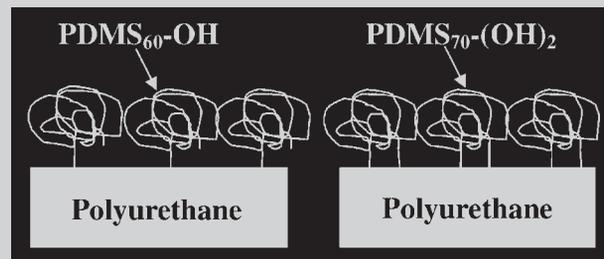


Summary: Polyurethane (PU) films with low water contact angle hysteresis (CAH) were prepared by employing less than 0.2 wt.-% of mono- or bihydroxyl-functionalized polydimethylsiloxane (PDMS) of 60–70 DMS repeat units. A Si content of as low as 0.03 wt.-% was sufficient to lead to a CAH of 20°. The curing temperature demonstrated strong effects on the wetting behavior of the PDMS-modified PU films: a relatively low curing temperature (40 °C) resulted in stronger surface segregation of PDMS than higher curing temperatures, giving rise to high water receding CAs and thus low CAH. It was found from angle-resolved X-ray photoelectron spectroscopy analysis that the surface silicon content was greater when cured at a lower temperature. The surface of PDMS-modified PU films was very smooth from AFM observations, but the Si content had strong effects on the surface phase contrast. The chain length of 60–70 DMS repeating units for both mono- and bifunctional PDMS

appeared to be long enough to prevent the surface reorganization during the CA measurements.



Schematic, simplified illustration of PDMS chains at the surface of PU films modified by PDMS₆₀-OH and PDMS₇₀-(OH)₂.

PDMS-Modified Polyurethane Films with Low Water Contact Angle Hysteresis

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Introduction

The liquid repellency (lyophobicity) is a very important property of organic coatings. Contact angles (CA) are commonly used to describe surface wettability,^[1] but CA alone is not enough to describe the lyophobicity of a coating. It is well known that the force (F) needed for a drop to move over a solid surface is determined by:^[2] $F \sim \gamma_{LV} (\cos \theta_R - \cos \theta_A)$, where γ_{LV} is the surface tension of the liquid and θ_R and θ_A are the receding and advancing CA of the liquid on the solid surface, respectively. The difference ($\theta_A - \theta_R$) is defined as the contact angle hysteresis (CAH), which governs the roll-off angle of a liquid droplet on a solid surface. CAH is generally considered to arise from three sources: chemical heterogeneity, surface roughness, and surface reorganization during the CA

measurement.^[3,4] The CAH may be viewed to be more important in making a surface lyophobic than the maximum achievable CA;^[5] for instance, the key to obtaining self-cleaning or superhydrophobic surface is to minimize the water CAH (in combination with proper surface roughness).^[5–14]

Fluorinated surfaces are widely used in a number of technological areas requiring low surface energy, low adhesion, and chemical inertness, among other desired properties. Bulk fluorinated materials can be used, but they are generally expensive and difficult to process. We recently prepared low surface-energy polyurethane (PU) films with surface rich in fluorinated species,^[15–17] on which the highest water θ_A was about 120° while the θ_R was only about 70° (with up to 4 wt.-% of fluorine in the films). The very large CAH is likely due to the fact that the

fluorinated chain (e.g., $C_8F_{17}-$) is not long enough to prevent the surface reorganization (i.e., to shield the polar urethane group from the interrogating liquid) upon contact with water during the CA measurements.^[18] When the water droplet is in contact with the film surface, the urethane group that originally sits below the top fluoroalkyl layer would have the opportunity to interact with water, leading to a low θ_R . We examined the top atomic layer of the fluorinated PU surface containing 1 wt.-% of fluorine by low energy ion scattering,^[19,20] and found only fluorine and carbon atoms are present, suggesting that oxygen and nitrogen atoms are primarily located beneath the top atomic layer.

Polydimethylsiloxane (PDMS), with a normally much longer chain than the perfluoroalkyl chain, has been introduced to various polymeric systems to modify surface properties, such as polystyrene,^[14] poly(methyl methacrylate),^[21] polycarbonate,^[22] and PU.^[23,24] The PDMS chains, in comparison with other components in the mixture, have the tendency to migrate toward the air/film interface to minimize the interfacial energy. The reported CAH in the copolymers or polymer blend systems is typically 35–40°,^[23,25] significantly greater than the CAH for pure PDMS^[26,27] (due to its flexibility pure PDMS has only been extensively used as elastomers). A low water CAH would be important to make a surface superhydrophobic, and may be helpful in designing marine biofouling-resistant coatings.^[28] In this paper we describe a simple method to prepare cross-linked PDMS-modified PU films with a small CAH by using less than 0.2 wt.-% PDMS (as such, the bulk properties of PU will be virtually unaltered).

Experimental Part

Materials

A polyisocyanate cross-linker, hexamethylene diisocyanate trimer (Desmodur N3600), was obtained from Bayer AG.

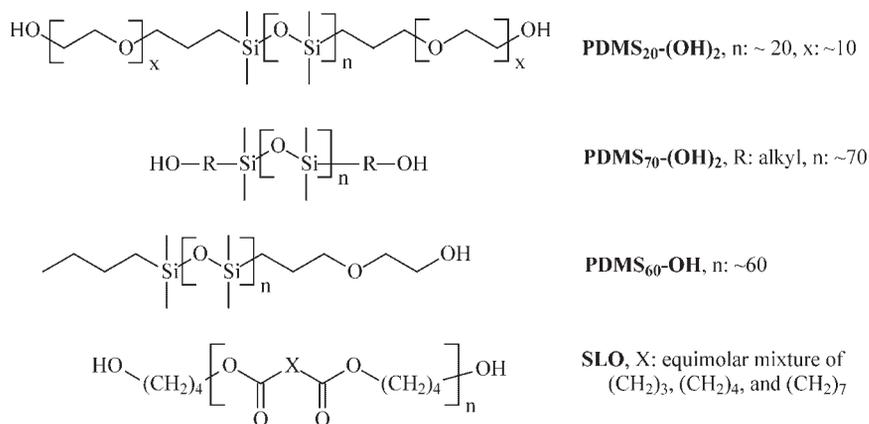
Three kinds of hydroxyl-terminated PDMS (Scheme 1) were used as received; PDMS₇₀-(OH)₂ and PDMS₆₀-OH were purchased from Sigma-Aldrich and PDMS₂₀-(OH)₂ was kindly provided by EFKA (The Netherlands). The synthesis of the hydroxyl-end-capped solventless liquid oligoester (SLO, Scheme 1) was reported elsewhere.^[15] Butyl acetate was obtained from Sigma-Aldrich and dried by molecular sieve before use. Other chemicals were purchased from Merck and were used as received.

