

A POLYURETHANE-BASED RETANNING AGENT WITH FLUORESCENT EFFECT

by

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ABSTRACT

A novel fluorescent waterborne polyurethane retanning agent (FWPRA) was prepared through chemical incorporation of fluorescer, disodium 4,4'-bis[4-anilino-6-hydroxyethylamino-6-(2-choloronilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonate (RSW), into polyurethane backbone as a chain extender. The chemical structure was characterized by FTIR, ¹H NMR and UV-vis spectrophotometer, and fluorescence performances of FWPRA, RSW together with resultant leather were investigated systematically. The results indicate that polymerization has a positive effect on optical performance; FWPRA shows enhanced fluorescence intensity in comparison with fluorescer RSW. In the retanning process, no decay of optical performance can be found when chromium(III) salt and chestnut extract are used together, which reveals that FWPRA presents good fluorescence stability to other chemicals. For wet blue retanned by FWPRA, the shrinkage temperature, thickness as well as mechanical properties are improved. Most importantly, the resultant leather exhibits magic fluorescence effect under UV lamp.

INTRODUCTION

Leather tanning has been known as the oldest human activities, where hides and skins are treated by natural materials.¹ Tanning process introduces crosslinks between collagen chains to irreversibly alter their structure, hence to increase the hydrothermal stability, antimicrobial ability and mechanical properties.² The common chrome tannage is advantageous to provide leather excellent stability and mechanical strength,³ nevertheless, it is not able to confer all the expected properties to leather. As one of the significant steps in leather manufacturing wet processing, retanning

follows the primary tanning process in order to overcome some drawbacks of chrome tannage, which levels out the structure of a skin or hide by filling the loose and empty parts to improve the cutting value as well as endows specific functional properties to the final leather, such as water-proof, fire-retardancy, anti-microbial, antifouling and so on.⁴⁻⁸

Waterborne polyurethanes is one of the best candidates for leather retanning because they can afford the resultant leathers excellent ductility and flexibility together with expected genuine leather feeling attributed to their unique structures.^{9,10} The properties of polyurethanes can be adjusted depending on the ratio of their soft segments and hard segments formed by diisocyanate and dihydric alcohols, and besides, the functional component can be easily incorporated into the structure due to the flexibility of molecular design, which provides a possibility to develop functional polyurethane based materials and functional leather products. For example, J. Reinerset *et al*¹¹ introduced tetrafluoroethane monomers with hydroxyl groups to polyurethane network, and this fluorinated polyurethane showed remarkable antifouling properties compared to conventional system. Sadu and coworkers¹² chemically prepared nAg-TiO₂/polyurethane composites with excellent antibacterial activity by attaching nano silver-doped titania (nAg-TiO₂) to polyurethane in the chain-extension step, and the composites showed washable antibacterial characteristics.

In this paper, a fluorescer, disodium 4,4'-bis[4-anilino-6-hydroxyethylamino-6-(2-choloronilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonate (RSW) was used as a chain extender, then a novel fluorescent waterborne polyurethane retanning agent (FWPRA) was prepared and used for leather retanning. The fluorescence performances of FWPRA and retanned leather were measured in detail. Simultaneously, the stability of FWPRA, shrinkage temperature, and mechanical properties as well as cross section morphologies of final leather was investigated.

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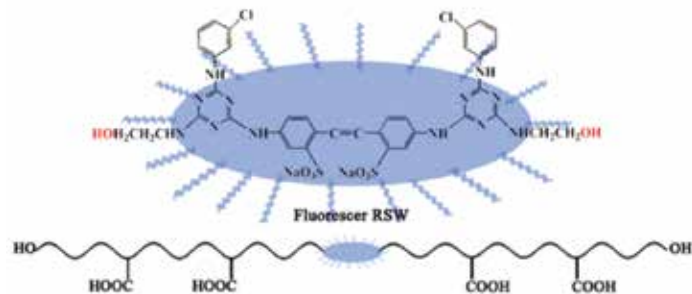
EXPERIMENTAL

