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# 폴리에스터-코튼 원단용 안티필링 피니싱제로서 폴리실록산 개질화 폴리우레탄의 합성 및 응용

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# Synthesis and Application of Polysiloxane-Modified Polyurethane as Anti-pilling Finishing Agent for Polyester-Cotton Fabric

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**Abstract:** The polysiloxane-modified polyurethane anti-pilling finishing agent (SA-PU) was synthesized with 2,4-tolylene diisocyanate (TDI), polyester diol (PDHA), and amino-terminated siloxane (SA) as raw materials. The structure of SA-PU was characterized by Fourier transform infrared spectroscopy (FTIR). Scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) showed that SA-PU had been successfully finished on the surface of the fabric. Moreover, the properties of SA-PU on the treated fabric were measured by Martindale abrasion, pilling tester, and Kawabata Evaluation System for Fabrics (KES-F). The results indicated that the anti-pilling property of polyester-cotton fabric was improved 2~3 grades after finishing. In addition, the surface properties and bending properties of polyester-cotton fabric were also improved.

**Keywords:** polysiloxane, polyurethane, polyester-cotton fabric, anti-pilling.

## Introduction

Polyester-cotton fabric is widely used in clothing industry and decoration field because it has high strength, good dimensional stability, and wrinkle-resistance.[1-3] However, polyester-cotton fabric is mechanically affected during daily wearing and laundering, which leads to pilling, a common phenomenon of polyester-cotton fabric.[4] In polyester-cotton fabric, short cotton fibers are easy to fuzz,[5,6] at the same time, polyester fibers are easy to accumulate static charge because of its hydrophobic character.[7] Under the impact of static interaction, polyester fibers will entangle with cotton fibers to form pills[8] and it is difficult for these pills to fall off the surface of the fabric because polyester-cotton fabric has high strength.[9] The pilling phenomenon has a bad effect on the appearance of the fabric.[10] Therefore, it is crucially important for polyester-cotton to obtain anti-pilling performance.

In order to solve this problem, usually, chemical treatments can be applied to the fabrics.[4,11] In recent decades, a series of approaches for the anti-pilling finishing of polyester-cotton fabric has been investigated. Fabio *et al.*[12] used a Si:Ox:Cy:Hz thin film, which was deposited on the fabric through PECVD using HMDSO-$O_2$-Ar gas mixture to promote pilling resistance. Hafiza *et al.*[13] were committed to produce a cellulose enzyme for bio-polishing of polyester-cotton fabric in order to improve pilling resistance. Montazer *et al.*[14] investigated the application of aminoplast resins along with a crosslinking agent to reduce pilling, etc.

Because of advantages including good film-forming ability, abrasion resistance, and adhesion, polyurethane (PU) can be applied to fabric as anti-pilling finishing agent.[15] However, the

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handle and the wearability of the treated fabric tend to be worse.[16] Amino-terminated siloxane (SA), as the most commonly used softener, has been greatly applied to impart a satisfactory handle to polyester-cotton textile for making the garment or fabric more appealing.[17] The SA molecular chain has better film-forming properties due to the presence of helical structure and methyl extending to the outside. Amino in the SA chain segment can interact with the hydroxyl and carboxyl on the fabric, therefore, SA can give the soft handle when its segments adsorb directly on the surface of the fabric.[18,19] However, the adhesive force of SA to fluffs on the fabric is poor.

By introducing PU to SA, siloxane modified polyurethane (SA-PU) which has both characteristics of PU and SA is synthesized. Therefore, SA-PU has not only good abrasion resistance, strong adhesive strength, satisfactory resistance to different climates but also excellent flexibility, low surface energy as well as good film-forming ability. As a result, research works on PU modified with SA has received substantial attentions. For example, Xu *et al*.[20] made a fabric finishing agent with cationic waterborne polyurethane (WPU) modified by silicone oil, then the finishing agent and the blocking polyether silicone oil were jointly used to treat cashmere knitted fabric. It was found that resistance to pilling of the treated cashmere knitted fabric was improved from a scale of 2~3 to 4 and its washing shrinkage rate was reduced from 11.2% to 3.3%. Lei *et al*.[21] used linear polyether-blocked amino silicone (LEPS) to modify WPU, and it was found that with an increase of the LEPS content in the WPU, the WPU film was more flexible, and the abrasion resistance of the WPU film was increased. Zhang *et al*.[22] successfully synthesized polydimethylsiloxanes- (PDMS-) modified WPU, and they proved that the PDMS-modified WPU had satisfactory film-forming property. Lian *et al*.[23] successfully incorporated SA into PU, then MR elastomer was finished with the product. The result was that the incorporation of SA into PU led to the decrease in friction coefficient of the finishing surface.

