



Developing a novel UV protection process for cotton based on layer-by-layer self-assembly

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ABSTRACT

A new approach for UV protection of cotton fabrics based on electrostatic self-assembly (ESA) technique was studied in this paper. Three fluorescent brightening agents (FBAs) and poly(diallyldimethylammonium chloride) (PDDA) were stepwisely fabricated on cationized cotton fabrics through direct layer-by-layer (LbL) deposition technique. Dyeing of the assembled cotton fabrics with anionic dyes shows regular and identifiable “odd–even” changes in color depth (K/S value), indicating the variation of surface polarities of the cotton substrates due to the alternate deposition of FBA and PDDA on them. The stepwise increases in UPF of treated cotton fabrics further revealed the growth of these LbL deposition multilayers. The assembled cotton fabrics could obtain excellent UV protection ratings of UPF > 40 after several bilayers of FBA/PDDA were fabricated, depending on the type of FBAs. Excellent durability to washing of the (FBA/PDDA)_n multilayers was obtained, which indicates good adhesion between the multilayer coatings and the cotton surfaces.

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1. Introduction

In recent years, there is a progressive increase in UV radiation on human skin caused by the depletion of the ozone in the earth's atmosphere. As long-term exposure to UV light can result in a series of negative health effects such as acceleration of skin ageing, photodermatitis (acne), erythema (skin reddening), and even severe skin cancer, developing textiles with UV protection functionality has been widely researched so far (Reinert, Fuso, Hilfiker, & Schmidt, 1997; Schindler & Hauser, 2004). UV radiation on or near the earth's surface is an invisible component of sunlight, divided into UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (200–280 nm). Fortunately, the very high energy of the UV-C photons is mostly absorbed by ozone in the higher regions of the atmosphere, decreasing their relative intensity on the earth surface to almost zero. Therefore, to be useful in protecting the wearers from solar UV radiation, the main UV rays that should be blocked by textiles are UV-A and UV-B. To date, many approaches have been investigated to improve the UV protection function of cotton fabrics because cotton textiles are the most regular summer clothes but having the least UV-blocking ability. Among them, organic UV absorbers (Akrman & Prikryl, 2008; Czajkowski, Paluszkiwicz,

Stolarski, Kazmierska, & Grzesiak, 2006; Riva, Algaba, & Pepio, 2006; Tragoonwichian, O'Rear, & Yanumet, 2008), nanoscaled inorganics such as ZnO (Becheri, Durr, Lo Nostro, & Baglioni, 2008; Vigneshwaran, Kumar, Kathe, Varadarajan, & Prasad, 2006) and titanium hydrosols (Xin, Daoud, & Kong, 2004; Xu, Liu, Wang, & Chen, 2006), dyestuffs (Gorensek, Sluga, & Urbas, 2007; Gorensek, Urbas, Strnad, & Parac-Osterman, 2007; Kim, 2006; Veatch & Gatewood, 2002), fluorescent brightening agents (Grancaric, Tarbuk, Dumitrescu, & Biscan, 2006; Pusic & Soljagic, 2008) and miscellaneous (Cheng, Li, Yuen, & Hu, 2006; El-Tahlawy, El-Nagar, & Elhendawy, 2007; Vigneshwaran et al., 2006) have been widely studied. Some UV absorbers with reactive groups that can covalently bond with cellulosic hydroxide groups have been industrially applied.

Much research on layer-by-layer (LbL) electrostatic self-assembly (ESA) of polyelectrolyte multilayers on charged surfaces has been conducted during the past decades, aiming at providing surfaces and materials with specific properties and functionalities (Decher & Schlenoff, 2003; Decher, Hong, & Schmitt, 1992; Lvov, Decher, & Moehwald, 1993). The polyelectrolytes with opposite charges could bond to each other with ionic bonds when the charged substrate is alternatively dipped in polyion solutions, forming multilayer ultrathin films on the substrate. ESA processing has advantages including no limitation on the requirement of size, shape and topography of the charged substrates, controllable functionalization through flexible utilization of polyelectrolytes or other charged substances, as well as a simple, cost-

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and energy-saving and eco-friendly process (Chen & McCarthy, 1997).