Materials

Poly(propylene glycol) with number-average molecular weight of 600 (PPG 600) and 2,2-Bis(hydroxymethyl) propionic acid (DMPA) were purchased from Aladdin Industrial Corporation (Shanghai, China) and were degassed and dried under high vacuum (0.8 mmHg) at 120°C overnight before use. Isophorone diisocyanate (IPDI), 2-Aminoethanol and bismuth octoate were provided by Energy Chemical Co., Ltd. (China, Shanghai) and were dehydrated with 0.5 nm molecular sieve for 24 h prior to synthesis. Triethylamine (TEA), acetone of A.R. grade were purchased from Xiya Reagent Co., Ltd (Chengdu, China) and used without further purification. Disodium 4,4'-bis[4-anilino-6-hydroxyethylamino-6-(2-chloronilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonate (RSW) was reagent grade and obtained commercially from Ciba Specialty Chemicals Co., Ltd. (Basel, Switzerland). Chromium powder, chestnut extract, formic acid, sodium formate and sodium bicarbonate were purchased from Dowell Science & Technology Inc. (Chengdu, China). LEVOTAN C used during the retanning process was brought from LANXESS Co. (Kolner, Germany). Distilled water was self-prepared.

Synthesis of FWPRA

The fluorescent waterborne polyurethane was synthesized via step growth polymerization. The schematic of the incorporation of RSW into FWPRA is shown in Scheme 1. Polymerization was performed in a 250 ml four-necked separable reaction flask with a mechanical stirrer, thermometer, nitrogen inlet and condenser with drying tube. 25g IPDI and 40g PPG 600 were charged into the reactor together with a drop of bismuth octoate, and the mixture was reacted with vigorous agitation at 80°C for 2 h. Thereafter, 3.2g DMPA was added to the mixture and the reaction proceeded at 80°C for another 2 h to form a linear prepolymer. During the prepolymerization, acetone was added properly to decrease the viscosity of the reaction system. Subsequently, 0.5g RSW dissolved in acetone was added and the reaction was carried out at 75°C under N₂ atmosphere for a duration of 2 h. Next, 6.66g 2-Aminoethanol was added into the system until the temperature was reduced to 50°C. Then, the carboxylic acid groups were neutralized by the addition of 1.88g TEA. Finally,



Scheme 1. The schematic of the incorporation of RSW into FWPRA.

the eventual mixture was dispersed by deionized water with vigorous stirring conditions for 1.5 h to ensure the complete reaction, and the solid content of the emulsion was approximately 30%. The fluorescent waterborne polyurethane retanning agent (FWPRA) was obtained after removing the acetone from the emulsion at room temperature by rotary vacuum evaporation under the reduced pressure. As a control, linear WPA without fluorescer was prepared.

Measurements

Fourier Transform Infrared Spectra

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet IS10 FTIR spectrometer (Thermo Scientific, United States) in the range from 400 to 4000 cm⁻¹ after 32 scans at 2 cm⁻¹ resolution using thin film prepared by painting WPA and FWPRA of the latex on KBr flake and then evaporating water by heating under lamp. As for fluorescer RSW in powder form, pressed KBr pellet technique was used to prepare the sample.

¹H Nuclear Magnetic Resonance (¹H NMR) Spectra

¹H nuclear magnetic resonance (¹H NMR) spectra of WPA and FWPRA were performed on a Bruker AV400 NMR (400 MHz) spectrometer operating in the Fourier transform mode at 30°C with deuterated dimethyl sulfoxide (DMSO-*d*₆, 99.9 atom% D) as the solvent and tetramethylsilane (TMS) as the internal reference.

The UV-vis Absorption Spectra

The UV-vis absorption spectra were measured by a UV-3600 spectrophotometer (Shimadzu Corporation) using a quartz cell with a pathlength of 10 mm and the wavelength was ranged from 350 to 420 nm with a medium speed scanning.