Preparation of Bifunctional PDMS-Modified PU Films

The hydroxyl number of SLO was determined to be 135 mg KOH per gram by titration, corresponding to an OH amount of $2.4 \times 10^{-3} \text{ mol} \cdot \text{g}^{-1}$. In the reaction mixtures comprising SLO, N3600, and bifunctional PDMS, the overall NCO/OH molar ratio was maintained at 1.1 to ensure the complete conversion of the hydroxyl groups. The content of the bifunctional PDMS was varied to obtain different silicon contents in the films. The reaction mixture was dissolved in dry butyl acetate (30 wt.-% of solid content), and applied on clean aluminum panels with a wet film thickness of $\approx 30 \mu\text{m}$ and then cured at 120, 80, and 40 °C for 2, 4, and 24 h, respectively. The thickness of the cured, dry films was about 10 μm , as measured using a Twin-Check thickness gauge by List-Magnetic GmbH.

Preparation of Monofunctional PDMS-Modified PU Films

To increase the miscibility of monofunctional PDMS (PDMS₆₀-OH) with other components, partially PDMS-modified isocyanates were synthesized via a one-step reaction between N3600 and PDMS₆₀-OH. To ensure that there is at least one NCO group for individual N3600 molecules after the reaction, the NCO group was in large excess (the NCO:OH molar ratio: 118:1).^[16] The reaction is described as follows: To a 50-mL three-necked round-bottom flask equipped with a magnetic stirrer, an addition funnel, a reflux condenser, a thermocouple, and a nitrogen inlet, was added 2.5 g of N3600, 1 mg of dibutyltin dilaurate (catalyst), and 9 g of dry butyl acetate.



Scheme 1. Chemical structures of three different kinds of PDMS and SLO.

After the flask was heated to 70 °C, 0.5 g of PDMS₆₀-OH, dissolved in 3 g of dry butyl acetate, was added dropwise through the addition funnel into the mixture. The reaction was maintained at 70 °C for 2 h under stirring and dry argon atmosphere. ¹H NMR was used to confirm the reaction: after reaction a small peak emerged at 4.1 ppm, corresponding to CH₂ from PDMS next to the urethane group, -OC(O)-NH-. The product (PDMS-NCO) was stored in a sealed container in a refrigerator under dry argon atmosphere to avoid any contact with atmospheric moisture.

Similar to the method described in Preparation of Bifunctional PDMS-Modified PU Films, films (≈10 μm thick) containing SLO, N3600, and partially PDMS-modified N3600 (PDMS-NCO) were prepared, except that the overall OH/NCO molar ratio was kept at 1.1 to ensure the complete conversion of isocyanate groups.

The PDMS-modified PU films were rinsed with acetone to remove the possible free PDMS chains that might not be covalently bonded to the cross-linked networks. It was found that the CA difference before and after the acetone rinsing was marginal, indicating that almost all the PDMS chains were chemically bonded to the PU films.

Characterization Techniques

Contact angles were measured with deionized water on a Dataphysics OCA30 instrument at room temperature. Dynamic advancing and receding CAs were recorded while water was added to and withdrawn from the drop, respectively, by a syringe pump. The CA reported was the average of values for 3–4 drops and the difference was normally within 2°. Real-time infrared spectra were recorded on a BioRad Excalibur spectrophotometer equipped with a deuterated tri-glycine sulfate (DTGS) detector, a MKII Golden Gate heated diamond 45° ATR top plate (Specac Ltd., Kent, England), and a 3000 series high stability temperature controller (Specac). After the reaction mixture was deposited on the diamond unit, infrared spectra (two scans per spectrum) were collected every 5–30 s at a resolution of 16 cm⁻¹. Atomic force microscopy (AFM) was used to examine the surface morphology of the PU films. AFM images (height and phase) were collected on a Nanoscope IV (Digital Instruments/Veeco Metrology Group, USA) instrument under tapping mode. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα X-ray source and a hemispherical analyzer with a five-channeltron detector. Spectra were obtained using the aluminium anode (Al Kα = 1486.6 eV) operating at 240 W and a constant pass energy of 20 eV with a background pressure of 2 × 10⁻⁹ mbar. Different takeoff angles (θ), 90, 60, 45, 30, and 20° (between the film surface and the axis of the analyzer lens) were used to collect the spectra at different probe depths. The analysis depth, *d*, is controlled by varying θ through the following equation: $d = 3\lambda \sin \theta$, where λ is the inelastic mean free path of the electrons traveling through the measured sample.^[29] For Si, the sampling depth at a takeoff angle of 90° corresponds to roughly 10 nm.^[29] All C 1s peaks corresponding to hydrogen carbon and silicon carbon were calibrated at a binding energy of 284.6 eV to correct for charging.

Results and Discussion

Thermal Curing of SLO with Isocyanates by In Situ ATR-FTIR

The reaction between hydroxyl and isocyanate groups was monitored by real-time ATR-FTIR. The evolution of IR spectra of the reaction mixture of N3600 and SLO at 80 °C is shown in Figure 1. The peak at 2272 cm⁻¹, corresponding to the NCO group, decreased steadily as the curing reaction proceeded; so did the peak at 3550 cm⁻¹ (OH stretching). New peaks emerged at 3380 cm⁻¹ (-NH-COO-) and 1520 cm⁻¹ (amide II, NH bending). On the other hand, the carbonyl group on the isocyanurate ring (1690 cm⁻¹) remained the same throughout the reaction, on the basis of which all spectra were normalized. The NCO conversion can be calculated from the disappearance of 2272 cm⁻¹ peak. The NCO conversion for the reaction between N3600 and SLO as a function of reaction time is shown in Figure 2. At 120 °C, the complete NCO conversion was reached in about 2 min, while it took about 20 min at 80 °C for the NCO conversion to reach ≈98%. The same reaction was also performed at 40 °C and only a 90% conversion for the NCO groups was reached after 120 min. The reaction between SLO, N3600, and 2 wt.-% of PDMS₇₀-(OH)₂ was also monitored at 80 °C, and the existence of PDMS did not show any significant effect on the cross-linking rate.

