

Synthesis, Film Morphology, and Performance on Cotton Substrates of Dodecyl/Piperazine Functional Polysiloxane

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ABSTRACT: A novel polysiloxane bearing dodecyl and epoxy side groups (DESO) was synthesized as an intermediate through hydrosilylation of polymethylhydrosiloxane with allyl glycidyl ether and 1-dodecene. Then, dodecyl/piperazine functional polysiloxane (DPSO) was prepared through the reaction of *N*-aminoethylpiperazine with DESO. The chemical structure of DPSO was characterized with FTIR and ¹H-NMR spectroscopy and its application performance on cotton fabrics was studied. DPSO with dodecyl side groups gifted the treated fabrics with good wettability and whiteness compared with piperazine functional polysiloxane, while with a slightly reduced softness as well as thickening handle. Film morphology, orientation, and performance on cotton substrates of DPSO were investigated by scanning electron microscope, atomic force microscopy, X-ray photoelectron microscope, and so on. Affected by the dodecyl side groups, DPSO formed relatively hydrophilic, macroscopically smooth but actually uneven films with many dodecyl side chain pillars on the treated substrate surfaces. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40186.

KEYWORDS: fibers; films; morphology; functionalization of polymers

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INTRODUCTION

Polysiloxanes have been used in textile industries as textile softeners for many years. The widely applications are mainly due to their outstanding fabric lubrication, softening properties as well as bounciness and anti-wrinkle properties.^{1–4} In general, these properties are believed to be related with their film morphology on fabric substrates.^{5,6} The most popular softener, amino silicone, can provide textiles with special smooth and softness probably because of its excellent film forming ability and morphology.^{7–9} However, some distinct drawbacks in the conventional amino silicone for textile finishing such as easy yellowing,^{2,10} strong hydrophobicity,¹¹ and uneven distribution of amino groups¹² severely restrict its scope of applications.

This research adopted hydrosilylation to synthesize piperazine functional polysiloxane to eliminate yellowing and uneven distribution of amino groups. Moreover, long alkyl side chains were introduced to the piperazine polysiloxane. It was interesting to find that the introduction of dodecyl groups could improve the whiteness and hydrophilicity of the treated textiles compared with those treated with single piperazine functionalized polysiloxane. Long alkyl chains are well known to be generally hydrophobic.^{13–15} How could the hydrophobic alkyl groups in piperazine polysiloxane make textiles more hydrophilic? There were very limited reports about the mechanisms. In this work,

we investigated the film morphology, molecular orientation of the synthesized polysiloxane on the wafers and cotton substrates using scanning electron microscope (SEM), atomic force microscopy (AFM), X-ray photoelectron microscope (XPS), and other instruments. Based on the analysis of the results, we proposed a possible interaction model between dodecyl/piperazine functional polysiloxane (DPSO) and cotton fibers.

EXPERIMENTAL

Materials

Four polymethylhydrosiloxane (PHMS) samples ($M_n = 10,000$ g mol⁻¹) were synthesized according to the method reported in the literature¹⁶ and their Si—H contents were 0.15, 0.35, 0.55, 0.75 mmol g⁻¹, respectively, determined by chemical titration. Allyl glycidyl ether (AGE) and 1-dodecene were purchased from Aladdin Reagent Company, and used as received. *N*-Aminoethylpiperazine (AEP) was kindly supplied by Zhejiang QuePing Textile Chemical Engineering Ltd.

Defatted cotton fabric with a density of 110 × 70 (the counts of warp × fill yarns for 10 × 10 inch) and a width of 59 inch was purchased from YingXiang Textile Mill Ltd. These cotton samples were treated according to the reference.¹⁷ Silicon wafer was cut into 0.5 cm × 1 cm strips, ultrasonic treated with ethyl acetate for 10 min prior to use, and immersed in a freshly

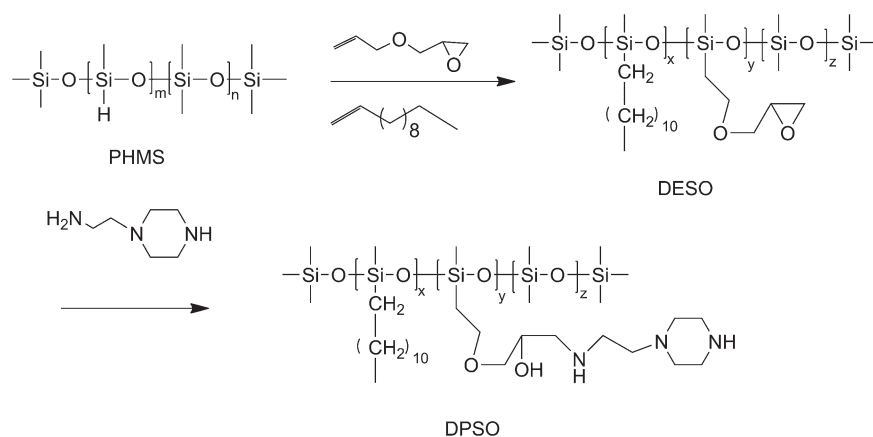


Figure 1. Synthesis route to DPSO.

prepared solution of 98% H_2SO_4 : 27% H_2O_2 = 3 : 1 (v/v) at room temperature for 20 min.¹⁸ They were then rinsed with ultra-pure distilled water and treated with 2% Na_2CO_3 aqueous solution for another 20 min. Followed by washing with large amounts of pure distilled water to pH = 7.0, the silicon wafer was dried at 120°C under N_2 atmosphere and then kept in a desiccator until being used.