Fluorescence Spectrometry

Fluorescence spectra were carried out by using a fluorescence spectrophotometer (Cary Eclipse, Varian Medical Systems) at excitation of 365 nm. The emission spectra were carried out in quartz cuvettes with a pathlength of 10 mm. Emission data were collected from 370 nm to 570 nm using 1-nm slit widths in excitation and emission (wavelength resolution of 1 nm), and corrected for nonlinear instrument response.

Scanning Electron Microscope (SEM) Examination

SEM (Hitachi Model S520, Japan) was employed to observe the cross-section morphologies of the leather. The images were observed in high vacuum mode under the operating condition of emission current 5 mA, working distance 9.5 mm, accelerating voltage 10 kV and a medium spot size.

Shrinkage Temperature (*T*_s) of Leather

The shrinkage temperature of leather samples were measured by a MSW-YD4 shrinkage meter (Yangguang Research Institute of Shanxi University of Science Technology) according to Chinese Industrial Standard (QB/T 2713-2005).

Mechanical Properties of Leather

Dumbbell shaped leather specimens of 50-mm length and 10-mm neck width were measured in tension mode with a universal material testing machine (model tensiTECH) supplied by Tech-Pro Inc. (Woodstock, USA) with a cross-head speed of 50 mm/min at 25°C. Each sample was measured five times and the average values along with their standard deviation were reported.

RESULTS AND DISCUSSION

Chemical Structure

The FTIR spectra of RSW, WPRA and FWPA are presented in Figure 1. As for RSW, there were some characteristic absorption peaks of triazine ring at 1361 cm^{-1} and 1572 cm^{-1} , moreover, a peak at 1242 cm^{-1} was detected, which corresponded to the stretching vibration of $-\text{SO}_3\text{Na}$. As for WPRA and FWPA, The distinct absorption peaks at 3332 cm^{-1} belongs to urethane N-H stretching, and at 1713 cm^{-1} referred to the C=O group in urethane. The absorption peak at 1107 cm^{-1} was ascribed to the stretching vibration of ether linkage in PPG600. Compared with WPRA, though the peak of $-\text{SO}_3\text{Na}$ in fluorescer RSW could not be distinguished distinctly as a consequence of band overlapping in the region of interests, new absorption peaks at 1573 cm^{-1} and 1360 cm^{-1} assigned to the stretching vibration of triazine ring in fluorescer RSW appeared in FWPA, which demonstrated the successful covalent conjugation of RSW into waterborne polyurethane backbone.

In addition to FTIR analysis, NMR experiment was also carried out to evidence the conjugation of RSW. As presented in Figure 2, the ^1H NMR spectra of both WPRA and FWPA were plotted for comparison. As for FWPA, it could be found that a new resonance signal peaking at around 3.66 ppm ascribing to the protons of Ar-NH- from RSW appeared, which also provided evidence for the successful incorporation of RSW into waterborne polyurethane chains.

Figure 3 displays the UV-visible absorption spectra of RSW, WPRA and FWPA. It is worthy to note that WPRA presented no optical absorption, while the absorption spectra of FWPA and RSW were exactly similar, which indicated that the absorption peaks of FWPA were in relation to RSW and simultaneously verified the insertion of RSW into polyurethane chain. Compared with FWPA, the absorption peak of RSW presented a red shift from 363 nm to 372 nm, which was ascribed to the $\pi-\pi^*$ transition from the conjugation between vinyl and the benzene rings.¹³

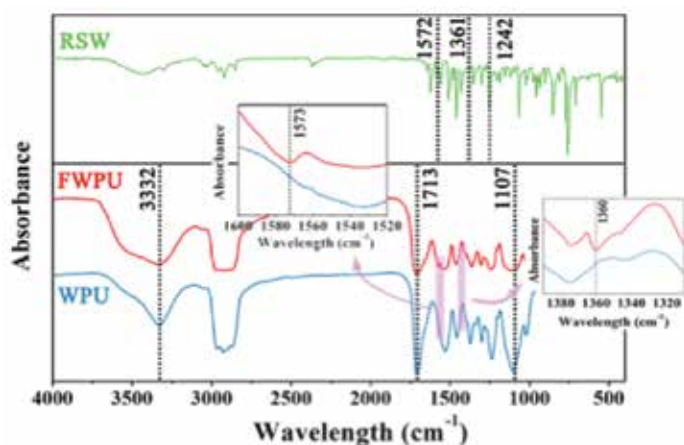


Figure 1. FTIR spectra of RSW, WPRA and FWPA.

