

Wear-resistant cotton fabrics modified by PU coatings prepared via mist polymerization

Wanchao Fan, Yanhui Zhu, Guanghui Xi, Meiqi Huang, Xiang Dong Liu

Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, College of Materials and Textile, Zhejiang Sci-Tech University, Xiasha Higher Education Zone, Hangzhou 310018, People's Republic of China
Correspondence to: X. D. Liu (E-mail: liuxd2007@gmail.com)

ABSTRACT: Cotton fabric was successfully modified using a simple mist polymerization with polyurethane (PU) prepolymer and ethylene glycol as the monomers. Scanning electron microscope showed the presence of a very thin polymer coating on the cotton fiber surface. Martindale abrasion tests revealed that the thin PU coating imparted to the cotton fabric a doubled wearing durability compared with the original fabric. Additional experiments demonstrated that the mist polymerization has little impact on the desired cotton properties such as water absorptivity, vapor transmissibility, mechanical property, and flexibility. Considering the excellent balance between the enhanced abrasion resistance and the cotton natures, this surface modification methodology has potential to fabricate wearing durable textiles. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43024.

KEYWORDS: coatings; surfaces and interfaces; textiles

Received 5 August 2015; accepted 4 October 2015

DOI: 10.1002/app.43024

INTRODUCTION

In recent years, many attempts have been made to endow cotton fabric with new functionalities, including antimicrobial activity,^{1–5} superhydrophobicity,^{6–10} and abrasion resistance.^{11–13} Various techniques, such as dip coating,¹⁴ solution immersion,^{15,16} sol-gel coating,^{17–20} spray deposition,^{21–23} chemical vapor deposition,^{24,25} and graft polymerization^{26–28} have been tried to modify cotton surface. Because cotton fibers are generally soft and sensitive to abrasive forces, the improvement of wearing durability is of particular importance in clothing industry. The common way to increase the abrasion resistance of cotton textiles is the application of protective coatings on the cotton fiber surface. For example, Rosace *et al.*²⁹ prepared abrasion-resistant cotton fabrics by depositing organosilicon compounds via low pressure plasma chemical vapor deposition technique, and demonstrated a remarkable improvement on the abrasion resistance of the fabric. Brzeziński *et al.*^{12,13} reported a sol-gel method to coat SiO₂/Al₂O₃ xerogel on fiber surface, and verified the excellent effect on improving wear performance of cotton or polyester/cotton blending fabrics. Zhou *et al.*³⁰ found that the combination of poly(vinyl alcohol) and the cross-linker of 1,2,3,4-butanetetracarboxylic acid can significantly improve the abrasion resistance of cotton fabric. However, these approaches have serious limitations for practical applications in textile industry. The drawbacks include large dosage of chemi-

cals, increased cost, difficulty in large scale production, deterioration in hygienic and aesthetic properties of cotton, and environmental concerns. These disadvantages motivate researchers to explore new protective materials and surface modification technologies for the textile finishing.

We recently developed a “mist polymerization” technique^{31,32} to modify solid substrate surfaces. Because the monomer feeding in this process is a mist stream atomized from a monomer solution, the thickness and the surface morphology of the resulting polymer layer are tunable by varying the polymerization factors like monomer concentration, solvent and mist feeding time. Additionally, this methodology for surface modification has the important practical advantages over conventional methods that it works with a wider range of monomers and substrates and consumes smaller quantity of monomer during the finishing process.

Based on the understanding that PU coatings are generally safe to human body³³ and have excellent wearing durability,^{34,35} the combination of the mist polymerization technique and PU polymers is researched. The abrasion-resistant coatings in present work are synthesized by successively feeding the mist streams atomized from the PU prepolymer and EG solutions in acetone to the cotton fabric surface, and heating at 60°C for 2 h. The resulting fabric samples are tested using a variety of characterization techniques, including field emission scanning

Additional Supporting Information may be found in the online version of this article.

© 2015 Wiley Periodicals, Inc.

Table I. Viscosity and Theoretical X_n of the PrePUs

PrePU	TDI/EG (mol/mol)	Viscosity (mL/g)	X_n
PrePU 1	2:1	1.19 ± 0.13	3
PrePU 2	1.5:1	1.35 ± 0.17	5
PrePU 3	1.25:1	1.54 ± 0.12	9
PrePU 4	1.15:1	1.76 ± 0.15	14

electron microscope (FE-SEM), Fourier transform infrared (FTIR) spectra, Martindale abrasion tests, water contact angle (WCA), tensile strength tests, water absorption tests, and vapor transmission tests. The experimental results show that the PU layers provide cotton fabrics with excellent abrasion resistance and hydrophobicity. Additionally, there are no significant damages on the cotton natures during the chemical treatment.

