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Synthesis of Linear Piperazine/Polyether Functional Polysiloxane and Its Modification of Surface Properties on Cotton Fabrics

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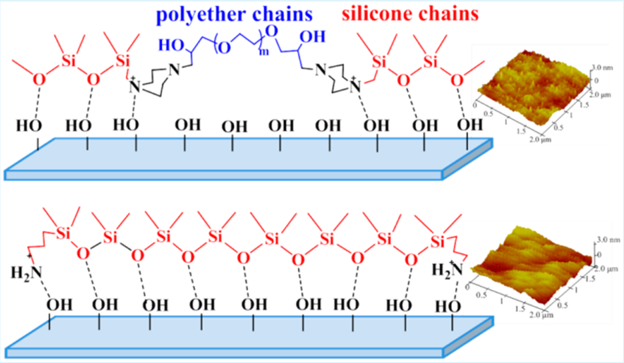
ABSTRACT: In this work, silicone softener (PTSO−PEG) was synthesized, with piperazine terminated polydimethylsiloxane (PTSO) and epoxy terminated polyethylene glycol (EPEG) as raw materials. Chemical structure of PTSO−PEG was characterized by ^{1}H NMR, FTIR, GPC, and TGA. Its application on cotton fabrics was studied. Morphologies of silicone modified surfaces on cotton fabrics and silicon wafers were investigated by SEM and AFM, respectively. The morphology images indicated that PTSO−PEG treated surface was macroscopically smooth and microscopically rough. Performance properties of silicone treated cotton fabrics, including hydrophilicity, whiteness, and softness, were tested. The results showed that PTSO−PEG treated cotton fabrics expressed better whiteness and hydrophilicity than traditional amino silicone treated sample. The piperazine and hydrophilic polyether groups on PTSO−PEG molecules disturbed the continuous and orderly arrangement of Si−CH_3 groups, giving the cotton a hydrophilic and rough surface. This work provided a cost-effective and environmental method to synthesize and apply high performance silicone softener.



KEYWORDS: *silicone softener, piperazine, hydrophilicity, whiteness, morphology*

1. INTRODUCTION

Silicones are widely used as softeners in textile finishing processing.[1,2] The silicone backbones have good flexibility, for the Si−O bonds are longer than C−C bonds and the steric effect between methyl groups on neighboring silicon atoms is weak.[3] Thus, silicones can give some typical properties such as softness, bounciness, and antiwrinkle properties to cotton fabrics and other materials.[1−4]

In fabric manufacturing industry, a lot of conventional amino silicones are widely applied, such as *N*-γ-aminopropylpolysiloxane, *N*-β-aminoethyl-γ-aminopropylpolysiloxane, etc.[5−7] They impart cotton fabrics with superior softness and highly smooth surface.[8] However, these conventional amino silicones involve some serious drawbacks that restrict their application, in both preparation process and application properties.

In preparation process, most traditional amino silicones are synthesized either effectively low or highly pollutive to environment. The typical methods to synthesize functional polysiloxanes include hydrolysis and condensation polymerization of siloxane with silane coupling agents, and hydrosilylation among polysiloxanes and functional chemicals containing double bonds. For example, Xu[9,10] synthesized a series of amino polysiloxanes through condensation polymerization of α,ω-dihydroxypolydimethylsiloxane and amino silane coupling agents. Hou[11−13] synthesized several amino polysiloxanes with similar structure through ring-opening polymerization. Some residual amino silane coupling agents remained in products because of the low conversion rate, and they negatively affected properties. Previously, we synthesized dodecyl/piperazine functional polysiloxane by hydrosilylation of dodecyl/epoxy modified polysiloxane with *N*-aminoethylpiperazine.[14] Fabrics treated by this silicone expressed good wettability and whiteness. But large amount of solvent was used during synthesis, which made the product purification process more complicated. More importantly, it is energy-consuming and not environmentally protective in industrial application.

In application properties, traditional amino silicones treated cotton fabrics express serious defects, such as strong hydrophobicity and easy yellowing under thermal condition or ultraviolet radiation. These amino silicones own protonated amino groups, thus can easily attach onto the negatively charged cotton fabric surface through electrostatic interactions.[15−17] Once exposed in high temperature or ultraviolet environment, the amino groups are easily being oxidized and lead to yellowing effect.

