Ultraviolet Resistant/Antiwrinkle Finishing of Cotton Fabrics by Sol-Gel Method

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ABSTRACT: Nano titanium dioxide (TiO_2) sols were prepared by sol-gel method with tetrabutyl orthotitanate (TBOT) as precursors, citric acid (CA) as inhibitors. Ultraviolet resistant capacity of finished cotton fabrics are greatly improved with good wrinkle-resistance, whiteness and tensile strength as well. The optimum molar ratio for preparing nano-TiO_2 sols in this study is $n[C_2H_5OH] : n[H_2O] : n[CA] : n[HCl] : n[TOBT] = 20 : 6 : 1.2 : 0.025 : 1$, at ambient temperature. Particle size distribution analysis of the sol reveals that the curve is right tailed with an average diameter of 72.8 nm. Factors affecting the performance of finished cotton fabrics by TiO_2 sols, such as concentration of sodium hypophosphite (SHP), triethanolamine (TEA) in finishing bath, curing temperatures and time lengths were investigated by orthogonal experiments. The optimum finishing results can be obtained with 3% SHP, 3% TEA, curing at 165°C for 3 min. Aggregated nano-TiO_2 particles on surfaces of finished cotton fibers both washed and unwashed were investigated by high resolution cold field emission scanning electron microscope and energy dispersive X-ray spectrometer. Esterification crosslinking between CA and cotton fibers were also demonstrated through infrared spectra. After a five-time's wash, ultraviolet protection factor of finished cotton fabrics with nano-TiO_2 sols is up to 117.42 and dry crease recovery angles increase by 30.2° with slightly improved whiteness, while the breaking strength decreases by 18.8%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2090–2098, 2011

Key words: crosslinking; dyes/pigments; fibers; nanoparticles; gelation

INTRODUCTION

Nowadays textiles with multifunctional purposes such as ultraviolet (UV) resistance, antiwrinkle, antimicrobial, etc., become more and more popular. In recent years, sol-gel technologies have been widely used to produce nanomaterials in the fields of electronics, ceramic, chemistry, biotechnology, composite materials, textiles, etc.[1,2] With the help of this technology, thin films of transparent, adhesive metal, or nonmetal oxides can be prepared on the surfaces of textile fibers, which greatly enhance textile performance through physical or chemical means.

As a method of wet chemical reaction, a sol-gel process starts from a chemical solution, which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Initial metal alkoxides or chlorides are dissolved in solvents (water or organic solvents) forming uniform solution, then the precursors undergo various forms of hydrolysis and condensation reactions, resulting in sols with particles of nanoscale. A sol is vaporized and turns into a gel, which will turn into nanoscale oxide powders when heated at a proper temperature.[3]

Nanoscale metal oxides play vital roles in precise ceramics, photovoltaic cells, magnetic recording materials, catalytic fields, etc.[4] Titanium dioxide (TiO_2) is widely used in textile industries. Because of the high surface activities, nano-TiO_2 can be used in organic dyes decoloration,[5] antimicrobial materials,[6] UV resistant textiles, etc. Under certain temperatures and pressures, the three crystalline forms of TiO_2–rutile, anatase, and brookite can transform into each other.[7]

Preparation, functional investigation and application of nano-TiO_2 have aroused extensive attractions of many researchers in recent years.[8] Generally, there are two ways to prepare nano-TiO_2: one is dry method such as physical crush method, chemical vapor deposition method; the other is wet method such as liquid phase neutralization method, colloid chemistry method.[9]
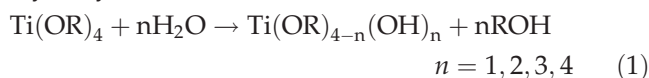
Hydrolysis and condensation of TOBT in proper mediums can generate gels in sol-gel processes. Main reactions in a sol-gel process refer to formula (1), (2), and (3):[10]

Hydrolysis:

$$Ti(OR)_4 + nH_2O \rightarrow Ti(OR)_{4-n}(OH)_n + nROH$$
$$n = 1, 2, 3, 4 \quad (1)$$

where $R = CH_3, C_2H_5, C_3H_7$, etc.

Condensation:

$$2Ti(OR)_{4-n}(OH)_n \rightarrow (Ti(OR)_{(4-n)}(OH)_{(n-1)})_2O$$
$$+ H_2O \quad n = 1, 2, 3, 4 \quad \text{(oxolation)} \quad (2)$$

$$2\, Ti(OR)_{4-n}(OH)_n \rightarrow (OH)_{(n-1)}(OR)_{(4-n)}$$
$$Ti\!-\!O\!-\!Ti(OR)_{(3-n)}(OH)_n + ROH$$
$$n = 1, 2, 3, 4 \quad \text{(alcoxolation)} \quad (3)$$
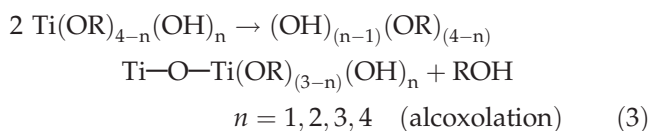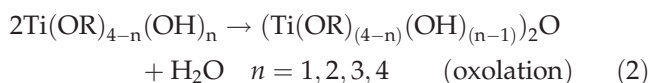
Unlike relatively faster nucleophilic hydrolysis under alkaline conditions, hydrolysis of TOBT in hydrochloric acid mediums is a much slower electrophilic reaction with final products of high purity. With increasing concentration of H^+ ions from hydrochloric acid, the equilibrium in formula (4) moves toward left side and higher concentration of $[M\text{-}(OH)_2]^{z+}$ will be achieved, which is beneficial to condensation with shorter gelation times.