Synthesis of DPSO

To a three-necked round bottom flask equipped with a nitrogen inlet tube, a reflux condenser, and a thermometer, a mixture of PHMS, AGE, 1-dodecene (the mol ratio of Si—H and C=C was 1 : 1) and appropriate amount of toluene (as solvent) were added and stirred with a magnetic stirrer. After a catalytic amount of H_2PtCl_6 in isopropanol solution was added, the mixture began to be heated to 65°C under N_2 protection. Some extra AGE was added to fully complete the reaction in 2 h. After another 2 h, the toluene and other low-boiling-point impurities in the mixture were removed under reduced pressure. Finally, a transparent, viscous fluid was obtained (DESO) and used as reactant in the next procedure. In this step, the epoxy content maintained constant through adding same amount of AGE, while the alky value increased along with the increasing Si—H content of PHMS, thus DESO with four levels of alky content was obtained (Figure 1).

In another three-necked round bottom flask charged with a reflux condenser and a thermometer, a mixture of DESO, AEP (mol ratio was 1 : 1.2), and isopropanol (as solvent) was added and heated to about 75°C, the mixture was maintained at 75–80°C for 6 h. The isopropanol and other unreacted raw materials were removed by vacuum distillation. Finally, a light yellow fluid (DPSO) was obtained (Figure 1). Thus, the synthesis of DPSO with constant amino value and varied alky value were accomplished.

Sample Preparation

Treatment of Silicon Wafers. DPSO was dissolved in ethyl acetate to form a 0.03 wt % ethyl acetate solution. A pretreated silicon wafer was impregnated into the above solution¹⁹ and kept vertically for several seconds, then dried at 80°C for 5 min and cured at 170°C for 3 min. Finally, the sample was kept in a desiccator to balance for 24 h and noted as DPSO/Sil (for the silicon wafer substrate).

Treatment of Cotton Fabrics. Amino polysiloxane softeners are usually used in textile industry as emulsions. A 10% DPSO emulsion (10 g DPSO emulsified with 5 g fatty alcohol polyoxyethylene ether and 85 g H_2O) was prepared and its pH was adjusted to about 5.5 by adding HAc during the process of emulsification.²⁰ Cotton samples were impregnated in a diluted aqueous bath (bath ratio, 10% DPSO emulsion : H_2O = 1.5 : 100) for about 20 min, padded to wet pick-up at about 70% on the weight of the dry fibers. The padded fibers were then dried at 100°C for 10 min and cured at 120°C for 2 min, kept in a desiccator to balance for 24 h, and noted as DPSO/cot.

Characterization

Molecular Structure and Physical Properties of DPSO. The amino contents were acquired by chemical titration, which was detailed in the literature.⁷ The number average molecular weight (M_n) was measured by gel permeation chromatography (GPC) Waters 1525/2414, using tetrahydrofuran (THF) as solvent. FTIR was performed on a Nicolet 560 spectrometer using KBr pellet technique. $^1\text{H-NMR}$ analysis was conducted with a Bruker 400MHz nuclear magnetic resonance spectrometer and was carried out with a 5% (by mass) content in CDCl_3 at room temperature. Thermogravimetry analysis (TGA) was performed on a Q500 thermogravimeter (TA Instruments Company) under nitrogen atmosphere at a heating rate of 20°C min^{-1} from room temperature to 900°C. The viscosity measurement was conducted on a NDJ-7 viscometer at room temperature. An Abbe Refractometer (2WAI) was used to determine the Refractive index n_d^{20} of DPSO.

Performance on Cotton Fabrics. Bending rigidity (BR) of the treated fabrics was measured with YG (B) 022D tester (Wen Zhou Darong Company). Whiteness of the fabrics samples was determined with WSB-3A digital display whiteness meter (Wenzhou Darong Company) and the average of five readings of each sample was used as the final results. Wettability was tested according to the literature.²¹

Characterization of DPSO Film. XPS analysis was performed on a Physical Electronics Model 5700 X-ray photoelectron spectrometer (PHI) equipped with monochromatic Al K α source (150 W, 15 kV, KE = 1486.6 eV). The water contact angle (WCA) was measured by JC 2000C static contact angle

Table I. Synthesized DPSO and Their Basic Properties

Name	Amino value (mmol g ⁻¹)	Alkyl value (mmol g ⁻¹)	Viscosity (mPa s)	Refractive index n_D^{20}
DPSO1	0.4532	0	2283	1.6487
DPSO2	0.4528	0.2	2467	1.6412
DPSO3	0.4519	0.4	2258	1.6477
DPSO4	0.4544	0.6	2372	1.6456

measurement instrument at $(22 \pm 2)^\circ\text{C}$. The injection volume of liquid was $5 \mu\text{L}$ and the average of five readings was used as the final contact angle of each sample. SEM measurement was performed on a S-570 scanning electron microscope (Hitachi) after the fiber samples were coated with gold in vacuum, the morphologic photographs were taken at magnification of 5000 times. AFM images were obtained with a Nanoscope IIIA AFM (Digital Instruments) in tapping mode. All the scanning was performed at 22°C and in air of relative humidity of 48%. The root-mean-square-roughness (R_q) of a $2 \mu\text{m}^2$ scanned area was calculated by the Nanoscope III software using the following equation:

