Synthesis, Characterization, and Film Morphology of Dodecylpolysiloxane

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Received 5 August 2005; accepted 13 January 2006
DOI 10.1002/app.24288
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel polysiloxane softener bearing dodecyl side groups (dodecylpolysiloxane [DDPS]) was synthesized by copolymerization of octamethylcyclotetrasiloxane with dodecyltrimethoxysilane and hexamethyldisiloxane. Chemical structure and film morphology of the synthesized polysiloxane are characterized and investigated by infrared spectrum, ^{1}H-NMR, field emission scanning electronic microscope, and atomic force microscope. The experiment results indicate that DDPS can form a hydrophobic film on both the cotton fiber and silicon wafer surface. At an amplification of $<$80,000 (of the original fiber) and the observation rule (working distance) of $>$200 nm, DDPS shows a relative smooth resin film on the treated fabric/fiber surface. But as the observation rule decreases to 2 nm—almost to a molecular scale—the DDPS film mostly exhibits an inhomogeneous structure and uneven morphology in its atomic force microscope images. There are many low or high peaks that appeared in DDPS topography. Consequently in 2 μm^2 scanning field, the root mean square roughness of DDPS film reaches to 0.199 nm, which is 2.46 times rougher as compared with that of polydimethylsiloxane film. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4480–4486, 2006

Key words: dodecylpolysiolxane; film morphology; AFM image; fabric softener

INTRODUCTION

Polysiloxanes are of great importance in textile industry. They are widely used as softeners to improve fabric softness, tactility, and other mechanical properties.[1–3] Usually, functional polysiloxanes give rise to different tactility on fabrics.[1] The most popular softener, amino functional silicone, can offer a unique, soft, smooth, silk-like, or cottony sensation for fabrics,[2] while the long alkyl functional polysiloxanes confer the treated fabrics with a fluffy, thickening, but less smooth sensation during evaluation by hand. Why do these occur?

One possible reason is film structure and modality. Film-forming ability is one of the characteristic properties of the polysiloxane softeners.[3,4] Film morphology not only influences the handling and performance of polysiloxane, but also provide the information about configuration and orientation of the film-forming molecule in adsorbed state,[5,6] which makes it possible for us to get a better understanding of the softening mechanism of the polysiloxane. Therefore, researches on the film morphology of functional polysiloxanes have attracted more attention recently.[7,8] However, the deforming properties of the fibers limit advanced instruments used in the field, thus there are little data available about the precise morphology and the film structures of the siloxane softeners, except those from scanning electronic microscope (SEM) observations.[3,4]

Dodecyl functional containing polysiloxane, as one of the important long alkyl functional polysiloxane softeners, can be used separately or in conjunction with amino functional silicone to confer the fabrics with fullness, fluffy, thickening, as well as somewhat rough handling. Especially the thickening and somewhat rough tactility makes the siloxane softening agent have great potential in ramie-like textile treatment or functional decorating cloth finishing. Thus, for understanding the truth, a new dodecylpolysiloxane (DDPS) softener was synthesized by us, then its film morphology and microstructure on cotton fabrics or on the imitated cellulose substrate, silicon wafer surface, were investigated by atomic force microscope (AFM), field emission scanning electronic microscope (FESEM), and other instruments.

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Contract grant sponsor: National Natural Science Foundation Committee of China; contract grant number: 50373025.

Contract grant sponsor: Science and Technological Department of Shaanxi Province, China; contract grant number: 2002K08-G10.