Hence, it becomes urgent to develop novel amino silicones that can be synthesized cost-effectively and environmental friendly. They should impart fabrics with excellent whiteness, hydrophilicity, and softness. Recently, various types of modified silicones were designed and synthesized with special proper-

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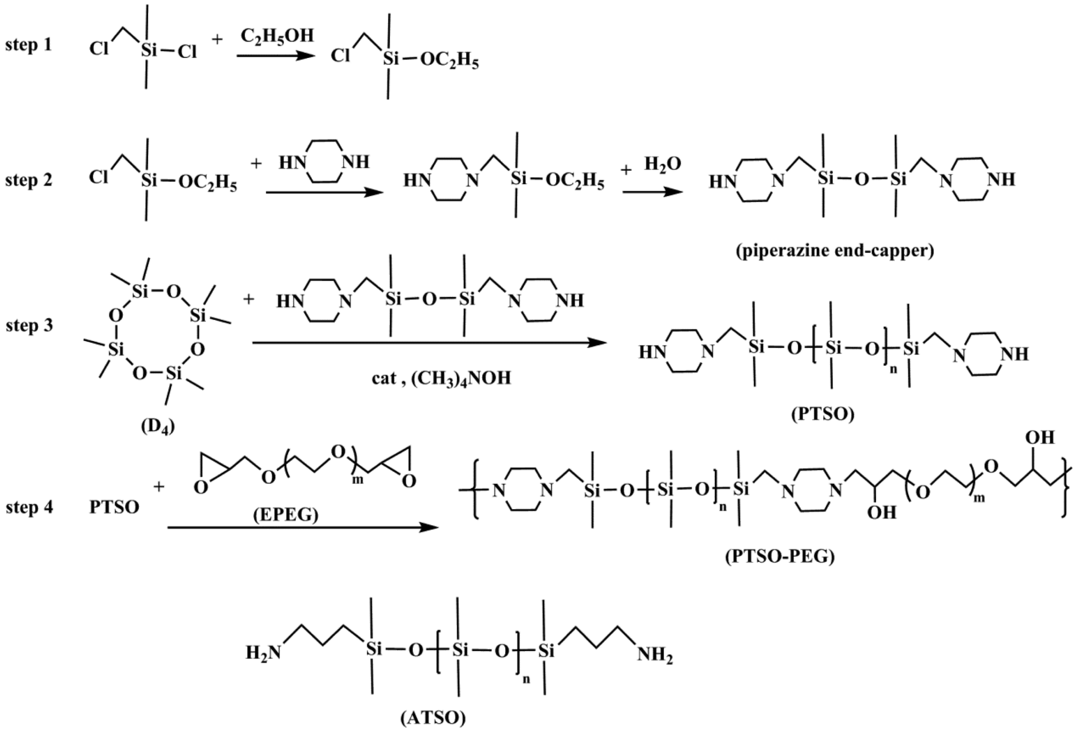
Scheme 1. Synthesis Route of PTSO−PEG



ties.[18,19] For example, secondary or tertiary amine modified silicones, such as γ-piperazinylpolysiloxane, give fabrics excellent whiteness.[10,20] Polyether grafted/blocked polysiloxanes, which contain hydrophobic segments (polysiloxane) and hydrophilic chains (polyether) together, express excellent performance in hydrophilicity and emulsification property during fabric treatment.[3,21−23] However, from industrial application perspective, there are still few silicones that combine all these advantages together in low cost. The solution is mainly focused on improvement in molecular structure design and synthesis methods.

In this work, we synthesized piperazine and polyether contained silicone softener by cost-effective and environmental friendly method. First, 1,3-bis(α-piperazinemethyl)-tetramethyldisiloxane was synthesized and used as end-capper. Then it reacted with octamethylcyclotetrasiloxane (D_4) via solvent-free ring-opening polymerization to obtain piperazine terminated polysiloxane (PTSO). The PTSO further reacted with epoxy terminated polyethylene glycol (EPEG) to produce piperazine/polyether functional polysiloxane (PTSO−PEG). The PTSO−PEG treated cotton fabrics expressed good properties, including whiteness, softness, and unlike traditional amino siloxane, they maintained good hydrophilicity. Surface morphology of PTSO−PEG treated cotton fabrics and silicon wafers was observed and studied by SEM and AFM.[2,9,20]

2. EXPERIMENTAL SECTION

2.1. Materials. Octamethylcyclotetrasiloxane (D_4, 98% purity), (chloromethyl)dimethylchlorosilane, epoxy terminated polyethylene glycol (EPEG), and fatty alcohol polyoxyethylene ether (XL, HLB ≈ 10.5), all industrial grade, were obtained from Zhejiang Xinan Chemical Industrial Group Co., Ltd., Hebei Taifeng Chemical Co., Ltd., Wuxi Huilong Electronic Materials Co., Ltd., and Zhejiang Ji Lida Chemical Co., Ltd., respectively. Piperazine, dioxane, acetic acid, ethyl acetate, and isopropyl alcohol, all analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd. Defatted cotton fabrics were obtained from Ying Xiang Textile Mill Ltd. Silicon wafers were purchased from Zhejiang Lijing Silicon Materials Co., Ltd. and used as substrate in AFM characterization.

