mm/min. The width of the specimen was 50 mm. The tensile and tear properties of the fabric were measured according to ISO13934.1: 1994 and ISO 13937.1:1995, respectively.

The conditional wrinkle recovery angle (WRA) was measured by a P500570 (SDL. Co.) according to AATCC Test Method 66-2003.

3. Results and discussion

3.1. Preparation of the functional cellulose fabrics based on reactive azobenzene Schiff base derivative

The azobenzene Schiff base molecule with a long conjugated system has a strong absorption of ultraviolet in 250–400 nm region. The UV absorption of BSPEA is shown in Fig. 1.

The molecular structure of cellulose has a lot of hydroxyl that may be employed in various activation processes (Hou, Wang, et al., 2009a; Xie, Zhang, & Yu, 2009b). The compound BSPEA containing two reactive groups, two p-[(2′-sulphatoethyl)sulphonyl groups, is able to form covalent bonds with cellulose under alkaline conditions. The chemical reaction of cellulose and BSPEA is shown in Scheme 2.

The element analyses of the functional cellulose fabrics were determined. The nitrogen and carbon contents of samples are listed in Table 1. Compared with the control sample, the nitrogen and

Table 1
Element analyses of functional and control cellulose fabrics.

Samples	Control	FC-1	FC-2
N (%)	0.050	0.064	0.070
C (%)	42.81	42.85	42.95

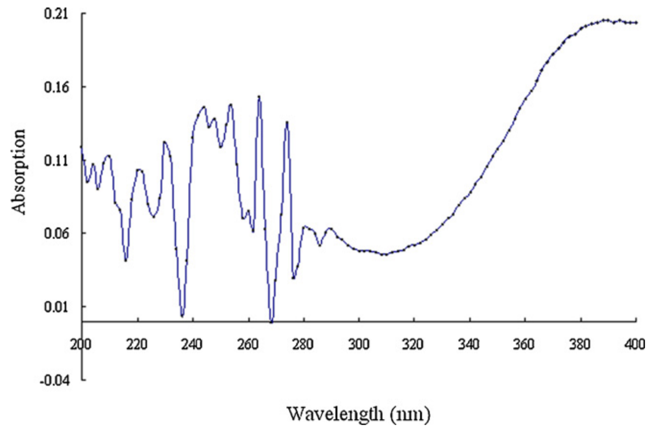


Fig. 1. UV absorption of BSPEA.

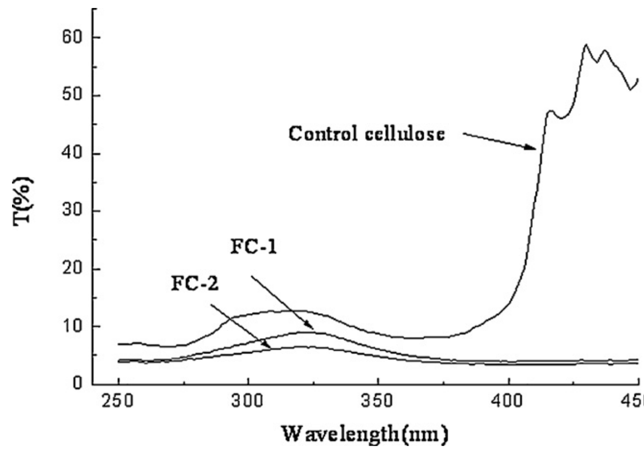


Fig. 2. Ultraviolet transmittance spectra of functional and control cellulose fabrics.

carbon contents of the functional cellulose fabrics increased. It can be seen that Schiff base compound was grafted to cellulose macromolecules. FT-IR spectra of the functional cellulose fabrics were also measured. FT-IR spectra of them assured the presence of –N=N– at 1583 cm^{-1}. This confirms that the Schiff base compound was able to form covalent bonds with cellulose fabrics.

3.2. Ultraviolet transmittance spectra and morphological structures of the functional cellulose fabrics

Ultraviolet transmittance spectra of the functional fabrics represent the UV-protection ability of the functional materials. Ultraviolet transmittance spectra of functional fabrics, FC-1 and FC-2, were measured and shown in Fig. 2. It can be seen that control sample had a high ultraviolet transmittance. This indicates that the resistance of control cellulose fabrics to ultraviolet ray was very poor. FC-1 and FC-2 had low ultraviolet transmittance (less than 5%). Generally, the UV-protective properties of fabrics would be evaluated as good or excellent when the ultraviolet transmittance was less than 5%.

