

Performance Research of Polyester Fabric Treated by Nano Titanium Dioxide (N ano-TiO₂) Anti-ultraviolet Finishing

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Abstract

Nano-TiO₂ sol and finishing agent was prepared by sol-gel method, during which tetrabutyl titanate was used as precursor and ethanol was used as solvent. The agent was penetrated into polyester fabric through a padding method, the anti-ultraviolet performance of the fabric was analyzed and the external morphology was carefully studied afterward. The results showed that indicated that the Nano-TiO₂ particles distribute evenly with fine dispersity and stability and the finished fabrics demonstrated exceptional anti-ultraviolet performance with a phenomenal UPF ascendance reaching up to 50+ without influencing the breaking strength.

Keywords: Sol-gel, Nano-TiO₂, Polyester, Anti-ultraviolet

1. Introduction

With the aggravating greenhouse effect and the getting-severer ozone depletion phenomenon emerge, the total amount of ultraviolet (UV) reached the earth surface increased year by year (Diffey.B, 2004). When intensely interact with human skin, central nervous system and ocular region, various pathological changes would be caused which makes doing research and development on Anti-ultraviolet fabrics a focal point in recent years(Wu, Dacheng, 2003). Nanometer particles are those superfine particles with sizing range around 1-100 nm. Based on the unique characteristics demonstrated by nanometer particles such as quantum size effect, small-geometry effect, surface effect and quantum tunnel effect, wide range of application are applying nanometer technology, e.g. catalyzing, optical filtering and absorbing, pharmaceutical, magnetic medium and novel material. Nano-TiO₂ possesses a multitude of advantages like small particle size, large specific surface area, strong magnetism, photocatalytic, exceptional absorbing property especially on UV, large surface activity, remarkable heat transfer performance and stable suspension liquid. In recent years, the research of function-fabric by application of the Nano-materials and application of Nano-technology were published (such as super-amphiphobic, super-amphiphilic, UV-protection, far-infrared healthy, antistatic, anti-bacterial)(Xin J H, 2004, p.97-100).

There are plenty of inorganic UV-absorbing nanometer material which could be used as UV-absorber, for example, Nano-TiO₂, Nano-ZnO, Nano-SiO₂, Nano-Al₂O₃, Nano-FeO and etc, among which Nano-TiO₂ is one stable, nontoxic and tasteless UV-absorber. By uniformly distributing Nano-TiO₂ into fiber molecules, the decomposition of the macromolecule chain could be effectively inhibited and free radicals could be reduced (Wang, Shimin, 2004, p.230-234). Nano-TiO₂ shows strong UV-absorbing capability and UVA, UVB could be effectively shielded while visible light could freely penetrate through. Nano-TiO₂ finishing agents could enhance the fabrics' UV-reflection and UV-scattering capability to a good extent and they are secure and pragmatic to use (Zhao, Jiaxiang, 2002, p.31- 34). Yalpani M and Johnson F(Yalpani, M, 1995) etc. have done deeply research on the preparation and performance of Nanometer Titanium Dioxide(Nano-TiO₂); Denghua(Deng, hua, 2007, p.40-42) have done the research about the treatment of cotton fabric using the Nanometer Titanium Dioxide(Nano-TiO₂), improving the performance of the anti-ultraviolet and anti-bacterial, Haixia Li(Li, Haixia, 2008, p.70-73) have discussed the performance of the Nanometer Titanium Dioxide, the research about the treatment of polyester fabric was so little. Thought the function of the anti-ultraviolet of polyester fabric is better than that of cotton fabric, the performance of the anti-ultraviolet still can not satisfy the anti-ultraviolet standard(AS/NZS) of fabric when the polyester fabric made into clothing.

2. Experimental

2.1 Material

Polyester fabrics with warp density 420p/cm, weft density 300p/cm and thickness 0.099mm.

2.2 Reagents

Tetrabutyl titanate, Anhydrous Ethanol, Nitrate, Distilled water.

2.3 Nano-TiO₂ prepared by sol-gel method

Add certain quantity of Tetrabutyl titanate precursor into the anhydrous ethanol with a 1:10 ratio, sufficient stir to get a fully resolved mixed solution A. Next put the catalyst HNO_3 into distilled water to make mixed solution B and then add A into B drop by drop under quick stirring state. Maintain that state under room temperature for a certain length of time and the uniformly distributed transparent Nano-TiO₂ sol could be prepared.