EXPERIMENTAL

Materials

The cotton fabrics were purchased from a local fabric store (60 ends/cm, 30 picks/cm, 0.42 mm thickness, 120 g/m² weight, 35.2 m²/g specific surface area). Before chemical modifications, the cotton samples (50 mm × 50 mm) were cleaned by ultrasonic washing in ethanol (30 min × 2 times) and deionized water (30 min × 2 times). Toluene diisocyanate (TDI), ethylene glycol (EG), and other chemicals were purchased from Shanghai Crystal Pure Industrial Co., Ltd (China) and used without further purification.

Synthesis of Polyurethane Prepolymer

The polyurethane prepolymer (PrePUs) were synthesized via the reaction of TDI and EG in acetone (Supporting Information Scheme 1). For example, EG (0.62 g, 10.0 mmol) and TDI (2.18 g, 20.0 mmol) were mixed in 40 mL acetone, heated with stirring to reflux for 4 h, and cooled to 25°C to obtain the PrePU 1 in acetone solution. The resulting PrePU solutions were directly utilized to the next mist polymerization procedure. The number-average degree of polymerization (X_n) of the PU prepolymers were controlled by adjusting the mole ratio of TDI/EG (Table I). Viscosity values of the PrePU solutions were measured by a Ubbelohde viscometer (JC522-1835, $\Phi = 0.5\text{--}0.6$ mm).

Mist Polymerization Procedure

The general mist polymerization procedure has two steps as shown in Supporting Information Scheme 2. First, a PrePU solution was atomized using an air compression-type atomizer (DH-M01, China), fed (0.36 mL/min) to a cotton sample (50 mm × 50 mm) for 3 min, and dried at 60°C for 2 h. Second, a EG solution (0.25 mol/L) in acetone was atomized, fed (0.24 mL/min) to the resulting cotton sample for 2 min, and dried at 60°C for another 2 h.

Solution Immersion Method

The pristine cotton fabric was immersed into a PrePU 3 solution (70 g/L) in acetone for 3 min, taken out to hang on a clotheshorse at 25°C for 10 min and dried at 60°C for 2 h. The resulting fabric was immersed into a EG solution (0.25 mol/L)

in acetone for 2 min, taken out to hang on a clotheshorse at 25°C for 10 min, and dried under 60°C for another 2 h.

Characterizations

FTIR spectra were collected from a Nicolet Fourier Transform spectrophotometer (AVATAR 5700, US) with an attenuated total reflection (ATR) accessory. Surface morphology was investigated by a field emission scanning electron microscope (FE-SEM, JSM-6700F, Japan) after gold coating (approximately 10-nm thickness). Static contact angles were measured using deionized water droplets (4 μ L) with a Kruss contact angle instrument (DSA 100, Germany) at 25°C. Average contact angle values were obtained by measuring three different positions on the same sample. Abrasion tests were performed using a Martindale abrasion instrument (HZ-8029A, China) according to DIN EN ISO 12947-3. Water absorption ability was measured basing on the weight increment of the cotton sample after soaking in plenty of deionized water for 10 min and hanging out for another 10 min. Water absorption rate is expressed as the weight ratio of adsorbed water to the cotton sample. Water vapor permeability was evaluated using ASTM E-96 (open cup test) method. The test fabric sample was placed tightly over a shallow dish distilled water. The weight loss of the test assembly over 24 h was measured and the vapor transmission rate (g/m²/day) was calculated as the water vapor permeability. All tests were performed at 20°C and 50% RH. Tensile strength tests were carried out on an electronic fabric tensile tester (YG065, China). The fabrics (rectangle shape, 200 mm × 50 mm) were stretched at a constant rate of 20 cm/min. Flexibility was determined by the flat loop method (IS 7016 Part¹¹). Fabric samples were cut from warp and weft directions (160 mm × 40 mm). A loop was made and was placed on a horizontal plane. The height of the loop was measured as an idea of the flexibility of the fabric. The lower the height of the loop, the greater is the flexibility. The laundering test was performed according to our previous work.³¹ The cotton fabrics (50 mm × 50 mm) were washed by an aqueous solution of sodium dodecanesulphonate (2.0%, w/w) in a beaker (500 mL) with stirring (300 rpm, magnetic stirrer, 9 mm × 25 mm) at 25°C for 10 min, rinsed with deionized water (25°C, 50 mL × 2 times), and dried at 60°C. The laundering fabric sample was subjected to the abrasion test after each washing cycle.