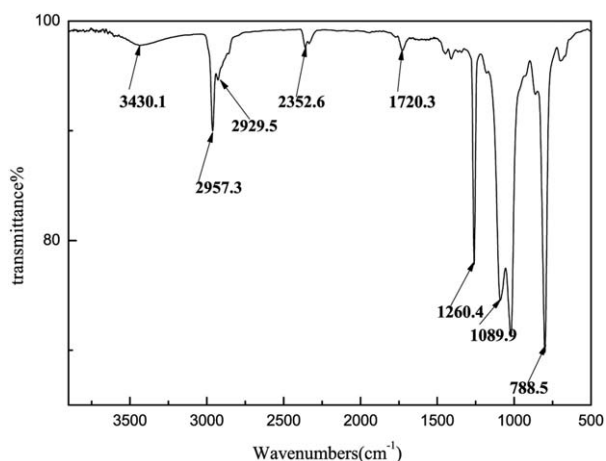
$$R_q = \sqrt{\frac{\sum Z_i^2}{n}}, \quad (1)$$

where Z_i is the height deviations with reference to the mean of n data points.²²

RESULTS AND DISCUSSION

Characterization of DPSO

We synthesized four DPSO samples having different alkyl contents. Table I provides the basic properties of the four synthesized samples. The amino was measured by chemical titration and alkyl values were calculated. There were no distinct differences in viscosity and Refractive index between four samples, this may due to their basically same M_n and similar molecular structures. Even though the polysiloxanes have different amount of dodecyl chains, the amount of dodecyl chain was so small (no more than 0.6 mmol g^{-1}) that its effect on amino values and viscosities can be ignored.

**Figure 2.** Infrared spectrum of DPSO.

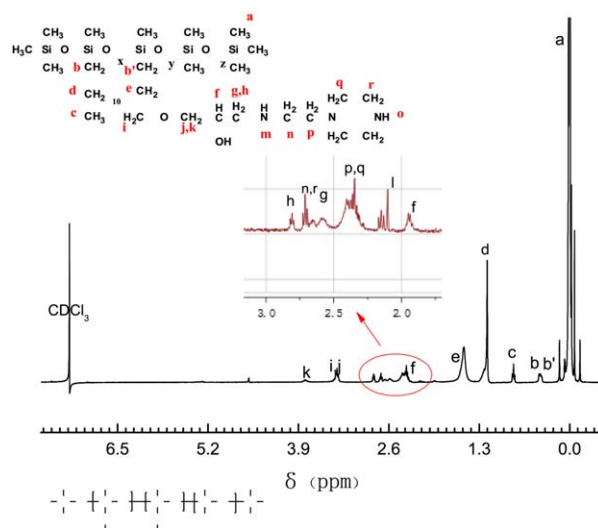
The chemical structure of the synthesized DPSO was determined by FTIR and ¹H-NMR Spectrometers. Take DPSO2 (alkyl value 0.2 mmol g^{-1}) as example, the IR spectrum and ¹H-NMR Spectrum of DPSO2 were shown in Figures 2 and 3.

The FTIR spectrum exhibits the characteristic stretching and distortion vibration peaks of C—H (CH_2) at $2957, 2929, \text{ and } 1467 \text{ cm}^{-1}$. The bands at $1089\text{--}1018 \text{ cm}^{-1}$ (Si—O—Si) and 801 cm^{-1} (Si—O—C) indicate that functional groups of Si—O—C and Si—O—Si exist in DPSO. The bands at 3430 cm^{-1} (N—H) and 1260 cm^{-1} (C—N) confirm that piperazine groups have been incorporated into the polysiloxane. The strong signal at 788.5 cm^{-1} ($-(\text{CH}_2)_n-$) suggests the presence of long alkyl chains.

The ¹H-NMR spectrum of DPSO2 demonstrates that the relevant chemical shift signals of the protons from dodecyl side chain clearly appear at $\delta 0.48$ (bH), 0.87 (cH), and 1.25 (dH), especially the absorption at $\delta 0.48$ identifies that Si— CH_2 —alkyl groups have been successfully bonded into DPSO skeleton. Chemical shift signals at δ (2.1–3.8) illustrate that AEP have been introduced into polysiloxane skeleton successfully. Therefore, the combination of IR and ¹H-NMR indicates that DPSO possessed the expected chemical structure shown as Figure 3.

Generally, there will be a thermocuring (120°C) stage at the end of the softness treatment for textiles. The finishing will be meaningless if the softeners decompose under treatment condition, so the study of the thermal stability of polysiloxane softeners is of great value. Thermogravimetry analysis (TGA) was implemented in this article and the results were shown in Figure 4.

