

Surface modification of polydimethylsiloxane elastomer for stable hydrophilicity, optical transparency and film lubrication



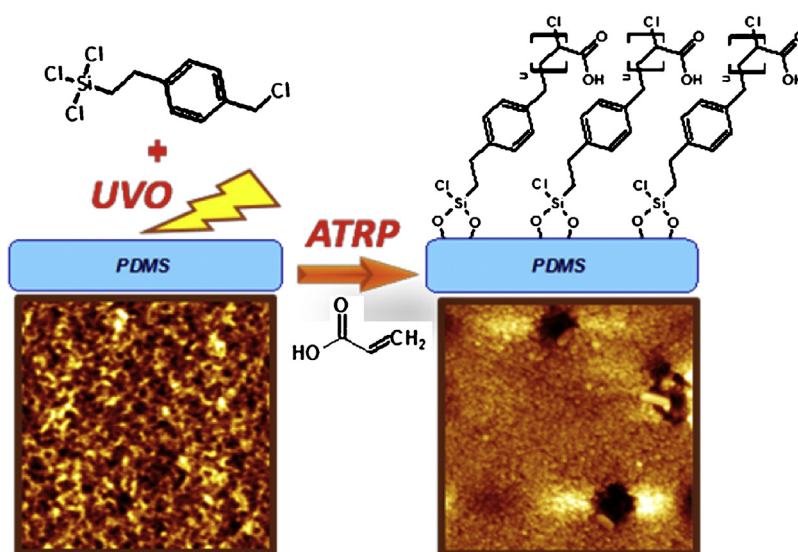
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HIGHLIGHTS

- PDMS surfaces have been hydrophilized by grafting a layer of polyacrylic acid.
- The hydrophilized PDMS maintained its original transparency and physical integrity.
- The hydrophilized PDMS surfaces are stable in air and have film lubrication behavior in aqueous condition.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface of polydimethylsiloxane (PDMS) elastomer was hydrophilized by poly(acrylic acid) (PAAc) using Surface Initiated Atomic Transfer Radical Polymerization (Si-ATRP). The ATRP initiator chosen was ((Chloromethyl) phenylethyl) trichlorosilane, which was immobilized on the surface of the PDMS through a simple but innovative method of drop coating, in contrast to the commonly used vapor deposition and solution-immersion methods. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS) were employed to examine surface properties of modified PDMS and confirmed presence of the PAAc chains covalently bonded to the PDMS surface. Physical properties and topography of the modified sample were characterized by water contact angle measurement and Atomic Force Microscopy. It is shown that the drop-coating of the silane initiator for ATRP modification with PAAc can result in good surface hydrophilization while causing minimum damage to the PDMS preserving its desired optical transparency. The resultant hydrophilic PDMS is stable in air and has film lubrication behavior in aqueous conditions and may be used in the development of advanced microfluidic devices and sensors where both surface hydrophilicity and bulk transparency are desired.

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1. Introduction

Tailoring the interfacial properties of the materials through surface modification by polymers without influencing the bulk material characteristics has attracted a great deal of attention in recent years. Such approach has been shown effective in fabrication and synthesis of versatile biomaterials, advanced sensing and microfluidic devices, and surfaces with outstanding tribological properties, *i.e.* friction and adhesion [1–6]. Polysiloxane elastomers are important engineering materials, having good thermal, environmental, and chemical stability over a wide range of temperatures [7]. They have been applied as sealants [7,8], thin films for encapsulation and packing of electronic devices [9], anti-fouling and releasing coatings [10], sacrificial layers and master-molds in soft lithographic micro-nanofabrication [11–13].

Among all studied polysiloxanes, poly(dimethylsiloxane) (PDMS) has exceptional chemical inertness and mechanical properties, such as flexibility and durability. These properties make PDMS an ideal platform for many applications especially those related to fabrication of different microstructures, microfluidic, and electrophoretic devices [12]. Use of PDMS in above-mentioned applications is further encouraged due to its low cost, ease of synthesis, and flexibility in processing [13,14]. Nonetheless, extreme inertness of the PDMS can counteract as a drawback together with its intrinsic hydrophobicity [15], and tendency to sorb, diffuse, and permeate bio-macromolecular compounds such as proteins [16,17]. Surface modification of PDMS with a hydrophilic polyelectrolyte such as PAAc can overcome these drawbacks and create an interesting interface. This modification can make the chemically inert PDMS surface to have a stable ionic conductive layer which is hydrophilic so to avoid the hydrophobic attraction with proteins and other biomolecules and is prone for fabrication of polyelectrolyte multilayers [18,19]. The resultant surface can act as a bioactive material for implantable miniature electronic and sensing devices [17], demonstrate improved wettability and electro-osmotic flow for microfluidic devices [20], and possess different smart and sustainable interfacial properties [21–26].

In literature, a great variety of techniques have been developed to modify and functionalize the surface of PDMS [27]. Many modifications rely on PDMS surface exposure to energy sources such as oxygen plasma [28], UV radiation [29], or corona discharges [30] to provide the hydroxyl functionalized surface needed for subsequent reactions. Noteworthy, recovery of the hydrophobic surface, due to PDMS oligomer rearrangement, occurs unless further reactions take place and utilize the hydroxyl groups [19]. Typical sequent reactions include integration of different coupling agents as surface initiators for graft polymerization [31–35], reaction of the hydroxylated surfaces with epoxy moieties [36], and coating the surface with hydrophilic polymers [17]. The two prior examples form covalent linkages while the latter example relies on weaker hydrogen bonding interactions.

In lieu of direct UV treatment of the PDMS surface, Hu et al. have opted for *in situ* polymerization of acrylates via UV treatment of PDMS in solvent with photo-initiator and monomer with success [14,29]. Many other research groups have utilized this *in situ* polymerization technique for grafting as well [20,37–39]. However, this method is solvent dependent and typically requires solvents that swell or solubilize PDMS [40]. Other strategies rely on sol-gel techniques or mixing of vinyl terminated ATRP initiators with PDMS and PDMS curing agent before curing. Roman et al. utilized a sol-gel method by solvating cured PDMS in tetraethyl orthosil-

icate followed by a condensation reaction in an aqueous solution of ethylamine to produce homogeneously distributed SiO₂ particles [41]. The incorporation of SiO₂ particles to the bulk and surface of PDMS exhibits a decline in water contact angle of 20° and no sorption for specific targeted compounds [41]. Alternatively, Wu et al. and other groups have mixed ATRP vinyl terminated initiators with PDMS resin and curing agent before curing to incorporate immobilized covalently linked ATRP initiators [42,43]. Unfortunately, by adding vinyl terminated ATRP initiators to the uncured PDMS, the PDMS curing agent must be increased to obtain similar crosslinking as opposed to not using vinyl terminated ATRP initiators.