EXPERIMENTAL

Synthesis and characterization of DDPS

In a 250 mL round bottom flask equipped with a thermometer, a mechanical stirrer and a condenser, 60 g octamethylcyclotetrasiloxane (D_4, Dow Corning Co., Shanghai, China), 12.6 g dodecyl trimethoxysilane (HD-111, Dadi Chemical, China), and a catalytic amount of potassium ethoxylate (analytical reagent) as well as a few drops of hexamethyldisiloxane (Dow Corning) were mixed and heated to 90–100°C to react for 3–4 h. Then the reaction temperature was enhanced to 130–140°C and the mixture was maintained at that temperature for another 2 h. After the low boiling point impurities were removed from the product by vacuum distillation at 13 kPa, a clear thick liquid fluid, DDPS, was obtained. The content of dodecyl groups in DDPS molecule is 0.6 mmol/g (expressed by mmol $C_{12}H_{25}$ per gram DDPS), the number average molecular weight M_n = 3405, the mass average molecular weight M_w = 7769.

As mentioned above, polydimethylsiloxane (PDMS, without dodecyl group pending in the side chain) was prepared and used as a contrast in the research of the film morphology of DDPS.

Characterization

Infrared (IR) spectrum was acquired on a Bruker VECTOR-22 spectrometer, KBr liquid film. ^{1}H-NMR spectra were recorded by INOVA-400 spectrometer (Varian), $CDCl_3$ as a solvent, and tatramethylsilane (TMS) as an internal standard. The average molecular weight was determined by a Waters GPC instrument, tetrafuran (THF) as solvent, and polystyrene of narrow average molecular weight used as a reference standard.

Observation of DDPS film on cotton fabric/fiber surface by SEM and FESEM

The best way to research the morphology of polysiloxane softener on fabrics is to observe the treated fabric surface directly by instruments. Therefore, SEM and FESEM were first utilized to research the treated fabric/fiber surface in the experiment.

Polysiloxane softeners are usually used in textile industry in emulsion. In accordance with this, a 30% DDPS emulsion (which involved emulsifying 10 g DDPS with 3 g of alkyl polyoxyethylene ether and 30.3 g H_2O) was used as a sample in the experiment to finish the fabrics and to form the expected siloxane film on the fabric/fiber substrate.

Fabric sample, 100% cotton fabrics with yarn counts of 474 × 235 (the number of warp and filling yarns, 10 cm × 10 cm), were impregnated in a diluted aqueous bath (bath ratio, 30% DDPS emulsion : H_2O = 1 : 100) containing about 1% DDPS emulsion sample, padded to wet pick-up at about 70% on the weight of the dry fabrics. Then the padded fabrics were dried at 100–105°C for 10 min, cured at 160°C for 30 s, and finally kept in a drier overnight.

The film morphology of DDPS anchored on the treated fabric/fiber surface was examined by Hitachi *S*-570 scanning electron microscope and SIRION 200 field emission scanning electron microscope (FEI) after the samples were coated with gold in vacuum.

Investigation of film morphology of DDPS on silicon wafer substrate by AFM

AFM is by far a powerful instrument in the observation of film morphology, it also provides a possible route to investigate the film of functional polysiloxane softener on nanometer scale. Since the natural fibers are easily deformed in AFM observation, a polished silicon wafer was used as a rigid substrate to research the film morphology and the microstructure of the DDPS. To obtain a substrate surface similar to the natural cellulose fiber, with many hydroxyl groups and carrying negative charges on its surface, the silicon wafers should be pretreated as follow.

Pretreatment of the silicon wafer

A polished silicon wafer was cut into 0.5 cm × 1 cm strips, washed with distilled water, immersed in a mixed solution of 98% H_2SO_4 : 27% H_2O_2 = 4 : 1 (w/w) at room temperature for 20 h, then rinsed with pure distilled water and treated with 2% Na_2CO_3 aqueous solution for another 1 h. Followed by washing with large amounts of pure distilled water, the silicon wafer was dried at 100°C and then kept in a desiccator until being used.

