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Novel Fluorous Hybrid Surface Modification Characterized by Wetting Dynamics, Morphology and Nanomechanics

Sithara Nair
Virginia Commonwealth University

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Novel Fluorous Hybrid Surface Modification Characterized by Wetting Dynamics, Morphology and Nanomechanics

A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science at Virginia Commonwealth University

Sithara S. Nair
Director: Dr. Kenneth Wynne
Professor of Chemical Engineering

Department of Chemical and Life Science Engineering
Virginia Commonwealth University
Richmond, VA 23284-3028
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Novel Fluorous Hybrid Surface Modification Characterized by Wetting Dynamics, Morphology and Nanomechanics

Sithara S. Nair

Department of Chemical and Life Science Engineering, Virginia Commonwealth University Richmond, VA 23284

Abstract

The surface response of a polymer substrate to external stimuli such as initial wetting is controlled by the outermost molecular layer. Thus, changes on the nanoscale may be engaged to control macroscale wetting behavior. Our work has predominantly focused on surface modification of conventional polyurethane coatings (HMDI-BD-PTMO). Studies on network constrained phase separation and facile polydimethylsiloxane surface functionalization led to the discovery of a simpler one-step and more general approach to functional polymer surfaces that we have designated as “Bottle-Brush Nanoglass” (BB-NG) after the two principle components: (a) a polyoxetane soft block “spine” with side chain “A” bristles and triethoxysilyl chain ends and (b) an alkoxy silane that together with BB chain ends comprise precursors to a “nanoglass”, NG phase. This paper focuses on the extent of modification for a conventional aliphatic polyurethane using a range of fluoropolyoxetane (poly(trifluoroethoxymethyl-methyl oxetane) diol) or 3F diol (1) based modifier concentrations. Upon generating a blend of the polyurethane with the modifier, the BB-NG which is a minor constituent of the blend, phase separates to provide the topmost layer of the coating. Initial results demonstrate that the modified polymer coatings exhibit an expected increase in contact angles with water. Wetting behavior was characterized using the sessile drop technique as well as Dynamic Contact Analysis (DCA, Wilhelmy Plate). Surface composition as well as near surface topology and morphology are characterized by X-ray
Photoelectron Spectroscopy (XPS) and Tapping Mode Atomic Force Microscopy (TM-AFM) respectively. Contrast in phase images reflect the surface modulus and viscoelasticity, from which physical form or compositional differences may be deduced. These characteristics have also been explored in our study by hardness tests via nanoindentation.
CHAPTER 1

1.1. Introduction

Distinctive combinations of properties make nanostructured sol–gel materials that are molecular hybrids of organic and inorganic components of mounting significance for a broad range of applications including catalysis, environmental science, electronics, biomedical science and industrial separations. Hence engineering the surface chemical composition and structure is one of the fundamental objectives of coatings research. This research focuses on a fluorous hybrid blended with conventional polyurethane to affect a novel approach to surface modification.

Linear polyurethanes are polymer chains created by an addition reaction between a diisocyanate and a polyl in the presence of a catalyst and other additives causing formation of urethane linkages. Polyurethanes are comprised of hard and soft segments that interact with each other leading to interesting surface and bulk morphologies. The resulting polymer can be polyurethane or a polyurethane-urea depending on whether the chain extender is a diol or a diamine. Hydrogen bonding between the urethane and urea moieties causes close packing in “hard segment domains”, which are rigid and provide toughness and strength to the polyurethane. The soft segments on the other hand grant flexibility. Phase transitions of polyurethanes provide information regarding the range of use temperatures. Fig. 1.1 depicts a model of a polyurethane.
Polyurethanes can be thermoplastics or thermosets, depending on the formulation. In a typical polyurethane synthesis, a polyol monomer is end-capped with a diisocyanate as shown in Scheme 1.1 to produce a polyurethane prepolymer. The prepolymer chains are reacted with a diol/diamine chain extender to form high molecular weight, linear polyurethanes.

 Scheme 1.1. Polyurethane synthesis using a diol chain extender
In polyurethanes, it is established that the soft blocks are driven to the air-polymer interface mainly due to a certain amount of immiscibility between the soft and the hard blocks.\textsuperscript{1-7} This phenomenon is thermodynamically driven so as to minimize surface energy as the soft block is usually nonpolar.