2.2. Synthesis Process of Piperazine End-Capper, PTSO, and PTSO−PEG. The synthesis process included four steps (Scheme 1):

Step 1. To a flask with (chloromethyl)dimethylchlorosilane (143 g, 1 mol), ethanol (50.6 g, 1.1 mol) was added dropwise over 5 h with stirring at 50 °C. After reaction for another 5 h, the crude product was purified by distillation to obtain a colorless fluid [(chloromethyl)-dimethylethoxysilane (125 g, 82% yield)].

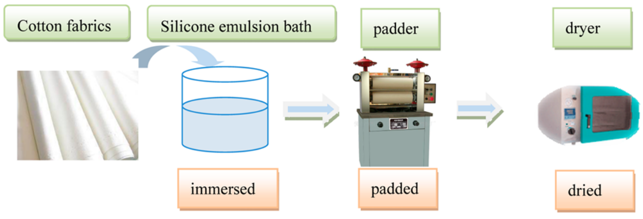
Step 2. To a three-necked flask equipped with a reflux condenser, a nitrogen inlet tube, and a dropping funnel, a mixture of piperazine (172 g, 2 mol) and dioxane as solvent (172 g) was added and heated to 80 °C. The (chloromethyl)dimethylethoxysilane (61 g, 0.4 mol) was added dropwise over 2 h and stirred for another 2 h. After reaction, the precipitate of piperazine hydrochloride was removed by filtration, and the solvent together with parts of piperazine was removed under reduced pressure. The crude product was further purified by vacuum distillation to obtain the α-piperazinemethyl dimethylethoxysilane (36.4 g, 45% yield). Finally, this silane was hydrolyzed at 50 °C for 5 h and further purified by distillation to obtain a transparent fluid of piperazine end-capper.[24]

Step 3. To a three-necked flask equipped with a reflux condenser, a nitrogen inlet tube, and a thermometer, a mixture of D_4 and piperazine end-capper was added, with solid tetramethylammonium hydroxide (0.02 wt %) as base catalyst. The reaction mixture was maintained at 90 °C for 10 h and heated to 150 °C for 0.5 h to decompose the catalyst. After the low boiling point impurities were removed under reduced pressure, a viscous fluid [piperazine terminated polydimethylsiloxane (noted as PTSO)] was obtained. The molecular weight of PTSO was controlled by the molar ratio of D_4 to piperazine end-capper.[25] Aminopropyl terminated polysiloxane (noted as ATSO), a conventional amino silicone, was synthesized through the same method.

Step 4. To a three-necked flask equipped with a reflux condenser, a nitrogen inlet tube, and a thermometer, a mixture of PTSO and EPEG (molar ratio, PTSO/EPEG = 1:1) was added and dissolved in isopropyl alcohol (40 wt %) at 80 °C. After a 5 h reaction, a transparent and viscous fluid (noted as PTSO−PEG) was obtained. A series of PTSOs−PEG with the same ether chain and different silicone chain length were synthesized by the same method.

2.3. Treatment Process of Cotton Fabrics. Scheme 2 showed the treatment process of cotton fabrics. The synthesized PTSO−PEG needs to be emulsified before fabric treatment.[26,27] The corresponding silicone emulsions were prepared by phase inversion emulsification method.[14] To a round-bottom flask, 10 g of PTSO−PEG and 3 g of XL (nonionic emulsifier) were added and mixed with magnetic stirrer for a few minutes. Then 10 g of 10 wt % HAc aqueous solutions were added dropwise to form a uniform and transparent water-in-oil emulsion. At last, 60 g of water was added slowly to obtain an oil-in-water silicone emulsion.[28]

Scheme 2. Treatment Process of Cotton Fabrics



The PTSO−PEG emulsions were diluted into 1 wt % silicone aqueous bath. Cotton fabrics were impregnated in the bath for 30 min (weight ratio, fabrics/bath = 1:10) and padded to wet pick-up at about 70 wt % on the weight of the dry fabrics. The padded fabrics were then dried at 80 °C for 120 s and at 130 °C for 60 s. Then they were kept in a desiccator to balance for 24 h (noted as PTSO−PEG/cot).[29,30]