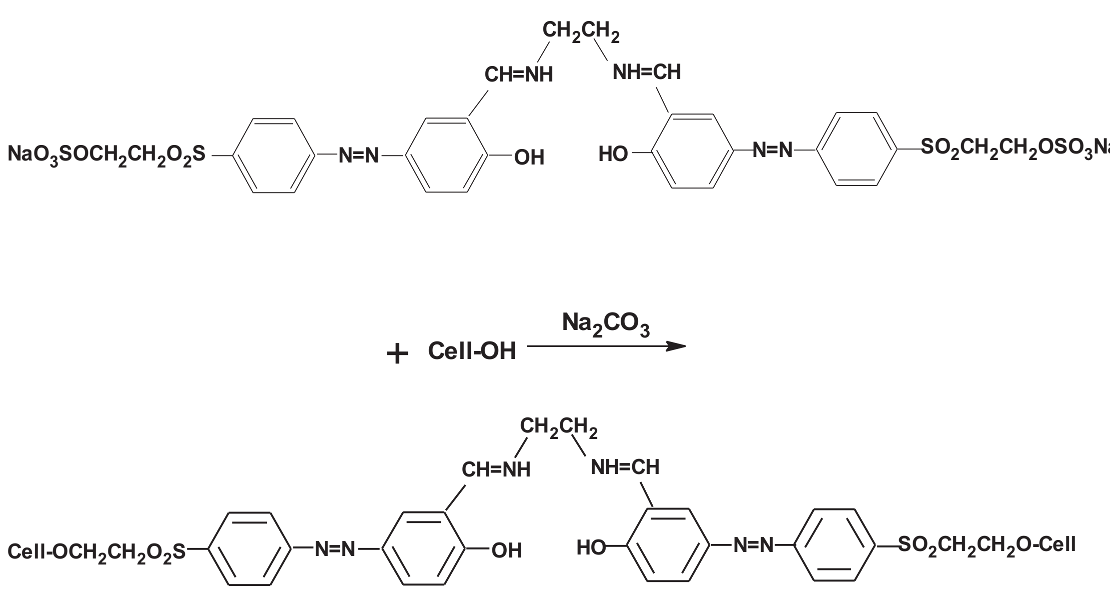
The morphological structures of the functional cellulose fabrics were analysed in this paper. SEM analysis of the functional cellulose fabrics was used to characterize the changes about the surface morphology of cellulose. Fig. 3(a and b) are the SEM of the control cellulose fiber and FC-2 sample, respectively. The surface of FC-2 is smoother than that of control sample. It can be seen that functional cellulose fabrics were swelled during being grafted process.

Table 2
UPF, T(UVA), T(UVB) of functional and control cellulose fabrics.

Samples	Concentrations (g/l)	UPF	T(UVA)	T(UVB)
Control	0	8.31	10.09	11.81
FC-1	2	18.72	4.29	5.17
FC-2	5	31.7	3.09	3.73

3.3. UV-protective properties of functional cellulose fabrics

Generally, the sun emits UV radiation across a broad spectrum from the high energy UVC band (wavelength below 280 nm) to the UVB (wavelength below 280–315 nm) band and UVA band (wavelength below 315–400 nm). Due to absorption of ozone layer in the upper atmosphere, UVC was filtered. UV radiations reaching the earth's surface mainly are UVB and UVA. Therefore, UPF, T (UVA), T (UVB) for the functional cellulose fabrics were measured. The results are summarized in Table 2. It shows that the control sample had a high ultraviolet transmittance and low UPF value. The modified cellulose samples, FC-1, and FC-2, had higher UPF value



Scheme 2. Mechanism of cellulose reacting with BSPEA.

Table 3
Physics properties of functional and control cellulose fabrics.