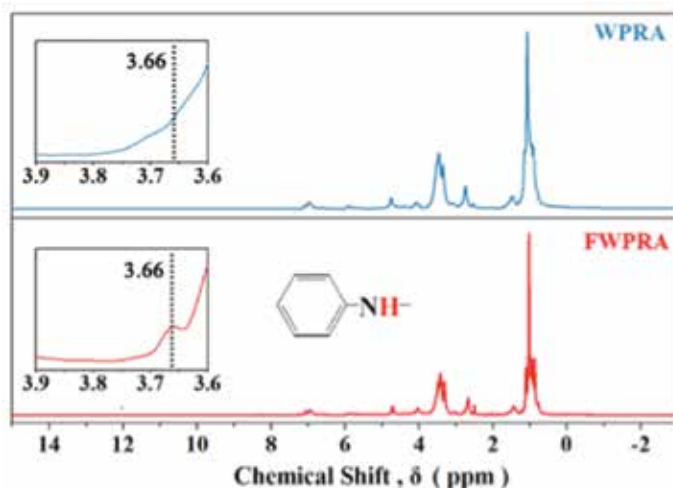


Figure 2. the ^1H NMR spectra of WPRA and FWPA.

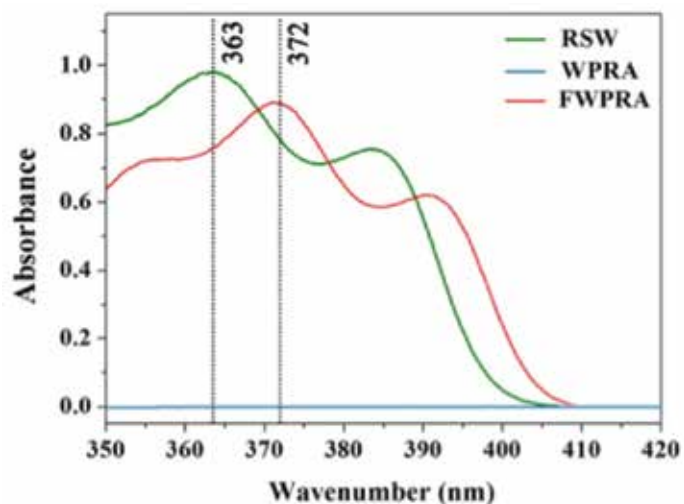


Figure 3. the UV-visible absorption spectra of RSW, WPRA and FWPA.

Fluorescent Properties

The fluorescence spectra of WPRA, RSW and FWPra with the same concentration of chromophores, which was assessed by the wavelengths 365 nm at 25°C, are displayed in Figure 4. It can be seen that WPRA without RSW unit shows no emission peaks, whilst the FWPra and RSW show strong absorption and similar emission shape that verified that the FWPra still maintained striking fluorescence after polymerization. Moreover, the fluorescence intensity of FWPra was increased slightly comparing with the RSW at the same fluorophore concentration.