$$[M - (OH)_2]^{z+} \Leftrightarrow [M - (OH)_2]^{z-1} + H^+$$
$$\Leftrightarrow [M - (OH)_2]^{z-2} + 2H^+ \quad (4)$$
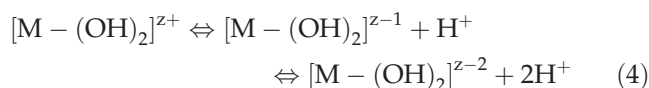
Citric acid (CA) contains multicarboxyl groups in the molecule, which provides potential complex bond-forming capabilities with transitional metal ions. CA, together with its salts, has relatively strong chelating capabilities over a wide pH range of 4–8. When the concentration of CA is elevated, more ionized COO^- ions are supplied to compound with titanium ions. Stereoscopic obstacles of the resultant complex compounds then delay the hyrolysis reaction behaving longer gelation times.

After dried at low temperatures, gels undergo a cure or incineration at high temperatures, and superfine TiO_2 particles with good purity and stable quality will be achieved. However, the high prices of titanium salts have greatly hindered the industrializing process of sol-gel methods.

UV-resistant finishing of textiles will shield UV radiation (UV-A 315–400 nm, UV-B 280–315 nm) in the ray of sunshine and lower the occurring probabilities of skin cancers and some other diseases. Most organic UV absorbers just absorb the energy of UV radiation and transform the energy into heat or other longer wavelength radiation. Inorganic UV-resistant agents such as TiO_2 and ZnO can modify the directions of incident UV radiation by scatter or reflect phenomenon, avoiding their penetrating through fabrics and hurting human skins.[11]

Antiwrinkle finishing can impart fabrics with good wrinkle recovery and easy care capabilities.

Formaldehyde-containing finishing agents such as 1,2-dimethylol-4,5-dihydroxyethyleneurea, N,N'-dimethylethyleneurea are restricted because of environmental and healthcare problems,[12] whereas formaldehyde-free finishing agents such as 1,2,3,4-buthanetetracarboxylic acid, CA, are widely concerned.[13,14] Despite of disadvantages of yellowing and inferior performance, cotton fabrics finished by CA are good solutions to obtain winkle recovery performance due to their relatively lower costs. Many researches have been executed on the reacting mechanisms between CA and cellulose molecules.[15,16] The esterification between cellulose and CA occurs in two steps: the formation of a five-membered cyclic anhydride intermediate by the dehydration of two carboxyl groups, and subsequent esterification between the intermediate and hydroxyl group in cellulose molecules. The reaction mechanism of crosslinking between cellulose and CA catalyzed with nano-TiO_2 under UV irradiation has been proposed.[17] Besides, CA can be used as a chelating agent in the preparation of nanometal oxides materials by sol-gel methods.[18]

In this study, preparation of nano-TiO_2 sols was investigated. Then, cotton fabrics were finished with nano-TiO_2 sols under different conditions. Ultraviolet protection factor (UPF), dry crease recovery angles (DCRA), breaking strength (BS), scanning electron microscopy (SEM) and energy dispersive X-Ray spectra (EDS), infrared (IR) spectra of finished samples were also investigated.

EXPERIMENTAL

Materials

Bleached twilled weave cotton fabric (110.8 g m^{-2}, warp direction 220 yarns/10 cm, weft direction 400 yarns/10 cm) were used throughout this study.

Tetrabutyl orthotitanate (TOBT, $Ti(OC_4H_9)_4$, C.P., Aladdin Reagent Co., Ltd., Shanghai, China); Citric Acid (CA, $C_6H_8O_7 \cdot H_2O$, A.R., Tianjin Damao chemical reagent factory, Tianjin, China); sodium hypophoshite (SHP, $NaH_2PO_2 \cdot H_2O$, A.R.), Triethylolamine (TEA, $(HOCH_2CH_2)_3N$, A.R.) from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

Ethanol (EtOH, C_2H_5OH), 37% Hydrochloric acid, etc are all analytical grades, without any further purifying in this study.