Based on the above discussion, in this research, we have tried to synthesize a polymer by introducing PU prepolymer to the amino-terminated SA molecular chain. At first, the PU was synthesized with 2,4-tolylene diisocyanate (TDI), polyester diol (PDHA), and then the PU was reacted with the SA to synthesize the SA-PU. Besides, the anti-pilling property, physical and mechanical properties of the polyester-cotton fabrics finished by SA-PU were studied.

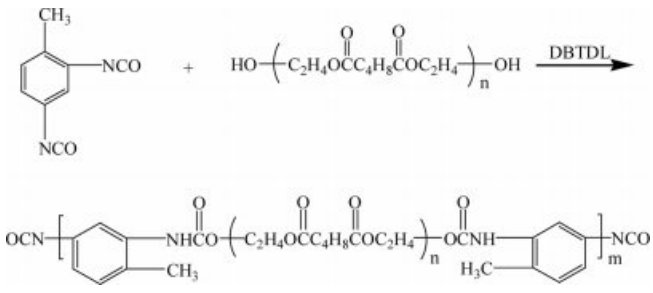
## Experimental

**Materials.** The woven polyester-cotton fabric (PTCO, 60% and 40%, 89 g/m$^2$) with the mesh density of 133×72 was used in this study. 2,4-tolylene diisocyanate (TDI) was provided by Sinopharm Group Chemical Reagent Co., Ltd. Polyester diol (PDHA-1500) was provided by Xin Yu Chemical Industry. Acetone (AT) was provided by Suzhou Qiang Sheng Chemical Reagent Co., Ltd. Dibutyltindilaurate (DBTDL) was analytical pure grade and obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. The amino-terminated siloxane (SA) was a self-produced laboratory product.

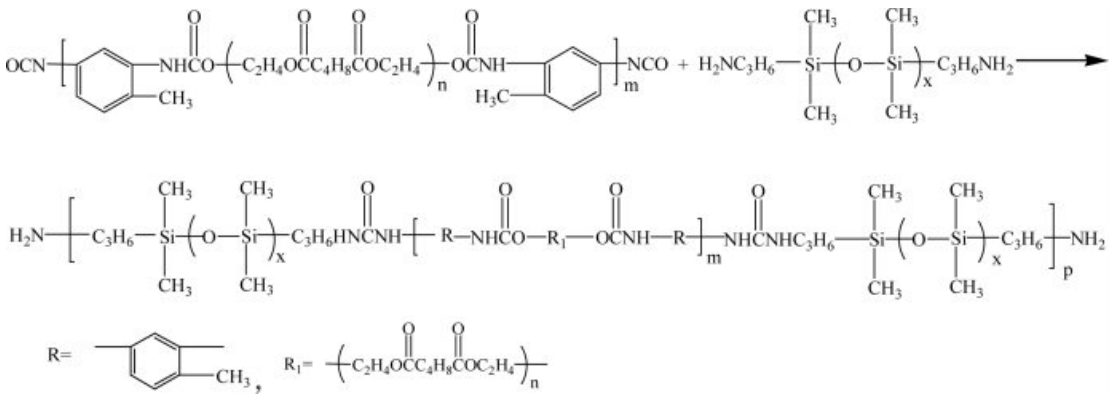
**Synthesis. Synthesis of the Polyurethane Prepolymer (PU):** Equation of synthesis reaction was shown in Scheme 1. In the preparation of the PU, DBTDL (0.10 g), vacuum dehydrated PDHA-1500 (15.00 g) and AT (5.00 g) were added in a four-necked flask equipped with a nitrogen inlet and outlet, stirring apparatus, thermometer and a condenser. Then, TDI (3.48 g) was added dropwise. The reaction was last for 2~3 h at 60 °C. The PU (16.45 g) was gained when the amount of NCO reached a certain value. During the reaction, the AT was used as solvent. The NCO content was determined by the standard dibutylamine back-titration method.[24]