RESULTS AND DISCUSSION

Protection Effect of the PU Coating Against Abrasion

PrePUs were synthesized by the reaction of TDI and EG in acetone (Supporting Information Scheme 1). X_n is calculated from the stoichiometric ratio, TDI/EG, basing on the Carothers relationship. As shown in Table I, the viscosity values of the PrePU solutions decrease with the increase of TDI/EG molar ratio. The decrease in viscosity is attributable to the decline of the theoretical X_n value. When the PrePUs were used to the mist polymerization, as shown in Table II, remarkable improvements on abrasion resistance are observed by comparing with the pristine cotton fabric. The PU coatings give the cotton fabric an effective protection against the abrasive motion exceeding 2.30×10^4 cycles in Martindale test, while the unmodified cotton fabric withstands not more than 1.30×10^4 cycles. The mole ratio of

Table II. Wearing Durability of the Modified Cotton Fabrics

Fabric	Mist solution	I II	Temperature (°C)	Abrasion cycles (10^4)
MM1	PrePU1	EG ^a	60	2.39 ± 0.25
MM2	PrePU2	EG	60	2.56 ± 0.34
MM3	PrePU3	EG	60	2.63 ± 0.22
MM4	PrePU4	EG	60	2.69 ± 0.32
MM5	PrePU3	EG	0	1.32 ± 0.23
MM6	PrePU3	-	60	1.98 ± 0.18
MM7	-	EG	60	1.25 ± 0.13
SM	PrePU3	EG	60	3.09 ± 0.39
Cotton	-	-	60	1.26 ± 0.19

^a0.25 mol/L EG in acetone.

TDI/EG, i.e., the theoretical X_n , has not a significant effect on the wearing durability, as the abrasion cycle numbers of the modified cotton fabrics fluctuate within a very tiny range (about ± 1500 cycles). However, the cotton fabric modified using the solution immersion method (SM), which can be taken as an extreme finishing method regardless of damage on cotton natures, exhibits a maximum of 3.09×10^4 cycles. The thickness of the PU coating is an important factor for the wearing durability. It is theoretically correlative to the mist feeding time, i.e., the quantities of the reactants (PrePU or EG). Therefore, the dependencies of the wearing cycle numbers on the mist feeding times of the reactants, PrePU and EG, are investigated. As shown in Figure 1(a) with the fixed EG feeding times, the cycle numbers sharply increase with increasing mist feeding time of the PrePU solution to 60 s, then gradually increase until 250 s. However, the effect of the EG feeding dosage on the wearing durability is different. Figure 1(b) with the fixed PrePU feeding times shows that the wearing cycle numbers gradually increase with increasing EG feeding time at first, but tend to be almost constant when the feeding time was over than 120 s. The highest wearing cycle numbers for the three fixed PrePU dosages are 2.41×10^4 , 2.62×10^4 , and 2.76×10^4 , respectively. Besides, Figure 1 also suggests another difference that

excessive TDI groups are helpful to enhance the wearing durability but exceeded EG not. Additional experiments were done to demonstrate the hypothesis. As shown in Table II, the absence of heat (MM5) or TDI (MM7) leads to no obvious change on the wearing cycle number, whereas the absence of EG (MM6) still results in a little increase. These results are presumably due to the cross-linking reactions of the isocyanate groups with the hydroxyl groups in cellulose chains or with themselves.³⁶

Figure 2 shows the ATR-IR spectra of the pristine cotton fabric [Figure 2(a)], the mist modified fabric [MM3, Figure 2(b)], and the modified fabric after a abrasion test [Figure 2(c)]. By comparing with the original fabric sample, the modified fabric MM3 exhibits two characteristic peaks at 1709 cm^{-1} and 1540 cm^{-1} , which are contributed to the covalent bonds of C=O and C-N, respectively. However, the characteristic peaks cannot be found from the ATR-IR spectrum [Figure 2(c)] of the modified fabric after the abrasion test (1.50×10^4 cycles). These IR spectra suggest the formation and the destruction of the PU coating on the cotton fiber surface.

The surface morphology changes after the mist polymerization were investigated by FE-SEM. From the low-magnification images, no significant difference can be observed between the original fabric [Figure 3(a)] and the modified fabric MM3 [Figure 3(b)]. In Contrast, few particles are found on the modified surface prepared using the solution immersion method [Figure 3(c)]. The high-magnification SEM images reveal that the original cotton fibers have smooth surfaces [Figure 3(d)], but the surfaces of the modified fibers are rough [Figure 3(e,f)]. The statistic average diameters of the fibers were calculated from the low-magnification SEM images. They are 14.5 ± 1.5 , 14.9 ± 1.2 , and $17.6 \pm 1.8 \mu\text{m}$ for the pristine fibers, the mist polymerization modified fibers, and the fibers modified using the solution immersion method, respectively. These data indicate that the mist polymerization results in a very thin polymer layer (about $0.4 \mu\text{m}$) on cotton fiber surface, while the solution immersion method produces a relatively thick coating (about $2.1 \mu\text{m}$). This is agreeable with the high wearing durability of the fabric fully modified using the solution immersion method.