Particle diameter distribution of TiO_2 sol was analyzed on Beckman Coulter N5 submicron particle size analyzer (Beckman Coulter, Inc., Brea, CA); X-rite Color-Eye 7000A computer color matching system (X-Rite Incorporated, Grand Rapids, MI) for fabric whiteness (Wh, Hunter whiteness); Model YG541B crease recovery angle tester for DCRA (Wenzhou Darong Textile Instrument Co., ltd., Wenzhou, China);

Model YG (B) 912E textile UV-resistant performance tester for UPF (Wenzhou Darong Textile Instrument Co., Ltd., Wenzhou, China); Model HD026N+ multi-functional electronic fabric strength tester (Nantong Hongda Experiment Instruments Co., Ltd., Nantong, China) for BS; M-6 pin tenter (Nantong Baolai Texitle Equipment Co., Ltd., Nantong, China) for fabric drying and curing; Royalstar XQB45-831G full automatic washing machine (Royalstar Home Appliances Co., Ltd, Hefei, China).

High resolution cold field emission scanning electron microscope (FESEM) (SEM, Hitachi S-4800, Hitachi High-Technologies Corporation, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS, EDAX Genesis 4000, Ametek, Inc., Mahwah, NJ) was used to investigate the areal microstructural morphology of samples; Nexus-6700 IR spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA) for analysis of IR spectra absorbing capabilities of sol finished fabrics.

Preparation of TiO_2 sols

(1) Under the condition of agitation, TOBT was dripped into the mixed solution of CA and 2/3 part of ethanol, after a certain period of time, transparent, yellowish solution, namely A, would appear; (2) Certain amount of deionized water, hydrochloric acid, 1/3 part of ethanol were mixed, resulting solution B; (3) Solution B was dripped slowly into solution A with intensive agitation, continued agitating after the conclusion of dripping for some times, then transparent sols could be achieved.[19]

Finishing methods with TiO_2 sols

Recipe: (w/w): 40% TiO_2 sols; 1–3% SHP; 1–3% TEA; x% deionized water, total up to 100%. (Counting as concentration of Titanium: 0.2353 mol L^{-1})

Technological process: Cotton fabric–> two-dip-two-pad, with 70% wet pickup–> drying (50°C, 5 min)–>cure (150–165°C, 2–5 min)–>wash –>performance test

Gelation time testing

Gelation time refers to time interval between the onset of the contact of dripping liquid with precursor and solidification of solution. Solidification of solution means the colloidal system will not flow while the container inclines at 45° angle.

UV resistant performance testing

Ultraviolet protection factor (UPF) of both finished and unfinished dry cotton fabrics was recorded and calculated according to American association of textile chemists and colorists 183 test method. UV transmittance data was recorded by the tester.

DCRA testing

Only delayed DCRA (wrap + filling) was recorded according to GB/T 3819-1997.

BS testing

Only BS was recorded according to GB/T 3923-1997. The tensile speed was 100 mm min^{-1}. BS decrease is calculated according Formula (5):

$$\text{Breaking strength decrease } \% = (BS_0 - BS_1)^*100/BS_0 \quad (5)$$

where the subscript 0 represents unfinished samples, 1 represents finished samples with or without wash.

RESULTS AND DISCUSSION

Preparation of nano-TiO_2 sols

In our preliminary studies of single-factor experiments of preparing TiO_2 sols, five factors are studied, which affect gelation time of sols, i.e., temperature for preparation, molar ratios of n[EtOH] : n[TOBT], n[H_2O] : n[TOBT], n[CA] : n[TOBT], n[HCl] : n[TOBT]. Generally, only sols can be used to finish fabrics and they should be relatively stable, which means gels will not occur in scores of hours or even longer in storage in the study.

For further study of the preparing conditions of TiO_2 sols at ambient temperature, a set of $L_9(3^4)$ orthogonal experiments are designed and carried out. All factors and levels are as follows:

- Factor A, molar ratios of n[EtOH] : n[TOBT], 16, 18, 20.
- Factor B, molar ratios of n[H_2O] : n[TOBT], 6, 7, 8.
- Factor C, molar ratios of n[CA] : n[TOBT], 0.8, 1.0, 1.2;
- Factor D, molar ratios of n[HCl] : n[TOBT], 0.025, 0.075, 0.125.

Experimental design and subsequent testing results are shown in Table I, with analysis in Table II.

Tables II and III reveal that compared with unfinished samples, UPF, DCRA, whiteness of finished cotton specimens by TiO_2 sols are greatly elevated, whereas BS decrease to different levels. The amount of hydrochloric acid is the most significant factor to UPF and BS. This is because hydrochloric acid greatly affects the hydrolysis velocity of TOBT and concurrent particle diameters of TiO_2, and then finally affects the scatter, reflecting of UV radiation on fiber surfaces. Cellulose macromolecules can be degraded more sensitively at high concentration of H^+ derived from hydrochloric acid. Concentration of