Fluorescence quantum yield (Φ_F) is employed to judge the ability of fluorescers to emit absorbed light energy. And furthermore, as the fluorescence intensity is enhanced, the numerical value of quantum yield turned larger.¹⁴ It is calculated using the equation:^{15,16}

$$\Phi_F = \Phi_{st} \frac{F_u}{F_{st}} \frac{A_{st}}{A_u}$$

Here Φ_{st} is the quantum yield of the standard, F_{st} and F_u represent the integrated emission band areas of the standard and sample, respectively, while A_{st} and A_u are the absorbance of the standard and sample at the excited wavelength, respectively, and subscripts st and u refer to the standard and unknown, respectively. Using Rhodamine B ($\Phi_F=0.89$) as a standard, the fluorescence quantum yields (Φ_F) of RSW and FWPra were calculated to be 0.35 and 0.49, respectively. The stronger fluorescence intensity of FWPra could be explained as that less exciplex was formed among the fluorophores due to the chemical conjugation of RSW into polyurethane chain.¹⁷

The Stoke's shift is a significant parameter caused by the energy loss between the excitation and the emission state arising from excited molecules experience vibrational relaxation or internal conversion along with the solvation effect,¹⁸ which can be calculated according to the following equation:¹⁹

$$\nu_A - \nu_F = (\lambda_A^{-1} - \lambda_B^{-1}) \times 10^7 \text{ cm}^{-1}$$

Where, λ_A is the maximum absorption and λ_F is the emission wavelengths. Hence, Stoke's shift of RSW and FWPra was calculated to be 3795 cm^{-1} and 3128 cm^{-1} , respectively. The $\Delta\nu$ of FWPra was less than that of RSW, implying less energy loss between the excitation and emission states.

Stability of Fluorescence

FWPra was supposed to possess outstanding stability of fluorescence during the retanning process. Some leather chemicals might have adverse impact on the fluorescence intensity of FWPra, herein, chromium (III) and chestnut

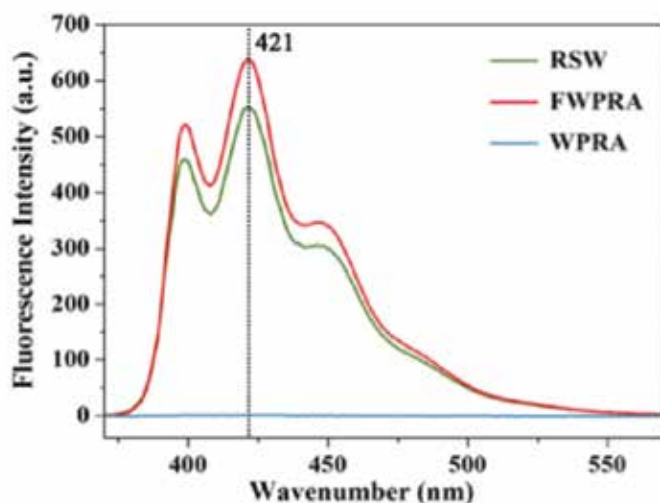


Figure 4. Fluorescence spectra of WPRA, RSW and FWPra with the same concentration of chromophores, $\lambda_{ex} = 365 \text{ nm}$, 25°C.