The chemistry of the sol-gel process can be represented as follows:

It is well-documented that titanium alkoxide react with water through the reactions shown in Eqs. (1) (2) (3) and (4). Hydrolysis:

$$Ti (OR)_n + H_2O \rightarrow Ti (OH)(OR)_{n-1} + ROH$$
(1)

Ti (OH) (OR)_{n-1} + H₂O
$$\rightarrow$$
Ti(OH)₂(OR)_{n-2} + ROH (2)

Condensation:

$$-\text{Ti-OH} + \text{HO-Ti} \rightarrow -\text{Ti-O-Ti} + \text{H}_2\text{O}$$
(3)

$$-\text{Ti-OR} + \text{HO-Ti} \rightarrow -\text{Ti-O-Ti} + \text{ROH}$$
(4)

3. Finishing process

The polyester fabric processed by plasma ion gas with power of 100KW, processing time of 10min, then dipping the fabric into the Nano-TiO₂ sol, at 60°C, processing time of 40 min, then dry out under 80°C.

4. Test and Characterization

4.1 Performance of the finishing agent

Dilute the Nano-TiO₂ Anti-ultraviolet finishing agent with 100 times of distilled water. The absorbency (A) and transmittance (T) were measured under different wave lengths by using TEC ultraviolet spectrophotometer. Test the particle distribution condition of Nano-TiO₂ sol and the surface potential characteristics of Nano-TiO₂ by using D10-BA38-1436 nanometer particle size analyzer. The crystallization phase situation of the prepared Nano-TiO₂ powder XRD diagram was characterized and analyzed by X-ray diffraction analyzer.

4.2 Performance of the finished fabric

The UV transmittance and obstructing rate in the wave section of UVA and UVB(Sliney.D.H., 2000, p.213-228) was got by using Camspec M350 SPF Spectrophometer in accordance with AATCC Test Method 183-1998), then evaluate the UV-protection effectiveness according to the value of ultraviolet protection factor (UPF) and the rate of UV-protection of fabric Use YG065/PC electronic strength tester by referring to GB/T3923.1-1997 testing method section 1(which is an introduction about the breaking strength and breaking elongation rate by undertaking stripe sampling method) to test the warp-wise breaking strength.

5. Results and Conclusions

5.1 Finishing agent's performance

The UV-Visible light absorbency spectrum and transmittance spectrum of Nano-TiO₂ anti-ultraviolet finishing agent show as fig.1 and fig.2.

Figure 1. shows that Nano-TiO₂ anti-ultraviolet finishing agent has a very limited UV-absorbing capability around the wavelength of 200nm with absorbency less than1, but when the wavelength surpasses 200nm, the absorbency ascends phenomenally and reaches a maximum value of 4.2 around 250nm. After that section, the absorbency gradually descends until around 320nm a precipitous decline appeared and the absorbency reaches to a minimum level of 0.1 around 360nm with no obvious absorbency change happened thereafter. In the whole visible light section, the finishing agent shows almost none absorption.

Figure 2. shows that a precipitous ultraviolet transmittance decline occurred since 200nm section and the transmittance comes almost to zero between wavelengths 250nm to 370nm. After 370nm section, the transmittance gradually ascends and around 400nm, the transmittance increases the fastest. The transmittance of visible light in all spectrums increases as the wavelengths increase.

So Nano-TiO₂ finishing agent has exceptional anti-ultraviolet effect and UVA, UVB section could be effectively shielded. In the visible light section, the agent has good transmittance and transparence.

5.2 The finishing agent's particle size and Zeta potential

Figure 3. shows that the average particle size of the nanometer particles is 23.3nm ranging uniformly between 5nm to 50nm which illustrates that high-purity Nano-TiO₂ sol could be readily prepared undertaking sol-gel method. The particle size distribution of Nano-TiO₂ could also affect the zeta potential: the smaller the Nano-TiO₂ particles are and the more uniformly they distribute, the larger the zeta potential absolute value will be and the more stable of Nano-TiO₂ sol will be. The zeta potential of Nano-TiO₂ tested is 31.97 with positive and large absolute value. The particle size is ideally small and well-distributed, therefore obtains a good distribution stability.