It can be seen clearly from this figure that the weight loss of four samples begins at around 450°C , the char yield of DPSO are all around 25% at 800°C under N_2 and the yield decrease slowly with the increasing of alkyl value. Even though there is a slight drop (about 10°C) in the initial decomposition temperature of DPSO after introducing dodecyl side groups (compare DPSO1 and DPSO2), this slight drop is so small that a conclusion can be drawn that the incorporation of long alkyl chains

**Figure 3.** ¹H-NMR spectrum of DPSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

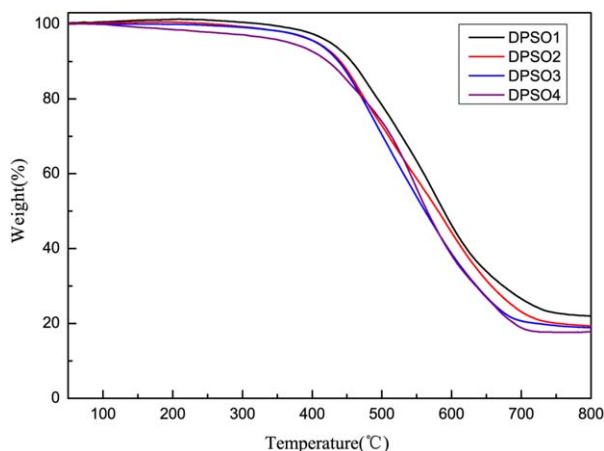


Figure 4. TGA curves of DPSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

has no obvious effect on initial decomposition temperature of piperazine functional polysiloxane, which is in accordance with references.^{23,24} Then the application area of piperazine functional polysiloxane will not be restricted by its thermal stability.

The Performance of DPSO on Cotton Fibers

Textile treatment is to improve or modify a certain property of the treated fabric. It is possible that some performance properties of the treated fabrics are improved, and others are changed negatively. Effect of textile treatment on its pristine color is expressed as whiteness of the fabrics before and after being treated, which can be determined by a whiteness tester. In addition, bending rigidity (BR) is one of the determining factors in assessing the fabric handle.²⁵ A decrease in the BR leads to a desirable fabric handle. On the contrary, an increase in BR would provide fabric with stiffer handle. BR, whiteness, and hydrophobicity of the treated cotton fabrics were investigated in this work to illustrate the effect of textile treatment, and the results are shown in Table II.

It can be seen from Table II that with the increased alky value, the softness of treated cotton declines slightly while the whiteness and the wettability of them increase greatly. The whiteness increases from 98.6° to 102.2° and the adsorbing time (wettability) drops from 57.8 s to 20.4 s. This suggests that the incorpo-

Table II. Performance of the Cotton Fabrics Treated by DPSO

Sample	BR (mN)		Whiteness (°)	Wettability (s)
	W	F		
Cot	199		102.1	19.9
DPSO1/cot	124		98.6	57.8
DPSO2/cot	135		102.0	22.3
DPSO3/cot	142		102.2	21.9
DPSO4/cot	148		102.2	20.4
ASO ^a /cot	132		98.2	55.8

^aASO (*N*- β -aminoethyl- γ -aminopropyl polydimethylsiloxane) is a kind of ordinary amino polysiloxane synthesized by traditional polymerization method. BR, bending rigidity; W, wrap; F, fill.

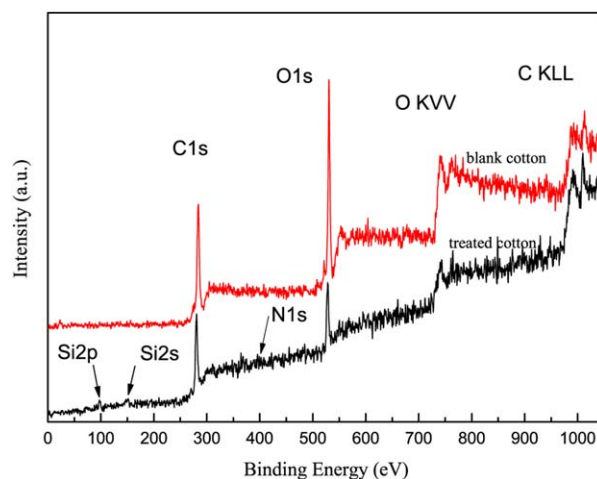


Figure 5. Wide scan X-ray photoelectron spectrum (XPS) for cotton substrates untreated and treated with DPSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ration of long alky chains gifts excellent yellowing resistance and strong hydrophobic resistance capability for the treated cotton at the expense of a slight loss of softness handle compared with that of DPSO1/cot (single piperazine functional polysiloxane).