**Synthesis of the Anti-pilling Finishing Agent (SA-PU):** Equation of synthesis reaction was shown in Scheme 2. At first, the amino-terminated siloxane (SA) (20.00 g) was added to the four-necked flask, after that, the PU (16.45 g) was added dropwise. With the protection of nitrogen, the reaction was kept about 3~5 h at the temperature of 20 °C. In the next step, the pH value of reaction system was adjusted to 6~7 by acetic acid. Finally, the product was emulsified with deionized water by vigorous stirring. And then SA-PU (32.81 g) with the yield of 85.27% was successfully synthesized.

**Application of SA-PU on Polyester-cotton Fabric.** The polyester-cotton fabrics were dipped in 80 g/L finishing liquid,




**Scheme 1.** Reaction equation of the PU.



**Scheme 2.** Reaction equation of SA-PU.

and nipped twice in a laboratory-scale padding machine at 5 kg/cm$^2$ and speed of 2 m/min to achieve 80% wet pickup. The bath ratio was 1:20. Then the padded fabric was dried in oven at 90 °C for 90 s and cured at 160 °C for 90 s. The testing samples were in the condition of atmosphere with temperature 20±1 °C and relative humidity 65±2% for 24 h before test.

**Characterization.** The chemical structures of the PU and SA-PU were characterized by Fourier transform-infrared (FTIR) spectroscopy (Nicolet 5700, Thermo Nicolet Corporation, USA). The surface morphology of the polyester-cotton fabric samples were measured by scanning electron microscope (S-4800, HITACHI, Japan) and energy dispersive spectrometer (EDS). The bending properties and surface properties which reflect the handle of fabric, were measured by Kawabata Evaluation System for Fabric (KESFB-AUTO-A, Japan). The coefficient of friction (MIU) was measured according to FZ/T 01054-2012. Bending rigidity (B) was measured according to GB/T18318.1-2009. All these measurements were repeated in both warp and weft directions, and the value was the average of both warp and weft directions. Each test was performed for three times. The anti-pilling property was measured by Martindale abrasion and pilling (Ning Bo Textile Instrument Factory) according to GB/4802.3-2008. Fabric whiteness was measured by Whiteness Meter (WSB-2) according to GB/T8424.2-2001. Each test was performed for three times. The breaking strength of fabrics were measured by Electrical fabric strength tester (YG026A) according to GB/T3819-1997. Air permeability was measured by gas permeability tester (Model YG461E) according to GB/T5453-1997. Each test was performed for three times. Moisture permeability was measured by moisture permeability tester (TEXTEST, Switzerland) according to GB/T 12704.2-2009. Each test was performed for three times.

## Results and Discussion

**FTIR Analysis.** It can be seen from Figure 1 that the characteristic absorption peak at 2270 cm$^{-1}$ assigned to -NCO group and the absorption peak at 3355 cm$^{-1}$ attributed to N-H of -NHCOO-, while the stretching vibration peak of C=O of the ester group was 1715 cm$^{-1}$. These indicated that the PU with the isocyanate group was synthesized. Compared (a) with (b), the methyl deformation vibration peak of -SiCH$_3$ appeared at 1257 cm$^{-1}$ in (b). 1091, 1020 cm$^{-1}$ belonged to the characteristic vibration peak of Si-O-Si. The flexural vibration peaks of Si-C appeared at 800 cm$^{-1}$. The absorption peak of -NCO at 2270 cm$^{-1}$ disappeared completely. It indicated that the PU was completely reacted and SA-PU was synthesized successfully.[25]

**EDS Analysis.** SA-PU was processed into polyester-cotton fabric, the distribution of elements on the surface of the fabric