2.4. Characterization. *2.4.1. Molecular Structure.* ^{1}H NMR spectra were recorded on a Bruker 400 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent. FTIR spectra were performed on a Nicolet 560 spectrometer using KBr pellet technique. Thermogravimetry analysis (TGA) was performed on a Q500 thermogravimeter (instrument, TA; heating rate, 10 °C/min; temperature range, 50−850 °C; nitrogen atmosphere). The molecular weights were obtained by gel permeation chromatography (GPC) (instrument, Waters 1525/2414; solvent, tetrahydrofuran). The amino content of PTSO was determined by chemical titration.

2.4.2. Performance Properties of Cotton Fabrics. Whiteness, softness, and hydrophilicity of cotton fabrics were measured by WSB-2 digital whiteness meter, LLY-01B electric rigidity tester, and JC 2000C static contact angle measurement instrument, respectively. These three properties were expressed as whiteness, bending rigidity (BR), and static water contact angle (WCA), respectively.[31]

2.4.3. Surface Morphology of Cotton Fabrics. Surface morphology of silicone treated cotton fabrics was studied by SEM. It was conducted on S-570 scanning electron microscope (Hitachi) at an accelerating voltage of 5 kV. The cotton fabrics were coated with gold in vacuum before scanning.

2.4.4. Surface Morphology of Silicon Wafers. In order to further study the difference in surface modification effects of functional polysiloxanes, the AFM tests were conducted on polished rigid silicon wafers. The observation was performed on a Nanoscope IIIA AFM (Digital Instruments) in tapping mode. The sample treatment process was as follows: oxidized silicon wafer was impregnated vertically into PTSO−PEG solution in ethyl acetate (0.03 wt %) for 10 s, dried at 80 °C for 2 min, cured at 130 °C for 60 s, and kept in a desiccator to balance for 24 h (note as PTSO−PEG/sil).[22]

3. RESULTS AND DISCUSSION

3.1. Molecular Structure Characterization. The molecular structures of functional polysiloxanes were characterized by ^{1}H NMR, FTIR, GPC, and TGA.

3.1.1. ^{1}H NMR Spectra. Piperazine end-capper (Figure 1) showed relevant chemical shift signals at δ 0.0 (aH), 1.75 (bH), 2.24 (cH), and 2.74 (dH).[24] The integrated area ratio of these four peaks was 2.96:1:1.98:1.93. It was consistent with the expected structure. PTSO3 (we took PTSO3 as an example) showed similar signals to that of piperazine end-capper. Its stronger intensity at δ 0.0 (aH) was due to the ring-opening polymerization of D_4. For PTSO3-PEG (we took PTSO3-PEG as an example), the relevant signals at δ 0.0 (aH), 1.82 (bH), and 2.10 (cH) were corresponding to polysiloxane chains, and those at δ 3.62 (i, jH) were corresponding to EPEG chains. The signal at δ 1.14 was attributed to isopropyl alcohol (solvent).

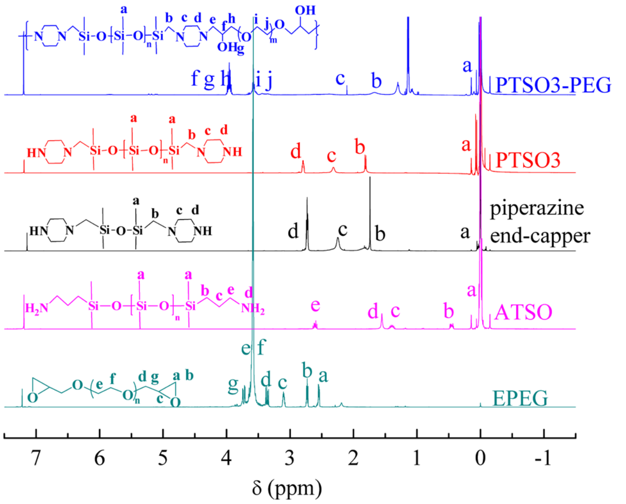


Figure 1. ^{1}H NMR spectra of piperazine end-capper, PTSO3, PTSO3-PEG, EPEG, and ATSO.