When comparing DPSO1/cot with ASO/cot, it is obvious that DPSO1 possesses better softness (lower BR) and whiteness ability on cotton substrates than ASO. This illustrates that DPSO1 synthesized through hydrosilation may have relatively more even distribution of amino groups than ASO synthesized by traditional polymerization method, which lead to the improvement of softness. Moreover, the lack of primary amine in DPSO1 molecules probably increases its yellowing resistance.²⁶

Film Morphology and Orientation on Substrates

X-ray photoelectron spectroscopy (XPS) probes the chemical composition and identity of the functional groups present within the outermost 2 nm of the film surface.⁷

Figure 5 shows a wide scan spectrum of cotton surfaces untreated and treated with DPSO. The spectrum of untreated cotton expresses no other elements other than carbon or oxygen. Comparatively, peaks of Si2p and Si2s appear at the treated cotton, and it proves that the DPSO is chemically connected on cotton's surface. There is so little nitrogen in the DPSO molecules that the spectrum of nitrogen cannot be seen clearly from Figure 5.

High resolution C1s X-ray scanning (Figure 6) is used to further define the surface coverage. For the untreated cotton substrate, there is a dominant C—C contribution at 283.1 eV, and small contributions due to the single C—OH and C—O—C groups (286.5 eV), and a large amount of hydrocarbon contamination (282.5 eV). This is consistent with previously reported XPS results for cotton fabrics.²⁷ For the cotton substrates treated with DPSO, there is a dominant C—Si contribution at 280.3 eV and small contributions due to the C—C and C—H groups (283.6 eV).

Contact angle is an important parameter in measuring surface hydrophobicity. It can be seen from Table III that the water

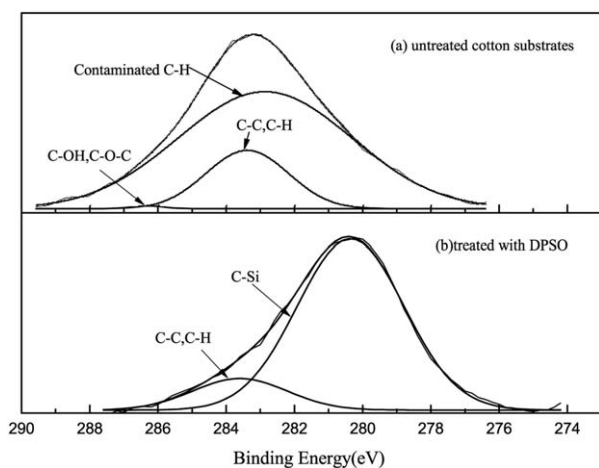


Figure 6. High resolution C1s X-ray spectrum for (a) untreated and (b) treated cotton substrates.

contact angle of the silicon surface treated with DPSO1 is 109.7° compared to 96.9° of the untreated surface, which due to the hydrophobicity of DPSO1. However, the water contact angles of the silicon surface treated with DPSO decrease along with the alky value increase. It is well known that amino functional groups have the tendency to react with $-\text{OH}$ on the surface of substrates. The water contact angle of DPSO1/Sil is larger than sil, it indicates that DPSO1 provides strong interaction at the silicon wafer-polysiloxane interface thus can form a complete hydrophobic film. Although when the dodecyl side groups are introduced into polysiloxane, the lower WCAs suggest that the existence of the hydrophobic $-\text{CH}_3$, $-\text{C}_{12}\text{H}_{25}$ groups may have negative impact on forming a complete hydrophobic and compact film^{15,17,28–30} thus improves the hydrophilicity of the DPSO film on silicon wafers.

It is well known that properties and application performance of a polymer depend largely on its structure or morphology on substrates.²⁵ Film morphology does not only affect the surface and performance properties of a polysiloxane but also provide information about the orientation of a film-forming molecule in

Table III. The Water Contact Angle of DPSO with Various Alky Values

Sample	WCA ^a (°)
sil	96.9
DPSO1/Sil	109.7
DPSO2/Sil	106.2
DPSO3/Sil	106.0
DPSO4/Sil	105.7

^aWCA refers to water contact angle.

an absorbed state, and reveal the film-forming mechanism.¹⁷ To reveal the reason why the incorporation of dodecyl side groups can improve the hydrophilic property of piperazine functional polysiloxane, the characterization of DPSO film is necessary.

Polysiloxanes possess low surface tension, which enables them to spread out easily and be adsorbed onto the hydrophilic fabric to form films. Through observing the treated fiber surface, the morphology of DPSO softener on the fiber surface can be determined.

Figure 7 is a series of SEM photographs of the cotton substrates (untreated vs. treated with DPSO2). Figure 7(b) shows the relatively smooth surface of the treated fiber (magnified 5000 times). In comparison with the untreated fibers [Figure 7(a)], a majority of grooves have disappeared or become shallower. Obviously, it results from the macro-smooth polysiloxane film coated on the fiber surface. As a consequence, DPSO2 provides the cotton fabrics with smooth handle.

The precise micro-morphology of the DPSO films on cotton substrates was studied by AFM. As natural fibers are easily deformed during AFM observation, a polished and rigid silicon wafer is usually used as substrate to observe film morphology and microstructures of functional polymer.¹⁹ And to ensure a monomolecular film coated on the substrate, 0.03% DPSO solution was used to treat the wafers by immersion. The AFM images of DPSO1 and DPSO2 were shown in Figures 8 and 9.