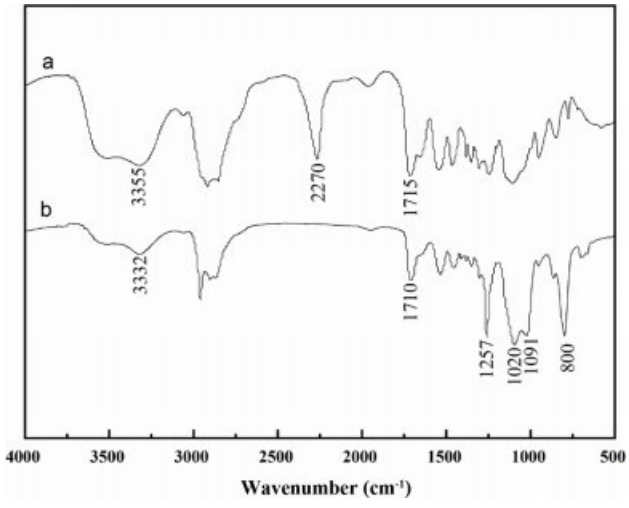



**Figure 1.** FIIR spectra of (a) PU; (b) SA-PU.

was presented in Figure 2. The EDS element distribution visually showed the distribution of the elements on the surface of the fabric after finishing. The atomic mass concentrations were listed in Table 1. As it can be seen, original fabric contained only C and O elements and the content of C and O elements on the surface of original fabric was 65.72% and 34.28%, respectively. With the finishing of SA-PU, the finished fabric was evenly distributed with N and Si elements. N and Si elements were derived from PU segment and amino-terminated siloxane, so the N and Si elements can be clearly seen. It also indirectly indicated the successful synthesis of SA-PU.

**SEM Analysis.** The morphological structures of original fabric, original fabric after friction, treated fabric by SA-PU after friction, treated fabric by SA-PU after 15 launderings and then by friction were shown in Figure 3. The fabrics were rubbed under the same test conditions. Compared Figure 3(a) with Figure 3(b), it was obvious in Figure 3(b) that the fibers in fabric were subjected to considerable destruction. Some fibers were broken and quite a number of the fibers got entangled with one another due to the repeated rubbing. Figure 3(c) indicated that SA-PU endowed the fabric with a relatively smooth surface. The morphology of the fibers had barely changed because the fabric had particular anti-pilling property. The anti-pilling mechanism of SA-PU was shown in the Scheme 3. The finishing agent formed a film on the surface of the fabric due to the good film-forming property of the PU component, which covered the fibers and fiber ends.[20] On the one hand, the film protected the fibers from being broken in friction, on the other hand, the film prevented the fiber ends from getting entangled with one another. At the same time, on account of favourable abrasive resistance of the PU component, the film scarcely got damaged in the experiment. Consequently, the anti-pilling property of the fabric finished by SA-PU had greatly improved. Figure 3(d) showed that the surface of the treated fabric by SA-PU after 15 launderings and