It should be noted that this new technique is not limited to polyelectrolytes. Some organic molecules with positive or negative charges have also been integrated into multilayers via LbL self-assembled deposition (Ariga, Lvov, & Kunitake, 1997; Chang-Yen, Lvov, McShane, & Gale, 2002). In view of this, it is reasonable that the textiles could be functionalized via incorporating various functional materials into ESA multilayer assemblies on fiber surfaces. However, few researchers so far have focused on textile substrates for their self-assembly functionalization (Dubas, Kumlangdudsana, & Potiyaraj, 2006; Dubas, Limsavarn, Iamsamai, & Potiyaraj, 2006; Hyde, Rusa, & Hinestroza, 2005). As the commonly used polyelectrolytes such as poly(sodium 4-styrenesulfonate) (PSS), poly(acrylic acid) (PAA), poly(dimethyldiammonium chloride) (PDDA), poly(allylamine hydrochloride) (PAH) and polyethyleneimine (PEI) have no special functions transferred to textiles, non-polyelectrolytes with negative charges such as nanoparticles (Dubas, Kumlangdudsana, et al., 2006) and dyestuffs (Dubas, Limsavarn, et al., 2006) were integrated into the LbL self-assembled multilayers together with polyelectrolytes to modify the surface antibacterial properties and dyeability, respectively. The present objective of this work is to fabricate anti-UV multilayer coatings on cationized cotton fabrics using the ESA technique. The alternating LbL buildup of three fluorescent brightening agents (FBAs) with anionic groups and polyelectrolytes on cotton substrates was performed. Three important aspects of the ESA anti-UV functionalization of cotton, i.e., characterization, growth and durability of multilayer ultrathin films on cotton, were evaluated.

2. Experimental

2.1. Materials

Well-prepared 100% cotton woven fabric was used in all experiments. 3-Chloro-2-hydroxypropyltrimethylammonium chloride (CR-2000, Dow Chemical Co., USA) is commercially available as a 65% (w/v) solution in water and was used as received. Three fluorescent brightening agents, Phorwite BA (CAS No. 4193-55-9, C.I. Fluorescent Brightener 28), Phorwite BBU (CAS No. 16324-27-9, C.I. Fluorescent Brightener 114) and Uvitex NFW (CAS No. 27344-41-8, C.I. Fluorescent Brightener 351) were used as UV-blocking agents. Poly(dimethyldiammonium chloride) (PDDA, 20%, w/w, Mw 100,000–200,000, Aldrich) and poly(sodium 4-styrenesulfonate) (PSS, 30%, w/w, Mw 70,000, Aldrich) were used as positively and negatively charged polyelectrolytes, respectively. They were used as received without further purification. Direct Red 80 (CAS No. 2610-10-8, C.I. Direct Red 80) was used for dyeing without further purification. The chemical structures of polyelectrolytes, FBAs and dyes used in this experiment are shown in Fig. 1. All chemicals were obtained from Fisher Scientific (Raleigh, NC) unless stated otherwise.

2.2. Preparation of cationized cotton substrates

For the purpose of multilayer film fabrication using the 'layer-by-layer' technique, the cotton fabrics were cationized using a cationizing agent (CR-2000). A solution containing 50 g/l of CR-2000 and 18 g/l sodium hydroxide was padded on the well-prepared cotton woven fabric. Then the padded fabric was wrapped in plastic film, slowly rotated at room temperature for 24 h, rinsed several times with water and finally the residual alkali on the fabric was neutralized with a dilute acetic acid solution (Hauser & Tabba, 2001).

2.3. Fabrication of self-assembled multilayers on cationized cotton surfaces

2.3.1. Direct deposition of multilayers

Polyelectrolyte multilayers were directly fabricated on the surfaces of the cationized cotton fabrics at room temperature according to the following procedure. Cotton swatches (4 cm × 4 cm, approximately 0.2 g each) were first immersed into a solution containing 1.0 mg/ml FBA in a plastic dish for 5 min followed by rinsing in deionized water for 5 min. Then the FBA-masked samples were transferred to PDDA solution (0.01 M by repeat unit) for 5 min followed by rinsing in deionized water for 5 min. After this, two monolayers or one bilayer were assembled on the surfaces of cotton fibers. The odd number denoted FBA layers, while the even number was PDDA layers. The above procedure was repeated cyclically until a (FBA/PDDA)_n multilayer thin film with the desired bilayer number (*n*) was deposited on the surface of the cationized cotton fabric.