TABLE I
$L_9(3^4)$ Orthogonal Experiments Design and Testing Results for Preparing TiO$_2$ Sols

| | A n[EtOH] : n[TBOT] | B n[H$_2$O] : n[TBOT] | C n[CA] : n[TBOT] | D n[HCl] : n[TBOT] | Testing results | | | |
					UPF	DCRA/°	Wh	BS/N
1	16	6	0.8	0.025	103.05	100.5	92.97	401
2	16	7	1.0	0.075	94.97	102.0	93.19	356
3	16	8	1.2	0.125	106.11	109.5	92.75	296
4	18	6	1.0	0.125	84.68	114.0	93.06	375
5	18	7	1.2	0.025	160.32	131.5	92.89	353
6	18	8	0.8	0.075	85.47	113.0	92.72	376
7	20	6	1.2	0.075	73.24	135.5	92.55	325
8	20	7	0.8	0.125	85.84	106.0	92.95	117
9	20	8	1.0	0.025	109.55	123.0	89.76	361

Note: (1) Unfinished sample: UPF 18.10, DCRA 90.2°, Wh 91.31, BS 453N∘.
(2) All fabrics are finished by each of prepared sols (that is, gels will never occur), 40% TiO$_2$ sols, 3% SHP, 3% TEA, curing at 150°C for 5 min.
(3) Gelation time of each prepared sol is longer than 12 h, so we do not use this data in this study.

CA determines the antiwrinkle performance of cellulose fabrics. Among the different weight of each desired performance of finished samples, UPF is the most important target, and then comes DCRA, while whiteness is the least important one. We select $A_3B_1C_3D_1$ as the optimum combination, i.e., n[C$_2$H$_5$OH] : n[H$_2$O] : n[CA] : n[HCl] : n[TOBT] = 20 : 6 : 1.2 : 0.025 : 1.

Finishing process experiments

To investigate the optimum finishing process of cotton fabrics with TiO$_2$ sols, we design another set of $L_9(3^4)$ orthogonal experiments. Conditions for preparing TiO$_2$ sols are adopted according to the conclusions in the above section. On basis of empirical estimation, factors and levels are selected as follows: Factor A, concentration of TEA, 1%, 2%, 3% (w/w); Factor B, concentration of SHP, 1%, 2%, 3% (w/w); Factor C, curing temperature, 150, 160, 165°C; and Factor D, curing time, 2, 3, 5 min. Experimental design and results of tests are shown in Table III, analysis in Table IV.

In Table IV, curing temperature is the most significant factor affecting UPF because it greatly affects the aggregating states of nano-TiO$_2$ on cotton fiber surfaces. In acidic medium, the interparticle forces are sufficient to cause considerable aggregation and/or flocculation prior to their growth.[20] After thorough hydrolysis, internal colloidal won't be enclosed with organic groups, whereas organic groups on the surfaces of condensates will be decomposed, volatilized during drying and curing. Curing temperature also affects the aggregating velocity, states and final particle sizes of nano-TiO$_2$ on fibers, whereas UPF of finished samples is closely related to the particle sizes in case of inorganic UV-resistant agents. The aggregation is demonstrated by the SEM micrographs in subsequent sections.

Concentration of SHP is the most significant factor to DCRA. In the antiwrinkle finish of cotton fabrics with CA, SHP is used as a catalyst, and its concentration affects the reaction velocity of dehydration, cyclization and anhydridisation of carboxyl groups inside CA molecules. As the amount of catalysts increases, anhydrized groups increase every unit time, so more CA molecules will react with macro molecular chains in cotton fibers, resulting enhanced crease recovery performance for fabrics.

Curing temperature is the most significant factor to whiteness. The wavelength of incident light demanded by catalyzing action of TiO$_2$ is about 380 nm. Reductive electrons e$^-$, which are negatively charged and highly reactive are formed in conduction bands of TiO$_2$ when stimulated by incident light, while positively charged, oxidative vacancies

TABLE II
Results Analysis of Orthogonal Experiments for Preparing TiO$_2$ Sols

		A	B	C	D
UPF	k_1	101.38	86.99	91.45	124.31
	k_2	110.16	113.71	96.40	84.56
	k_3	89.54	100.38	113.22	92.21
	R	20.62	26.72	21.77	39.75
DCRA/°	k_1	104.0	116.7	106.5	118.3
	k_2	119.5	113.2	113.0	116.8
	k_3	121.5	115.2	125.5	109.8
	R	17.5	3.5	19.0	8.5
Wh	k_1	92.97	92.86	92.88	91.87
	k_2	92.89	93.01	92.00	92.82
	k_3	91.75	91.74	92.73	92.92
	R	1.22	1.27	0.88	1.05
BS/N	k_1	351	367	298	372
	k_2	368	275	364	352
	k_3	268	344	324.67	263
	R	100	92	66	109

TABLE III
$L_9(3^4)$ Orthogonal Experiments Design and Testing Results for Finishing Process of Cotton Fabrics

	A TEA/%	B SHP/%	C Curing temp./°C	D Curing time/min	Testing results			
					UPF	DCRA/°	Wh	BS/N
1	1	1	150	2	79.32	108.0	92.55	320
2	1	2	160	3	106.60	117.0	92.69	360
3	1	2	165	5	86.59	138.0	92.74	360
4	2	1	160	5	161.92	118.0	92.51	348
5	2	2	165	2	87.70	125.0	93.37	357
6	2	3	150	3	113.15	121.5	93.59	399
7	3	1	165	3	102.41	122.0	92.66	388
8	3	2	150	5	116.87	118.0	93.38	414
9	3	3	160	2	117.07	134.5	92.22	387