3.1.2. FTIR Spectra. The FTIR spectra showed relevant signals of stretching and distortion vibrations of functional groups (Figure 2). For PTSO3-PEG, the bands at 2965, 1260, 1018−1098, and 800 cm^{-1} indicated the presence of C−H (−CH_3, −CH_2), Si−CH_3, Si−O, and Si−C groups, respectively.[32] The PTSO3 and ATSO had similar signals to PTSO3−PEG. It resulted from the overlap of vibrations attributed to C−O groups from EPEG chains (1107 cm^{-1}) and Si−O groups (1098 cm^{-1}) from polysiloxane chains. From ^{1}H NMR and FTIR spectroscopies, the chemical structures of samples were confirmed.

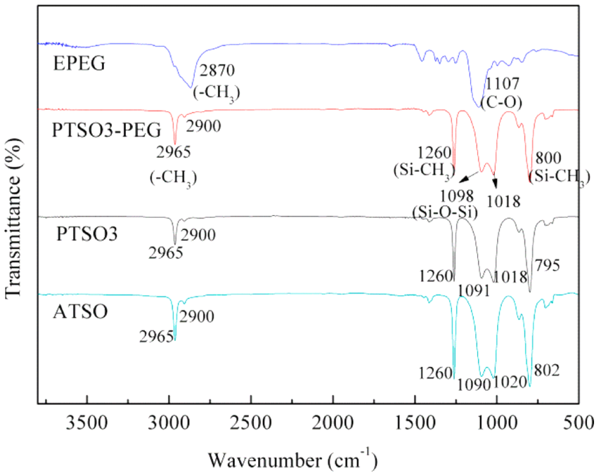


Figure 2. FTIR spectra of ATSO, PTSO3, PTSO3-PEG, and EPEG.

3.1.3. Molecular Weight. Piperazine terminated polydimethylsiloxanes (PTSO) with different designed molecular weight (Mn) were synthesized via solid tetramethylammonium hydroxide (Me_4NOH) catalyzed ring-opening polymerization. The molecular weights of PTSO were determined by GPC and chemical titration of amino contents (Figure 3 and Table 1). There were some deviations of Mn between these two methods, for Mn measured by GPC is a relative value. The PDI (polydispersity index) of PTSO was between 1.8 and 2.1, indicating that PTSO synthesized via solid Me_4NOH catalyzed polymerization had a wide molecular weight distribution. It resulted from the poor solubility of solid Me_4NOH catalyst in D_4. After PTSOs reacted with EPEG, three kinds of piperazine/polyether functional polysiloxanes (PTSO−PEG) with different siloxane chain length were obtained. The molecular weights of PTSOs−PEG were much larger than PTSOs according to GPC results. ATSO is a traditional amino silicone and owns primary amino groups. It was used to compare with PTSO−PEG in fabrics treatment effects. ATSO has different chemical structure with PTSO−PEG.

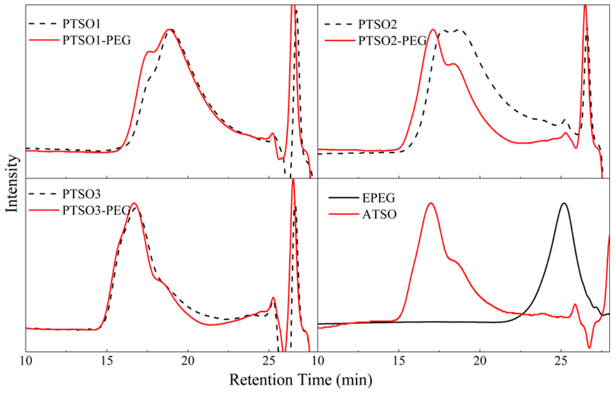


Figure 3. GPC curves of PTSOs, ATSO, EPEG, and PTSOs−PEG.

Table 1. Molecular Weight of PTSOs, ATSO, EPEG, and PTSOs-PEG

sample	designed Mn (g/mol)	Mn[a] (g/mol)	Mn[b] (g/mol)	PDI[c]
PTSO1	5000	4940	5290	1.86
PTSO1−PEG			7370	2.17
PTSO2	10000	8160	11840	1.80
PTSO2−PEG			16250	2.03
PTSO3	20000	18180	23950	2.11
PTSO3−PEG			28900	1.94
ATSO	20000	17950	17430	1.62
EPEG		640	620	1.30

[a] Mn values of PTSOs and ATSO were determined by chemical titration, for amino groups locate at the end of the molecules; thus, the amine content is proportional to their molecular weight. Similarly, Mn of EPEG can be determined from epoxy content. [b] Mn means the results from GPC. [c] PDI values were acquired according to GPC testing results.