2.3.2. Pre-mixed deposition of multilayers

Since each FBA has fewer negative charges compared with common polyelectrolytes, a new path was designed for fabrication of multilayers incorporating FBAs on the cotton surface. Each anionic FBA was mixed with a polycation (PDDA) in advance according to varied ratios, to form an interpolyelectrolyte complex that bears a net positive charge, (PDDA–FBA)⁺. The mole ratios of FBA to PDDA monomeric unit were 1:80, 1:50 and 1:10, corresponding to concentrations of 0.12, 0.19, and 0.96 mg/ml for Phorwite BA, 0.13, 0.22, and 1.08 mg/ml for Phorwite BBU and 0.06, 0.10, and 0.52 mg/ml for Uvitex NFW, respectively. The cationized cotton specimens with same dimensions as above were LbL self-assembled with PSS solutions and these mixed PDDA–FBA solutions. The specimens were first dipped in PSS solutions for 5 min to invert the surface electric properties from positively charged to negatively charged. After a rinsing in deionized water bath for 5 min, the PSS-coated specimens were transferred to the PDDA–FBA interpolyelectrolyte solutions and left for 5 min. They were then removed to a deionized water bath and rinsed for 5 min. This process produced ultrathin PSS/(PDDA–FBA) bilayer films on the cotton surfaces. After the assembly procedure was repeated multiple times to form functional FBA multilayers on the substrates, the specimens were air-dried.

2.4. Dyeing characterization of self-assembled multilayers deposited on cationized cotton surfaces

The surface polarity of the cationized cotton substrate deposited with self-assembled multilayers of polyelectrolytes was investigated by monitoring the change in color depth of the dyed cotton fabrics according to our previous report (Wang & Hauser, 2009). Cotton specimens were dyed using 7.5% owf anionic dye (Direct Red 80) with a liquor ratio of 150:1. The dyeing was performed in beakers without stirring at ambient temperature for 120 min to approach a dyeing equilibrium. All dyeing experiments were performed without additional auxiliary chemicals in order to evaluate dyeability without external interference.

The relative color depth of the dyed fabrics, expressed as *K/S*, was measured by the light reflectance technique using the Kubelka–Munk equation.

$$\frac{K}{S} = \frac{(1 - R)^2}{2R}$$

The reflectance (*R*) of the dyed fabrics was measured at the maximum absorbance wavelength on a Datacolor Spectraflash SF600 Plus spectrophotometer.