Note: Unfinished sample: UPF 18.10, DCRA90.2°, Wh 91.31, BS 453N。

h^+ are in valence bands, thus photo electron-hole pairs are formed. Because of abundant atoms on surfaces of nano-TiO_2 particles with high surface energy, reductive effect could occur due to transition of electrons from internal to external surface of particles.[21,22] Colored materials derived from CA molecule such as aconitic acid, itaconic acid, or furoic acid at high temperatures will be restricted by photo electron-cavity pairs. As a result, fabric whiteness is much heightened than that without TiO_2. Concentration of TEA is the most significant factors to BS. In the antiwrinkle finish of cotton fabrics with CA, TEA can partly neutralize the acidity of hydrochloric acid and CA, preventing fabrics from suffering from excessive strength loss. However, excessive amount of TEA affords strong alkalinity and hinder the catalyzing of SHP, so the antiwrinkle capabilities will decrease.

Considering the above-mentioned weight of each desired performance, combination of $A_3B_3C_3D_2$, i.e., 3% SHP, 3% TEA, curing at 165°C for 3 min, is the optimum choice of finishing process.

TABLE IV
Results Analysis of Orthogonal Experiments for Finishing Process of Cotton Fabrics

		A	B	C	D
UPF	k_1	90.84	114.55	103.11	94.70
	k_2	120.92	103.72	128.53	107.39
	k_3	112.12	105.60	92.24	121.80
	R	30.08	10.83	36.29	27.10
DCRA/°	k_1	121.0	116.0	115.83	122.5
	k_2	121.5	120.0	123.17	120.2
	k_3	124.8	131.3	128.33	124.7
	R	3.8	15.3	12.5	4.5
Wh	k_1	92.66	92.57	93.17	92.71
	k_2	93.16	93.15	92.47	92.98
	k_3	92.75	92.85	92.92	92.88
	R	0.50	0.58	0.70	0.27
BS/N	k_1	347	352	378	355
	k_2	368	377	365	382
	k_3	396	382	368	374
	R	49	30	13	27

Demonstrating experiments of the optimum finishing process

As the demonstrating experiments of conclusions proposed in *finishing process experiments* section, fabrics are finished with 40% TiO_2 sols, 3% SHP, 3% TEA, curing at 165°C for 3 min. A series of tests have been executed and the results are shown in Table V.

After a five-time's wash, UPF of the nano-TiO_2 sols finished cotton fabrics is up 117.42, DCRA increased by 30.2°(120.4–90.2 = 30.2) with slightly improved whiteness, while BS decrease by 18.8% (calculated according to (453–368)/453*100% = 18.8%). The UV transmitting characteristics of finished and unfinished samples are shown in Figure 1. The curves of Figure 1(b,c) demonstrate the sound UV resistant capabilities of cotton fabrics finished by nano-TiO_2 sols.

Since TiO_2 has a relatively higher refractive index (n_1 = 2.488, anatase; n_2 = 2.583, brookite; n_3 = 2.609, rutile), the scatter capability in UV radiation is good. According to quantum mechanisms, the larger the particle size of the semiconductor compound is, the lower the forbidden band energy will be. Stamatakis[23] believes that the optimum particle size of

TABLE V
Results of Demonstrating Experiments of the Optimum Finishing Process

Samples	UPF	DCRA/°	Wh	BS /N
Unfinished	18.10	90.2	91.31	453
Finished, without wash	137.03	136.5	91.71	381
Finished, wash five times	117.42	120.4	92.26	368

Note: (1) Washing conditions: water temperature 20°C, industrial soap 2 g L^{-1}, liquor ratio 100 : 1, on washing machine. Standard washing procedure, wash→rinse→centrifugation.
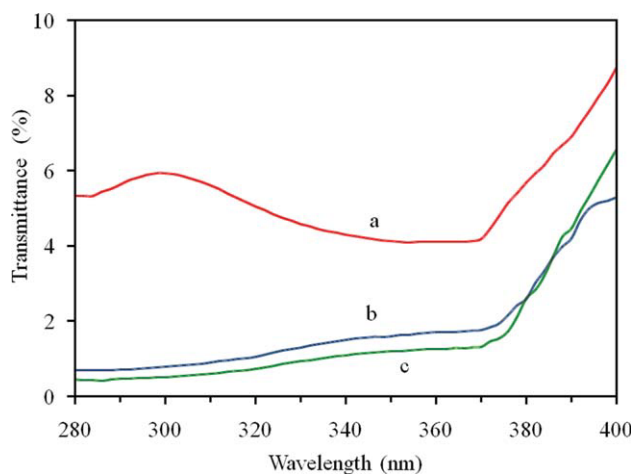(2) Lapping cloth is of the same kind as unfinished cotton fabrics.