Surface Properties of PDMS-Modified PU Films

Surface Wettability of PDMS₂₀-(OH)₂-Modified PU Films

We first used PDMS₂₀-(OH)₂ to modify PU films. Because of the long hydrophilic poly(ethylene oxide) moiety,

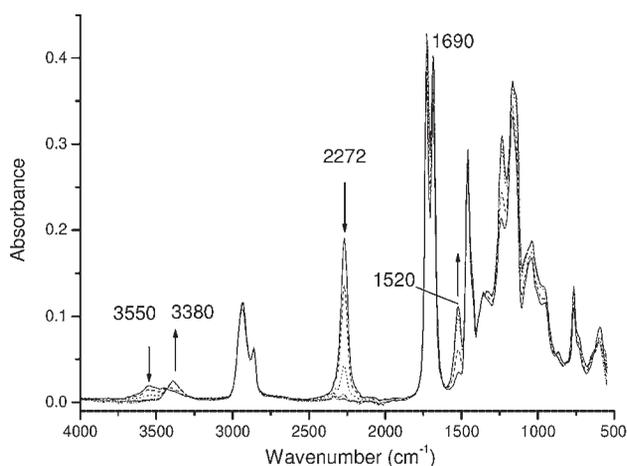


Figure 1. Real-time ATR-FTIR spectra for the thermal curing of SLO by N3600 at 80 °C (the OH/NCO ratio was 1.1 to ensure the full disappearance of NCO group).

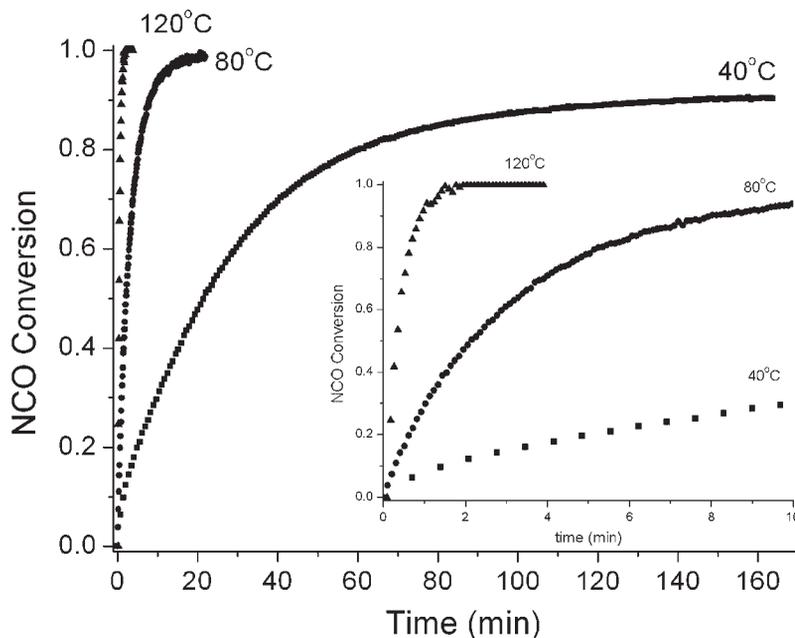


Figure 2. NCO conversion for reactions between N3600 and SLO at different temperatures.

PDMS₂₀-(OH)₂ appeared to be miscible with other components. So the amount of PDMS₂₀-(OH)₂ that could be incorporated into the reactive mixture without phase separation was much higher than the other two PDMSs. The water CA on the PU films containing PDMS₂₀-(OH)₂ as a function of the silicon content is shown in Figure 3. As the Si content was increased to ≈ 0.25 wt.-% (the Si content was estimated from the recipe with the assumption that all the starting materials were incorporated into the final films, which has been to some extent proven by the acetone rinsing test), the water θ_A and θ_R increased to 100 and 65°, respectively. The θ_A was lower than that for a pure PDMS,

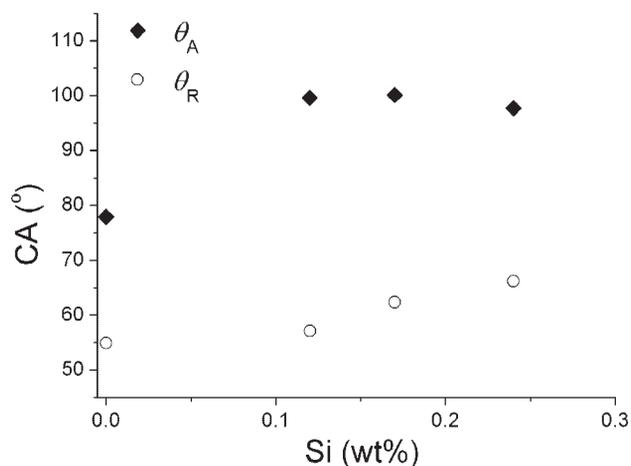


Figure 3. Water CA on (PDMS)₂₀-(OH)₂-modified PU films cured at 60 °C for 4 h.

while the CAH (about 35°) was much greater; on a pure PDMS surface (made from, for instance, hydrosilane and vinylsilane) the water CAH is usually less than 10°. [26,27,30,31] The relatively low water θ_A and high CAH for the PDMS₂₀-(OH)₂-modified PU films is likely due to the combination of the presence of the hydrophilic PEO segment and the short PDMS chain, which may be too short to prevent the surface reorganization during the CA measurements.