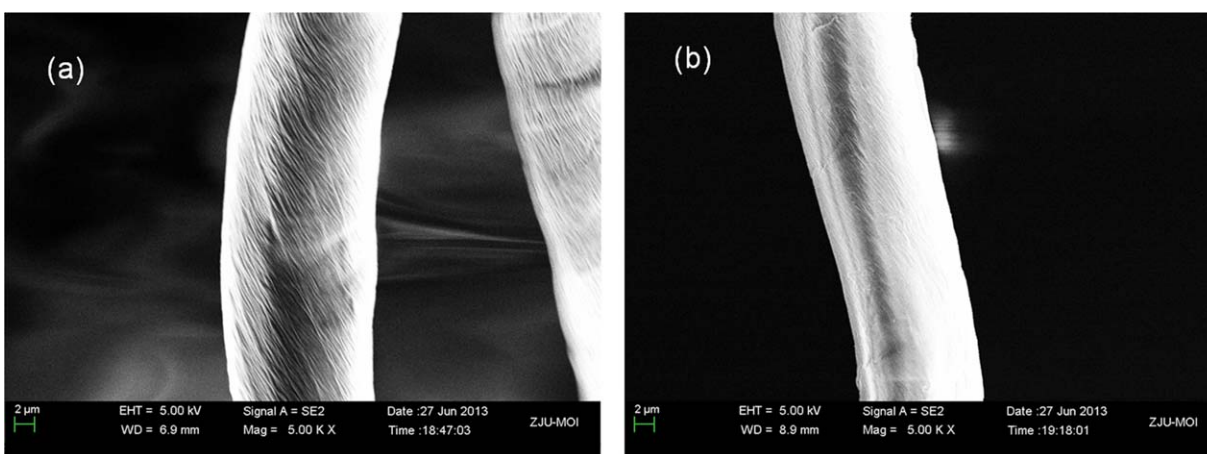


Figure 7. SEM photographs of cotton fiber: (a) untreated ($\times 5000$); (b) treated with DPSO2 ($\times 5000$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