The surface response of a substrate to external stimuli such as initial wetting is controlled by the outermost molecular layer. Desirable functionality at the surface may be derived by directing specific functional groups to the air-polymer interface.\textsuperscript{8-11} Changes on the nanoscale may thus be engaged to control macroscale wetting behavior.

An important focus of the Wynne research group is surface modification of conventional polyurethane coatings.\textsuperscript{12} HMDI-BD-PTMO (Fig. 1.2) thermoplastic elastomers are often employed as the bulk or “base” polyurethane. Here HMDI = hexamethylenediamine, BD = butanediol, PTMO = poly(tetramethylene dioxide).

![Fig. 1.2. The “base” polyurethane HMDI-BD-PTMO](image)

Oxetanes are heterocyclic organic compounds having a four membered ring. 3-bromomethyl-3-methyl oxetane (BrOx) is a useful starting material for many oxetane monomers. BrOx is synthesized on a large scale from 1,1,1-tris(hydroxymethyl) ethane by undergoing a bromination followed by subsequent treatment with NaOH to yield the product, which is then reacted with the respective alcohol by Williamson synthesis to produce the desired
oxetane monomer (Scheme 1.2, a). R stands for any functional side group that is desired for the specific application. If R denotes a semifluorinated moiety, the monomer is 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane designated 3Fox, which undergoes a cationic ring opening polymerization to produce the polyoxetane, P(3FOx) (Scheme 1.2, b). Since, the reaction entails chain termination by incorporating hydroxyl moieties at the chain ends, the P(3FOx) polyoxetane will also be referred to as 3F diol in this study.

![Scheme 1.2. Synthesis of a) Polyoxetane b) 3F diol](image)

As a unique class of materials, fluoropolymers possess a combination of properties, including high thermal and chemical stability, low surface energy, low flammability and low coefficient of friction.\(^{13}\) While surface modifiers with C\(_6\)F and C\(_8\)F side chains have been used\(^ {14}\) to impart low surface energy via phase separation as well, these moieties can degrade to perfluorooctanoic acid (PFOA) which is bioaccumulative.\(^ {15}\) Thus, the surface modifier approach has an extra challenge of surface modification with short fluorocarbon side chains.\(^ {16}\) Hence our work focuses on employing a C\(_1\)F fluorous polyoxetane block (3F) for surface modification.

The fluoropolyoxetane P(3FOx) (poly(trifluoroethoxymethyl-methyl oxetane) diol) is a commercially available soft block precursor. Purification of 3F diols is a crucial procedure to be conducted before modifier synthesis. This is essential to get rid of the cyclics and other low
molecular weight species that are generated during ring-opening polymerization of the fluoropolyoxetane. These species can prove to be contaminants in the polyurethanes as they diffuse to the water surface and interfere with accurate determination of contact angles by reducing water surface tension. Such contamination is problematic for potential use in biomaterials and microfluidics that necessitate minimal or negligible leaching. Fig. 1.3 shows the gel permeation chromatography data for 3F-4.5 diol before and after liquid-liquid extraction.

**Fig 1.3.** GPC chromatogram for 3F-4.5 diol A) As-received with high amount of cyclics B) After 8 extractions with negligible cyclic content (adapted from Zhang, W.; Henke, D.; Presnall, D.; Chakrabarty, S.; Wang, C.; Wynne, K. J. *Macromol. Chem. Phys.* **2012**, *213*, 1225-1238)
1.2. Polymer Characterization Methods

1.2.1. Goniometry

The goniometer, an instrument employed for contact angle measurement\textsuperscript{23} at a liquid-solid interface, utilizes the sessile-drop method.\textsuperscript{24} Here a single reading is taken on a static sessile drop shortly after its deposition. As a thermodynamic equilibrium is reached at the solid, liquid and the gas phase (at the contact line), a static contact angle is captured. Young's equation is used to describe the interactions between the forces of cohesion and adhesion and measure what is referred to as surface energy.

\[
\gamma^\text{lv} + \gamma^\text{sl} = \gamma^\text{hv} \cos \theta \quad \text{(Eqn. 1.1)}
\]

\[ \theta \] is the contact angle
\[ \gamma^\text{sl} \] is the solid/liquid interfacial free energy
\[ \gamma^\text{sv} \] is the solid surface free energy
\[ \gamma^\text{lv} \] is the liquid surface free energy