To the best of our knowledge, the majority of published works have focused only on the feasibility of the chemical modification itself. Although effective, the consequential effects of the modification procedures on optical and physical properties of the resultant PDMS have not been elaborated. For instance, solvent induced swelling can be a detrimental technique for modification of the PDMS samples embroidered with fine micro/nano-scale structures, due to their susceptibility to irreversible deformation. Naturally, gas phase deposition or other non-invasive procedures gain more attention to maintain the physical structures of the PDMS sample. However, depositing the coupling agent or graft polymerization of the initiator (*e.g.* silane coupling agents) causes discoloration and opacity of the PDMS film which are unfavorable for applications where *in situ* monitoring of the surface or any other optical responses is required. Recently, Dirany and coworkers reported a surface modification technique without impacting the viscoelastic properties of the bulk PDMS [44]. In this work, we aim to hydrophilize the PDMS surface using reagents and a procedure having benign effects on the bulk properties of the PDMS, in particular, the optical transparency property. For this, we developed a simple drop-coating method to immobilize a silane compound on the PDMS surface as an initiator for the ATRP grafting of the PAAc. Systematic chemical and physical characterizations were performed, showing that the drop-coating of the silane initiator for ATRP modification with PAAc was effective in terms of hydrophilization of PDMS surface to promote film lubrication behavior in aqueous conditions while preserving its desired optical transparency.

2. Experimental

2.1. Materials

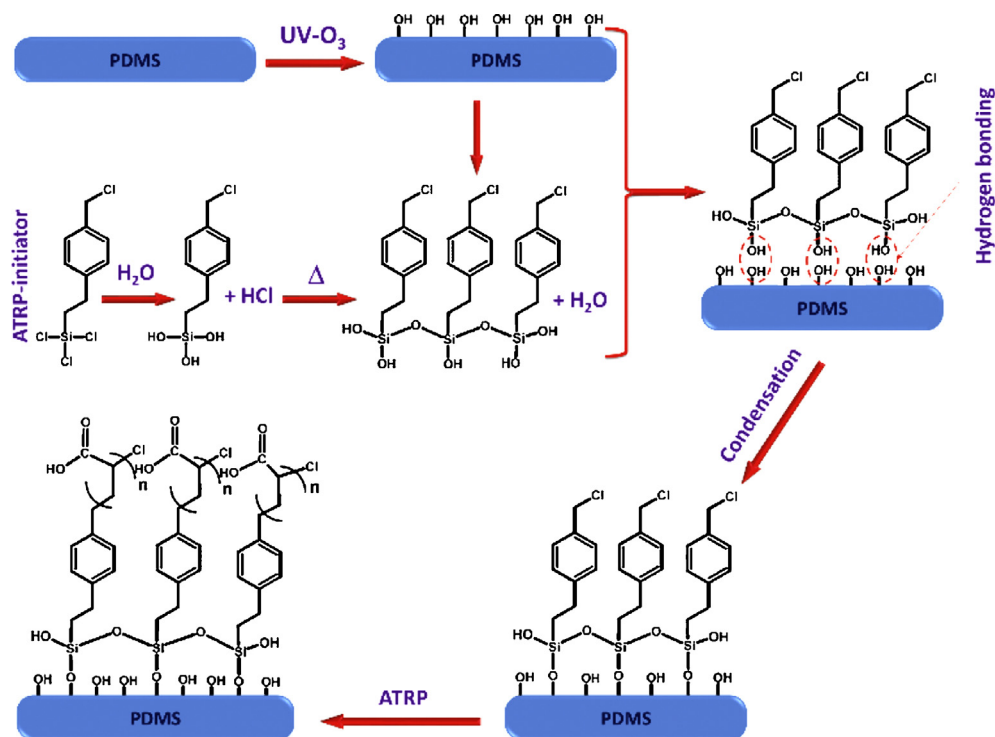
PDMS elastomer kits (Sylgard 184, Dow Corning) were used to make flat PDMS substrates. ((Chloromethyl) phenylethyl) trichlorosilane (Gelest, ≥95%) was used to form surface immobilized ATRP initiators on the surface of the flat PDMS samples via condensation reactions with hydroxylated PDMS. In one method, toluene (Honeywell, HPLC grade, ≥99.8%), was used to dilute the silane coupling agent. Sodium chloride (ACS grade, EMD Chemicals), sodium hydroxide (Sigma–Aldrich, ACS grade, ≥97%), copper(I) bromide (Aldrich, 99.999% trace metals basis), 2,2'-bipyridyl (BIPY, Sigma–Aldrich, ≥99%), and acrylic acid (Alfa Aesar, 99.5% stabilized with *ca.* 200 ppm 4-methoxyphenol) in water, that was purified through a Direct-Q Millipore purification system, were used for surface initiated atom transfer radical polymerization (SI-ATRP).

2.2. Experimental procedure

Flat PDMS substrates were obtained by casting Sylgard 184 PDMS prepolymer with its cross-linking catalyst at 10:1 (w/w) ratio, after 20 min of degassing *via* vacuum, on a clean microscope glass slide. The cross-linking took place at 100 °C for 1 h. After that, the PDMS was peeled from the microscope glass slide and kept in

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Scheme 1. PDMS surface modification via surface immobilization of silane for SI-ATRP of acrylic acid.

a desiccator for several days to ensure complete cross-linking so as to minimize effect of time on surface properties. The flat PDMS substrates were placed into an ultraviolet-ozone (UVO) chamber for 2 h so that hydroxylation could occur.