Surface Wettability of PDMS₇₀-(OH)₂-Modified PU Films

PDMS₇₀-(OH)₂, a bihydroxyl PDMS that contains a longer PDMS chain and no PEO spacer, was used instead of PDMS₂₀-(OH)₂. The water θ_A and θ_R on PDMS₇₀-(OH)₂-modified PU films are shown in Figure 4. The highest θ_A , irrespective of the curing temperatures, reached 110°, similar to that on pure PDMS, but only with as low as 0.03 wt.-% of Si in the film. The highest Si content in this study was 0.072 wt.-%, corresponding to a PDMS₇₀-(OH)₂ content of 0.2 wt.-%. The use of a Si content greater than 0.1 wt.-% would lead to visually observable, macroscopic phase separation. On the other hand, the curing temperature demonstrated a strong effect on the water θ_R ; the higher the curing temperature, the lower the θ_R , as clearly shown in Figure 4. The lowest water CAH was about 20° for the film cured at 40 °C, which is significantly lower than that for the PDMS₂₀-(OH)₂-modified PU films. This reduced CAH is likely due to the relatively long PDMS chain from PDMS₇₀-(OH)₂, which may to some extent shield the polar urethane group from the interrogating water during CA measurements. On the other

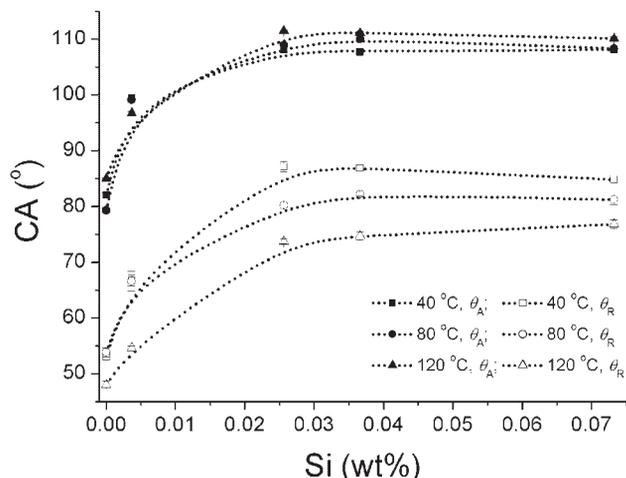


Figure 4. Water θ_A and θ_R on PDMS₇₀-(OH)₂-modified PU films cured at different temperatures as a function of the silicon content in the films. The dotted lines are added merely as an aid to the eyes.

hand, the CAH is not as low as the CAH for the pure PDMS, indicating that some polar parts are exposed to water and/or the surface reorganization may occur at some parts of the surface upon contact with water. It is known that while the θ_A is sensitive to the hydrophobic moiety, the θ_R is more dependent on the hydrophilic moiety.^[3,23] As long as there is hydrophilic part on the surface or surface reorganization takes place during CA measurements, the θ_R would be low and the CAH would thus be high.

Surface Wettability and Morphology of PDMS₆₀-OH-Modified PU Films

Monohydroxyl-terminated PDMS₆₀-OH, containing a PDMS chain of the comparable length to the bifunctional PDMS₇₀-(OH)₂, was also used to prepare PDMS-modified PU films. The structure of PDMS₆₀-OH was confirmed by matrix-assisted laser desorption ionization time-of-flight MS (MALDI-TOF MS). It was anticipated that, due to the monofunctionality of PDMS₆₀-OH, the PDMS chains may better orient at the film surface than its bifunctional counterpart. In this series of experiments, the highest PDMS₆₀-OH content was about 0.2 wt.-%, corresponding to a Si content of about 0.074 wt.-%. The water θ_A and θ_R on PDMS₆₀-OH-modified PU films are shown in Figure 5. The CAs showed similar dependence on the curing temperature to the PDMS₇₀-(OH)₂-modified films: only the θ_R was strongly affected by the curing temperature. The highest θ_A and θ_R (107 and 87°, respectively) reached at a silicon concentration of as low as 0.02 wt.-% for the film cured at 40 °C were comparable to the PDMS₇₀-(OH)₂-modified PU films also cured at 40 °C. It is interesting to notice that the increase of θ_A appeared to be much “more rapid” than the increase for the θ_R , as the silicon content was increased to about 0.02 wt.-% (the similar trend was observed for the PDMS₇₀-(OH)₂-modified PU films). This

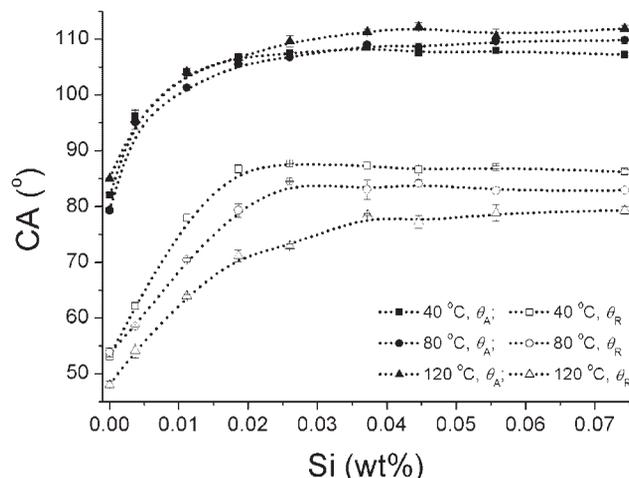


Figure 5. Water θ_A and θ_R on PDMS₆₀-OH-modified PU films cured at different temperatures. The dotted lines are added merely as an aid to the eyes.

phenomenon is again likely due to the fact that the θ_A is more sensitive to the low surface-energy species, whereas the θ_R is more dependent on the high surface-energy moiety at a film surface.^[3,23] This also indicates that, to some extent, the surface coverage by PDMS for the PU films at low silicon contents (<0.01 wt.-%) was low, leading to the CAH as high as 40° (Figure 6). The lowest CAH was about 20° when the film was cured at 40 °C with at least 0.02 wt.-% of Si in the film.