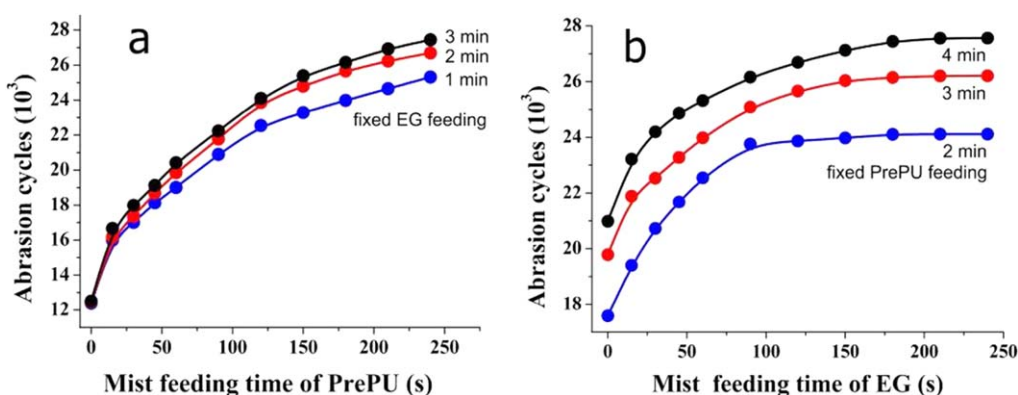


Figure 1. Effects of mist feeding time of (a) PrePU and (b) EG on the wearing durability. The modification condition: PrePU 3 (70 g/L), EG (0.25 mol/L). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

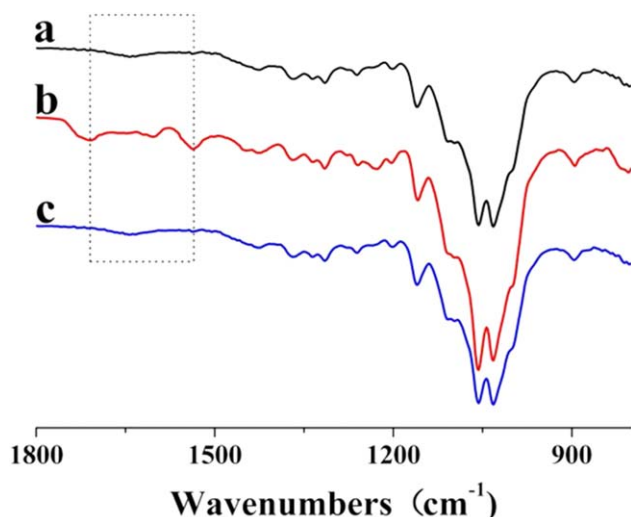


Figure 2. ATR-IR spectra of (a) the original cotton fabric, (b) the modified fabric MM3, and (c) its worn sample underwent 1.50×10^4 abrasion cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For a finishing process in practical applications, damages on cotton natures should be concerned. To investigate the mechanism of the abrasion damages, FE-SEM, ATR-IR, and WCA were employed to analyze the changes in morphology and the composition of the surface. Figure 4 shows the SEM images of the modified cotton fabrics subjected to Martindale abrasion test for various rotation cycles. After 1.50×10^4 abrasion cycles, the PU layer seems to be peeled off from the fiber surface. This suggests that the fragments on the fiber surface shown in Figure 4(b,c) are caused by the damage of the PU coating. The fiber

damages shown in Figure 4(e,f) are agreeable with previous work,³⁷ which demonstrated that the fiber damage by abrasion has a harm sequence of deformation and rupture. This hypothesis obtained further evidences based on WCA measurements and ATR-IR spectra. As shown in Figure 5, the WCA sharply drops to zero, (the WCA of the original cotton fabric is zero) after about 1.40×10^4 abrasive cycles. Because the high WCA is contributed to the PU coating, the rapid change in WCA means that the PU layer was completely peeled off from the fiber surface, and replaced by the hydrophilic cellulose. As mentioned above [Figure 2(c)], the disappeared after 1.50×10^4 abrasive cycles, indicating again that the main chemical component in the fiber surface was changed to cellulose from the PU polymer. Basing on these experiments, it is proposed that the abrasion damage mechanism consists of two steps, peeling of the PU coating and scathe of the cotton fiber. The thin PU coating provides strong protection against abrasion, resulting in the doubled wearing durability of the modified cotton fabric in Martindale abrasion test.