Immediately after the hydroxylated PDMS substrates were removed from the UVO chamber, drop-coating technique was used to immobilize the silane coupling agent. This method simply required drop-coating of 100% silane coupling agent on the PDMS substrate for 1 min, rinsing the sample with toluene, and drying with nitrogen. No visible swelling was observed after deposition of the initiator on the surface. However, a very slight bending and swelling of the sample was observed during the rinsing with toluene. The samples were kept in a desiccator at 70 °C at least for 24 h to make sure that de-swelling of the PDMS is complete.

Surface-initiated atom transfer radical polymerization of acrylic acid on immobilized silane initiator modified PDMS substrates was carried out in 100 mL round bottom flask with an aqueous solution of acrylic acid, CuBr, and BIPY, NaCl and at the pH of 13. In a typical experiment, 3.3303 g (0.0462 mol) of acrylic acid, 10.3 mg (0.0718 mmol) of CuBr, and 26.0 mg (0.1665 mmol) of BIPY were dissolved in 40 mL water. Afterwards, pH of the mixture was raised to *ca.* 13 via slow introduction of NaOH pellets. Once pH 13 was reached, 6.9 g (0.1181 mol) of NaCl was added. With NaCl fully dissolved, the mixture was deoxygenated via argon bubbling for 2 h at 0 °C using an ice-bath. The resulting solution was subsequently transferred through needle and syringe to an Argon purged 100 mL round bottom flask containing the immobilized silane initiator modified PDMS substrates, and the reaction was allowed to proceed at 50 °C for 1 to 5 h. After polymerization, the aqueous reaction mixture was removed; and, the PAAc grafted PDMS substrates were rinsed thoroughly with ultrapure water, and then dried in a stream of argon. Schematics of the graft polymerization procedure by the SI-ATRP have been shown in Scheme 1. Note that, the initiator immobilization takes place in three steps. Hydrolysis of the silane compound by the present humidity in the reaction media, hydrogen bonding between hydroxyl groups on the surface of the

sample and silane compounds, and the subsequent condensation assisted by thermal treatment in which water is eliminated over time [45,46].

2.3. Chemical characterization

ATR-FTIR was used to qualitatively determine the surface composition of the resultant samples. ATR-FTIR analysis was performed using a Bruker TENSOR 27 with LN-MCT detector. The ATR device was manufactured by PIKE technologies and is made of diamond crystal.

XPS was used to confirm presence of acrylates on the modified samples using a Thermo Scientific K-Alpha XPS spectrometer (ThermoFisher, E. Grinstead, UK). The samples were run at a take-off angle of 90° (relative to the surface). A monochromatic Al K α X-ray source was used, with a spot area (on a 90° sample) of 400 μ m. Charge compensation was provided using the combined e⁻/Ar ion floodgun. Position of the energy scale was adjusted to place the main C 1s feature (C–C) at 285.0 eV. Survey spectra were taken (PE – 200 eV, 1 eV step, 50 ms dwell, 1 scan), followed by spectral regions of interest collected at low energy resolution (PE – 150 eV, 0.2 eV step, 50 ms dwell; Si 2p–1 scan, Cl 2p–5 scans, C 1s–1 scan, O 1s–1 scan and Na 1s–5 scans; from which the relative atomic percentage At% were obtained. High resolution spectra were further obtained (PE – 25 eV, 0.1 eV step, 50 ms dwell) for Cl 2p (20 scans), C 1s (10 scans) and O 1s (10 scans). The instrument and all data processing was performed using the software (Avantage vs. 4.84) provided with the instrument as well as the appropriate sensitivity factors (modified Scofield).

2.4. Characterization of surface properties

Global surface topography of the native and modified PDMS samples were characterized using an Rtec optical profiler (San Jose, CA). We performed the interferometry with 10X magnification. The samples were gently pressed and adhered to microscope slides to

ensure flat orientation on the scanning spot. The scanning range was kept at 1 mm.

The water contact angle on dry samples was measured to monitor the change in hydrophobic nature of the original PDMS at each step of modification. Sessile contact angle measurements using a custom made apparatus was employed for this purpose. Droplets of about 10 μL were deposited on the samples with the rate of 20 mL/hr. At least four images of the liquid droplets deposited on the surfaces were analyzed to extract the contact angle at the three-phase contact line.

The peak force tapping mode AFM was used to determine the surface morphology and the roughness of a small spot on the dry PDMS sample before and after modification with silane compound and PAAc. The tests were carried out using a Dimension Icon Scanning Probe Microscope (SPM) (Bruker, USA) at room temperature with a silicon tip/silicon nitride cantilever (Bruker, USA), which has a resonant frequency of 70 kHz and a spring constant of 0.4 N/m. To have a better insight about configuration changes of the grafted polymer chains to the PDMS samples, we also performed the AFM tests under immersed conditions. For this, the prepared PAAc grafted PDMS samples were tested by AFM while immersed in a NaOH solution of pH 12.

A series of friction tests were carried out to determine the effect of surface modification on the film lubrication behavior in terms of coefficient of friction (COF) of the samples. Tests were performed by a custom-made setup equipped with two perpendicularly arranged load-cells recording the force and displacement. One set of tests were done using a hemispherical PDMS lens with 6 mm diameter as a probe. In another series of friction tests, similar probes but modified with PAAc were used. A sequence of friction test includes: (1) approaching a probe towards the sample with the constant velocity of 1 $\mu\text{m/s}$, (2) indenting the sample to the preload of 2.5 mN, and (3) sliding the sample under the probe with the constant velocity of 500 nm/s. The normal force was kept constant during the sliding and both lateral force and displacement were recorded by the lateral load cell. All friction tests were carried out in aqueous condition in a liquid cell. As the pK_a of the acrylic acid is about 4.5, we chose two extreme acidic and basic conditions to detect any possible response to solution conditions. For this, dilute solutions of HCl with pH of 2 and NaOH with pH of 12 were prepared both having the ionic strength of 0.01.