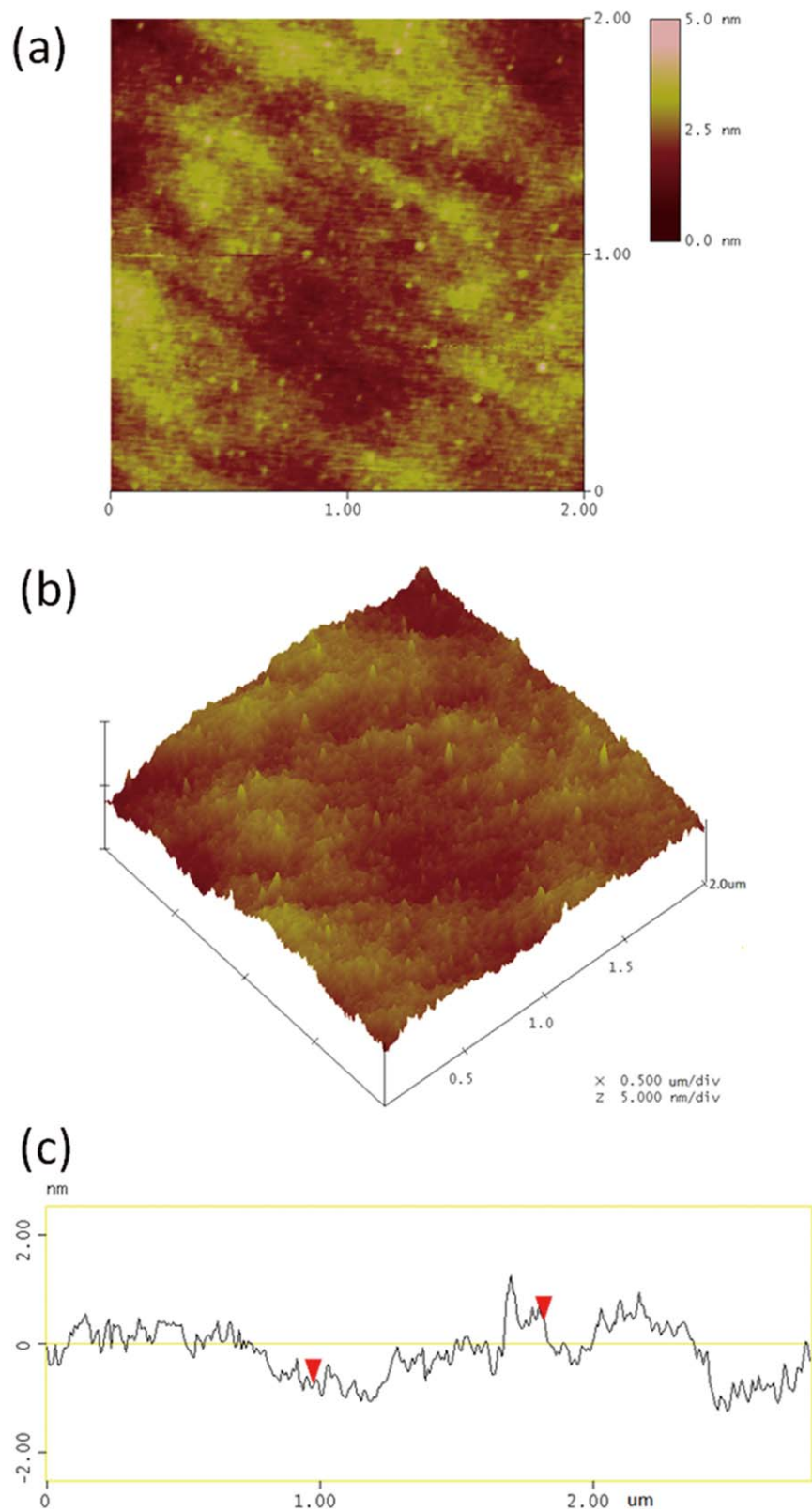


Figure 8. The AFM images of DPSO1/Sil (a) flattened, (b) three-dimensional, and (c) the surface profile along a line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

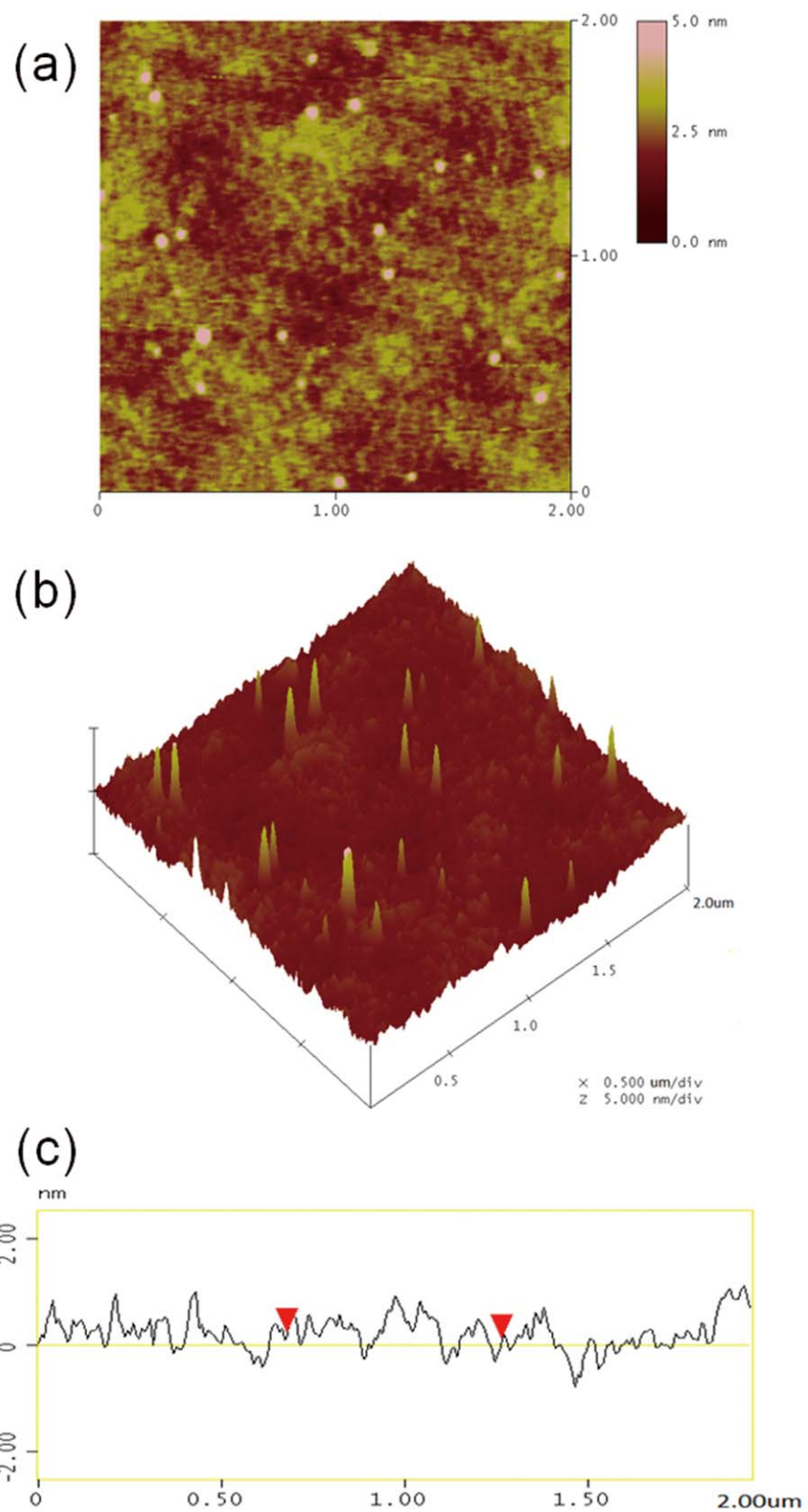


Figure 9. The AFM images of DPSO₂/Si (a) Flattened, (b) three-dimensional, (c) the surface profile along a line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Root-Mean-Square-Roughness (R_q) of Silicon Wafer Substrates Untreated and Treated with DPSO with Varied Alky Values

Sample	Img. R_q (nm)	Box R_q (nm) ^a
Sil	0.427	0.283
DPSO1/Sil	0.340	0.243
DPSO2/Sil	0.365	0.263

^aThe box R_q values were chosen from $1 \mu\text{m}^2$ smooth area.