5.3 The XRD of Nano-TiO₂ powder

The Nano-TiO₂ powder used for XRD is deserved under a drying condition lower than 50°C Because of a low drying condition, the crystal form could be considered as intact without any breakage. Figure 4 shows that a maximum diffraction peak in the pattern appeared when the diffraction angle(2 θ) reaches 25.3°, which just correspondence of the diffraction peak of the crystal plane of anatase type TiO₂(101) . Different diffraction peaks appeared when the diffraction angle reaches 37.9°, 48° and 55° matching along separately with the crystal plane of anatase type TiO₂(004), (200) and (211) which illustrates that the prepared Nano-TiO₂ has all been crystallized with phase structure of anatase crystal type. If the maximum diffraction peak of Nano-TiO₂ is narrow-and-acuate-oriented, the half-peak width would be narrow-oriented accordingly and the corresponding crystallinity would be better with comparatively intact crystal form.

5.4 Performance of the finished fabrics

5.4.1 Anti-ultraviolet performance of the finished fabrics

In Table1, ①Finished fabrics are fabrics which have prepared Nano-TiO₂ finishing agent without plasma ion; Get the polyester fabric processed by plasma ion and then impregnate the fabric into the Nano-TiO₂ finishing agent, got ②Finished fabrics. In Table.1, compared with the unfinished fibers, the UPF values of ①Finished fabrics did not increase, and the anti-ultraviolet performance of polyester fabrics did not obviously improve; ②Finished fabrics on the whole UV spectrum finished by Nano-TiO₂ is very high, especially for UVB reaching 98.8%. The UPF value of polyester fabrics finished elevates from 15.1 to 65.3 and UPF rate elevates from15 to 50+ belonging to exceptional protecting class which illustrates that the anti-ultraviolet performance of polyester fabrics enhanced to a good extent after being firstly pretreated by plasma and retreated by the finishing agent.

5.4.2 SEM analysis

Figure 5 and Figure 6 are the fiber surface topography after 1000 times of magnification. By comparing the two images, we can see that the unfinished fiber surface is smooth and sleek while the finished has deposited Nano-TiO₂ on the fiber surface ranging in an inconsecutive way with some aggregation formed due to the minimal-particle-size-led self-aggregating phenomenon of Nano-TiO₂. Consecutive Nano-TiO₂ particles ranged in a dispersed way leading to an irregular surface.

Nano-TiO₂ anti-ultraviolet mechanism analysis: (1) the valence band of Nano-TiO₂ is formed by the electron-filled-O_{2p} track and the conduction band is formed by the unoccupied Ti_{3d} orbital, which jointly configures a typical n-type semiconductor band gap. Based on its broadband-absorption performance, the energy of photonic (UV wavelength less than 410nm) would exceed the band gap if being radiated by UV when the energy of UV would be transformed into excitation energy to overcome the band gap. e⁻ is going to be stimulated and transit into a high-power conduction band from the valence band to form a e⁻ - h⁺ hole and impart the TiO₂ the power of UV absorption. (2) Nano-TiO₂ also has a remarkable capability of UV-scattering. The particle size of Nano-TiO₂ is smaller than the wavelength of UV and when the UV energy propagates into the Nano-TiO₂ particles in the form of electromagnetic wave to collide with the electrons within the Nano-TiO₂ particles, vibration would be triggered in the frequency of the incident UV thus becoming a source of propagation of the electromagnetic wave and scatter UV light in all directions (Cao, Jianjun, 2005). Due to the powerful UV absorption and scattering capability, fabrics finished by Nano-TiO₂ would be imparted with excellent UV-shielding performance.

5.4.3 Breaking strength

Mark: F(N)-Breaking strength; $\Delta L(mm)$ -breaking elongation; L(%)-elongation at break; W(J)-fracture work; T(s)-Breaking Time.

Table 2 shows that the breaking strength of the finished polyester fabric has decreased because the surface etching when being pretreated by plasma has caused damage to the fabric. The breaking force descending magnitude is fairly slight because of a low-level etching.

6. Conclusions

(1) The particle size of Nano-TiO₂ prepared by sol-gel method distributed fairly evenly showing fine dispersion and stability and has a remarkable shielding performance on the ultraviolet of UVA and UVB section.

(2) Finished Fabrics demonstrate excellent anti-ultraviolet performance with a UPF value over 60 and UPF rate over 50+.

(3) Discontinuous and unevenly distributed Nano-TiO₂ particles were deposited on the fabric surface after being finished by Nano-TiO₂.

(4) The breaking strength of the fabrics finished has decrease with a fairly slight or even unperceivable magnitude.