3.1.4. TG Analysis. The treatment process of cotton fabrics with silicones included a thermal curing stage at 130 °C; thus, the silicones' thermal stability was also very important. The weight loss curves (Figure 4) showed that EPEG, ATSO, and all the PTSO−PEG samples were stable before 150 °C. The decomposition temperature of EPEG ranged from 150 to 420 °C. During this temperature period, the curves of PTSOs−PEG decreased slowly with about 7−15% weight loss. It was attributed to the decomposition of ether chains and the volatilization of low boiling point siloxanes. The obvious decomposition temperature (20% weight loss) for ATSO and the PTSO−PEG samples began at about 420−450 °C, compared with EPEG's 180−200 °C. The results suggested that the synthesized silicones expressed much better thermal stability than EPEG.

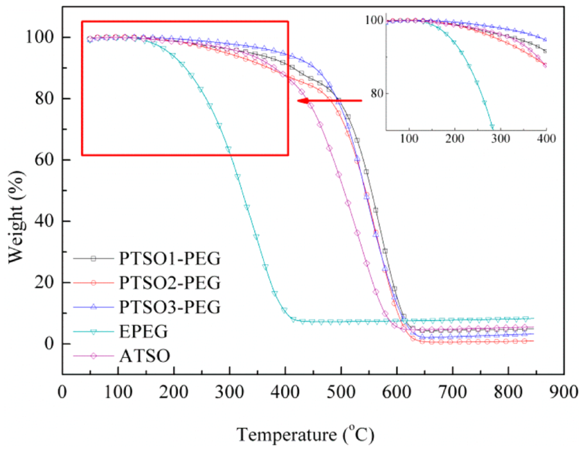


Figure 4. TGA curves of PTSO−PEG, ATSO, and EPEG.

3.2. Performance Properties and Surface Morphology of Treated Cotton Fabrics. The main performance properties of treated cotton fabrics include whiteness, softness, and hydrophilicity.

Whiteness of cotton fabrics was measured by whiteness meter. Figure 5A showed that PTSO−PEG treated fabrics almost remained the same whiteness as untreated raw cotton fabrics. However, ATSO treated fabrics showed relatively lower whiteness compared with other samples. The difference of whiteness could even be observed by the naked eye. This phenomenon resulted from primary amino groups (contained in ATSO), which are easier to yellowing than secondary and tertiary amino groups (in PTSO−PEG).[10] The primary amino groups contain highly reactive amino hydrogen, and they are easy to be oxidized and become dark in color once exposed to high temperature or ultraviolet radiation.

Softness of cotton fabrics was tested and characterized by bending rigidity (BR).[31] The low BR value represents good softness of fabrics. Figure 5B showed that all the PTSO−PEG treated cotton fabrics expressed lower BR values compared with untreated one (although slightly higher than ATSO treated sample). According to the GPC results (Table 1), the molecular weight of ATSO was close to PTSO2−PEG. Considering the difference in molecular structure, the ATSO was terminated by primary amine, while the PTSO2−PEG contained secondary/tertiary amine (from piperazine), together with polyether segments. The primary amine was helpful to increase softness, and the polyether segments led to negative effects. Besides, taking the molecular weight into consideration, the molecular weight of PTSO−PEG follows the order PTSO3-PEG > PTSO2-PEG > PTSO1-PEG, and the softness of corresponding treated cotton fabrics increased with their molecular weight. The long siloxane chain was beneficial in enhancing softness.

Water contact angles (WCA) on the surface of cotton fabrics were measured to characterize hydrophilic property (Figure 6). Untreated cotton fabrics had good hydrophilicity due to

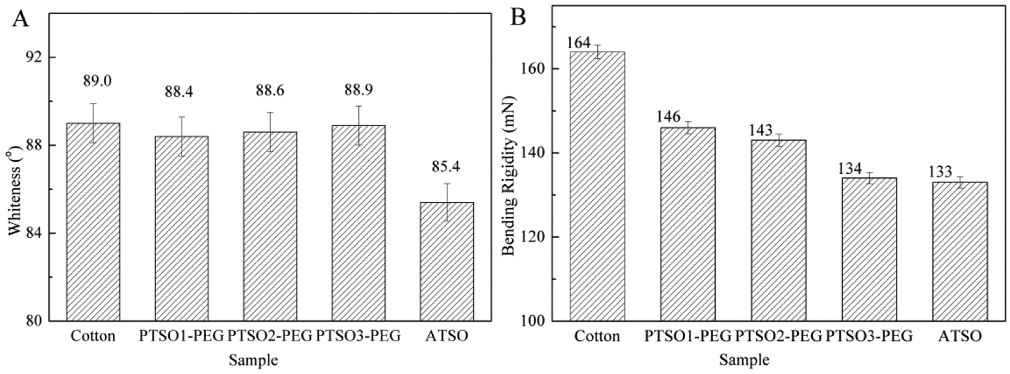


Figure 5. Properties of untreated and silicones treated cotton fabrics: (A) whiteness; (B) bending rigidity.