3. Results and discussion

3.1. Spectroscopic characterizations of the SI-ATRP modification process

The PAAc-hydrophilized PDMS was characterized by different analytical techniques to ensure the success of the chemical modification and acquire a better understanding of the modification process. Fig. 1 shows the ATR-FTIR spectra for unmodified PDMS (a), silane treated PDMS (b), and the PAAc grafted PDMS (c) that has undergone 5 h SI-ATRP reaction. Two peaks at 754–870 cm^{-1} and 1230–1280 cm^{-1} belong to stretching vibration of Si-CH₃. The peak at 1170–1200 cm^{-1} belongs to stretching vibration of Si-(CH₂)_x-. Characteristic peaks at 990–1130 cm^{-1} belong to stretching vibration of Si-O-Si. PAAc grafted PDMS exhibited a broad peak at 2900–3500 cm^{-1} which belongs to -OH stretching. This broad peak might include several species including surface absorbed water. Typical characteristic peaks for stretching vibration of carboxylic acid OH should be seen at 2500–3400 cm^{-1} . Typical characteristic peaks for stretching vibration of Si-OH should be seen at 3200–3400 cm^{-1} . Thus, broadening of the peak to frequencies higher than 3400 cm^{-1} can be indicative of characteristic peak for stretching vibration of OH in water. This water may be absorbed

to the surface as the surface is hydrophilic. Note that we have not seen any visible trace of water condensation on the surface of samples over time. More subtly, there appeared two small peaks at the wavenumber *ca.* 1620 cm^{-1} and 2850 cm^{-1} on the PAAc grafted PDMS spectrum which are characteristic peaks for carbonyl and methylene stretching, respectively. Thus, as the carbonyl distinctively belongs to the acrylates in our system, the presence of PAAc may be confirmed. It is worth noting that the depth of penetration in an ATR-FTIR test may influence the intensity of the peaks. The depth of penetration, d_p in an ATR-FTIR test is defined as:

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2 \theta - n_2^2)^{\frac{1}{2}}} \quad (1)$$

where n_1 and n_2 are the refractive indices of sample and ATR crystal, respectively. λ is the wavelength of the incident IR beam and θ is the angle of incidence of the IR beam relative to a perpendicular from the surface of the crystal. For 1000 cm^{-1} and 45° incident angle for a diamond probe, the depth of penetration is around 2.0 μm . This might be why there is no discernible difference between the unmodified PDMS and silane treated PDMS samples; perhaps the penetration depth of ATR-FTIR is far beyond the surface layer of immobilized silane. The strong absorption of PDMS beneath the surface may have masked the absorption peaks of the immobilized silane species. Likewise, the low intensity of the characteristic peaks for the modification species suggests that the modification reactions are limited to the surface [44,47,48].

Fig. 2(a) shows the XPS results for of the native PDMS (i), immobilized silane PDMS (ii), and PAAc grafted PDMS (iii–iv). Emphasis is placed on the Cl 2p signal at binding energy of about 200 eV indicating the successful immobilization of the silane initiator to the PDMS surface. The native PDMS (i) has no Cl 2p peaks, but the Cl 2p peak is present after silane treatment. As SI-ATRP is initiated, there appears a decline in Cl 2p peak intensity by the time. Both Fig. 2(b) and Fig. 2(c) represent the high-resolution XPS spectra for the Cl 2p and C 1s peaks of all four samples. Spectra (ii), (iii) and (iv) in Fig. 2(b) confirms the presence of covalently bonded chlorine atoms due to the characteristic peak at *ca.* 200 eV. The reduction of the Cl 2p signal intensity from spectrum (iii) to (iv) is indicative of the depletion of immobilized chlorine compound due to the ATRP reaction. There is a slight decrease in the intensity of the Cl 2p signal after 1 h polymerization. However, the Cl 2p signal intensity decreased significantly (almost disappeared) after 5 h polymerization reaction, indicating the most of chlorine had been depleted. The following studies focused on the samples treated with 5 h polymerization time. In Fig. 2(c), a small hump around 289 eV binding energy in both spectra (iii) and (iv) unequivocally buttresses the presence of carboxylates and accordingly PAAc on the surface of the PDMS samples, as reported in other works in the literature [38,48].

3.2. Influences of the modification on the optical, roughness, topological properties of PDMS

Fig. 3(a–d) demonstrates the optical interferometer images and a photograph of the neat and modified PDMS sample obtained from drop-coating silanization. According to Fig. 3(a), the roughness value, RMS, for the neat PDMS sample, on a scanning range of 1 mm, was determined to be 49 ± 3 nm. According to Figs. 3(b–c), immobilization of the initiator followed by aqueous SI-ATRP caused a noticeable increment of roughness. The drop-coating of the initiator had a slight effect on the roughness of the native sample changing the RMS to 210 ± 22 nm. Fig. 3(d) shows a photograph of the modified PDMS samples. Clearly, the PDMS sample has retained most of its optical and surface properties.

We compared the efficiency of initiator immobilization using drop-coating technique to that of other common techniques such as

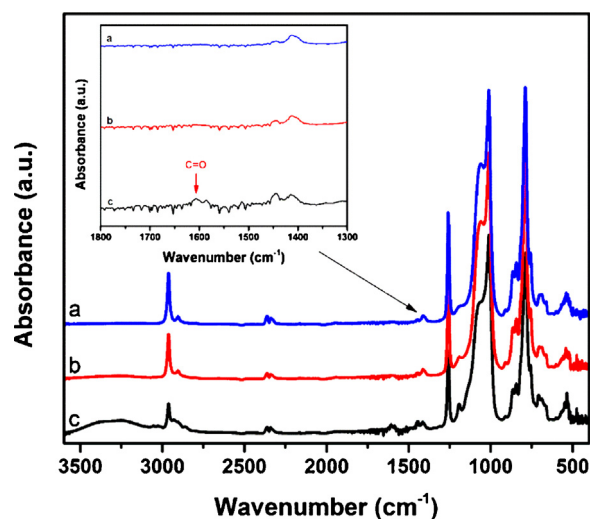


Fig. 1. FTIR-ATR spectra of (a) unmodified PDMS, (b) immobilized silane modified PDMS, and (c) PAAc grafted PDMS (5 h SI-ATRP reaction time). The inset graph shows magnified spectra between 1300 and 1800 cm⁻¹ to highlight the subtle changes of the carbonyl group peak at 1620 cm⁻¹.