The underwater stability of the PU films modified by mono- and bifunctional PDMS (containing ≈ 0.04 wt.-% Si and cured at 80 °C) was compared. After being submerged in deionized water for 48 h, the films were naturally dried at ambient conditions and subjected to contact angle measurements. For both films, the water θ_A and θ_R values

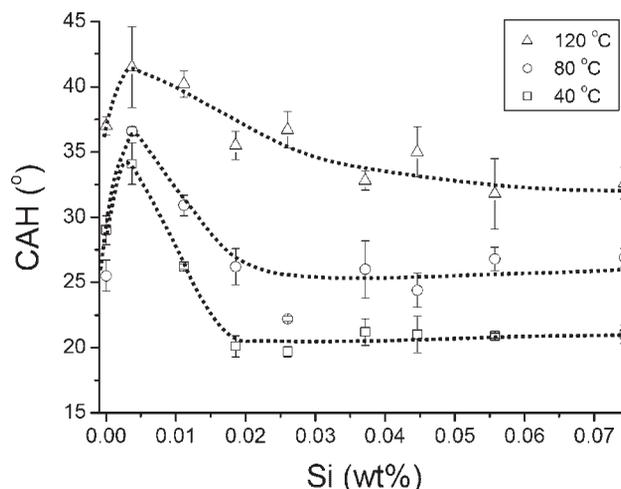


Figure 6. Water CAH for PDMS₆₀-OH-modified PU films cured at different temperatures. The dotted lines are added merely as an aid to the eyes.

were found to be similar to those on the films before the water submersion test, indicating that the PU films modified by both mono- and bifunctional PDMS demonstrate good underwater stability.

Tapping mode AFM was used to examine the surface morphology of PDMS₆₀-OH-modified PU films. Typical AFM height images shown in Figure 7 were essentially featureless in a scan box of $100 \times 100 \text{ nm}^2$. There appeared to be no significant difference in the surface roughness for the films containing different silicon contents and cured at different temperatures. This is not surprising since PDMS is a known leveling agent for coatings.^[32] This also sug-

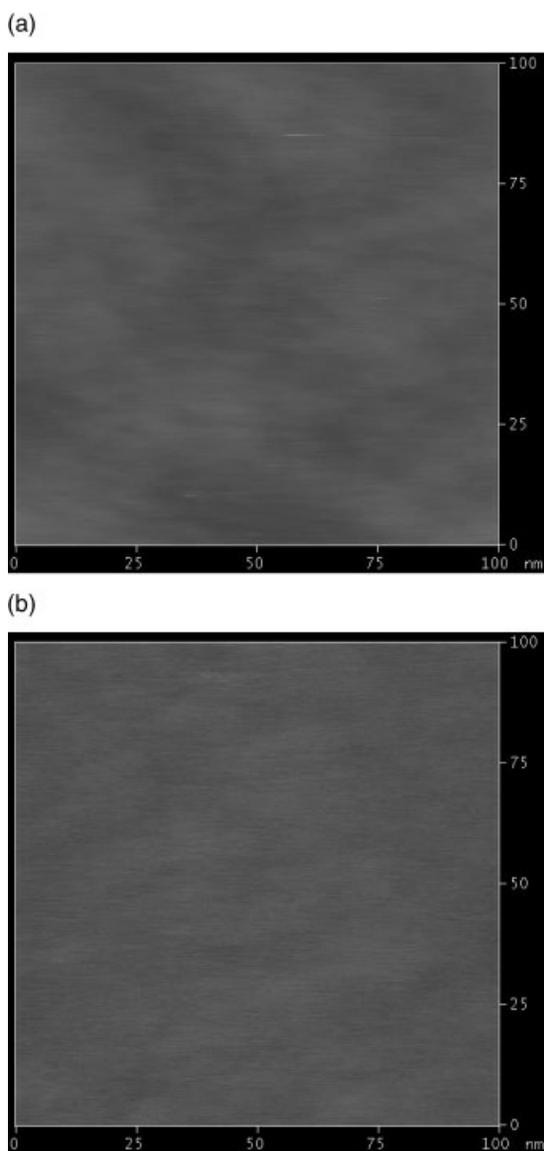


Figure 7. Tapping mode AFM height (data scale: 10 nm) images of PDMS₆₀-OH-modified PU films (a) containing 0.074 wt.-% Si and cured at 80 °C, and (b) containing 0.026 wt.-% Si and cured at 120 °C.

gests that the CAH variation observed above was not related to surface roughness.

On the other hand, the AFM phase images were affected by the silicon contents, as shown in Figure 8. In the absence of PDMS, the phase image of the film appeared to be featureless [Figure 8(a)]. With a very small amount of Si (0.004 wt.-%) present in the film, there was discernible phase contrast [Figure 8(b)]; the dark area may correspond to the relatively soft polymer segment,^[16,33] in this case, PDMS-rich domain. The phase contrast is indicative of the surface chemical heterogeneity (the XPS results below showed that the surface Si content was indeed low), which agrees well with the large CAH observed (Figure 6). As the Si content was increased to 0.037 wt.-%, the portion of the relatively dark area increased slightly [Figure 8(c)]. Only when the Si content was further increased to 0.074 wt.-%, the phase contrast became quite obvious [Figure 8(d)]. This is likely due to that, once the PDMS concentration at the surface is high enough, the PDMS chains start to form aggregates. As mentioned earlier, if the Si content was greater than 0.1 wt.-%, macroscopic phase separation would have been observed. In a recent investigation by Majumdar and Webster,^[24] a biphasic structure (strong phase separation) was reported at a PDMS content of 10 wt.-% (in contrast, the PDMS content in this study was 0.2 wt.-%).

The curing temperature also showed some effects on the phase contrast, but a systematic analysis appeared to be difficult and was not attempted.

Surface Chemical Composition of PDMS-Modified PU Films

The surface chemical compositions of the films were obtained by XPS. The C 1s, Si 2p, and N 1s regions of the XPS spectra for PDMS₆₀-OH-modified PU films are shown in Figure 9. With the increasing PDMS content in the films, the Si 2p peak intensity increased while the N 1s peak intensity decreased; in the meantime, the peak intensity corresponding to C=O (only present in the PU part) also decreased, clearly indicating the increasing enrichment of PDMS at the surface. The atomic percentages of Si or N were calculated from the XPS spectra by comparing the intensity of Si 2p or N 1s peak and the summation (excluding H) of the intensities of the Si 2p, N 1s, O 1s, and C 1s peaks in combination with the sensitivity factors for different elements.^[34] Typical statistical error for Si and N atomic concentration was estimated to be 1 and 4 atom%, respectively.