Preparation and observation of DDPS film on the silicon wafer

Emulsion is not suitable for the formation of the polysiloxane film on silicon wafer, because the residual emulsifier deposited on the silicon substrate could contaminate the probe of AFM and interfere with the AFM image. Thus, an organic solution of functional polysiloxane was utilized to coat the silicon wafer. Meanwhile, to avoid the multilayer of polysiloxane softener from being deposited on the silicon substrate, a thoroughly diluted polysiloxane in ethyl acetate solution was utilized in the following procedure, and the film formation on silicon wafer surface was performed by referring to Langmuir film preparation and literature methods.[9]

DDPS (0.03 g) or PDMS (accurate to 0.0001 g) was, respectively, placed in two beakers, then dissolved in

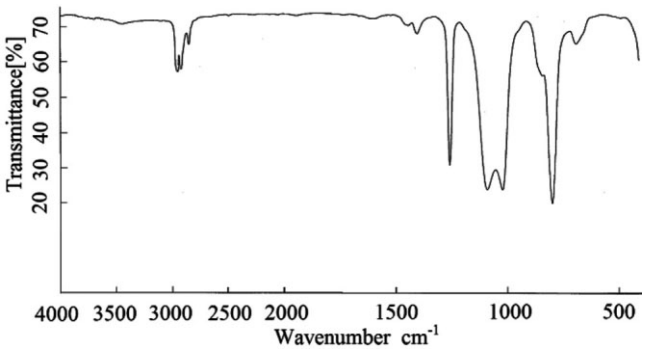


Figure 1 Infrared spectrum of DDPS.

ethyl acetate solvent (analytical reagent, redistilled before use) to form a 0.03% polysiloxane solution. The dried clean silicon wafer was vertically dipped in the polysiloxane solution for several seconds, then drawn out and immediately dried at 100°C for 10 min, cured at 160°C for 2 min, then conditioned in a desiccator for 24 h at room temperature.

The topographic images of the polysiloxane films immobilized on silicon substrate were observed by Nanoscope IIIA. atomic force scanning microscope (Digital Instruments) at 22°C in air with relative humidity of 48%, and all the scanning was performed in tapping mode.

RESULTS AND DISCUSSION

Characterization results of DDPS

Molecular structure is the primary influencing factor on film morphology. So the chemical structure of the synthesized polysiloxane should be determined. Since DDPS is not sophisticated and relatively simple in chemical structure, the characterization was conducted by the IR and nuclear magnetic resonance (NMR) spectrometers.

Figure 1 is the IR spectrum of DDPS. From Figure 1, it could be clearly detected that four groups of middle and strong absorption bands appeared separately at 2963–2856 cm^{-1} ($\nu_{C—H}$, —CH_3 and —CH_2—), 1260cm^{-1} (s, $\delta_{C—H}$, Si—CH_3), 1092–1024 cm^{-1} (s,$\nu_{Si—O}$), and 801cm^{-1} ($\nu_{Si—C}$, Si—CH_3, Si—CH_2—), which indicates that functional groups such as Si—CH_3, Si—O, —CH_3, —CH_2— have existed in the molecule of DDPS.

Figures 2 and 3 are ^{1}H-NMR spectra of DDPS. These spectra demonstrate that the relevant chemical shift signals of the protons from dodecyl side chain clearly occur at δ 0.48 (bH), 0.87 (dH), and 1.25 (cH), especially the absorption at δ 0.48 can identify that Si—CH_2—alkyl groups have been successfully boned into DDPS skeleton. Therefore, the combination of IR and ^{1}H-NMR indicates that DDPS possesses the expected chemical structure shown as follow.

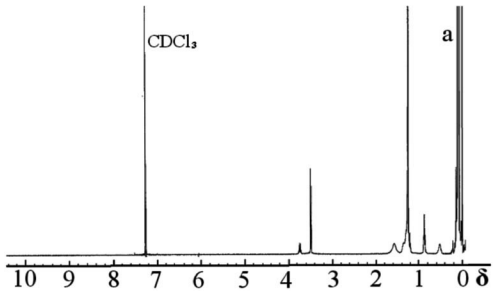
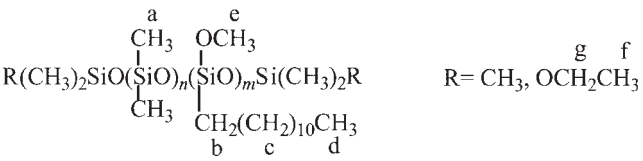


Figure 2 ^{1}H-NMR Spectrum of DDPS.



