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Properties of Anti-UV-finished Cotton Fabrics Cured by Blue Light Irradiation

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Abstract: To decrease the pollution discharge and energy consumption resulting from textile finishing using the conventional pad-dry-cure process, a blue light-curable digital finishing for textile was innovatively proposed. Based on the mechanism of blue light curing technique, a combination of the blue light curing process and anti-UV finishing was established in this study. A blue light-curable anti-UV finishing solution containing oligomers, monomers, photoinitiators, and anti-UV agents was padded onto the surface of the cotton fabrics, and then cured to form a tough film under blue light irradiation. The ultraviolet protection factor (UPF) value of the finished cotton fabrics was 50, the top level of international standards, demonstrating excellent UV resistance. The finished cotton fabrics also showed good rubbing and washing durability, and acceptable handle. The integration of an anti-UV finishing with the blue light curing technique presents some unique advantages in terms of environmental protection and application potential.

Keywords: Anti-UV finishing, Blue light curing, Rubbing and washing durability, Anti-UV property, Fabric handle

Introduction

Functional finishing of textiles can endow fabrics with specific properties, enhancing the added value of the textiles [1]. Functional finishing is traditionally achieved by the pad-dry-cure process. Although this process is already quite well established, the problems of energy consumption, pollution discharge, and low utilization of functional chemicals still remain. Those problems cannot be entirely solved by adjustments to the finishing process, so there is considerable demand for new ideas and technologies. To alleviate these problems, we propose the new concept of digital functional finishing by blue light curing of textiles. The process involves two main steps: 1) the finish solution comprising photoinitiators, photopolymerizable oligomers and monomers, and functional substances is digitally injected onto the fabric surface; and 2) the finish solution is photoinduced *in situ* by blue light irradiation to form a polymerised film on the fabric. This functional finishing process using blue light curing and digital finishing can achieve single-side and selective-location finishing, with low energy consumption, high chemical utilization, and low pollution discharge. It is worth noting that blue light curing is key to this innovative blue light-curable digital finishing technique, because it determines the finishing durability, fabric handle, and other mechanical properties of the finished fabric. As is known, light-curing reactions can be divided into two types, depending on the wavelength of the radiation: UV curing and visible light curing. Although UV curing has been developed and used in many fields for a considerable time, the problems of ozone formation, potential harm to fibers and people's health, and limited curing depth still exist. For years, blue light curing, one of the visible light curing, has been extensively developed in the field of dental materials because it is safe and highly efficient. Based on this point, we have endeavored to develop a high-efficiency blue light curing technique. An efficient, three-component initiating system has been proposed, presenting low oxygen inhibition, and a novel visible light initiator has been synthesized and characterized [2-4]. Moreover, we have demonstrated a blue light-induced polymerization system that produces cured film with excellent tensile mechanical properties and flexibility; we have applied blue light curing to textile digital printing, indicating that the printed fabric samples had fine patterns and satisfied rubbing fastness and soft fabric handle requirements [5-7]. Thus, a preliminary blue light curing system with good performance has been established. Anti-UV finishing is currently receiving more attention because of the increased risk of exposure to ultraviolet radiation [8]. It is necessary to develop an anti-UV finishing process with low energy consumption. In this paper, a blue light-curable anti-UV finishing was introduced as a typical representative of blue light-curable functional finishing, and the anti-UV properties, handle, rubbing and washing durability of the finished fabrics were evaluated.

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Experimental

Materials

Camphorquinone (CQ), a photoinitiator, was purchased from Sigma-Aldrich Co (St. Louis, MO, USA). Ethyl 4-dimethylaminobenzoate (EDB) was obtained from Meryer Co., Ltd., (Hangzhou, Zhejiang, China). 2-hydroxyethyl methacrylate (HEMA), a monomer, and nano zinc oxide

(ZnO) were provided by Aladdin Industrial Inc. (Shanghai, China). Aliphatic polyurethane acrylate (PUA), an oligomer, and benzotriazole TF615 were obtained from Sanmuchem Co., Ltd. (Yixing, Jiangsu, China) and Zhejiang Transfar Co., Ltd. (Hangzhou, Zhejiang, China) respectively. The finishing experiments were performed using 100 % plain cotton fabrics (115 g/m^2, Furun Printing & Dyeing Co., Ltd., Zhejiang, China). All materials were used as received.