The surface chemical compositions of the PDMS₇₀-(OH)₂-modified PU films cured at 80 °C are shown in Figure 10. The takeoff angles of 90 and 30° correspond to the estimated probe depth of 10 and 5 nm, respectively. Apparently, because of the preferential surface enrichment

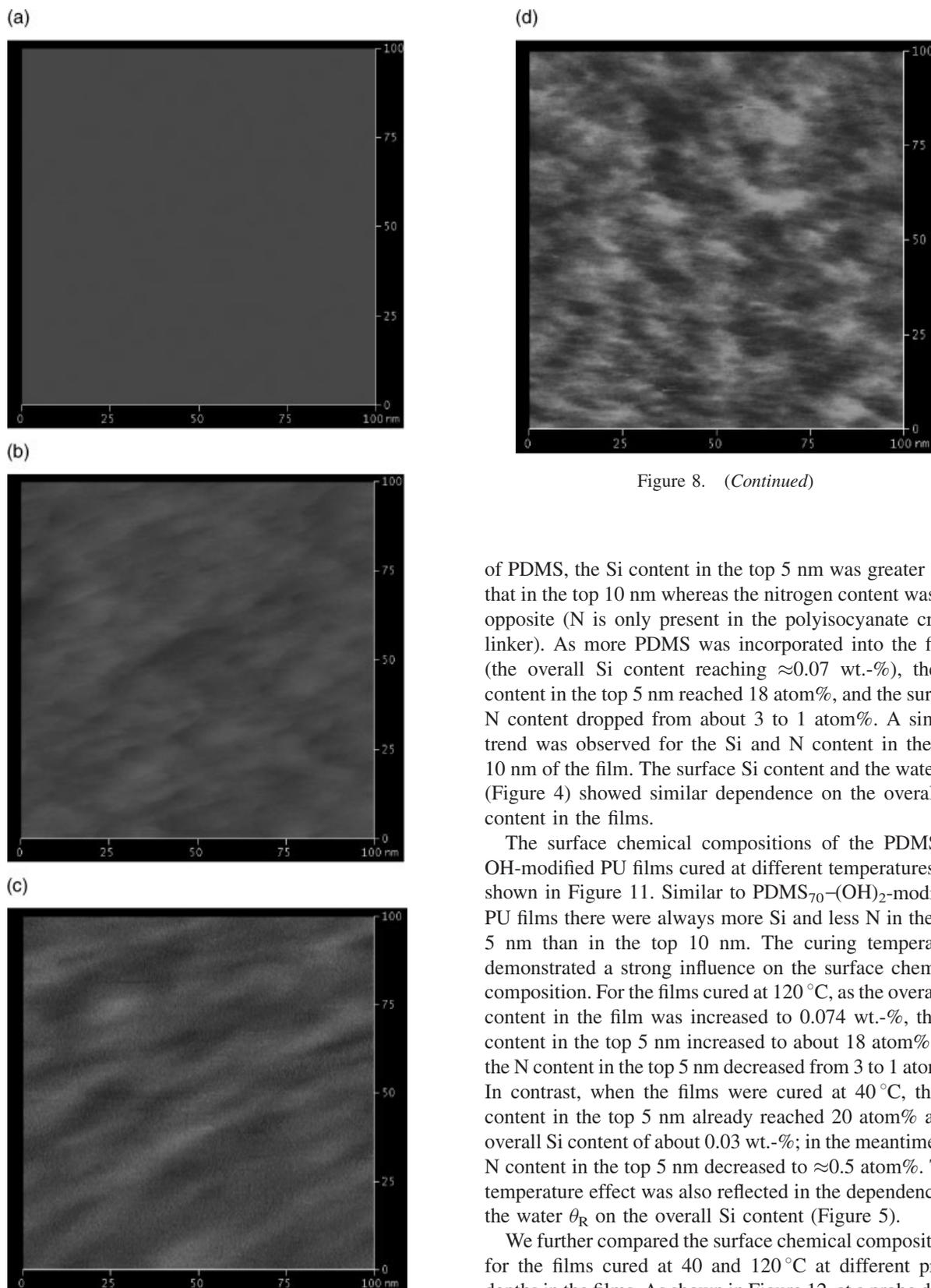


Figure 8. (Continued)

of PDMS, the Si content in the top 5 nm was greater than that in the top 10 nm whereas the nitrogen content was the opposite (N is only present in the polyisocyanate cross-linker). As more PDMS was incorporated into the films (the overall Si content reaching ≈ 0.07 wt.%), the Si content in the top 5 nm reached 18 atom%, and the surface N content dropped from about 3 to 1 atom%. A similar trend was observed for the Si and N content in the top 10 nm of the film. The surface Si content and the water θ_A (Figure 4) showed similar dependence on the overall Si content in the films.

The surface chemical compositions of the PDMS₆₀-OH-modified PU films cured at different temperatures are shown in Figure 11. Similar to PDMS₇₀-(OH)₂-modified PU films there were always more Si and less N in the top 5 nm than in the top 10 nm. The curing temperature demonstrated a strong influence on the surface chemical composition. For the films cured at 120 °C, as the overall Si content in the film was increased to 0.074 wt.-%, the Si content in the top 5 nm increased to about 18 atom% and the N content in the top 5 nm decreased from 3 to 1 atom%. In contrast, when the films were cured at 40 °C, the Si content in the top 5 nm already reached 20 atom% at an overall Si content of about 0.03 wt.-%; in the meantime the N content in the top 5 nm decreased to ≈ 0.5 atom%. This temperature effect was also reflected in the dependence of the water θ_R on the overall Si content (Figure 5).