Morphology of DDPS on fabric or fiber substrate

Polysiloxanes possess low surface tensile strength. This property makes them easily outspread and they can be adsorbed on the hydrophilic fabric surface and form films of molecular dimensions. As such films sheath the fibers, more or less modified morphology of the treated fibers should be observed in experiment. Thus, from observation of the treated fiber surface, we can get the information about the morphology of the polysiloxane softener on the fiber substrate.

Figures 4–6 are a series of SEM and FESEM photographs of 100% cotton fabrics/fibers treated or untreated by DDPS. Figure 4 clearly shows that relatively smooth surfaces are visualized on the treated fibers at the amplification of 5000 times (the observation rule = 6.0 μm), in comparison with the untreated fibers. Figure 5 FESEM photographs demonstrate that a polysiloxane resin film has been coated on the treated fiber surfaces. And a majority of the grooves have disappeared on the treated fiber surface or become shallower; moreover, the edges of some fiber surface look blunt and smoother.

Although the amplification has already reached to 80,000 times (based on the original) and the observa-

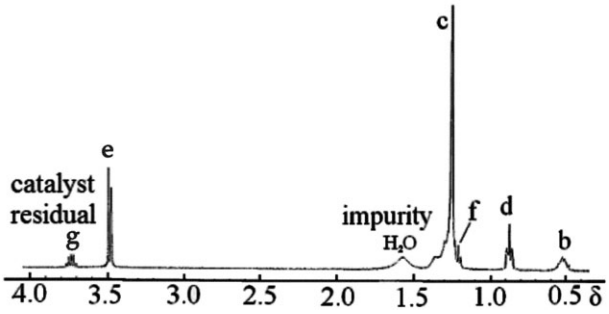


Figure 3 The magnified ^{1}H-NMR spectrum of DDPS.