A surface with a stable, sessile drop water contact angle over 90° is hydrophobic. This condition is exemplified by poor wetting, poor adhesiveness and a low solid surface free energy. A surface with a low contact angle is hydrophilic. This condition reflects water drop spreading, better adhesiveness, and higher surface energy. Fig. 1.5\textsuperscript{25} shows the sessile drop images of water and hexadecane with a condensation-cured polydimethylsiloxane coating. From these results, it
was evident that the surface was hydrophobic with a contact angle of 115° with water and at the same time, modestly oleophilic, with a hexadecane contact angle of 23°.

**Fig 1.5.** Sessile drop images and contact angles of water and hexadecane with a condensation cured PDMS coating

### 1.2.2. Atomic Force Microscopy (AFM)

In AFM (Fig. 1.6) the sample is scanned by a microfabricated tip that is mounted to a cantilever. While scanning, the force between the tip and the sample is obtained by monitoring the deflection of the cantilever. A topographic image for the sample is obtained by plotting the deflection of the cantilever versus its position on the sample. Alternatively, it is possible to plot the height position of the translation stage. This height is controlled by a feedback loop, which maintains a constant force between tip and sample. Image contrast arises because the force between the tip and sample is a function of both tip–sample separation and the material properties of tip and sample.
Near-surface phase separation in polyurethanes has been the subject of several Tapping Mode – Atomic Force Microscopy (TM-AFM) studies. In this mode the oscillating cantilever contacts the surface of the sample intermittently and the lateral friction between the tip and the sample is insignificant. This not only reduces wear of the tip but causes only minimal damage to the sample. If soft and hard blocks are well phase separated, then at light tapping (\( r_{sp} > 0.95 \)) only the surface soft domain interacts with the AFM tip, resulting in a featureless phase image. If the proximal interaction with the sample is increased by decreasing the setpoint ratio (\( r_{sp} \)), that is, tapping harder, then near-surface hard blocks are observed in artificial color images as yellow domains in a brown background. If the polymer is poorly phase separated, then hard domains are resolved even at light tapping.

**Fig. 1.6.** Schematic of operation of an AFM (adapted from Butt, H. J.; Cappella, B.; Kappl, M. *Surface Science Reports* 2005, 59, 1-152)
Fig. 1.7\textsuperscript{11} shows the AFM images of the base polyurethane HMDI-BD(50)/PTMO under light tapping. The lighter yellow domains represent the hard blocks and the dark background indicates soft blocks.

![AFM Images](image)

**Fig 1.7.** TM-AFM height (1 x 1 µm) images of base polyurethane HMDI-BD(50)/PTMO  

a) \( r_{sp} = 0.97 \)  
b) \( r_{sp} = 0.95 \)  
(adapted from Kurt, P.; Gamble, L. J.; Wynne, K. J. *Langmuir* 2008, 24, 5816-5824)

### 1.2.3. Dynamic Contact Angle Analysis

Dynamic Contact angle (DCA) analysis follows the Wilhelmy plate technique.\textsuperscript{31} Wettability analysis via force distance curves is illustrated schematically in Fig. 1.8. This technique can also elucidate whether or not contamination of the interrogating liquid occurs via the material being tested. A thin plate of known dimensions is suspended from a computer-monitored microbalance over a vessel containing liquid of known surface tension. Wetting force on the plate is measured as it is immersed in or withdrawn from the liquid, and is used to calculate surface tension using the Wilhelmy equation:

\[
\gamma = \frac{F}{l \cdot \cos \theta}, \quad \text{(Eqn. 1.2)}
\]
where $F$ is the force derived from respective mass ($m$) changes on immersion and emersion, $g$ is the gravitational constant, $P$ is the perimeter, $\gamma$ is the liquid surface tension, and $\theta$ is the contact angle.