We further compared the surface chemical compositions for the films cured at 40 and 120 °C at different probe depths in the films. As shown in Figure 12, at a probe depth of about 3.4 nm, the Si content was about 21.3 atom% and the N content was less than 0.2 atom% when the film was cured at 40 °C. This suggests that the top surface of the film

Figure 8. Tapping mode AFM phase (data scale: 20°) images of PDMS₆₀-OH-modified PU films cured at 80 °C, containing different Si contents (wt.-%): (a) 0, (b) 0.004, (c) 0.037, and (d) 0.074.

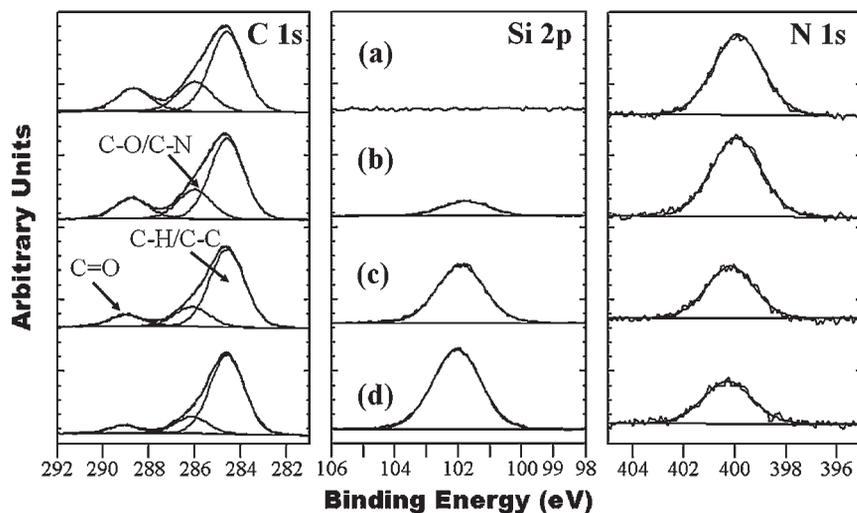


Figure 9. XPS spectra (takeoff angle: 90°) for the PDMS₆₀-OH-modified PU films cured at 40 °C and containing different Si contents (wt.-%): (a) 0, (b) 0.004, (c) 0.019, and (d) 0.045.

is primarily composed of PDMS chains (the Si content in a pure PDMS would be close to 25 atom%). The Si content was significantly lower and the N content was higher at different probe depths when the films were cured at 120 °C. The strong temperature effect is likely the result of the competition between the surface segregation of PDMS and the formation of the cross-linked network.^[35] Although at a high curing temperature (e.g., 120 °C) the diffusion of PDMS may be faster,^[17] the formation of the cross-linked network is also markedly faster than cured at a lower temperature (Figure 2). As a consequence of the rapid reaction, the viscosity of the reactive mixture would increase rapidly, limiting the diffusion of PDMS toward the surface. On the contrary, when the film was cured at a lower

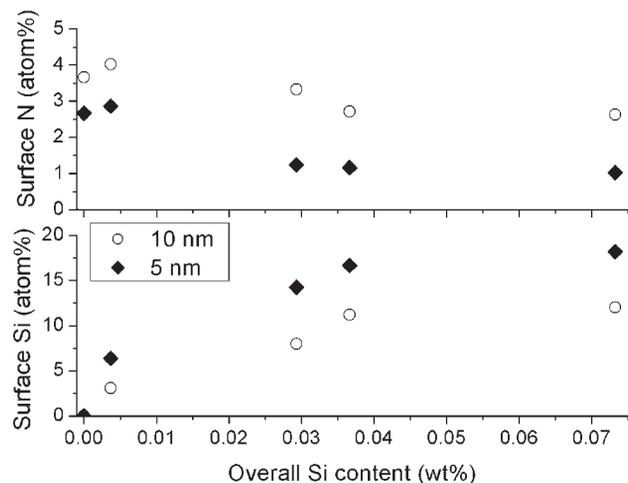


Figure 10. Surface chemical compositions (Si and N) for PDMS₇₀-(OH)₂-modified PU films cured at 80 °C.

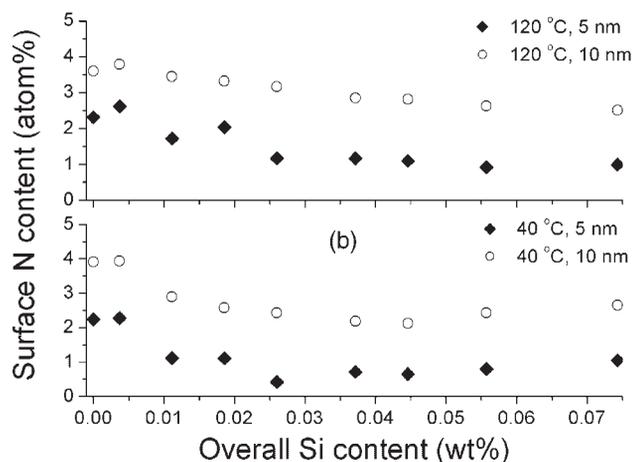
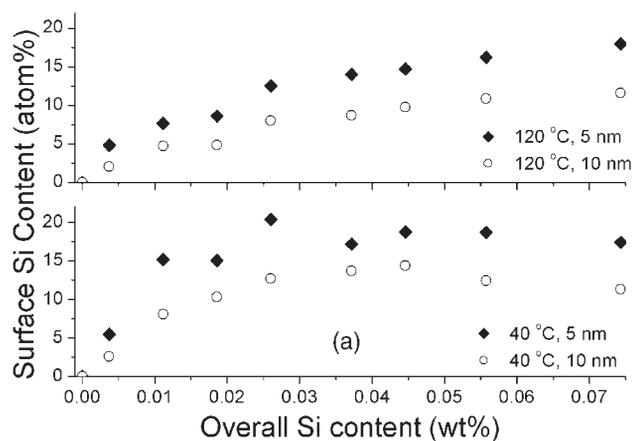


Figure 11. Surface compositions of (a) Si and (b) N for PDMS₆₀-OH-modified PU films cured at different temperatures.