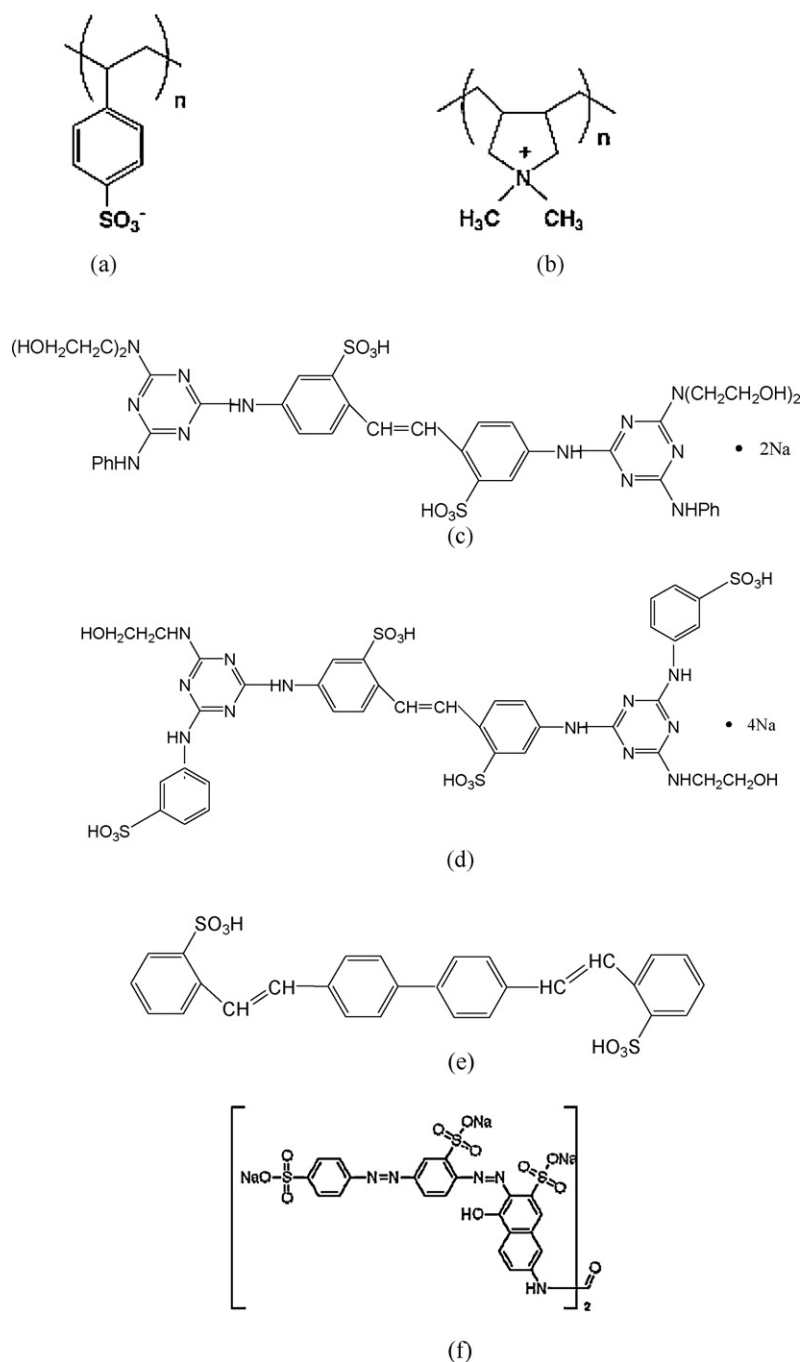


Fig. 1. Chemical structures of (a) PSS, (b) PDDA, (c) Phorwite BA, (d) Phorwite BBU, (e) Uvitex NFW and (f) Direct Red 80.

2.5. Test of UV protection ability of assembled cotton fabrics

Accurate assessment of the amount of UV protection provided by the fabrics requires measurement of the spectral transmittance (%T) of each fabric across the wavelength range 280–400 nm (UV-R), which includes the UVB and the UVA. Furthermore, the ultraviolet protection factor (UPF), which is defined as the ratio of the erythemally weighted UV radiation irradiance at the detector with no specimen to the erythemally weighted UV radiance at the detector with a specimen present, was measured by a Varian Cary 300 UV spectrophotometer (Varian, CA, USA). The spectrophotometer was fitted with integrating sphere and fabric holder accessories. The mean UPF and transmittances of UV-A, UV-B and UV-R of the fabrics can be calculated according to the Australian/New Zealand

Standard (AS/NZS 4399:1996 *Sun protective clothing—Evaluation and classification*, Standards Australia, Sydney) using an automatic analysis software for UV protection of fabrics (UPF Easy Menu software package 0.200). Typically, a fabric with a UPF of ≥ 40 is considered to provide excellent protection against UV radiation according to this standard.

2.6. Durability test

The anti-UV durability to washing was determined following the AATCC Test Method 61-1996 test using an AATCC Standard Instrumental Atlas Launder-Ometer LEF. One 45 min washing in Atlas Launder-Ometer LEF is roughly equal to five typical home launderings according to the AATCC test method. For easy under-

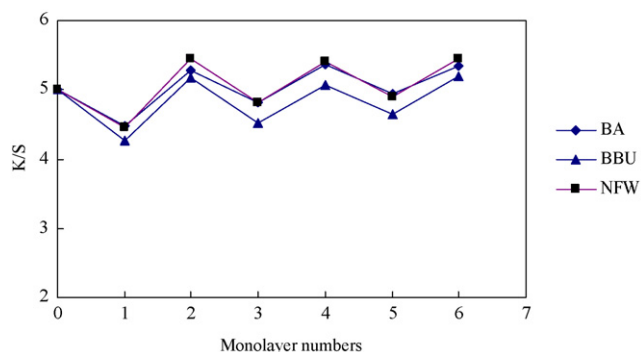


Fig. 2. K/S of assembled cotton with FBA and PDDA vs. the number of monolayers (the odd number was attributed to the FBA layers, while the even number to PDDA layers). The solid lines are to guide the eye to outline the alternative changes of surface polarities.

standing, we adopt the equivalent number of home launderings in this paper. It should be noted that a 2001 AATCC Standard Reference Detergent WOB (without FBA) was used in this test in order to avoid the effect of FBAs in the detergent on the precise assessment of UV protection function caused by the self-assembled multilayers. The specimen that was not assembled with polyelectrolytes/fluorescent brightening agents was used as the blank.