In a typical experiment, a coated slide is attached to an electrobalance and a beaker of water is placed on the stage, which is raised/lowered at a specified rate. The resulting advancing (adv) and receding (rec) force distance curves (fdc’s) provide $\theta_{\text{adv}}$ and $\theta_{\text{rec}}$ via Eqn. 1.2. Extrapolating the fdc to the point of immersion eliminates the need for a buoyancy correction to $F$. Multiple cycles may be conducted without disturbing the system. Contact angle hysteresis is calculated as the difference between $\theta_{\text{adv}}$ and $\theta_{\text{rec}}$. Interpretation of fdc’s can contribute to chemical and physical information about surface heterogeneity, surface roughness, surface cleanliness, surface polarity, and surface stability. DCA measurements by the Wilhelmy Plate method allows for determination of wetting behavior over the entire surface of the coated slide and thus provides valuable information regarding contact angles as well as potential contamination of the interrogating liquid.$^{32}$

---

**Fig 1.8. Dynamic Contact Angle analysis**

A) Advancing angle data  
B) Receding angle data
An important step after performing DCA measurements is determining whether water is contaminated during DCA analysis. Fig. 1.9\textsuperscript{17,22} schematically illustrates this process. Post-DCA test water is checked with a freshly flamed glass coverslip. If water insoluble organic components have leached from the coating, diffusion to the water surface is rapid and fdcs are characterized by varying degrees of hysteresis (Fig. 1.9, A). If no water-insoluble coating constituents leach, overlapping advancing and receding fdcs are observed (Fig. 1.9, B). With no leaching, the wetting behavior for the flamed glass slide is identical to that for the initial test of water surface tension on Nanopure water.

\textbf{Fig. 1.9.} Surface tension test of post-DCA water with a flamed glass slide A) fdc hysteresis due to leaching B) Overlapping curves due to no leaching
1.2.4. X-Ray Photoelectron Spectroscopy (XPS)

XPS, or Electron Spectroscopy for Chemical Analysis (ESCA) is a quantitative spectroscopic technique used to analyze the surface chemical composition and chemical or electronic state of each element. The first high quality X-ray induced photoelectron spectra were produced by K. Siegbahn and his associates in Uppsala, Sweden, revealing the potential of XPS. A typical XPS system is shown in Fig. 1.10. The sample is placed in an ultrahigh vacuum environment and exposed to a low-energy, monochromatic x-ray source. The incident x-rays cause the ejection of core-level electrons from sample atoms. The energy of a photoemitted core electron is a function of its binding energy and is characteristic of the element. Energy analysis of the emitted photoelectrons is the primary data used for XPS. Since each element has a unique set of binding energies, XPS can be used to identify the elements on the surface. Also, peak areas at nominal binding energies can be used to quantify concentration of the elements.

![Diagram of XPS system](image)

**Fig 1.10.** A) Block diagram of a typical XPS system B) Schematic Principle of XPS (adapted from Yoon, S. C. R., B. D Macromolecules 1986, 19, 1068-1079)
For polyurethanes, the extent of phase separation of the domains depends on compositional variables such as the symmetry of aromatic diisocyanate, the type of chain extender (diamine or diol), the number of carbons in linear low molecular weight chain extender, the type of soft segments (polyether or polyester), and the chain lengths of these soft segments. In 1985, S.C Yoon and B.D. Ratner utilized XPS to analyze the surface chemistry of fluorine-containing segmented polyurethanes as a means to study extent of phase separation.\textsuperscript{1} They not only used it to evaluate the presence of hard segments at the surface but also find the effect of chain length on surface aggregation of the soft segments.

\textit{1.2.5. Nanoindentation}

Nanoindentation is a method to measure the mechanical properties such as stiffness of materials at the nanoscale. It is a technique performed using an AFM instrument. In this technique, the area for testing is located using AFM, and the indentations are imaged after testing. The hardness test measures the resistance to the penetration of a material by a microfabricated tip.\textsuperscript{34} As the indenter impinges on the sample, elastic and plastic deformation occurs, which results in the formation of a hardness impression conforming to the shape of the indenter. The tip penetration depth is recorded as a function of applied load, generating force-displacement curves that determine properties including hardness and elastic moduli. By measuring the force required to push the tip into the material compared to the depth, the hardness of the sample can be determined. The degree to which the material returns to its previous shape determines elastic modulus. Hardness is thus calculated using the following equation:

\[
H = \frac{P_{\text{max}}}{A}
\]  
(Eqn. 1.3)
Where \( H \), \( P_{\text{max}} \) and \( A \) are hardness, peak indentation load, and projected area of the impression, respectively. Since the development of several nanoindentation techniques,\(^{35-37}\) mechanics at the nanoscale have been studied for various polymers, nanocomposites, biomaterials, single biological cells and tissues. For example, Kurland, et al., have used this technique to study biological systems (Fig. 1.11\(^{38}\)).