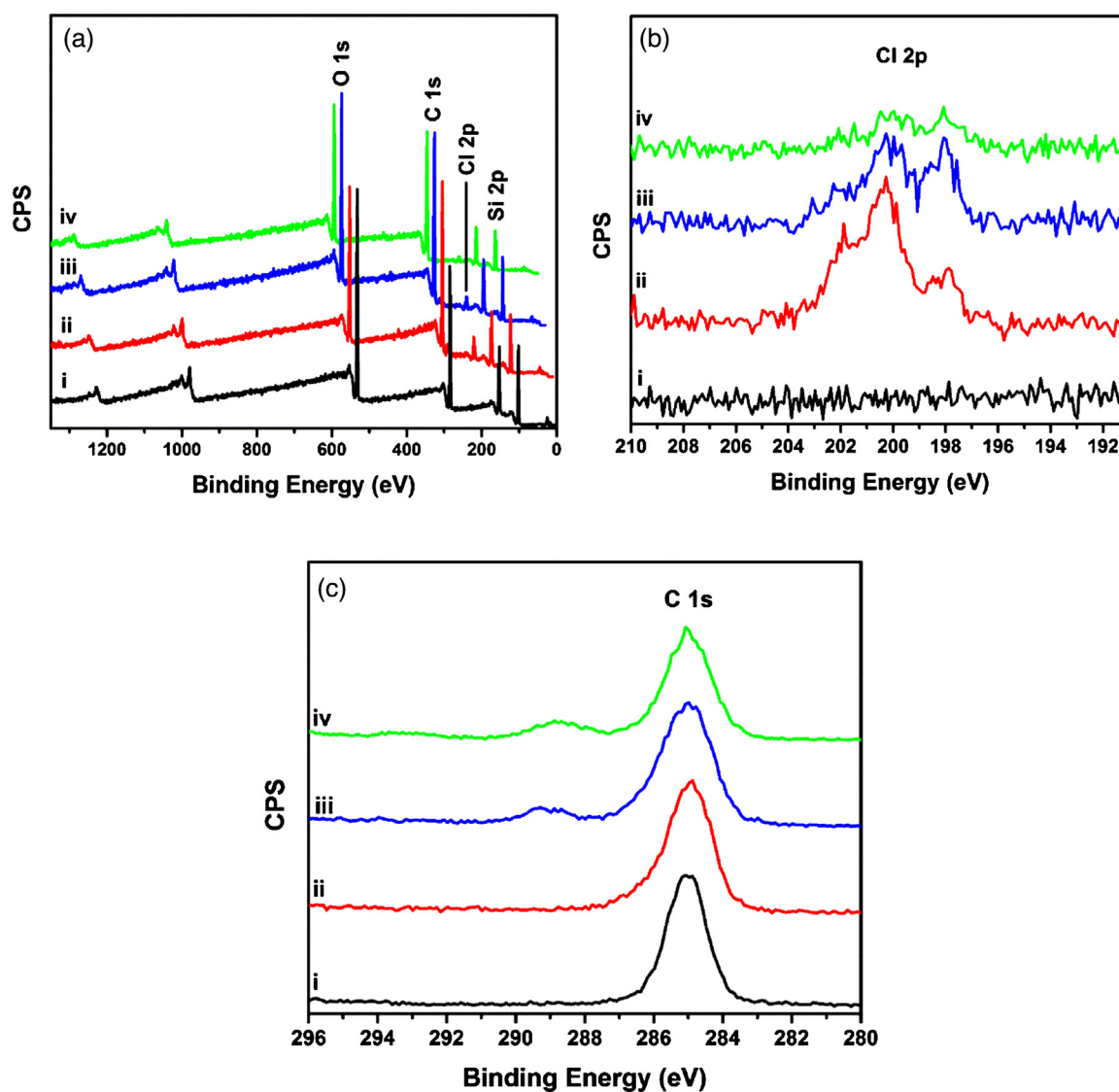


Fig. 2. (a) XPS wide scan spectra, (b) high resolution XPS spectra for the Cl 2p spectral line region, and (c) high resolution XPS spectra for the C 1s spectral line region; (i) unmodified PDMS, (ii) immobilized silane modified PDMS, (iii) PAAc grafted PDMS after one hour of SI-ATRP, and (iv) PAAc grafted PDMS after five hours of SI-ATRP.