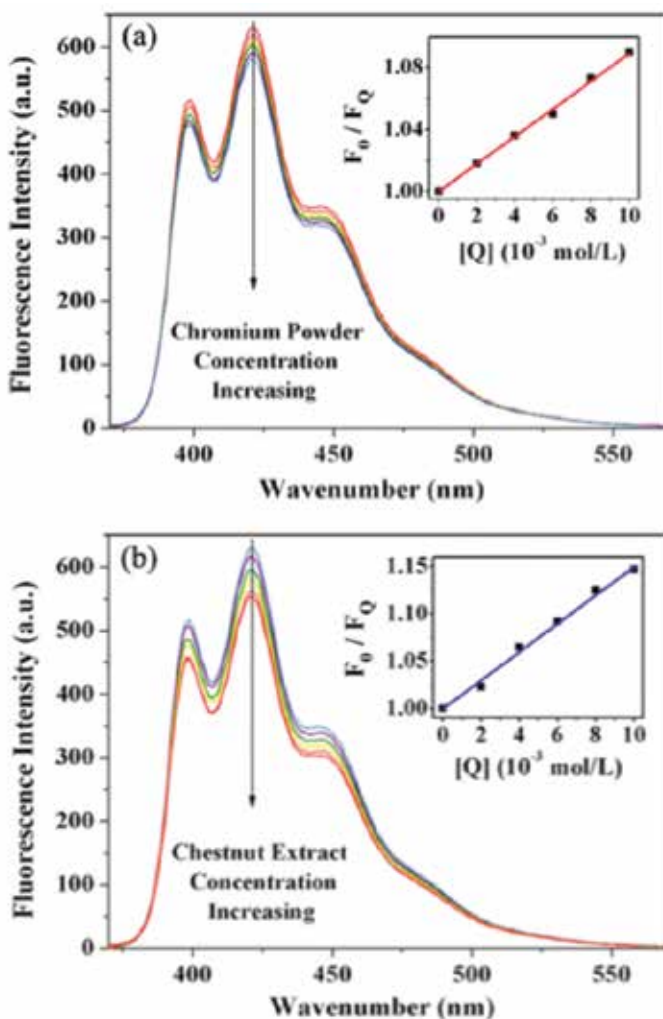


Figure 5. (a) Fluorescent spectra of FWPra in increasing concentration of chromium(III) and the plot of F_0/F_Q vs. concentration of chromium(III); (b) Fluorescent spectra of FWPra in increasing concentration of chestnut extract and the plot of F_0/F_Q vs. concentration of chestnut extract, $\lambda_{ex} = 365 \text{ nm}$, 25°C.

extract were selected to investigate the fluorescence stability of FWPRA. According to the Stern–Volmer equation:²⁰

$$\frac{F_0}{F_Q} = 1 + K_{SV} [Q]$$

Where F_0 and F_Q are the fluorescence intensity of FWPRA without and with leather chemicals, respectively, and $[Q]$ represents the concentration of leather chemicals, while K_{SV} refers to the Stern–Volmer constant. Normally, the value of K_{SV} decreased with the improving of fluorescence intensity. As presented in Figure 5, the fluorescence intensity gradually weakened with the concentration of chromium (III) and chestnut extract increasing from 0 to 10×10^{-3} mol/L, but the magnitude of the reduction only changed within a small range. Moreover, the calculation based on the Stern–Volmer equation showed the K_{SV} of chromium(III) and chestnut extract were 8.96 and 14.84, respectively. The small value of K_{SV} demonstrated that the fluorescence of FWPRA was stable and not sensitive to chromium(III) as well as chestnut extract.

Application of FWPRA in Retanning Process

The wet blue was retanned in terms of the following process listed in Table I. As a control, WPRA was simultaneously utilized to treat the leather with the same technology. All chemicals were applied based on the quantity of evenly shaved wet blue.

Figure 6 shows digital pictures of waterborne polyurethane and retanned leather. No matter leather or polyurethanes showed no fluorescent characteristics and little difference under visible light. But under UV light, both FWPRA and leather treated by FWPRA emitted a bluish-violet light, which reveals that retanning process has little effect on fluorescent effect of resultant leather.

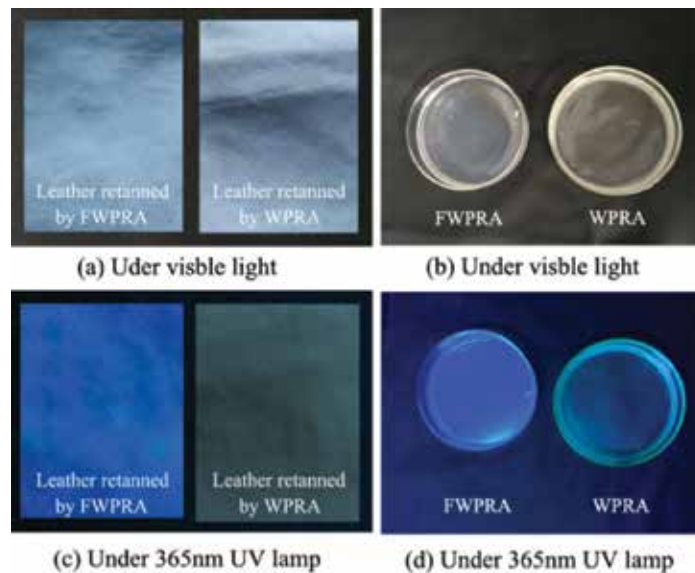


Figure 6. Digital pictures of (a) Leather retanned by FWPRA and WPRA under visible light; (b) FWPRA and WPRA under visible light; (c) Leather retanned by FWPRA and WPRA under a 365nm radiation UV lamp; (d) FWPRA and WPRA under a 365nm radiation UV lamp.