Figure 1 Comparisons of UV transmittance of cotton fabrics (a) unfinished, (b) finished, after wash five times, and (c) finished, without wash. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
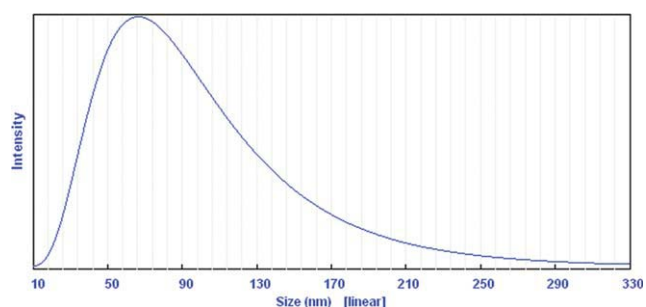

Figure 2 Screenshot of particle size distribution analysis of TiO_2 sol Conditions of preparation: $n[C_2H_5OH] : n[H_2O] : n[CA] : n[HCl] : n[TOBT] = 20 : 6 : 1.2 : 0.025 : 1$, at ambient temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

spherical TiO_2 is between 50 and 120 nm to attenuate the UV rays in the wavelength range of 300 and 400 nm. In case of attenuating UV rays of longer wavelength, scattering plays a vital role than absorbing, and vice versa. Mean particle size of the TiO_2 sol prepared according to the optimum method is 72.8 nm (See Fig. 2), so we can infer that the finished cotton fabrics should present good UV resistant performance. The differences of transmittance between finished and unfinished fabrics by the nano-TiO_2 sol
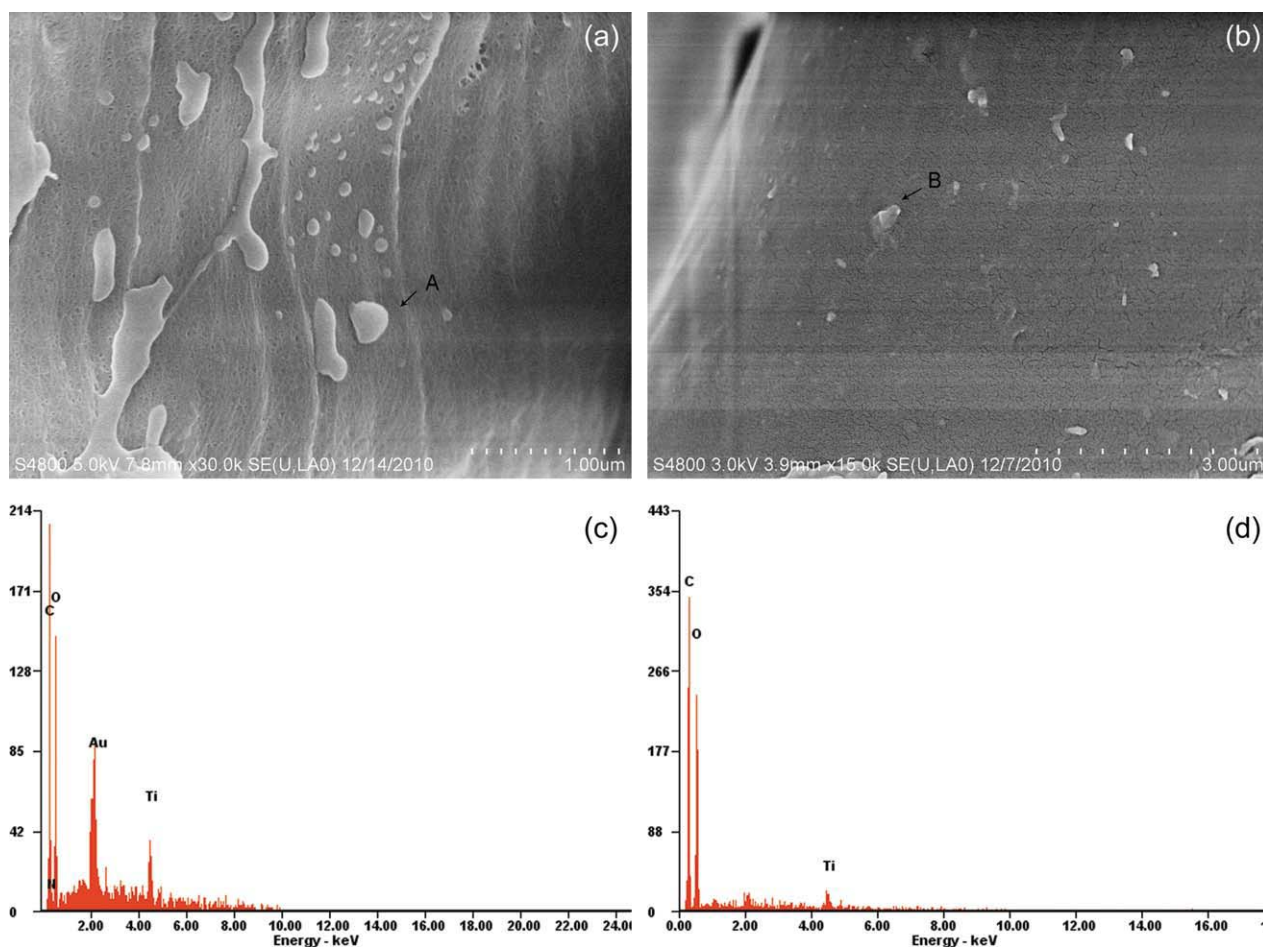