3. Results and discussion

3.1. Direct deposition of FBA/PDDA multilayers

3.1.1. Characterization of FBA/PDDA-assembled cotton surfaces

It is well known that the alternating charge reversal on the substrate surface is the main driving force for the fabrication of ESA multilayers (Hammond, 1999; Schönhoff, 2003). The electrical properties of the cotton surface would change alternately between positively charged and negatively charged after LbL electrostatic assembly of polyelectrolytes. Therefore, it is valuable to determine the change in surface polarity of assembled cotton to demonstrate the stepwise buildup of FBA/PDDA multilayers. According to our previous work, a dyeing method in terms of K/S values has been proven a simple and quick means to characterize the change of surface polarities of LbL self-assembled textile substrates on basis of the attraction or repulsion between the anionic dye and polyelectrolytes (Wang & Hauser, 2009). As shown in Fig. 2, the regular changes in color depth of assembled cotton substrates indicate that the surfaces were alternately deposited with every FBA and PDDA layers. As the outermost layer alternated between FBA and PDDA, the K/S values present distinct “odd–even” regular oscillations, revealing that the surface coverage of FBA by PDDA and vice versa are enough to change the surface polarities. The results also show that organic small molecules with fewer charges compared to the common polyelectrolytes such as PSS, still could be multilayeredly fabricated on the cationized cotton substrates via ESA deposition. This is because the three FBAs with 2–4 sulfonic groups are not only strong organic electrolytes, but also have intermolecular interactions with PDDA, which are referred to as substantivity. Therefore, a corresponding FBA molecule/polyelectrolyte system would have better self-assembly characteristics. This result is in accordance with several reports involving organic molecules/polyelectrolytes self-assembly system (Ariga et al., 1997; Dubas, Limsavarn, et al., 2006).

3.1.2. UV protection function of FBA/PDDA-assembled cotton

Both UPF and percentage of transmission are main parameters for assessing UV protection ability of the fabric. However, UPF is commonly used due to the consideration of its calcula-

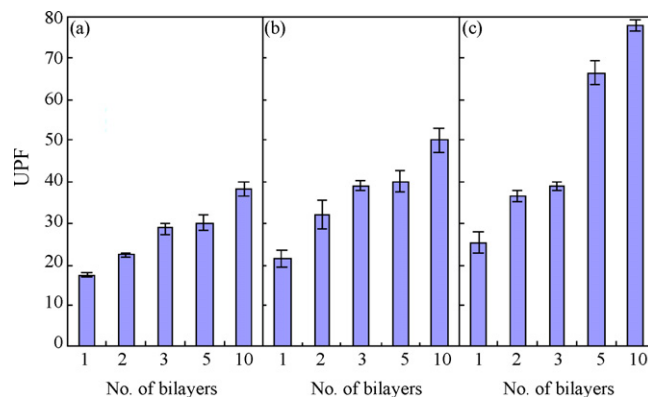


Fig. 3. Direct self-assembled (FBA/PDDA)_n multilayers on cationized cotton. FBAs are (a) BA, (b) BBU and (c) NFW.

tion on erythral spectral effectiveness and irradiance at a certain wavelength. Therefore, it also could be defined as the ratio of the potential erythral effect to the actual erythral effect transmitted through the fabric by the radiation (Schindler & Hauser, 2004).

As shown in Fig. 3, all the cotton fabrics assembled with FBA/PDDA multilayers show increases in UPF values. When the cotton samples were firstly dipped in each anionic FBA solution, the FBA molecules were adsorbed on the cotton surface with positive charges, leading to an immediate increase in the UPF due to the UV absorption capability of aromatic structure in the FBA molecules (Fig. 4). As more FBA and PDDA were alternatively adsorbed on the cotton substrates, the UPF values were increased correspondingly. When the bilayer numbers of BA/PDDA, BBU/PDDA and NFW/PDDA multilayers were up to ten, five and three, respectively, the corresponding assembled cotton fabrics all obtain UPF of ≥ 40 . According to the Australian/New Zealand Standard AS/NZS 4399: 1996, these fabrics could be classified as excellent protection classification compared to uncationized and cationized fabrics with a low UPF rating of less than 15, which is classified as non-ratable.