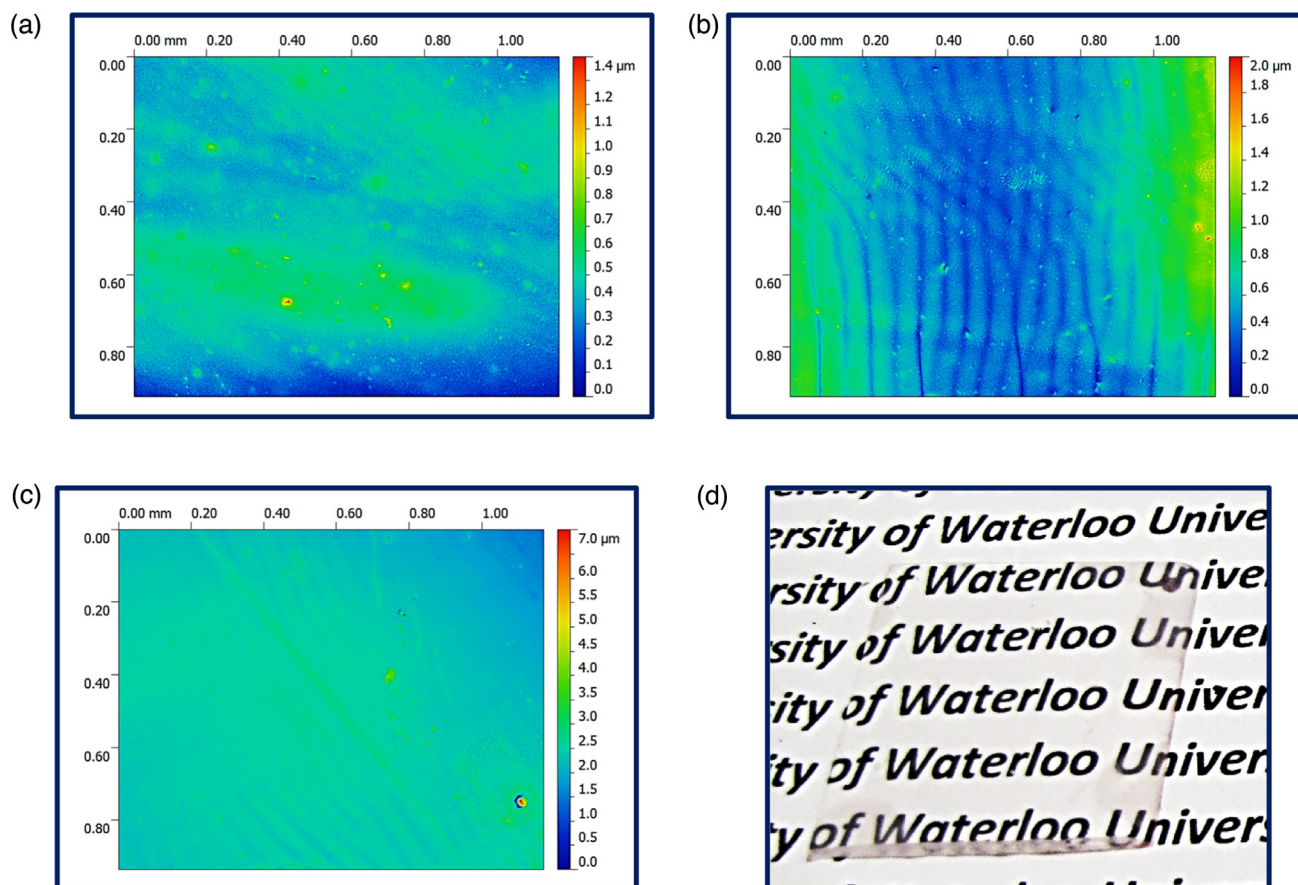


Fig. 3. Optical interferometry images for (a) neat PDMS, (b) initiator immobilized PDMS by drop-coating technique, and (c) PAAc grafted PDMS. Figure (d) shows a photograph of the PAAc grafted PDMS sample.

gas phase and liquid phase chemical deposition. Notably, the drop-coating method has the most non-invasive effect on the physical and optical properties of the PDMS. In fact, a very short period of deposition of the silane compound on the PDMS renders the chemical reaction and immobilization of the initiator to the PDMS but restricts the reaction only to the surface of the material. As a result, the modified sample remained flat and unbent; and, it retained its transparency after both silanization and polymerization processes. In contrast, the use of organic solvents is indispensable for the liquid phase chemical deposition of initiator. As a result, the PDMS piece swells and becomes significantly larger than its original size. Although recovering to its original size after post drying, the sample will be bent, cracked on the surface, opaque, and significantly stiffer. We speculate that the swelling of the PDMS facilitates the chemical reaction of the initiator even in the bulk of the PDMS sample. This can potentially change the chemical properties and also discoloration of the bulk PDMS. Likewise, for gas phase deposition of the silane compound, the flat PDMS sample becomes blunted, rough, opaque, and stiffer. Damage to the surface of the modified PDMS through a similar route is also observed by Xiao et al. [31]. The vapor phase deposition and solution based techniques lead to drastic roughening of the surface with visible discoloration and bumps on the surface leading to RMS values of several micrometers [49].

After topographical analysis of the initiator-immobilized samples, AFM tests were employed to scrutinize the surface topography of the PDMS at the molecular scale before and after modification. As the pK_a of PPAc is around 4.5, we postulated that the chain conformation of the grafted PAAc chains might be altered and more tangibly detected by AFM when exposed to different pHs. For this, we performed AFM tests in both dry and immersed conditions using

a liquid cell. Fig. 4(a–d) shows topographical change of the PDMS surface before and after modification. The scanning range for these images is $2\ \mu\text{m}$ and the standard deviation for measurements of 3 arbitrary spots on each sample was within less than 25% margin. The surface of the native PDMS is homogenous and smooth with RMS roughness of about 1.3 nm (Fig. 4(a)). Note that the deviation of RMS in this set of images from those obtained by optical interferometer is due to the difference in the scanning size. As can be seen in Fig. 4(b) the surface of the silane modified sample is fairly homogenous but it has become rougher and shows lumps sporadically dispersed on the surface. We believe these lumps are results of the sudden deactivation of the silane initiator when they get exposed to humidity and absorbed or poised on the surface of PDMS [49]. The RMS estimated for this sample is 2.21 nm indicating very slight change in RMS comparing to the native PDMS through drop-coating method. Fig. 4(c) indicates the topography of the PAAc grafted PDMS sample. Interestingly, wave-like clusters of polymer chains with sharply defined grain boundaries appeared on the surface after polymerization and the RMS increased to 8.37 nm. The increment of the roughness compared to that of the previous steps confirms the grafting of the PAAc chains on the silane modified samples. Moreover, the presence of such collapsed conformation for polymer chains on the surface can be attributed to the drying process after polymerization [39]. Fig. 4(d) shows the topography of the PAAc grafted PDMS sample immersed in NaOH solution with pH of 12. RMS value has not changed dramatically and is close to the value obtained in dry condition, i.e. 7.14 nm. Note that change in the conformation of long grafted polymer chains when exposed to a proper medium could result in a tangible change in surface roughness values. This is not the case in our experiments. This suggests a