Figure 3 SEM-EDS investigation of cotton fabrics finished with nano-TiO_2 sols: (a) SEM image, without wash; (b) SEM image, after wash 5 times; (c) EDS of area A showing strong C peaks (44.28 wt %), O peaks (22.97 wt %) and medium Ti peaks (4.62 wt %); (d) EDS of area B showing strong C peaks (54.82 wt %), O peaks (29.18 wt %) and weak Ti peaks (1.53 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
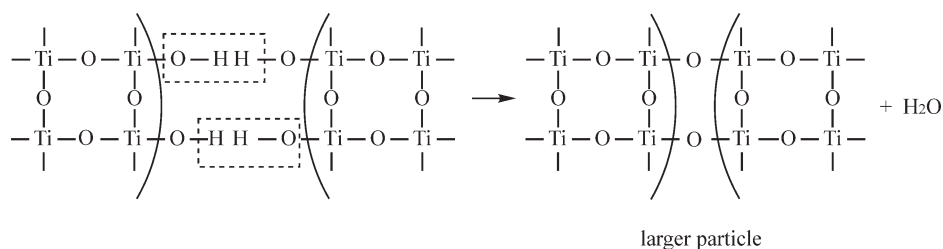
Figure 4 Schematic diagram of larger TiO_2 particle occurs due to "solid aggregation" between small particles.

near 400 nm is small; this is because the particle size is much less than the wavelength of visual light (380–780 nm), and scatter by nanoscale particles will not occur. Experimental results are well agreeable with expectations.

Particle size distribution of nano-TiO_2 sols

The TiO_2 sol prepared according to the optimum method is dispersed in doubly distilled deionized water, after 5 min stability at 25°C, the particle size distribution is analyzed. Figure 2 shows that the curve is right tailed with an average diameter of 72.8 nm. Accordingly, cotton fabrics finished by nano-TiO_2 particles of this size range can supply efficient UV resistance to human skins. Particles size distribution of TiO_2 sols is affected by the dripping speed of reactants, agitation, temperature and time length of reaction, etc. Further investigation has not been referred to in this study.

SEM-EDS investigation of cotton fabrics finished by nano-TiO_2 sols

SEM micrographs and EDS spectra of cotton fabrics finished by nano-TiO_2 sols both unwashed and after wash five times are shown in Figure 3. Figure 3(a) shows more nano-TiO_2 particles partly aggregated on surfaces of cotton fibers than that in Figure 3(b). When fabrics padded with sols are drying at low temperature, small precipitates (<1 μm) in the gelation first appear and sizes of these precipitates gradually increase leading to increases in aggregation. As the gelation goes on or cure at higher temperatures, larger aggregates become immobile on the surface or inside the hollow cotton fibers.

Hydroxyl groups linking Ti atoms between molecules in formula (2), (3) can dehydrolyze and form complicated networks. When nano-TiO_2 particles approach each other closely, abundant hydroxyl groups on the surfaces of particles may dehydrate and "solid aggregation" takes place (See Fig. 4). The dehydration occurs when the temperature is above 100°C and has been demonstrated by many differential scanning calorimetry (DSC) analysis.[24,25]

Washing can only partly remove these aggregates, leaving small size of nano-TiO_2 particles attached on fiber surfaces with less aggregation. This is demonstrated by the results of EDS spectra in Figure 3(c,d). The Au element is attributed to the vacuum-deposited coating of the fibers. After a five-time's wash, the weight percentage of Titanium decreases from 4.62 to 1.53%.

Multihydroxyl groups in the cellulose molecules of cotton fibers make the fiber much hydrophilic, so the hydrophilic nano-TiO_2 particles can easily adhere to the hydrophilic surfaces of cotton fibers through hydrogen bonds, Van Der Waals forces, or even chemical bonds (See Fig. 5), etc. Similar covalent bonds formed between the abundant hydroxyl groups on surface of TiO_2 and methylmethacrylate, $Ti(O-iso–Pr)_2(OCO–CH_2–C_{16}H_{33})(OCO–C(CH_3)=CH_2)$ have been demonstrated by many researchers.[26,27] This explains the phenomenon of washed samples still remain UV resistant performance [See Fig. 1, curve(b)].