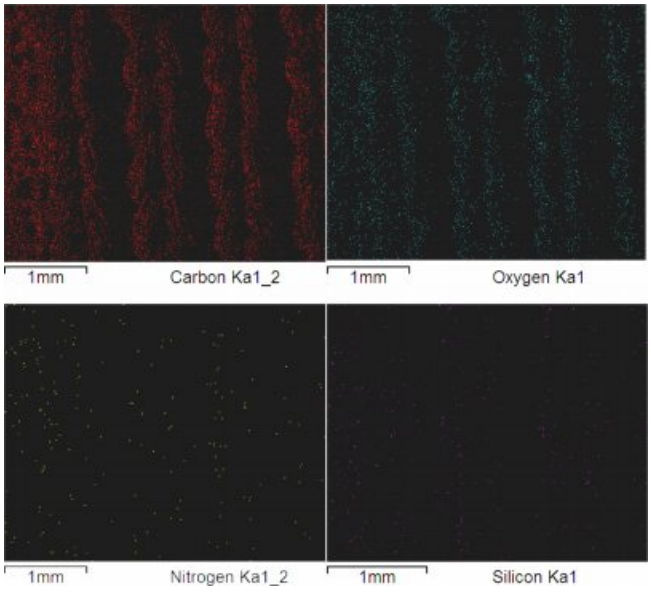



**Figure 2.** EDS analysis of the polyester-cotton fabric after finishing.

**Table 1. Chemical Compositions of Original Fabric and Original Fabric after Finishing**

| Samples | Mass concentration (%) | | | |
|---|---|---|---|---|
| | Carbon | Oxygen | Nitrogen | Silicon |
| Original fabric | 65.72 | 34.28 | 0 | 0 |
| Original fabric after finishing | 61.92 | 31.06 | 2.86 | 4.16 |

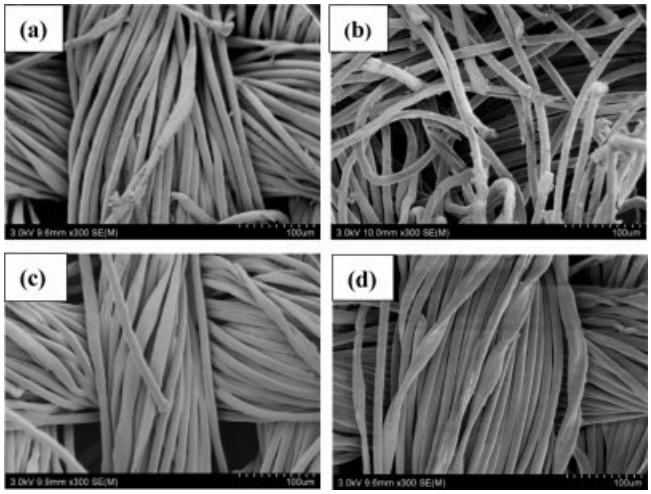
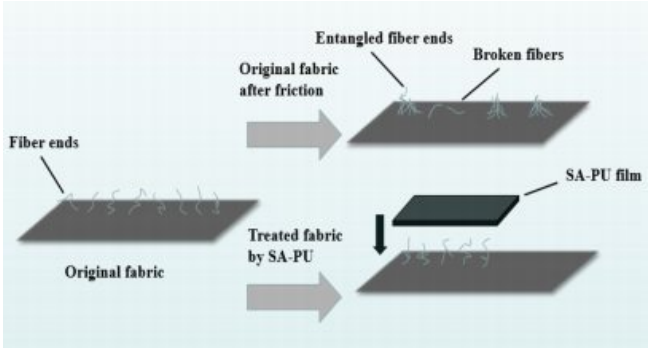



**Figure 3.** SEM micrographs of (a) original fabric; (b) original fabric after friction; (c) treated fabric by SA-PU after friction; (d) treated fabric by SA-PU after 15 launderings and then by friction.




**Scheme 3.** The anti-pilling mechanism of SA-PU.

then by friction remained smooth to a large extent, moreover, the fibers were not broken and didn't get drastic snarled. The above results stated that the anti-pilling property of fabrics finished by SA-PU had satisfactory washing fastness.

**Fabric Anti-pilling Performance and Handle Evaluation.** Surface properties including the coefficient of friction (MIU) and surface roughness (SMD) were measured. The surface roughness (SMD) indicated the variation in surface geometry of the fabric in units of microns, the coefficient of friction (MIU) referred to the friction between the fabric surface and a standard contactor.[26] The lower the MIU value is, the less the friction is, and the lower the SMD value is, the better the smoothness is.[27] In Table 2, the results showed that the MIU value and the SMD value on the warp and weft direction of fabric treated by SA-PU were reduced. On polyester-cotton fabric, the SA molecular chain had low surface energy and could rotate freely due to the presence of helical structure and methyl extending to the outside. Therefore, the MIU value and the SMD value decreased, namely, the softening property of the fabric after treatment was improved.[27] After curing (120 °C, 2 min), SA-PU film formed on the surface of the fiber. The film could reduce the friction between fibers and attach the fluffs to the surface of the fiber.[20] During the use of the fabric, the number of fluffs decreased. The above results stated that the fabric finished by SA-PU had better anti-pilling property.