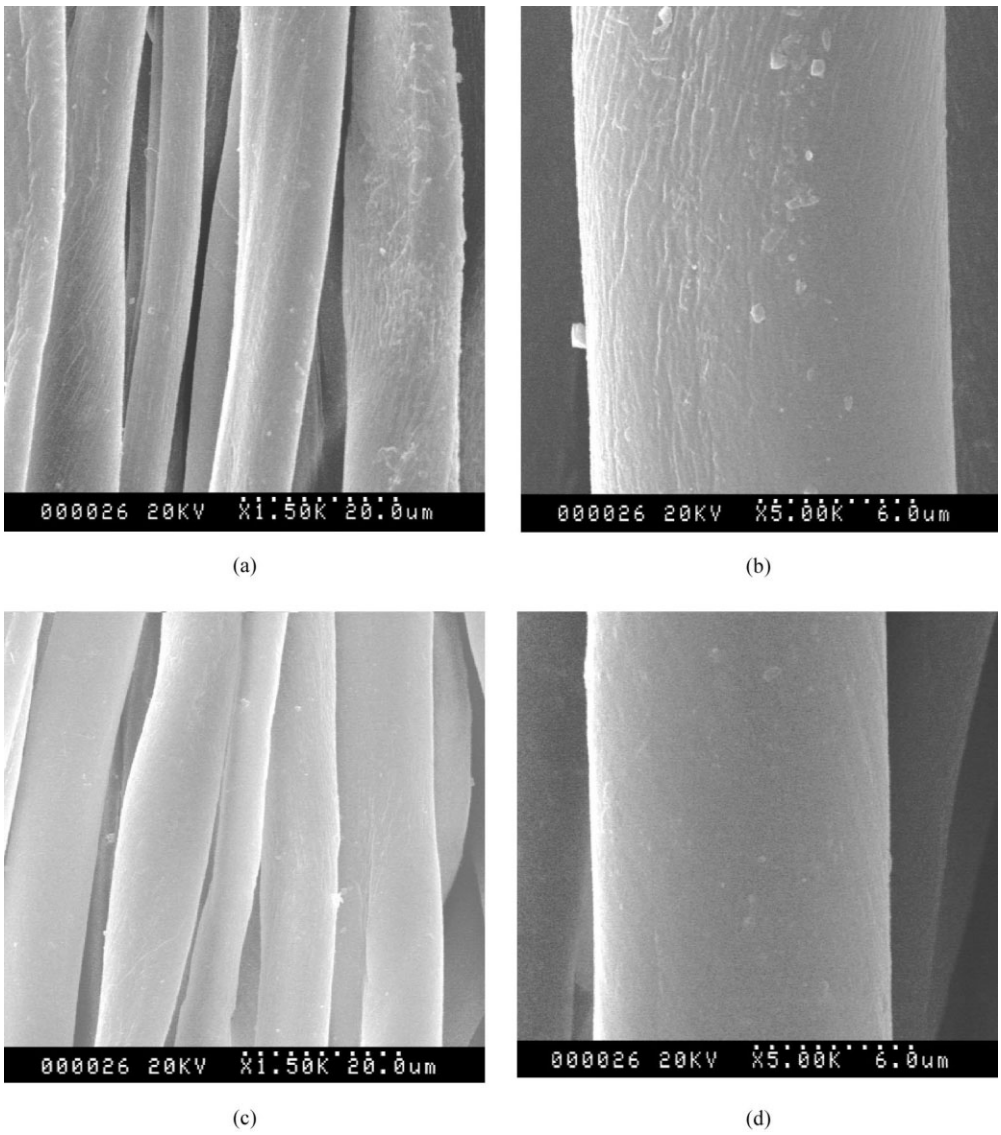


Figure 4 SEM photographs of 100% cotton fabric. (a) Untreated (×1500), (b) Untreated (×5000), (c) DDPS (×1500), (d) DDPS (×5000).

tion rule working distance decreased to 200 nm, FESEM could not yet give the precise morphology of DDPS film on the fiber substrate, partly because the DDPS film on the treated fiber surface is of the molecular dimension and too thin to be observed by such direct methods.

The precise film morphology and orientation of DDPS on silicon substrate

The precise morphology and microstructure of DDPS film on the imitated cellulose substrate, silicon wafer surface, were studied by atomic force telescope (AFM), and the results are shown in Figure 6. In addition, the AFM images of the contrast PDMS film are also shown in Figure 7.

Comparing Figure 6 with Figure 7, it is distinctively discovered that DDPS has formed an inhomogeneous structure film on the silicon surface. There are many high or low bright peaks that appeared in its three dimensional topography (Fig. 6). And in 2 μm^2 scanning field, the average roughness of DDPS film (expressed by the root mean square roughness, Rq.) reaches to 0.199 nm.

From the point of view of the chemical structure, DDPS is a typical nonionic siloxane polymer with PDMS skeleton and pending dodecyl side groups. Therefore, when DDPS is spread on the hydrophilic silicon wafer and forms a hydrophobic film on its surface, the PDMS skeleton would preferentially be forced to take such a molecular orientation that the dipolar Si—O bonds point to the silicon surface, while