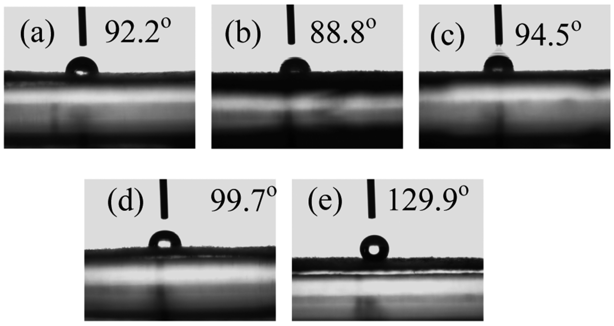


Figure 6. Water contact angles of cotton fabrics: (a) untreated cotton; (b) PTSO1-PEG/cot; (c) PTSO2-PEG/cot; (d) PTSO3-PEG/cot; (e) ATSO/cot.

abundant −OH groups on the surface. PTSO−PEG treated cotton fabrics (Figure 6b−d) had similar hydrophilic degree to the untreated cotton fabrics (Figure 6a). The WCA were affected by the siloxane chain length of PTSO−PEG, and the longer the chain length, the bigger the WCA value was. The ATSO treated cotton fabrics (Figure 6e) expressed much larger WCA than other samples. Considering the difference in molecular structures, the ATSO was terminated by primary amino groups and contained only long siloxane chain, while the PTSO−PEG was piperazine terminated and contained both siloxane and polyether segments. It was found that the terminal group (such as primary amino group) played a key role in enhancing WCA value. Compared with ATSO treated sample, the polyether segments in PTSO−PEG kept the WCA the same as untreated cotton.

The difference of hydrophilic degree resulted from the molecular functional group orientation, and it was further described by the proposed schematic model shown in Figure 7. Polydimethylsiloxane molecules have low surface tension; thus, they spread widely and covered closely on hydrophilic cotton fabric surface.[8,33,34] The silicone molecules may arrange as follows: the dipolar Si−O groups and protonated amino groups were attached closely onto the negatively charged cotton fabrics surface mainly via electrostatic interactions and hydrogen bonding.[28,35] Conversely, the hydrophobic Si−CH_3 groups pointed outward against surface.[36] For ATSO treated cotton fabrics, a relatively smooth and hydrophobic surface was formed because Si−CH_3 groups were arranged orderly on the surface. For PTSO−PEG treated samples, a less complete surface was formed because piperazine and polyether groups disrupted the continuous and sequentially oriented Si−CH_3 groups and reduced the hydrophobicity. Besides, the polyether groups were hydrophilic. Thus, water can be more easily adsorbed onto the PTSO−PEG samples' surface than ATSO sample.

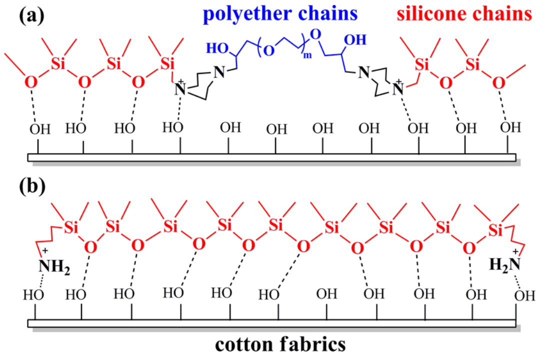


Figure 7. Proposed schematic model for silicones adsorbed on cotton fabrics: (a) PTSO−PEG treated cotton; (b) ATSO treated cotton.

SEM observation was useful to investigate the surface morphology of cotton fabrics. Figure 8 showed SEM images of untreated, PTSO3−PEG, and ATSO treated cotton fabrics. The surface of untreated fabrics (Figure 8a) was much rougher than the other treated two, with many grooves on surface. After being treated by silicones, both of the fabric surfaces (Figure 8b and Figure 8c) became relatively smooth and the grooves disappeared compared with untreated sample.