Controllable Damages on the Desired Properties of Cotton Fabric

To evaluate the damages accompanied with the mist polymerization, we examined some important properties of original cotton fabrics, including water absorptivity, vapor transmissibility, mechanical properties, and flexibility. As shown in Table III, the original cotton fabric absorbs more than 245% water in weight, while the mist modified cotton fabrics show a medium-level water absorptivity ranging from 230 to 190%. In contrast, the fabric modified by the solution immersion method absorbs less than 135% water in weight. Similarly, the mist polymerization process slightly affects the vapor transmission rate of the modified cotton fabrics. The mist modified fabrics show vapor

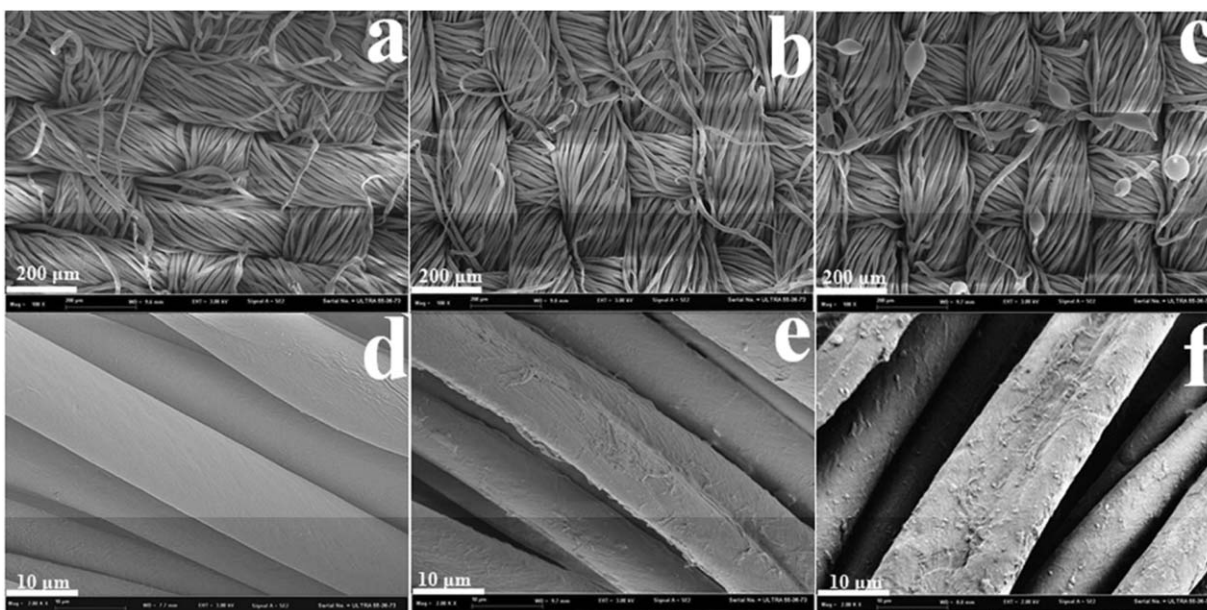


Figure 3. Low magnification SEM images (a–c) and high magnification SEM images (d–f) of the original cotton fabric (a and d), the modified fabric MM3 (b and e), and the modified fabric SM (c and f), respectively.