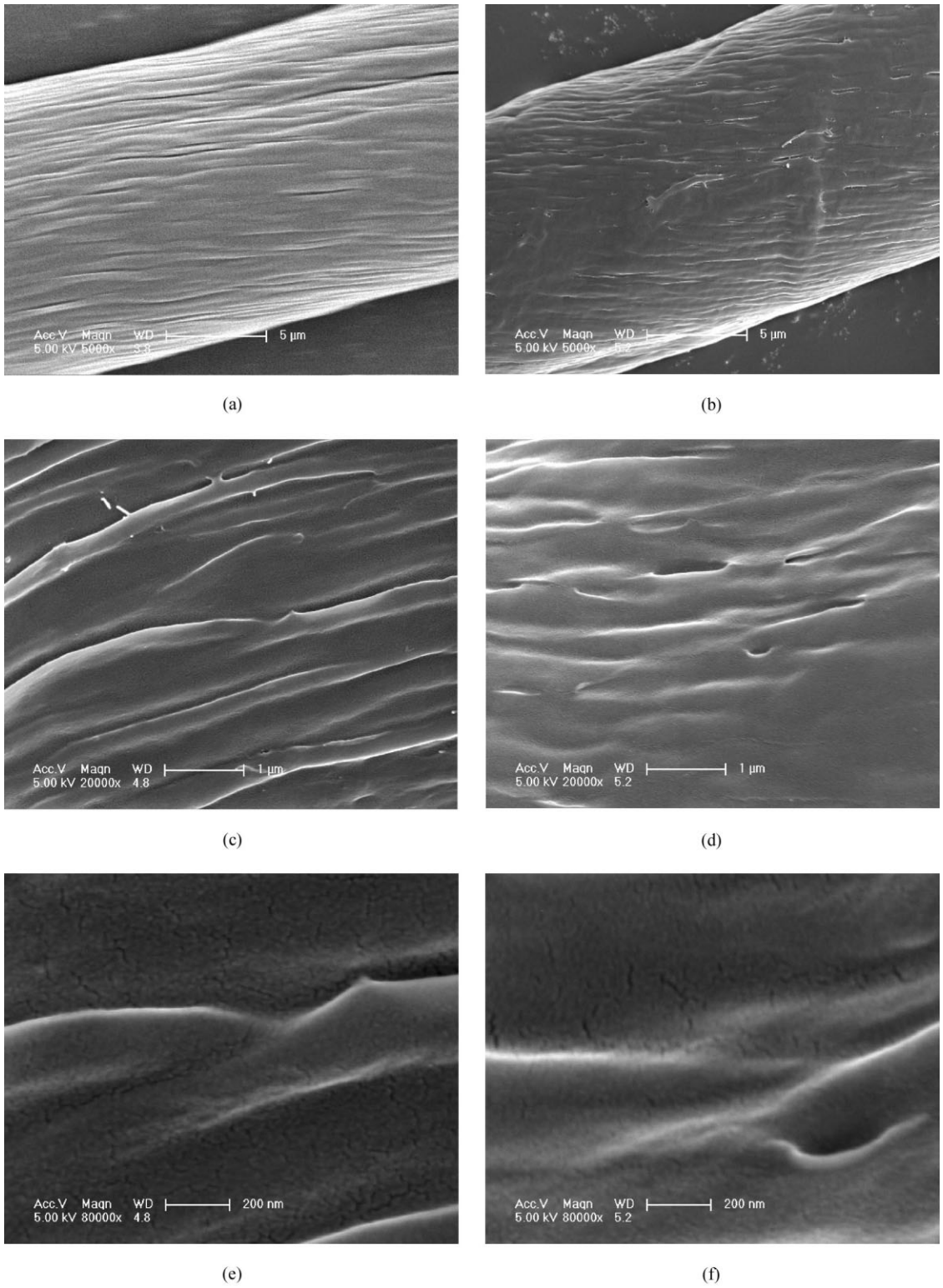


Figure 5 FESEM photographs of 100% cotton fiber treated or untreated by DDPS. (a) Untreated (×5000), (b) DDPS (×5000), (c) Untreated (×20,000), (d) DDPS (×20,000), (e) Untreated (×80,000), (f) DDPS (×80,000).

the hydrophobic —CH_3, —$C_{12}H_{25}$ groups are point away from the silicon surface and project out toward air (as shown in Fig. 8). However, dodecyl is a bulky group as compared with methyl, it possesses different configurations such as the random and extended configurations in space, which makes DDPS easily give rise to an uneven film on the silicon wafer surface. As a result, an inhomogeneous polysiloxane film with