Acknowledgement

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References

AS/NZS 43991996 Sun protective Clothing-Evaluation and classification. Published jointly by Standards Australian and Standards New Zealand.

Cao, Jianjun,Guo,Gang & Wang,Binhua. (2005). Use rutile Nano-TiO₂ to improve the photo-ageing performance of powder coating material. *Iron steel vanadium titanium*, Vol. 26, No.1, 2005, p. 34239.

Deng, Hua, Deng Baoxiang and Xiao, Changfa. (2007). Nano-materials in UV protection textiles. *Textile Asia*. June 2007, p. 40-42.

Diffey.B. Climate change. (2004). Ozone depletion and the impact on ultraviolet exposure of human skin. *Physics in Medicine and Biology*, Vol. 49, No.1, 2004, p. R1-R11.

Li, Haixia & Deng, hua. (2008). Preparation of Nano-titanium dioxide and its application in cotton fabric. *The eighth symposium of functional textiles and nanotechnology*, April 2008, p. 70-73.

Sliney.D.H. (2000). Ultraviolet radiation exposure criteria.Radiation Protection Dosimetry, No. 91, p. 213-228.

Wang, Shimin, Xu, Zuxun & Fu, Jing. *Nanometer material preparing technology*, Beijing: Chemistry Industry Press. P. 230-234.

Wu, Dacheng & Du, Zhongliang and GaoXushan. (2003). Nanometer fiber. Beijing: Chemistry Industry Press.

Xin J H & Daoud W A. (2004). A new approach to UV-Blocking treatment forcotton fabrics, Vol. 72, No. 2, TRJ, 2004, p. 97-100.

Yalpani, M, Johnson, F & Roblnson, L E. (1995). Advances in chitinand chitosan. *Elsevier Applied Science*, 1995, p. 543-561.

Zhao, Jiaxiang.(2002) The status quo of skin protecting fabrics research in Japan. *Textile Science Research*, Vol. 13, No. 2, 2002, p. 31- 34.

Table 1. Anti-ultraviolet performance of the finished and unfinished fabrics

Sample	UVA blockage%	UVB blockage%	UPF value	UPF rate
Unfinished fabrics	81.4	95.6	15.1	15
①Finished fabrics	84.5	96.2	17.4	15
^② Finished fabrics	94.3	98.8	65.3	50+

Table 2. Strength comparison of fabrics

Sample	F(N)	$\Delta L(mm)$	L(%)	W(J)	T(s)
Original polyester fabric	227.7	20.8	20.80	2.3	12.48
Polyester fabric finished	225.9	21.2	21.20	2.3	12.75

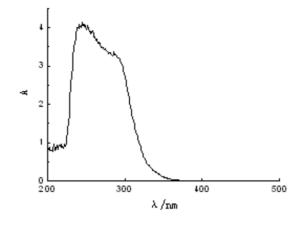


Figure 1. UV-absorbance spectra of Nano-TiO₂ sol

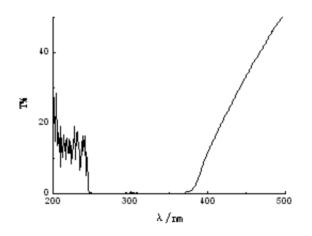


Figure 2. UV-transmission spectra of Nano-TiO₂ sol

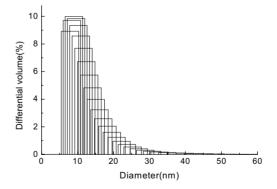


Figure 3. The Nano-TiO₂ particle size distribution

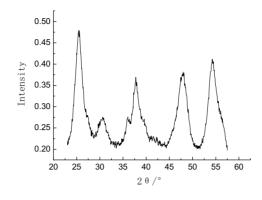


Figure 4. X-ray diffraction patterns of Nano-TiO₂ crystals

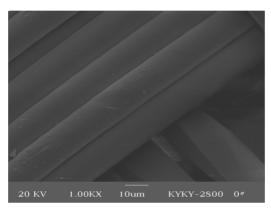


Figure 5. SEM image of the surface distribution of unfinished polyester fabrics

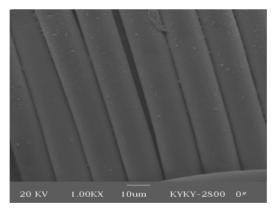


Figure 6. SEM image of the surface distribution of finished polyester fabrics