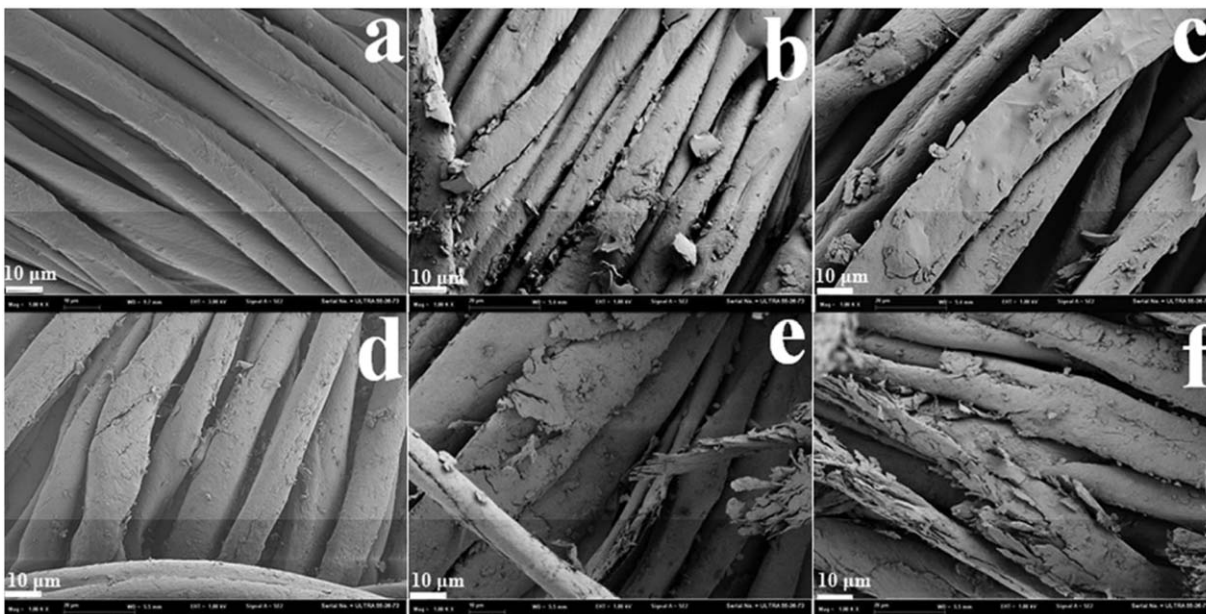


Figure 4. SEM images of (a) the modified fabric MM3 and its worn samples underwent (b) 0.50×10^4 , (c) 1.00×10^4 , (d) 1.50×10^4 , (e) 2.00×10^4 , and (f) 2.50×10^4 abrasion cycles.

transmission rates more than $1320 \text{ g/m}^2/\text{day}$, the decrease is less than 12% by comparing with the unmodified cotton fabric. In contrast, the solution immersion method makes a significant loss about 44% (Table III, SM). In the tensile tests, the mist polymerization induces about 3% decrease (Table III, MM3) when compared with the original cotton fabric, indicating that the mechanical damage is quite small. The optic images (Figure 6) show that the loop height of the original cotton fabric [Figure 6(a)] was 11.5 mm, while the modified fabric MM3 was 12.0 mm. This result means that the flexibility of the mist modified fabric is still good enough. Figure 6(c) shows the water droplets (0.1 mL, stained with blue ink) placed on the modified cotton surfaces. When the water droplet was placed on the unmodified cotton surface, it completely disappeared

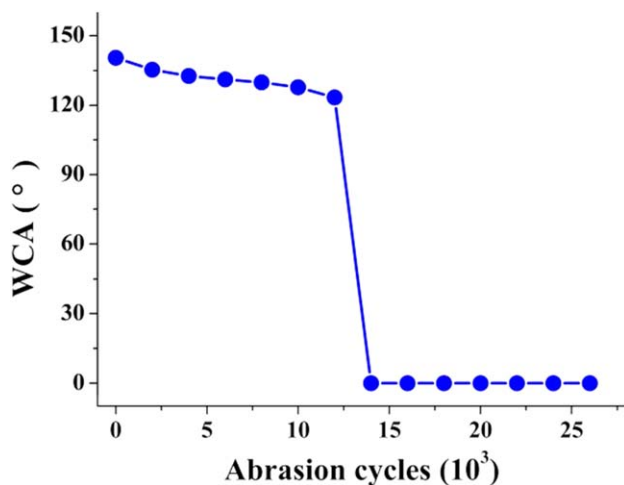


Figure 5. The WCA of the modified fabric MM3 underwent various abrasion cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. The Important Natures of the Modified Cotton Fabrics

Fabric	Water absorptivity (%)	Vapor transmissibility ($10^3 \text{ g/m}^2/\text{d}$)	Tensile strength (N)
MM1	232 ± 12	1.45 ± 0.30	-
MM2	220 ± 14	1.42 ± 0.50	-
MM3	206 ± 11	1.37 ± 0.50	602 ± 9
MM4	192 ± 16	1.32 ± 0.50	-
SM	134 ± 15	0.85 ± 0.60	-
Cotton	246 ± 12	1.51 ± 0.50	619 ± 6

and left only a water mark. However, the water droplets on the modified cotton surface kept the spherical shape for a long time (about 20 min). These results demonstrate that the mist polymerization does not affect the opposite face of the modified surface, but results in an asymmetric wettability on the modified side. Figure 7 shows the laundering durability of the