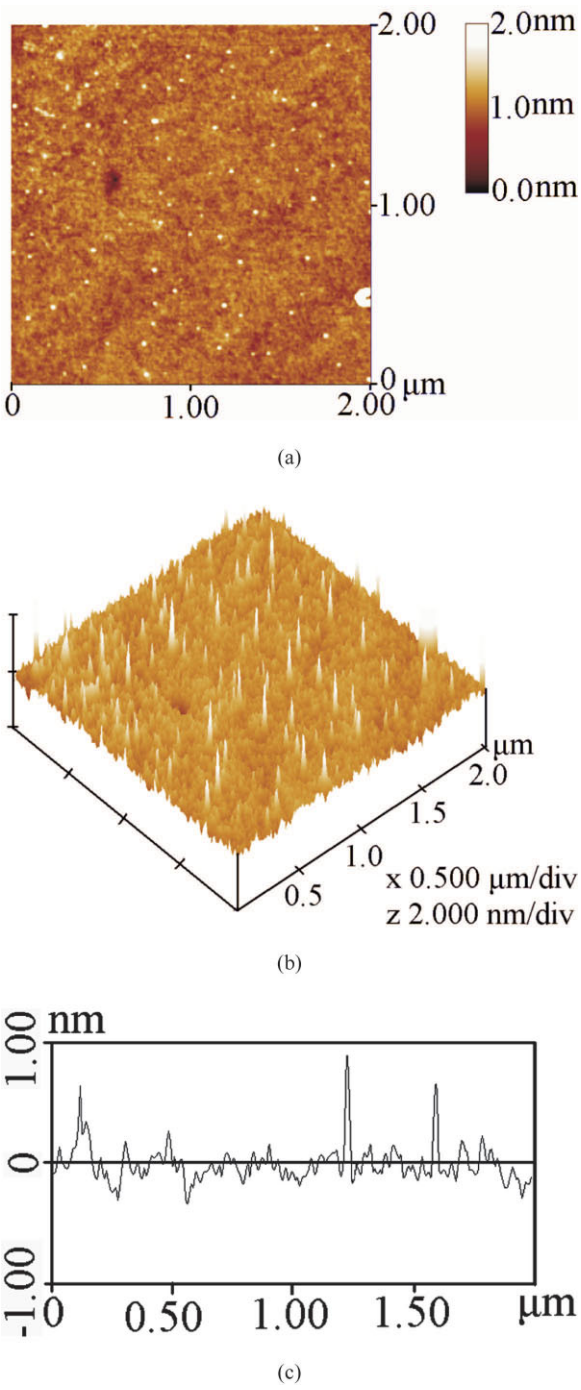


Figure 6 The AFM images of DDPS film with a R*q*. of 0.199 nm. (a) Flatten, (b) Three dimensional, (c) The surface profile along a line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

many peaks is clearly observed in the three dimensional AFM image of DDPS (Fig. 6). The brighter peaks are estimated to generate from the side chains, dodecyl groups, and the dim continuous phase may be arisen from the PDMS skeleton.

The characteristic inhomogeneous microstructure makes DDPS film less smooth and seems to be a bit rough as compared with PDMS (Fig. 7). Consequently, R*q*. of DDPS film reaches to 0.199 nm in 2 μm^2 scanning field, which is 2.46 times bigger than that of the contrast, the uniform PDMS film (with an Rq. of only 0.081 nm).