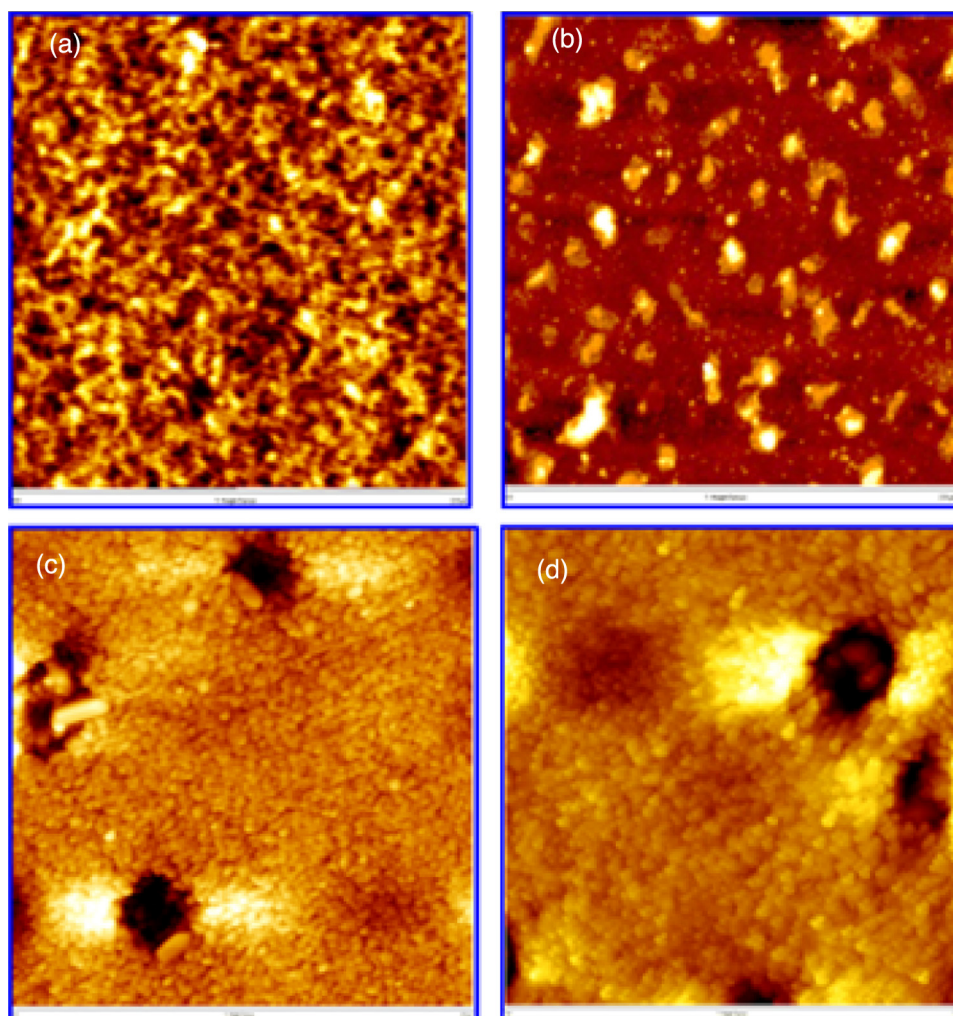


Fig. 4. Tapping-mode AFM images obtained from test on the (a) native PDMS film, (b) silane modified PDMS film, (c) PAAc grafted PDMS film in dry condition and (d) PAAc grafted PDMS film in fully immersed condition. The scan size for all tests were kept 2 μm .

low degree of polymerization of PAAc in our experiments. Further modification of the polymerization process is needed in order to achieve longer polymer grafted chains.

3.3. Water contact angle characterization of the hydrophilized PDMS surfaces

The hydrophilicity of the modified PDMS samples were characterized in terms of static water contact angle. Fig. 5 shows the water contact angles measured for each step of modification. The contact angle for the native PDMS sample was found to be $117^\circ \pm 2^\circ$, which is fairly in accordance with the values reported in the current literature. UVO treatment of the PDMS sample led to full spreading of water on the hydroxylated PDMS, showing dramatic shift of the surface properties from hydrophobic to hydrophilic. However, as expected, we observed that the hydrophilic surface of UVO-treated samples is not stable; it became hydrophobic in a very short period (*ca.* 30 mins). The hydroxylated PDMS sample then was treated with silane initiator. The contact angle for this sample raised to $104^\circ \pm 5^\circ$. The successful treatment of the hydroxylated PDMS facilitates condensation of the chlorines bonded to silicon atoms. Thus, we expect that the chloro-methylene groups attached to the phenyl group are exposed to the water which results in increment of contact angle to hydrophobic condition. Moreover, the surface of the silane modified PDMS sample is rougher compared to that of both

native PDMS and the UVO treated sample. This might also have effects on the contact angle of this sample. Finally, the contact angle for the PAAc grafted PDMS sample was obtained to be $67^\circ \pm 5^\circ$, verifying the success of hydrophilization of the hydrophobic PDMS surface. Note that the contact angle measurements were carried out on the hydrophilized sample stored in an evacuated desiccator one week after the treatment. Thus, the hydrophilization of PDMS is irreversible. This is because of the successful covalent bonding of the PAAc chains to the initiator molecules immobilized on PDMS during the ATRP [20,31,38].

3.4. Friction behavior of the hydrophilized PDMS surfaces

The effects of polymer brushes on the tribological properties of the polymers have been extensively studied in the literature. It has been shown that the repulsion between polymer brushes grafted on tribo-pairs when swollen in a solvent can preserve a thin fluid layer at the interface so as to reduce the friction [50]. We had speculated that the hydrophilic layer on the modified PDMS surface can be hydrated in water and act as a lubrication layer so as to reduce the hydrophobic interaction between PDMS surfaces and lower the friction at them. To test this, a series of friction tests was performed in aqueous conditions. The normal load during the friction was kept at 2.5 mN and the variation of the friction force against lateral displacement was recorded to determine the coefficients of friction.

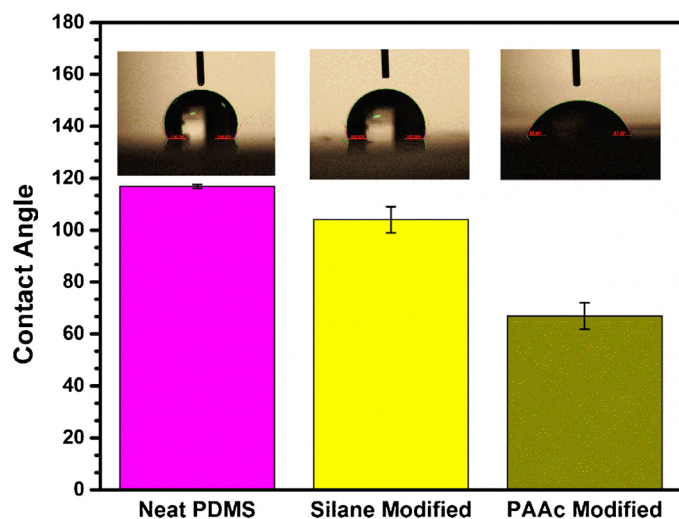


Fig. 5. Results of the contact angle measurement tests on PDMS sample before and after surface modification.