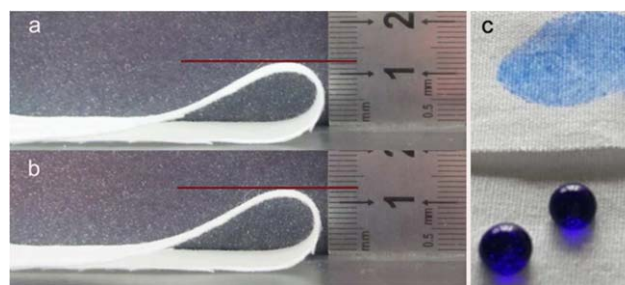


Figure 6. Flexibility of (a) the pristine cotton fabric and (b) the MM3 fabric, and (c) the asymmetric wettability of the MM3 fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

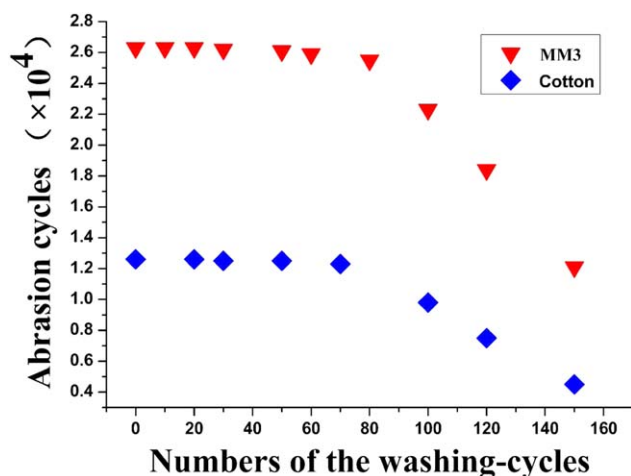


Figure 7. The abrasion cycles of the modified fabric MM3 and pristine cotton fabric underwent various numbers of washing-cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modified cotton fabric (MM3) with comparison to the pristine cotton fabric. The modified fabric exhibits good anti-abrasion behaviors before 80 washing-cycles, but then tends to decrease in the abrasion cycle number. Because the pristine cotton fabric has a similar degradation behavior after 70 washing-cycles, the degradation in wear-resistance may attribute to the loosening in fabric structure during the washing process. Therefore, this result suggests that the PU layer coated on the cotton surface has enough durability to washing.

In summary, the PU coating prepared by the mist polymerization process can significantly improve abrasion resistance of cotton fabrics with well controlled damages on the desired cotton natures such as water absorptivity, vapor transmissibility, mechanical properties, and flexibility.

CONCLUSIONS

Cotton fabrics were modified using a mist polymerization with PrePU and EG. The resulting PU coating on the cotton surface provides a strong protection act against abrasion. SEM images exhibited that the thickness of the PU coating on cotton fiber surface is about $0.4 \mu\text{m}$. In Martindale abrasion tests, the PU-modified cotton fabric successfully resisted more than 2.50×10^4 abrasion cycles; in contrast, the original cotton fabric only corresponds less than 1.30×10^4 cycles. Notably, the thin PU layer on the cotton fiber surface does not significantly affect cotton original natures such as flexibility, water absorptivity, and vapor permeability. Considering the excellent balance of the wearing durability with the desired natures of cotton fabrics, we believe the mist polymerization process has potential to fabricate wearing durable textiles.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (51573167), Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry (1101603-C).