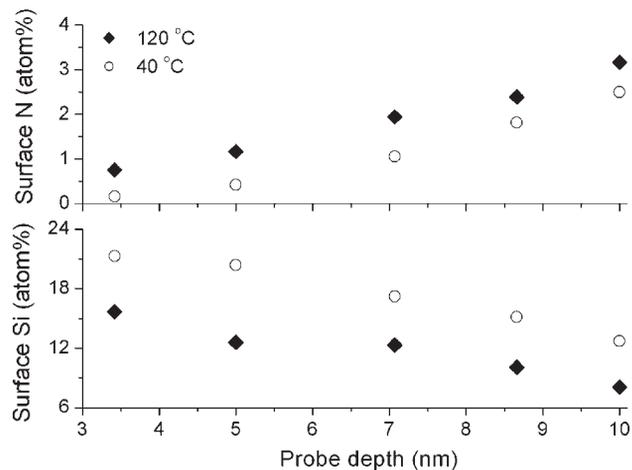


Figure 12. Chemical composition (N and Si) at different probe depths of PDMS₆₀-OH-modified PU films with 0.07 wt.-% of Si and cured at 40 and 120 °C.

temperature (e.g., 40 °C), the diffusion of PDMS would be slower, but the relatively low mixture viscosity, due to the slow reaction rate, would allow the PDMS chains to diffuse for a much longer period of time, leading to the more significant surface segregation of PMDS in the top surface.

Discussion

As mentioned earlier, we expected to observe some difference for the PU films modified by mono- and bifunctional PDMS. But the CA data (Figure 4 and 5) demonstrated that the difference was insignificant between the films modified by PDMS₆₀-OH and PDMS₇₀-(OH)₂, which have comparable PDMS chain length. We examined the surface chemical composition of the two films, as given in Figure 13. Obviously, both the Si and N contents in the top surface appeared to be similar for the two films, especially in the top 5 nm. The use of the monofunctional PDMS did not provide any extra advantage.

We attempted to estimate the thickness of a PDMS chain for the case of a complete surface segregation. By assuming that the PDMS chain adopts a random coil configuration, we estimated the root-mean-square (rms) radius of gyration^[36] for a PDMS chain containing 60 repeating

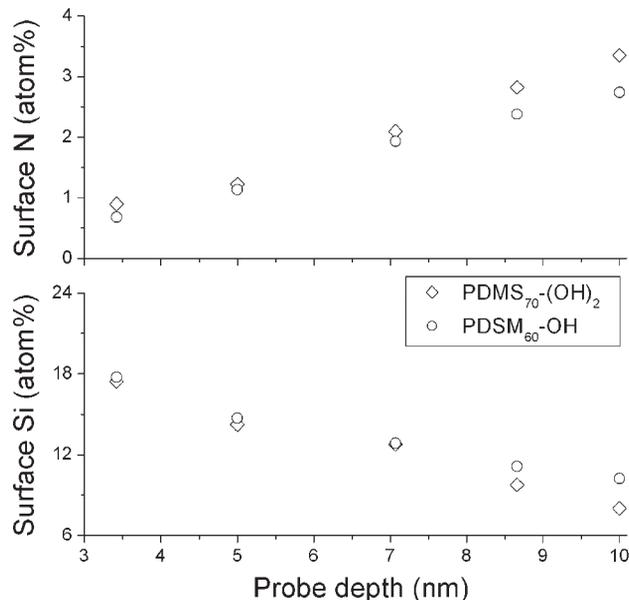


Figure 13. Surface chemical composition (N and Si) of the PU films cured at 80 °C and modified by PDMS₆₀-OH or PDMS₇₀-(OH)₂ (both containing about 0.07 wt.-% of Si).

units to be about 0.9 nm (the parameters used:^[37] the Si-O bond length, 0.164 nm; the O-Si-O bond angle, 110°; and the Si-O-Si bond angle, 143°). Therefore, if a PDMS chain were located at the film surface, the thickness of the PDMS layer would be roughly 1.8 nm, no matter if the chain is connected to the film via one point or two points [Figure 14(a) and 14(b)]. This may explain why PDMS₆₀-OH- and PDMS₇₀-(OH)₂-modified PU films demonstrated similar wetting behavior. The use of bifunctional PDMS may be even advantageous due to the two anchoring points to the bulk PU film.

For the PDMS₂₀-(OH)₂-modified PU films, because of the much shorter PDMS chain, the thickness of PDMS-rich layer should be much thinner [Figure 14(c)], leading to a much higher CAH than the other two systems. Nonetheless, because of the cross-linking during the film formation, the actual PMDS chain orientation would be far from the ideal random coil configurations shown in Figure 14; the CAH for the PDMS-modified PU films is still relatively high compared to pure PDMS (the presence of the polar urethane group also contributes to the high CAH).

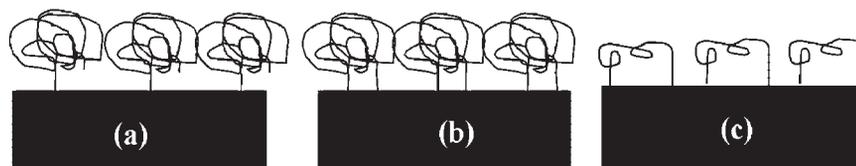


Figure 14. Schematic, simplified illustration of PDMS chains at the surface of PU films modified by (a) PDMS₆₀-OH, (b) PDMS₇₀-(OH)₂, and (c) PDMS₂₀-(OH)₂.

Conclusion

It has been demonstrated in this paper that PDMS-modified PU films with low CAH ($\approx 20^\circ$) could be successfully prepared by thermally curing a mixture of hydroxyl-end-capped liquid oligoester, a polyisocyanate cross-linker, and mono- or bihydroxyl-functionalized PDMS. It has been shown that a low amount of Si (≈ 0.03 wt.-%) is sufficient in producing low CAH when the PDMS chain contains about 60–70 repeating units. Although the curing temperature did not show much effect on the water θ_A , its effect on the θ_R was significant; the lower the curing temperature, the greater the θ_R and thus the lower the CAH. A relatively low curing temperature appeared to favor a strong surface segregation of PDMS, as demonstrated by angle-resolved XPS. The low CAH may be very helpful in designing marine biofouling-resistant coatings.^[28]

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