NFW-coated cotton presents the highest UPF among all the FBA-coated samples after the similar deposition of FBA layer, which is in accordance with their corresponding UV absorption spectra (Fig. 4). At the same time, NFW has a more linear structure and more decentralized charged groups, which might be benign for assembling functional multilayers.

In addition, the transmission between 400 and 800 nm, i.e., visible light section, of the assembled cotton fabrics did not show significant decrease compared to untreated cotton (Fig. 5), indicating that the chemicals are only deposited on the fiber surface and not in the spaces between fibers and yarns. This means that the enhancement in UV protection of cotton substrates derives from

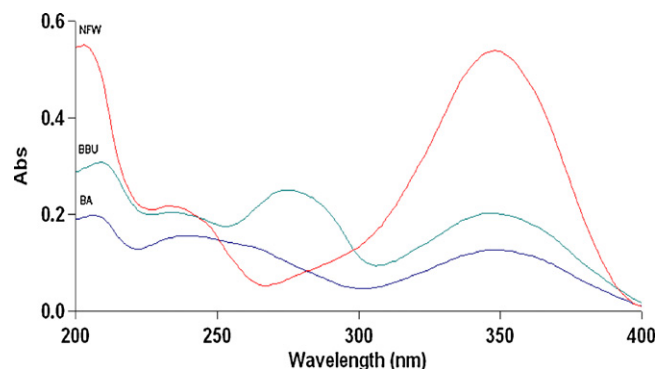


Fig. 4. UV absorption spectra of three FBAs.

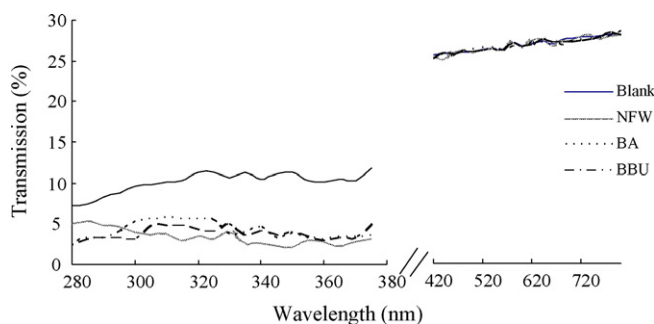


Fig. 5. Transmission of FBA-assembled cationized cotton. A UG11 filter (Schott, Mainz, Germany) was fixed closely against the fabric when the transmission spectrum was measured over the UV range of wavelengths, which ensured the elimination of the effects of fluorescence from the FBAs present in the fabric.

UV absorption of the aromatic structure of the FBAs rather than from the physical blocking of the interstices between fibers.

3.2. Pre-mixed deposition of PSS/(FBA-PDDA) multilayers

Considering that anionic FBA molecules contain fewer charges compared to common polyanions, we assessed another assembly method for the integration and fabrication of FBA-containing multilayers on the cotton surface. Referring to the assembling of some organic small molecules having single charge (Chang-Yen et al., 2002), a stepwise pre-mixed self-assembled deposition of FBA-containing multilayers was investigated in this work. As shown in Fig. 6, the deposition films for the three FBAs show similar growth trends when they were pre-mixed with PDDA and then together assembled into multilayers with PSS, forming PSS/(PDDA-FBA) multilayer deposition. For each FBA, the UPF values were increased with increasing ratio of FBA to PDDA and bilayer number of deposition multilayers because more FBAs were integrated into (PSS/FBA-PDDA)_n multilayers.

However, unlike organic molecules with single charge, each FBA used in this paper has at least two charges per molecule. These charges are enough for the reversal of surface electric properties for a successful fabrication of self-assembled multilayer, as demonstrated in above direct LbL deposition. In this case, compared with direct assembly of FBA, pre-mixed interpolyelectrolyte complexes (PDDA-FBA) which contain less FBA according to the ratio of FBA to PDDA, would incorporate less FBA onto the (PSS/FBA-PDDA)_n multilayers. Consequently, all the cotton samples that underwent pre-mixed self-assembly show correspondingly lower UV protection abilities.