Modification of the Nano ZnO

The nano ZnO was modified with methacryloxypropyltrimethoxysilane (MPS, Aladdin Industrial Inc., Shanghai, China), a silane coupling agent. The modification process was as follows: 6 % (the ratio of MPS and nano ZnO) MPS was added to 30 m*l* weakly acidic water. After 0.5 h ultrasound treatment, 1 g nano ZnO was added to the solution, and the mixture was agitated in a water bath at 80 ^{o}C for 2 h. The obtained sample was rinsed twice with deionized water, dried, milled, added to 50 m*l* deionized water, and ultrasonically dispersed for 0.5 h. After standing for 1 h, the upper layer of floating powder was removed and dried to obtain the modified nano ZnO.

Blue Light-curable Anti-UV Finishing for Cotton Fabrics

The blue light curing system comprising 0.01 g CQ, 0.01 g EDB, 0.8 g HEMA, and 1.2 g aliphatic PUA was mixed and ultrasonically dispersed. The anti-UV finishing solution was then prepared by adding a certain amount of the UV agents (the modified nano ZnO and benzotriazole TF615) to the curing system. The finishing solution was diluted with 10 g ethanol, and simultaneously ultrasonically dispersed to obtain a homogeneous mixture. After padding with the prepared mixed solution, the resultant cotton fabrics were stood for approximately 0.5 h to ensure the complete evaporation of the ethanol and then cured under blue light irradiation (16 mW/cm^2) for 300 s in a nitrogen atmosphere. All those steps were carried out in a dark environment except curing process.

Curing Efficiency of the Blue Light Curing System

The curing efficiency of the finishing solution was tested using a photo differential scanning calorimeter (Q2000, TA. Inc., USA) equipped with a photo calorimetric accessory (OmniCure S2000, Lumen Dynamics. Inc., Canada). Blue light radiation from a mercury arc lamp was delivered by quartz light guides with a 400-500 nm band-pass filter at 16 mW/cm^2.

Characterization of Coated Fabrics

Scanning electron microscopy (SEM) images of the fabrics were taken by using a field emission scanning electron microscopy (ULTRA55, Carl Zeiss. Inc., Germany) at an accelerating voltage of 1.5 kV with a magnification of 1500×. A UV-proof test was performed using an ultraviolet transmittance analyzer (UV-2000F, Labsphere. Inc., USA). Ten random points on the cotton fabric were tested and the mean value was chosen as the ultraviolet resistance of the cotton fabric. The fabric handle was tested using a fabric style instrument (Nucybertek Phabromet, Nu Cybertek. Inc., USA). With reference to the ASTM D 5035-1995 (2003) standard, the mechanical properties were measured by the universal material testing machine (Instron2365, Instron. Inc., USA). According to the AATCC 8-2007 standard, the rubbing durability was tested by rubbing 20 times (standard rubbing times), and the test of double the standard time was also implemented.

With reference to the AATCC 61-2003 standard, the washing durability of the anti-UV-finished fabric was evaluated by detecting the change in the anti-UV property with increasing washing times.

Results and Discussion

Surface Micro-topography

The micro-topographies of the finished cotton fabrics are shown in Figure 1. The pristine cotton fabric surface is smooth (Figure 1(a)). After coating with the pure curing system, the fabric became slightly rough and the fibers adhered to each other. This phenomenon is well observed and demonstrates the adhesive role of the curing system. The same results occurred when TF615 was added to the curing system, as shown in Figure 1(c), because TF615 is an organic liquid and fuses in the molecular state. Compared with the pristine example, the cotton fabric treated with the curing system comprising the modified nano ZnO exhibited particles on the surface, and the particle distribution was compact and uniform, which verified the good dispersity of the modified nano ZnO in the curing system. The nano ZnO was modified using MPS to improve the compatibility between the nano ZnO and the oily curing system [9]. It can be inferred from the SEM images that the anti-UV agents were attached to the fiber surface, endowing the cotton fabrics with anti-UV property.

Ultraviolet Resistance

The anti-UV properties of the cotton fabrics treated with the various finishing solutions are listed in Table 1. As can be seen, the UPF value of the untreated cotton fabric was only 6, and the transmittance levels in the UVA band (320-400 nm) and the UVB band (280-320 nm) were high, while the anti-UV properties of the cotton fabric with the pure curing system were slightly improved. However, the transmittance in the UVA band remained high. The chromophore and auxochrome in the structure of the cured film selectively absorb high-energy ultraviolet light, leading to a dramatic decrease in UVB transmittance [10]. When the two anti-UV agents were added, the UPF value almost reached the highest international standard value of 50, and the transmittance in