TABLE I
Retanning process.

Process	Chemicals	%	Time
Weighing			
Bleaching	Water (35°C)	200	15 min
	HCOOH	0.2	
Discharging the solution			
Neutralizing	Water (30°C)	150	40 min, pH 4-4.5 60 min, pH 5-5.5
	HCOONa	1	
	NaHCO ₃	0.4-0.5	
Discharging the solution			
Retanning	Water (35°C)	100	60 min
	WPRA/FWPRA	8%	
	LEVOTAN C	8%	
Horse up			

SEM can be used to observe the morphologies of the leather fibers before and after retanning. Figure 7 displays the cross section morphologies of wet blue and leather retanned by FWPRA. The image of wet blue presented the dense fibers and small gaps between collagen fiber bundles. However, the fibers were separated from each other in the image of leather treated by FWPRA, which was on account of excellent lubricating and filling of polyurethane between collagen fibers.

Shrinkage temperature (T_s) is an important parameter to evaluate the hydrothermal stability of leather. As presented in Table II, the T_s of the wet blue was 105.8°C, after retanned by FWPRA it increased to 108.3°C. This improvement was owing to the reaction between -COOH in polyurethane and chromium(III), consequently forming chemically coordination bonds between collagen chains. The thickness of leather increased after retanning process, and furthermore, they displayed development in mechanical properties, especially elongation at break because of excellent lubricating and filling of polyurethane between collagen fibers.

TABLE II
 T_s , average thickness and mechanical properties of leather.

	Wet blue	Retanned by FWPRA
T_s (°C)	105.8	108.3
Average thickness (mm)	0.903	1.433
Tensile strength (MPa)	15.195	17.386
Elongation at break (%)	34.37	71.499

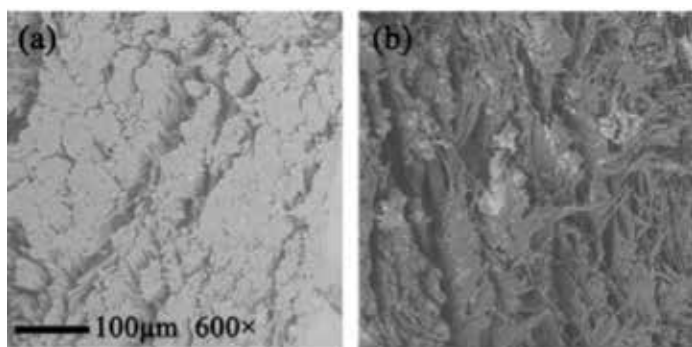


Figure 7. Cross-section morphologies of (a) wet blue; (b) leather retanned by FWPRA.

CONCLUSION

(1) Disodium 4,4'-bis[4-anilino-6-hydroxyethylamino-6-(2-choloronilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulphonate (RSW) was used as chain-extender, then a novel fluorescent waterborne polyurethane(FWPU) retanning agent was successful prepared.

(2) The polymerization and retanning process had little effect on its fluorescence properties. FWPRA shows enhanced optical performance in contrast with RSW. Coexistence with chromium (III) salt and chestnut extract, FWPRA still remains its fluorescence characteristics, showing splendid fluorescence stability to other leather chemicals.

(3) As for wet blue retanned by FWPRA, the collagen fiber was separated more evenly and the shrinkage temperature, thickness as well as mechanical properties were improved, most of all, the resultant leather exhibited obvious fluorescence effect.

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