REFERENCES

- Sundrarajan, M.; Selvam, S.; Ramanujam, K. *J. Appl. Polym. Sci.* **2013**, *128*, 108.
- Liu, Y.; Jiang, Z.; Li, J.; Liu, Y.; Ren, X.; Huang, T. *J. Appl. Polym. Sci.* **2015**, *132*, 42023.
- Airoudj, A.; Ploux, L.; Roucoules, V. *J. Appl. Polym. Sci.* **2015**, *132*, 41279.
- Pedrosa, M.; Mouro, C.; Nogueira, F.; Vaz, J.; Gouveia, I. *J. Appl. Polym. Sci.* **2014**, *131*, 40997.
- Xi, G. H.; Xiu, Y. L.; Wang, L.; Liu, X. D. *J. Appl. Polym. Sci.* **2015**, *132*, 41824.
- Wang, B.; Li, J.; Wang, G.; Liang, W.; Zhang, Y.; Shi, L.; Guo, Z.; Liu, W. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1827.
- An, Q.; Xu, W.; Hao, L.; Fu, Y. S.; Huang, L. X. *J. Appl. Polym. Sci.* **2013**, *128*, 3050.
- Zhou, X.; Zhang, Z.; Xu, X.; Guo, F.; Zhu, X.; Men, X.; Ge, B. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208.
- Xi, G. H.; Fan, W. C.; Wang, L.; Liu, X. D.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **2015**, *53*, 1862.
- Wang, J.; Chen, Y. *J. Appl. Polym. Sci.* **2015**, *132*, 42614.
- Alongi, J.; Malucelli, G. *Polym. Degrad. Stab.* **2013**, *98*, 1428.
- Brzeziński, S.; Kowalczyk, D.; Borak, B.; Jasiorski, M.; Tracz, A. *J. Appl. Polym. Sci.* **2012**, *125*, 3058.
- Brzeziński, S.; Kowalczyk, D.; Borak, B.; Jasiorski, M.; Tracz, A. *Fibers Text East Eur. Fibres* **2011**, *6*, 83.
- Lin, J.; Zheng, C.; Ye, W. J.; Wang, H. Q.; Feng, D. Y.; Li, Q. Y.; Huan, B. O. *J. Appl. Polym. Sci.* **2015**, *132*, 41458.
- Li, S.; Zhang, S.; Wang, X. *Langmuir* **2008**, *24*, 5585.
- Liu, H.; Szunerits, S.; Pisarek, M.; Xu, W.; Boukherroub, R. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2086.
- Abidi, N.; Cabrales, L.; Hequet, E. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2141.
- Chernyy, S.; Ulah, S.; Sørensen, G.; Tordrup, S. W.; Pedersen, P. B.; Almdal, K. *J. Appl. Polym. Sci.* **2015**, *132*, 41955.
- Yin, Y.; Guo, N.; Wang, C.; Rao, Q. *Ind. Eng. Chem. Res.* **2014**, *53*, 14322.
- Škoc, M. S.; Macan, J.; Pezelj, E. *J. Appl. Polym. Sci.* **2014**, *131*, 39914.
- Sparks, B. J.; Hoff, E. F.; Xiong, L.; Goetz, J. T.; Patton, D. L. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1811.
- Xiong, L.; Kendrick, L. L.; Heusser, H.; Webb, J. C.; Sparks, B. J.; Goetz, J. T.; Guo, W.; Stafford, C. M.; Blanton, M. D.; Nazarenko, S.; Patton, D. L. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10763.
- Steele, A.; Bayer, I.; Loth, E. *Nano Lett.* **2009**, *9*, 501.
- Hilt, F.; Boscher, N. D.; Duday, D.; Desbenoit, N.; Levalois-Grutzmacher, J.; Choquet, P. *ACS Appl. Mater. Interfaces* **2014**, *6*, 18418.
- Ma, M.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. *Macromolecules* **2005**, *38*, 9742.
- Kaur, I.; Bhati, P.; Sharma, B. *J. Appl. Polym. Sci.* **2014**, *131*, 40415.

27. Meng, X.; Yu, B.; Cong, H.; Shuai, L.; Yuan, H.; Xu, X.; Xu, S. *J. Appl. Polym. Sci.* **2015**, *132*, 41617.
28. Jian, N.; Xu, T. *J. Appl. Polym. Sci.* **2014**, *131*, 41193.
29. Rosace, G.; Canton, R.; Colleoni, C. *Appl. Surf. Sci.* **2010**, *256*, 2509.
30. Zhou, W.; Yang, C. Q.; Lickfield, G. *J. Appl. Polym. Sci.* **2004**, *91*, 3940.
31. Wang, L.; Xi, G. H.; Wan, S. J.; Zhao, C. H.; Liu, X. D. *Cellulose* **2014**, *21*, 2983.
32. Wan, S. J.; Wang, L.; Xu, X. J.; Zhao, C. H.; Liu, X. D. *Soft Matter* **2014**, *10*, 903.
33. Yuliya, B.; Marie, U. In *Modern Polyurethanes: Overview of Structure Property Relationship*; Patil, A.; Ferritto, M. S., Eds.; American Chemical Society: Washington, DC, **2013**; Vol. *1148*, Chapter 4, p 65.
34. Chang, W. H.; Scriven, R. L.; Peffer, J. R.; Porter, S. *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12*, 278.
35. Chattopadhyay, D. K.; Raju, K. V. S. N. *Prog. Polym. Sci.* **2007**, *32*, 352.
36. Delebecq, E.; Pascault, J. P.; Boutevin, B.; Ganachaud, F. *Chem. Rev.* **2013**, *113*, 80.
37. Zeronian, S. H.; Alger, K. W.; Ellison, M. S.; Al-Khayatt, S. M. In *Studying the Cause and Type of Fiber Damage in Textile Materials by Scanning Electron Microscopy*; Comstock, M. J., Ed.; American Chemical Society: Washington, DC, **1986**; Vol. *212*, Chapter 4, pp 77.