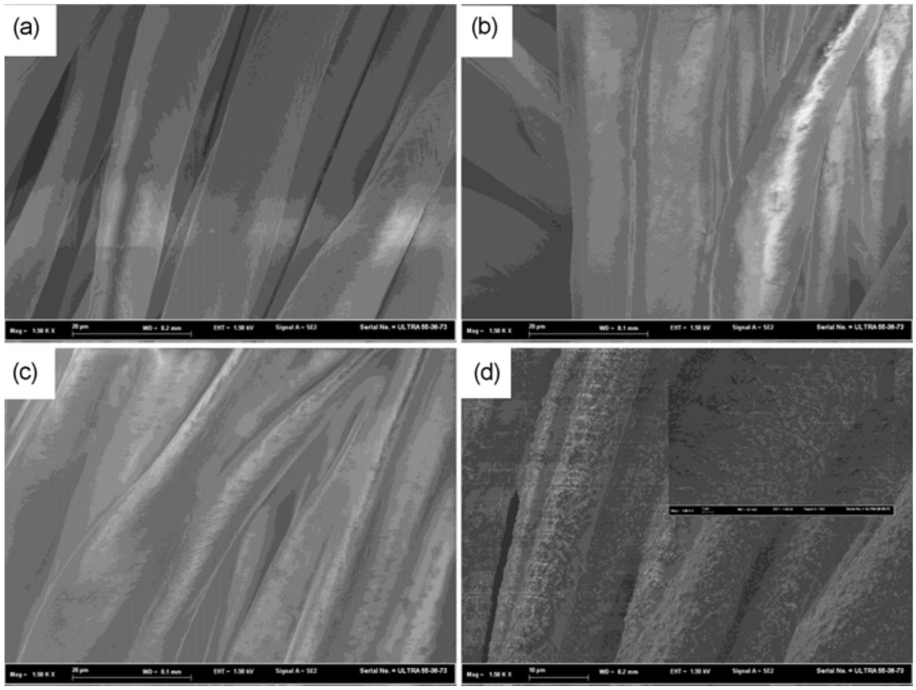

Figure 1. SEM images of; (a) cotton fabric, (b) cotton fabric with curing system, (c) cotton fabric with curing system and TF615, and (d) cotton fabric with curing system and modified nano ZnO.

Table 1. Anti-UV properties of the treated samples

Samples	UPF value	UVA value (%)	UVB value (%)
Cotton fabric	6.00	23.57	14.54
Cotton fabric with curing system	12.52	26.34	6.00
Cotton fabric with curing system and the modified nano ZnO	45.55	7.84	1.83
Cotton fabric with curing system and the TF615	51.84	5.20	1.72

the two bands was low on account of the intramolecular action of TF615 and the quantum size effect of the nano ZnO [11,12]. This indicates that the cured film has similar properties to the binding agent, and the nano ZnO and benzotriazole coating imparts anti-UV performance to the fabrics. It can be concluded from Table 1 and the SEM images shown above that this blue light curing finishing method is able to endow cotton fabrics with anti-UV property, regardless of the type of anti-UV agents used.

Fabric Handle

Fabric handle, an important indicator, was evaluated to judge the quality of the finished fabric. The handle results of the cotton fabrics that had been treated with the various finishing solutions are listed in Figure 2. Compared with the original cotton fabric, the stiffness of the treated fabrics increased to some extent, while the softness and smoothness declined slightly. As presented, the addition of TF615 slightly reduced the difference on account of its dilution. In general, there was little difference between the original fabric and the treated fabrics. This can probably be attributed to the quick dilution of the mixture in ethanol during the finishing process, which led to the formation of a thinner film. The same changes in the handle properties occurred as in traditional anti-UV finishing, i.e., flexibility declined and

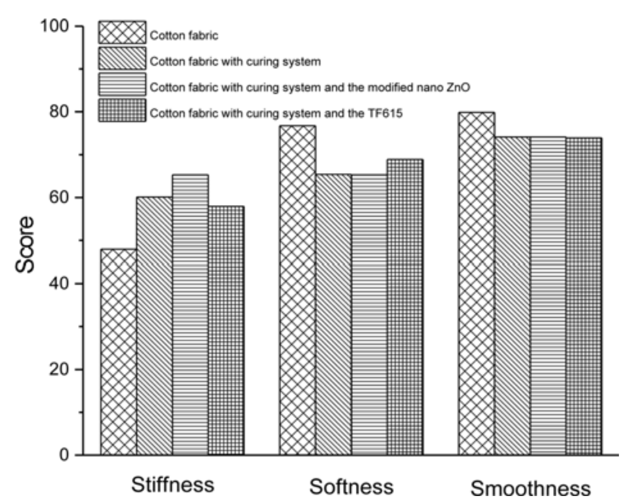

Figure 2. Fabric handle of the treated samples.