Bending rigidity (B) indicated the ability of a fabric to resist bending.[14] The value on the warp and weft direction of the treated fabric was reduced from 0.0582, 0.0579 gf·cm$^2$/cm to 0.0561, 0.0568 gf·cm$^2$/cm, respectively. The flexibility and handle of the fabric were enhanced because the introduction of PU segments was beneficial to improve the flexibility and the elastic recovery of the fabric. The anti-pilling property of the polyester-cotton fabric treated by SA-PU was improved 2~3 grades. The polar groups such as -NHCOO-, -$NH_2$ could form intermolecular hydrogen bonds with the hydroxyl on the polyester-cotton fabric.[28] Therefore, the polyester-cotton fabric finished by SA-PU had good washing durability. Even after 15 launderings, the anti-pilling property of the fabric finished by SA-PU was still good and had good fastness.

**Physical and Mechanical Performance Changes in the Fabrics after Finishing.** The experimental results of physical and mechanical properties were shown in Table 3. Compared with those of the untreated polyester-cotton fabric, the whiteness, air, and moisture permeability of the polyester-cotton fabric finished by SA-PU dropped slightly. The whiteness of fabric decreased mainly due to the introduction of amino polysiloxane to cause fabric yellowing. The decrease of air permeability could be explained by the formation of the compact SA-PU film on the surface of the fabric by curing (120 °C, 2 min). The SA molecular chain had low surface energy, therefore, the fabric finished by SA-PU had low surface energy and had slight moisture absorption. The moisture permeability of fabric treated by SA-PU was declined. In addition, the existence of SA-PU film limited the relative slip of fibers, so the

**Table 2. Fabric Anti-pilling Performance and Handle Evaluation**

| Samples | | Untreated fabric | Treated fabric | Treated fabric after 15 launderings |
|---|---|---|---|---|
| Anti-pilling grades | | 1~2 | 4 | 3~4 |
| SMD (μm) | warp | 4.277 | 3.106 | 3.648 |
| | weft | 3.702 | 2.951 | 3.344 |
| MIU | warp | 0.206 | 0.170 | 0.181 |
| | weft | 0.243 | 0.188 | 0.201 |
| B (gf·cm$^2$/cm) | warp | 0.369 | 0.215 | 0.235 |
| | weft | 0.133 | 0.109 | 0.114 |

**Table 3. Physical and Mechanical Performance Changes of the Fabric after Finishing**

| Samples | | Untreated fabric | Treated fabric | Treated fabric after 15 launderings |
|---|---|---|---|---|
| Whiteness (%) | | 78.2 | 75.6 | 76.1 |
| Air permeability (mm/s) | | 1617 | 1388 | 1438 |
| Moisture permeability (g/h·m$^2$) | | 1325 | 1019 | 1130 |
| Break strength (N) | warp | 1107 | 1311 | 1286 |
| | weft | 552 | 713 | 689 |

breaking strength on the warp and weft directions of fabrics finished by SA-PU had acquired mild improvement.

## Conclusions

A polysiloxane modified polyurethane anti-pilling finishing agent (SA-PU) for polyester-cotton fabric was successfully synthesized. After the pad-dry-cure finishing process, the anti-pilling property of the fabrics had increased 2~3 grades. In addition, the MIU values on the warp and weft direction of the treated fabric were reduced from 0.206, 0.243 to 0.170, 0.188, respectively. The SMD values on the warp and weft direction of the treated fabric were reduced from 4.277, 3.106 μm to 3.702, 2.951 μm, respectively. The B values on the warp and weft direction of the treated fabric were reduced from 0.0582, 0.0579 gf·cm$^2$/cm to 0.0561, 0.0568 gf·cm$^2$/cm, respectively. It showed that SA-PU had a great effect on the bending properties, surface roughness and the coefficient of friction. Even after 15 launderings, they were affected slightly. It indicated that the polyester-cotton fabric finished by SA-PU exerted good durable anti-pilling property. Moreover, the breaking strength of the treated fabric improved mildly. But the whiteness, air and moisture permeability of the treated fabric dropped slightly.

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