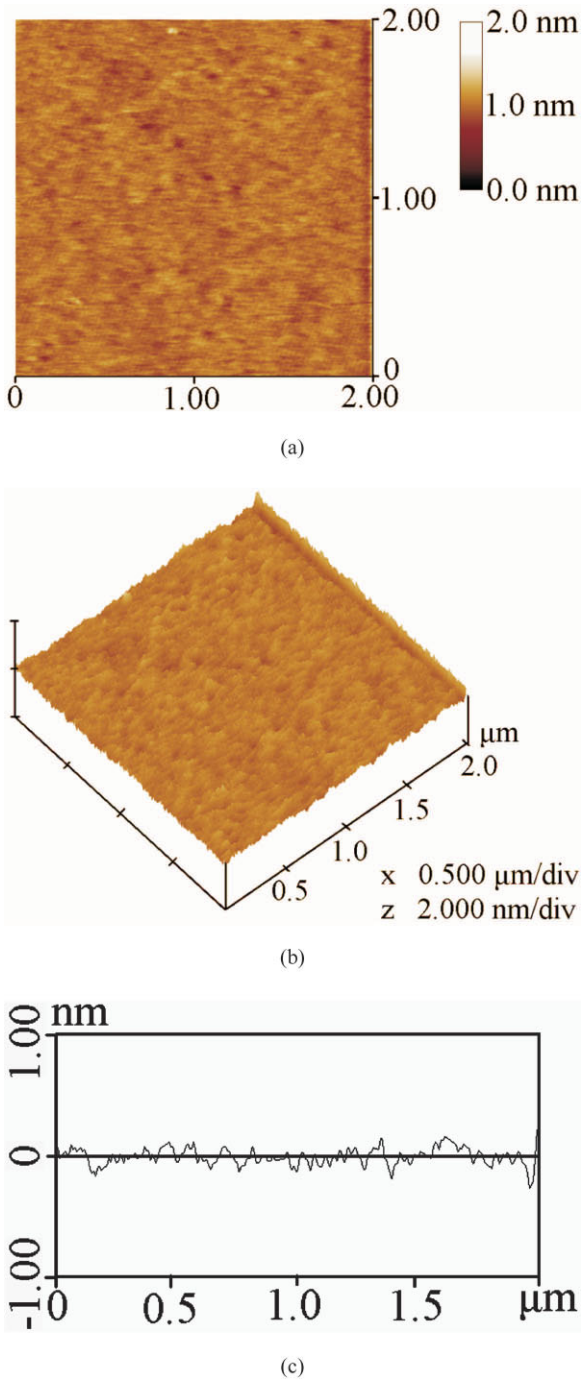


Figure 7 The AFM images of PDMS film with a R*q*. of 0.081 nm. (a) Flatten, (b) Three dimensional, (c) The surface profile along a line. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

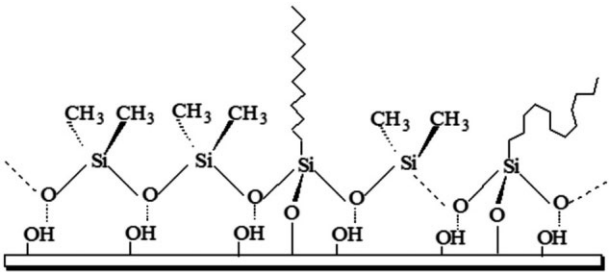


Figure 8 The orientation of DDPS molecule on the hydrophilic silicon wafer substrate.

CONCLUSIONS

DDPS can form film on silicon and cotton fabric substrate. At an amplification of <80,000 (of the original fiber) and an observation rule (working distance) of >200 nm, the DDPS film on cotton fiber surface shows a relative smooth morphologic outline in FESEM observation. But as the observation rule decreases to 2 nm, the macroscopic relative smooth DDPS film substantially exhibits an inhomogeneous structure, there are many low or high peaks that appeared in its three dimensional AFM image and in 2 um^2 scanning field, and the film average roughness (Rq.) reaches to 0.199 nm. Film morphology could influence the tactility and other performance of functional polysiloxane softener. The particular film morphology of DDPS may be the crucial factor why DDPS could offer a fluffy, thickening, but less smooth tactility for the treated fabrics.

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