Table 2. Mechanical stretching properties of the treated samples

Samples	Breaking force (N)		Ultimate elongation (mm)	
	Wrap	Weft	Wrap	Weft
Cotton fabric	300.59	123.26	25.49998	27.99969
Cotton fabric with curing system	307.12	143.7	19.00011	20.49983
Cotton fabric with curing system and the modified nano ZnO	328.35	152.62	20.5003	20.50018
Cotton fabric with curing system and the TF615	333.9	160.71	20.49995	20.46005

stiffness increased after padding [13]. On the whole, the handle of the fabrics treated using this finishing method was acceptable.

Mechanical Stretching Properties

The mechanical stretching properties of the cotton fabrics treated with the various finishing solutions are listed in Table 2. As can be clearly seen, after finishing, the breaking forces of the warp and weft improved, while the ultimate elongations of the warp and weft decreased. The cured film formed on the surface of the cotton fabric had a certain strength, which led to the increase of the mutual force between the film and the fabric fibers. However, a number of stable covalent cross-linkages were introduced to the microstructural unit of the fabric during the curing process, so that mobility between each unit was subject to some restrictions. This resulted in non-uniform stress, which led to the decrease in the breaking elongation of the fabric. Comparing the cotton fabrics treated with various anti-UV agents, the breaking force and ultimate elongation results were similar, indicating that the type of agents has no effect on the mechanical stretching properties. In a sense, the blue light curing finishing method enhanced the mechanical properties of the fabrics.

Anti-UV Properties after Rubbing and Washing

Rubbing and washing fastness are the most important indicators of the functional finishing in textiles, and are mainly determined by the mechanical stretching properties of the cured film and the polymerization efficiency. Commonly, the maximum polymerization rate and conversion are two standard evaluations of polymerization efficiency.

The curing efficiencies of the systems with various anti-UV agents are presented in Figure 3. It can be seen that the efficiency of the system was improved by the addition of the modified nano ZnO. The improvement may be attributed to the enhanced intensity arising from the light scattering among the modified nano ZnO particles. However, the addition of TF615 reduced the curing efficiency slightly. TF615 contains phenyl groups that can partly absorb light, leading to a decrease in curing efficiency. On the whole, it is acceptable that the addition of UV agents has a slight impact on the efficiency of the curing system.

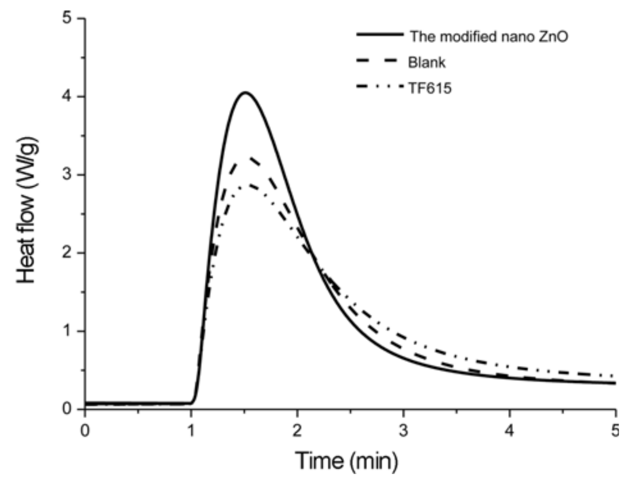

Figure 3. Effect of the anti-UV agent types on the curing system.

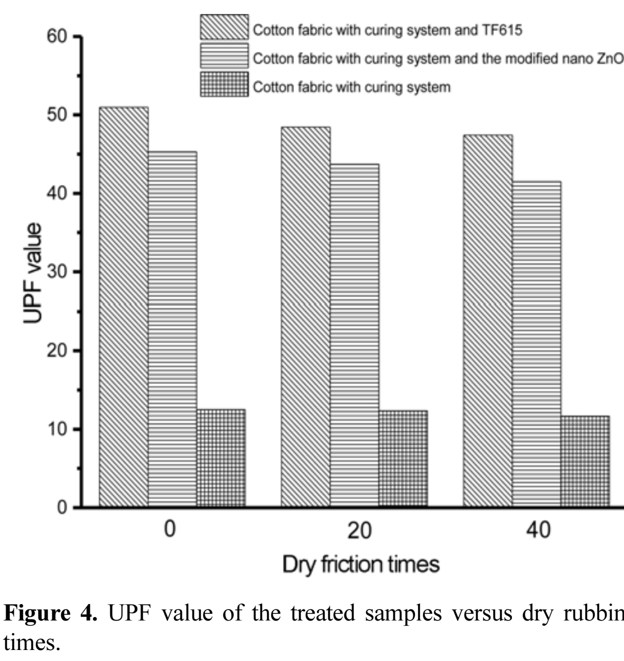

Figure 4. UPF value of the treated samples versus dry rubbing times.