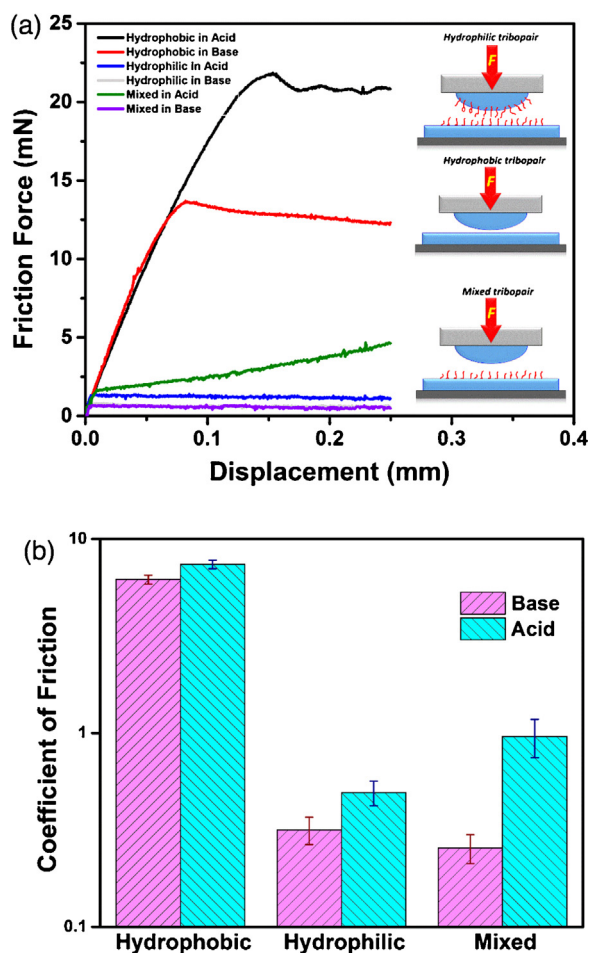


Fig. 6. (a) Friction force vs displacement graphs and (b) variation of COF for friction tests between three different tribopairs immersed in two different solutions.

We used the average value of the friction force in the pseudo-steady region of the friction curve and divided it by the normal force to obtain the coefficient of friction. Fig. 6(a) shows typical friction force vs displacement graphs; Fig. 6(b) represents the average coefficient of friction for a stroke of 250 μm for three tribopairs: (1) native PDMS probe vs native PDMS sample (hydrophobic), (2)

native PDMS probe vs PAAc modified PDMS sample (mixed), and (3) PAAc modified PDMS probe vs PAAc modified PDMS sample (hydrophilic). The hydrophobic tribopair has the highest friction force, while both mixed and hydrophilic tribopairs have remarkably lower friction force. Apparently, there was no lubrication layer between the hydrophobic tribopair; the interface is rather dry displaying noticeably higher coefficient of friction. Note that there is just a slight difference between hydrophilic and mixed tribopair arrangements. That is, the friction force can be reduced only if one side (either sample or probe) of the tribopair is hydrophilic. These results are in accordance with the observations by Bongaerts et al., who studied the tribological behaviors of PDMS–PDMS contacts [51].

The significant reduction of friction upon the hydrophilization of PDMS was observed in both acid and base conditions as shown in Fig. 6(b). Compared to this large reduction, the influence of acid/base condition of the aqueous solutions is secondary; and the friction in the basic conditions is always lower than that in acidic conditions. The friction coefficient of the unmodified hydrophobic PDMS in the basic condition is 16% lower than that in the acidic condition. We suspect that immersing of the PDMS in acid and base solutions might have different effects on the physical properties of the neat PDMS. The coefficient of friction for the hydrophilic tribopair in the basic condition is 36% lower than that in acidic condition. PAAc chains can undergo repulsion and consequently extension when exposed to solvents with $\text{pH} > \text{pK}_a$ (≈ 4.5) or they collapse when the pH of the surrounding solvent is lower than pK_a . Since the PDMS is modified with poly(acrylic acid), a greater level of deviation is anticipated between the friction force in basic and acidic conditions. The coefficient of mixed tribopair in the basic condition is 76% lower than that in acidic condition, showing the largest difference among the three tribopairs. Likely, both the responses from the surface PAAc layer and the bulk PDMS contributed to the difference. Compared to the effect of surface PAAc hydrophilization of PDMS on its overall friction behavior which reduced the friction about 20 times, the effect of solution pH is secondary. However, these friction results indicate that application of PAAc-modified PDMS in aqueous conditions may need to consider both the bulk and surface responses to the solution conditions. Future research work needs to decouple these surface and bulk effects by using a pure PDMS and examining the effect of amount or grafting density of PAAc on the PDMS surface. Nevertheless, the friction behavior of the hydrophilized PDMS surfaces suggested that the ATRP Modification with poly(acrylic acid) through the developed drop-coating method of immobilization of the silane Initiator can effectively render the PDMS to be hydrophilic and to have low friction that are desired properties for the applications of polysiloxanes in such areas as soft tribology and microfluidic devices.

4. Conclusions

Surface of the PDMS films was hydrophilized by a benign ATRP modification with poly(acrylic acid) while preserving its optical transparency. For this, a simple but effective drop-coating method of immobilization of the silane initiator was developed. Immobilization of the initiator was followed by the atomic transfer radical polymerization of the acrylic acid. Grafting of the PAAc chains from the PDMS sample was confirmed through ATR-FTIR, XPS chemical analyses. The results confirmed successful immobilization of the silane initiator through the new drop-coating method and also successive grafting of the PAAc chains. The hydrophilicity of the modified PDMS was investigated by the water contact angle tests and friction tests in aqueous conditions. The hydrophilization of PDMS reduced the water contact angle from 116° to 67° , which is stable over weeks. The induced hydrophilicity leads to a drastic

reduction of the coefficient of friction due to facilitated full-film lubrication. One great advantage of our technique is that it limits the chemical reaction near the surface with minimal damage to the PDMS surface which preserves its transparency.

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