Samples	Tensile strength (N)	Elongation at break (mm)	Tearing strength (N)	WRA (°, w+f)
Control	383.6	24.35	15.82	206.1
FC-1	377.4	22.64	14.13	213.5
FC-2	375.6	22.12	13.82	218.6

and lower ultraviolet transmittance. Especially, UPF of FC-2 sample reached 31.7. The UV protective properties of fabrics would be evaluated as good when the ultraviolet transmittance was less than 5% and UPF reached 10–30. It can be seen that the azobenzene Schiff base compounds could be used to improve the fabric performance of ultraviolet resistance. The UV-protective properties of the functional cellulose fabrics were mainly attributed to absorbing UV radiation of azobenzene Schiff base, which caused change of the molecular structure based on its cis–trans isomerization and intermolecular proton transfer.

Physical properties of functional cellulose fabrics were measured. The tensile strength, the wrinkle recovery angle (WRA) and tearing strength of the control sample and functional cellulose fabrics are presented in Table 3, respectively. It indicates that the tensile strength, the elongation at break and the tearing strength of functional cellulose fabrics showed a slight decrease. However, WRA of the functional cellulose fabrics had slight improvement. It can be contributed that the BSPEA contained two reactive groups, p-[(2′-sulphatoethyl)sulphonyl phenylazo, which was able to crosslink cellulose. The elastic recovery of the cellulose fabrics which crosslinking was introduced had been improved due to the inhibition of slippage between the molecules when forces were applied. It is also found that the functional cellulose fabrics had not significant influence on the physical properties.

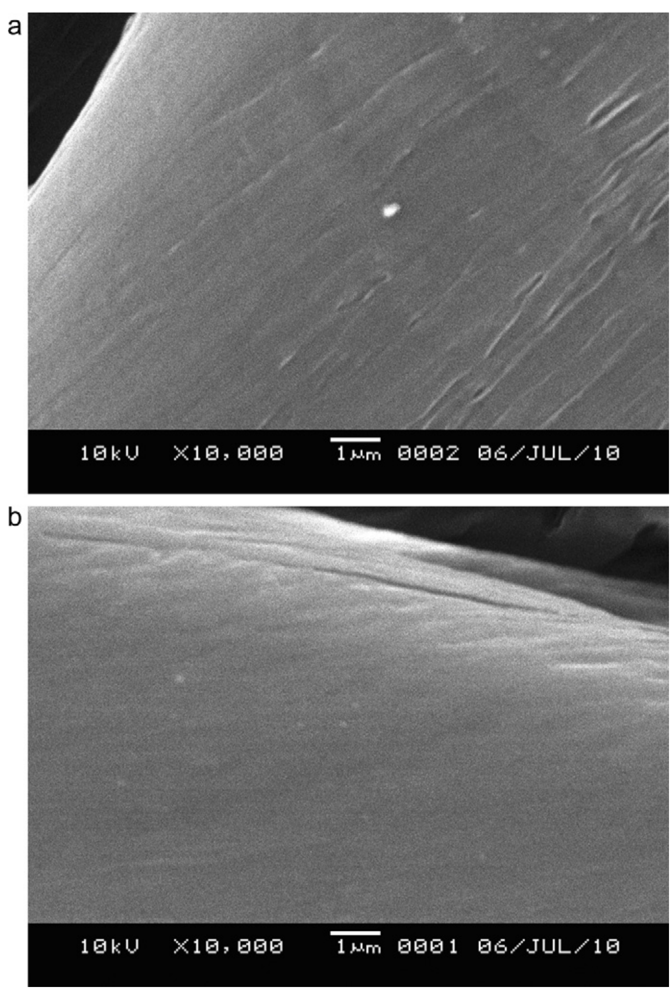


Fig. 3. SEM of control cellulose fiber and FC-2 sample.

4. Conclusions

The functional cellulose fabrics containing azobenzene Schiff base were prepared with grafting reaction. The nitrogen and carbon contents of the modified cellulose significantly increased. The functional cellulose fabrics had higher UPF value and lower ultraviolet transmittance, so had excellent UV-protection properties. The morphological structure of the functional cellulose fabrics is smoother than that of control sample. The functional cellulose fabrics had not significant influence on the physical properties.

There is a growing demand in the market for apparel textiles and biomaterials that offers comfort and UV-protection from the harmful effects of the UV radiation. The multifunctional cellulose fabrics based on reactive azobenzene Schiff base will have potential application in textile and functional materials. Other properties of functional cellulose fabrics based on reactive azobenzene Schiff bases will be further investigated.

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