3.3. AFM Images of Silicon Wafers. To further study the morphology of silicone treated surface in microscopic scale, AFM observation was adapted (with silicon wafers as model substrates). The results are shown in Figure 9. The roughness pictures (Figure 9b, Figure 9d) illustrated the height change on the surface. PTSO3−PEG treated wafer (Figure 9a) was microscopically rough with obvious peaks, for the piperazine and polyether groups disrupted the continuously oriented Si−CH_3 groups. ATSO treated wafer (Figure 9c) was relatively smooth because of the more orderly arranged Si−CH_3 groups. It demonstrated different molecular orientations of PTSO−PEG and ATSO on silicon wafer substrates. And it is consistent with the proposed schematic model for silicones adsorbed on cotton fabrics shown in Figure 7.

4. CONCLUSIONS

Linear piperazine and polyether functional polysiloxanes (PTSO−PEG) have been synthesized via reaction between epoxy terminated polyethylene glycol (EPEG) and piperazine terminated polydimethylsiloxane (PTSO). Their applications on cotton fabrics as silicone softeners were studied. Results

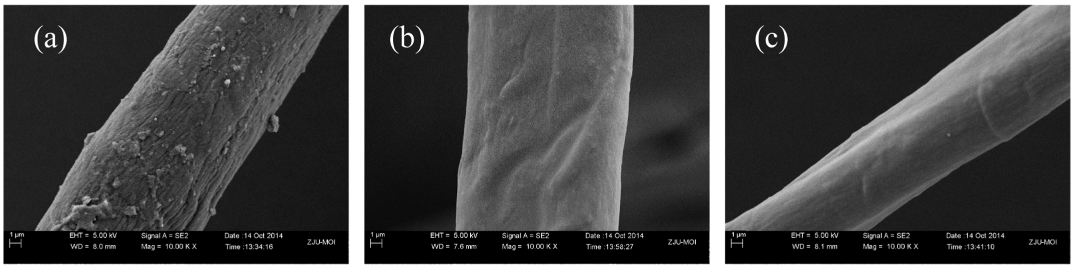


Figure 8. SEM images of cotton fabrics (×10 000): (a) untreated cotton; (b) PTSO3-PEG/cot; (c) ATSO/cot.

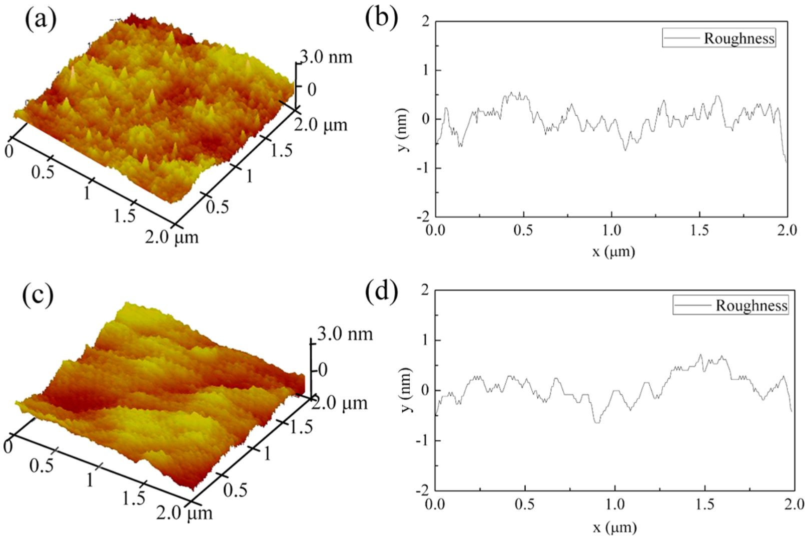


Figure 9. Three-dimensional AFM images and roughness of the silicon wafer surface along a line: (a) PTSO3-PEG/sil (3D); (b) PTSO3-PEG/sil (roughness); (c) ATSO/sil (3D); (d) ATSO/sil (roughness).

indicated that compared with traditional ATSO treated cotton fabrics, the PTSO−PEG treated samples expressed better whiteness while maintaining good softness. The water contact angles (WCA) showed that PTSO−PEG treated cotton fabrics maintained as good hydrophilicity as untreated fabrics, but ATSO treated sample had a high hydrophobic surface. SEM images showed that the PTSO−PEG treated cotton fabrics expressed smooth surface.

The different performance properties and surface morphology between PTSO−PEG and ATSO treated samples were related to the molecular structure of silicones and their orientation on the surface. It was discovered that the PTSO−PEG treated silicon wafer surface was rougher than ATSO treated sample, for the introduction of piperazine and polyether groups on PTSO−PEG molecules disrupted the continuous and orderly orientation of Si−CH_3 groups.

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Notes

The authors declare no competing financial interest.

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