The relationships between the UPF values and the rubbing times of the three treated cotton fabrics are presented in Figure 4 and Figure 5. As can be seen, there was a tiny decrease in the UPF value after rubbing 20 times (the

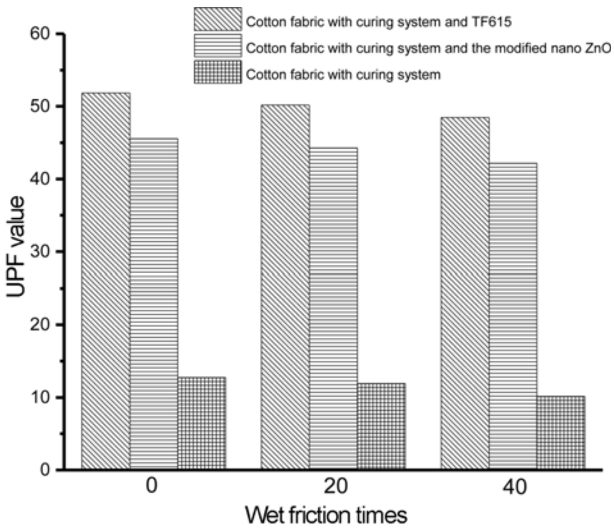

Figure 5. UPF value of the treated samples versus wet rubbing times.

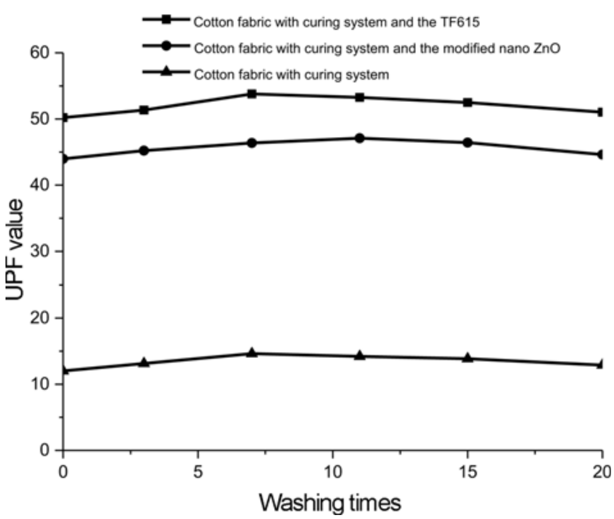

Figure 6. UPF value of the treated samples (after 20 times dry rubbing) versus washing times.

international standard). A similar result appeared after rubbing for twice the international standard rubbing time. The cotton fabrics and the anti-UV agents were coated together by the polymerization system after curing, so that the binding force between the fabrics and the anti-UV agents was sufficiently large, resulting in the slight decrease in the ultraviolet resistance after rubbing. Moreover, the curing efficiency in Figure 3 also confirms that the quality of the cured film was unaffected by the addition of the agents.

The relationships between the UPF values and the washing times of the dry rubbed fabrics are presented in Figure 6. The anti-UV properties increased slightly with increasing washing times. Because of the frictional resistance among the fibers, the fabrics remain in a state of contraction during the drying process, leading to an increase in the thickness of those finished fabrics [14]. Moreover, anti-UV properties were slightly enhanced, possibly owing to the partial exposure of the anti-UV particles [15]. After washing 20 times, the anti-UV properties of the treated fabrics were still excellent. In general, this finishing method can ensure good washing durability of the anti-UV properties.

Conclusion

In this work, blue light-curable anti-UV finishing of cotton fabrics was studied. An anti-UV finishing solution was induced by blue light to rapidly form a polymerised film on the surface of cotton fabrics instead of the thermal curing traditionally used in pad-dry-cure step. Compared with traditional anti-UV finishing techniques, this method is simple, energy-efficient, and environmentally friendly. The addition of anti-UV agents hardly affected the curing efficiency, and anti-UV performance was successfully imparted to the fabrics. After finishing, the handle of the fabrics deteriorated slightly in comparison to the original fabric, but the rubbing and washing durability were excellent.

This novel technique is also applicable to other finishing methods. By adding various functional agents, different functions, even multiple functions, can be achieved and it is possible to endow fabric with multiple functions. Moreover, this approach can be also assisted with digital inkjet printing technique, realizing an on-demand functional finishing. The blue light-curable digital functional finish for textiles will have wide application prospects.

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