IR spectra analysis

IR spectra of (a) unfinished cotton fabrics and (b) nano-TiO_2 finished cotton fabrics after thoroughly washed are shown in Figure 6. The strong, broad peak near 3406.61 cm^{-1} results from O—H
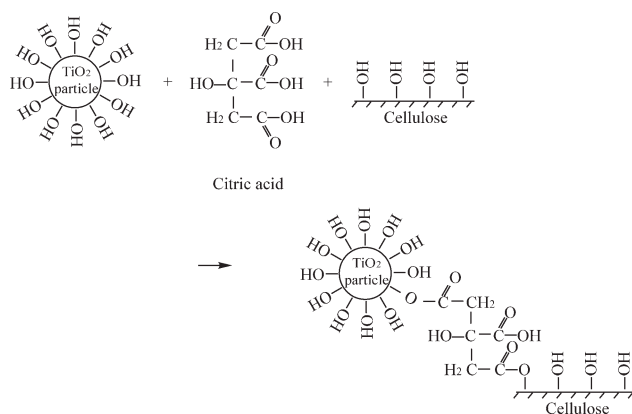

Figure 5 Schematic diagram of process of TiO_2 particles fixed on cotton fibers by CA molecules.
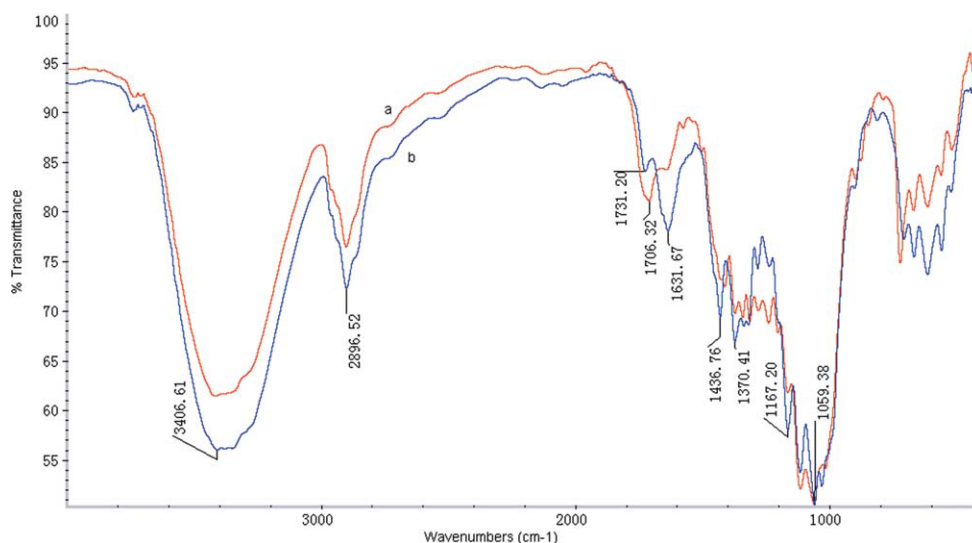
Figure 6 IR spectra of (a) unfinished cotton fabrics and (b) cotton fabrics finished with nano-TiO$_2$ sols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stretching vibration in cellulosic molecules; 2896.52 cm^{-1} shows C—H stretching vibration. The stretching vibration C=O at 1706.32 cm^{-1} in the spectrum of unfinished cotton samples (which occurs due to the formation of potential aldehyde groups during the oxidative bleaching process of cotton fabrics with hydrogen peroxide) weakens after finished by nano-TiO$_2$ sols, whereas the deformation vibration of O—H are greatly strengthened at 1631.67 cm^{-1}; carbonyl groups in noncyclic ester stretching vibration at 1731.20 cm^{-1} appears in finished samples. Stretching vibration of C—O—H near 1059.51 cm^{-1}, C—O—C asymmetrical stretching vibration at 1370.41 cm^{-1}, symmetrical stretching vibration at 1117.51 cm^{-1} are also observed. These evidences reveal crosslinking esterification between carboxyl groups in CA molecules and hydroxyl groups in cellulose molecular chain. Cotton fabrics are imparted antiwrinkle capabilities by CA chemically.

CONCLUSIONS

Cotton fabrics with good UV resistance, antiwinkle, relatively high whiteness are achieved by finishing with nano-TiO$_2$ sols. The optimum molar ratio for preparing nano-TiO$_2$ sol is n[C$_2$H$_5$OH] : n[H$_2$O] : n[CA] : n[HCl] : n[TOBT] = 20 : 6 : 1.2 : 0.025 : 1, at ambient temperature. Particle size distribution analysis of the sol reveals that the curve is right tailed with an average diameter of 72.8 nm. The optimum finishing process of cotton fabrics with nano-TiO$_2$ sols is: 40% nano-TiO$_2$ sols, 3% TEA, 3% SHP, two-dip-two-pad with 70% wet pickup, drying at 50°C for 5 min, then curing at 165°C for 3 min. Aggregated nano-TiO$_2$ particles on fiber surfaces of finished cotton fabrics are studied by FESEM-EDS. IR spectra demonstrate esterification crosslingking between CA and cellulose and provide good antiwrinkle capabilities to cotton fabrics.

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