Comparing Figure 8 with Figure 9, it is distinctively discovered that DPSO2 has formed an inhomogeneous film on the silicon wafer surface. There are many high or low bright peaks that appear in its three-dimensional photography (Figure 9). In $2 \mu\text{m}^2$ scanning field, the average roughness of DPSO2 film (expressed by the root mean square roughness, R_q) reaches to 0.365 nm, which is a little higher than DPSO1 (0.340 nm), but still lower than untreated silicon wafer (0.427 nm, shown in Table IV).

From the aspect of the chemical structure, DPSO2 is a typical cationic siloxane polymer with PDMS skeleton, pending piperazine side groups and dodecyl side groups. Therefore, when DPSO2 spreads on the hydrophilic silicon wafer and forms a hydrophobic film on its surface, the DPSO2 skeleton would preferentially be forced to take such a molecular orientation that the dipolar Si—O bonds point to the silicon surface, the ammonium groups point to the silicon surface to react with —OH on the surface^{3,5,7,8} while the hydrophobic —CH₃, —C₁₂H₂₅ groups point away from the silicon surface and point out toward air (as shown in Figure 10).

When notice the surface profile along a line (Figures 8 and 9), we may find that the peak values of the lines are less than 1.5 nm, we can conclude that the DPSO film coated on the wafer should be a monolayer.¹⁷ Because of the steric hindrance caused

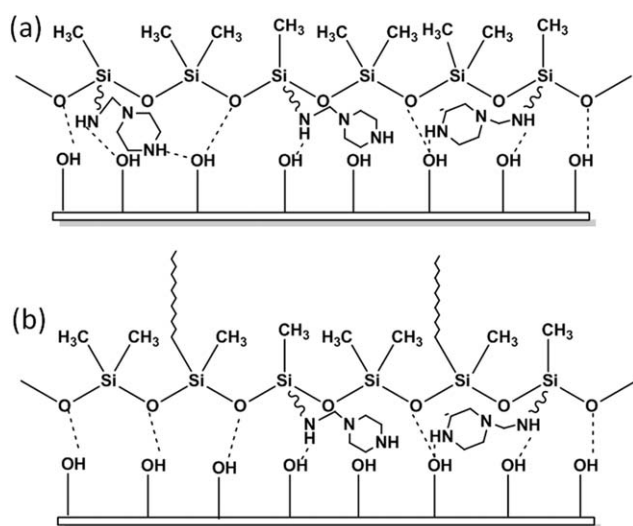


Figure 10. Proposed schematic model for the orientation of DPSO adsorbed on silicon-wafer substrates (a) DPSO1 without dodecyl side groups; (b) DPSO2 with dodecyl side groups.

by long alkyl chain, the amount of deposition of polysiloxanes should be reduced, thus not completely compact monolayer films were formed. There is no doubt that the formation of not completely compact films lead to the improvement of whiteness and wettability performance of DPSO softener.

As dodecyl side groups have random and extended configuration in space, it makes DPSO2 easily give rise to an uneven film on the silicon wafer surface.⁹ As a result, an inhomogeneous film with many high or low bright peaks are clearly observed in the three-dimensional AFM image of DPSO2 which are not exist in the image of DPSO1. Thus, the brighter peaks are estimated to originated from the long alky side chains. This may be used to explain the strange phenomenon that the introduction of dodecyl side groups can make the piperazine functional polysiloxane less hydrophobic.

The characteristic inhomogeneous microstructure makes the DPSO2 film less smooth as compared with DPSO1 (Figure 8). Consequently, the root mean square roughness R_q of DPSO2 film reaches to 0.365 nm in $2 \mu\text{m}^2$ scanning field, which is a little bigger than that of DPSO1, the relatively more uniform film (with a R_q of 0.340 nm). Moreover, compared with the untreated silicon-wafer substrates, the treated silicon-wafer either treated with DPSO1 or DPSO2, can get much smoother surface, which is accordance with the SEM results.

CONCLUSIONS

DPSO with pendant long alky chain and piperazine groups has been successfully synthesized via hydrosilation. TGA analysis shows that the introduction of dodecyl groups has no negative impact on its thermal stability. Application performance of DPSO on cotton fabrics illustrates that along with alky value increases, the hydrophilicity and whiteness of the treated fiber increase while the softness of it suffers a slight decline. What's more, amino polysiloxane softener synthesized through hydrosilation possessed better application performance than those synthesized via traditional polymerization method, especially in terms of softness modification.

SEM and AFM observations demonstrate that DPSO form a macro-smooth but actually uneven siloxane film on the treated cotton fiber surface. Though seems rough in micro-topography, the DPSO film still able to minimize the root mean square roughness of the treated silicon wafer. DPSO may take such an orientation to form film on the cotton substrates that the —CH₃, —C₁₂H₂₅ groups projected outward into air while the piperazine groups pointed inward to the substrate, interacting with the hydroxyls of the cotton in ester or hydrogen bonds. The formation of this not completely compact film would be more hydrophilic than those films without long alky chains.

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