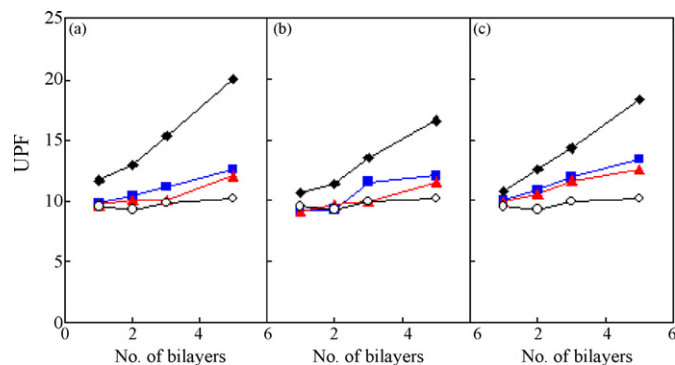


Fig. 6. Pre-mixed self-assembled (PSS/FBA-PDDA)_n multilayers on cationized cotton. FBAs are (a) BA, (b) BBU and (c) NFW. Molecule ratios of FBA to PDDA monomeric unit were (▲) 1:80, (■) 1:50 and (◆) 1:10. (○) without FBA. The solid lines are to guide the eye to outline the changes of surface polarities.

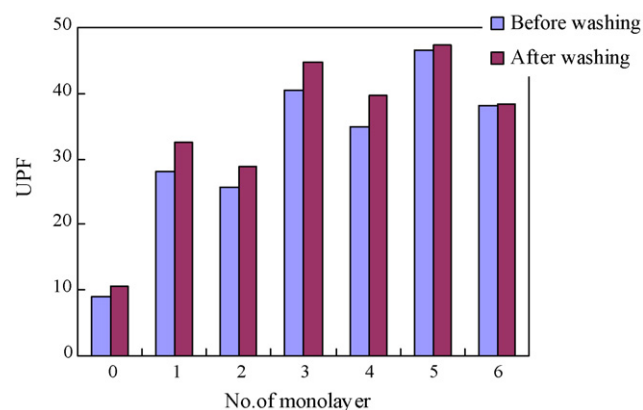


Fig. 7. Durability of NFW/PDDA-assembled cotton after five home washings.

3.3. Durability

UV protection treatments for textile goods have the same need for washing fastness as dyestuffs. Laundering trials should be carried out with all new formulations or processes to confirm that the claimed UV protection is actually active during the life of the garment. The washing fastness was tested after five home laundries of the blank and cotton assembled with NFW and PDDA. As shown in Fig. 7, the UPF values of all the samples after washing were not decreased, but were increased more or less. The results indicate that the cotton fabrics assembled with FBA/PDDA multilayers had good durability to washing, no matter the outermost layer is FBA or PDDA. The increases in UPF after washing could be ascribed to the slightly increasing cover factors (the fraction of the surface area of the fabric covered by yarns) of the cotton samples caused by washing because cotton has a tendency to shrink to increase its cover factor after washing (Davis, Capjack, Kerr, & Fedosejevs, 1997; Riva & Algaba, 2006; Wang & Hauser, 2009). This also can be proven by comparing the UPF values of the blank (monolayer number is 0) before and after washing.

In summary, the strong ionic bonds formed between FBA and PDDA enhanced the stability of organic molecule/polyelectrolyte multilayers against washing, resulting in no decline in UV protection function.

It should be noted that the UPF values of the PDDA-coated cotton samples decreased compared to previous NFW-coated ones. This is because a given amount of previously adsorbed NFW was extracted by exposure to a PDDA solution. Other research involving polyelectrolyte-dye self-assembled thin films had reported this "extraction" effect (Kharlampieva & Sukhishvili, 2004; Tedeschi, Caruso, Mhwalld, & Kirstein, 2000).

4. Conclusions

Anti-UV functionalization of cationized cotton was achieved by using LbL ESA deposition of fluorescent brightening agents (FBAs) and polycations (PDDAs). It was demonstrated by characterizing the surface polarities and multilayer growth of assembled cotton substrates through color yields of cotton surfaces and UPF data, respectively. The assembled cotton fabrics could obtain excellent rating of UV protection when the (BA/PDDA)₁₀, (BBU/PDDA)₅ and (NFW/PDDA)₃ bilayers were built-up on the cotton substrates, respectively. Good durability to washing revealed the stability of multilayer films on the cationized cotton, which is important for actual application of textiles. Further detailed assessment for processing factors of this new approach is ongoing.

In summary, as effective UV absorbers but with less negative charges, all the three FBAs presented good self-assembly abilities

with PDDA, indicating functional organic molecules with fewer charges could also be integrated into multilayers as polyelectrolytes via LbL ESA deposition. This conclusion is benign for the application of self-assembly technique in textile functionalization.

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