**Fig. 1.11.** Schematic representation of nanoindentation - An AFM tip with radius of curvature, \( R \), under the influence of a vertical, compressive load indents a biological sample to a depth, \( \delta \)  
(adapted from Kurland, N. E.; Drira, Z.; Yadavalli, V. K. *Micron* 2012, 43, 116-128)

**The Oliver-Pharr Model**

One of the most successful methods of nanoindentation analysis was developed by Oliver and Pharr.\(^{39}\) These elasticity-based analyses (Fig. 1.12\(^{40}\)), preferable for relatively thicker samples,\(^{39}\) are normally applied to the unloading data for an indentation measurement. The underlying assumptions of this analysis method include:

1. The unloading behavior of the material is characterized purely by elastic recovery
2. The sample is an elastic infinite half-space
3. The sample is homogeneous and isotropic
The procedure for this analysis is fitting a power law function to the unloading segment. This yields the contact stiffness, $S^*$, as slope of this function at maximum load. It thus becomes possible to derive the indentation modulus and the indentation hardness.

Siedlecki, et al., used nanoindentation via AFM to characterize the surface mechanical properties of poly(urethane urea) biomaterials in air and in water. Indentation force displacement curves were obtained that determined the depth profile of mechanical properties. These results confirmed an outermost soft segment layer covering hard domains located 2–20 nm subsurface in air. Regions having intermediate modulus values lying between the hard and soft domains were found at the boundaries of hard and soft domains. This research confirmed earlier studies of Runt, et al.; but provided quantitative depth profiling.

Fig. 1.12. Force-displacement curve according to the Oliver-Pharr Analysis, where $S^*$ is the slope of the tangent to the unloading curve at the peak indentation load ($P_{\text{max}}$) (adapted from VanLandingham, M. R. Journal of Research of the National Institute of Standards and Technology 2003, 108, 249-265)
CHAPTER 2

2.1. Introduction.

Only a small quantity of fluorinated species is needed to provide a surface with low surface energy as the fluorinated species migrate toward the air/film interface to minimize interfacial energy.\textsuperscript{42-49} In recently reported research,\textsuperscript{50} the modification of conventional polyurethane was described using fluorous polyurethanes (requiring several steps in synthesis) that serve to surface-concentrate the soft block.\textsuperscript{12,51,52} Interesting topology in terms of complex rugosity resulting in high contact angles with water (of about 107° $\theta_{\text{adv}}$) was observed for the “neat” 3F-polyurethane, i.e U-3F-4.5, where U-3F denoted the fluorous polyurethane and 4.5 the number average molecular weight in kDa.

The main focus of the present study was to

a) Further investigate some of the preliminary results of this work

b) create modified surfaces with a 3F phase separated domain where the bulk polyurethane is changed from higher modulus (U50) to lower modulus (U30)

The thermodynamically driven tendency of the fluorous groups to surface concentrate has been employed to “chaperone” other functional groups and to provide advantageous functionality, giving potential for use in commercial applications. Such studies on “network constrained phase separation”\textsuperscript{11} have paved the way to the discovery of a simpler and more general approach to functional polymer surfaces. Instead of using fluorous polyurethane for modification, a more efficient method was sought. This led to the discovery of a single-step hybrid approach, that has been designated “Bottle Brush-Nanoglass” (BB-NG, Fig. 2.1) after the two principal components: (a) a polyoxetane soft block main chain “spine” with side chain “A”
bristles and triethoxysilyl chain ends and (b) an alkoxy silane that together with BB chain ends comprise precursors to a “nanoglass”, NG phase.

**Fig 2.1.** “Bottle Brush-nanoglass” hybrid surface modification (For U50, x= 3, y= 2, z= 1; while for U30, x= 3, y= 2, z= 1.2)

In this study, the BB-NG system using hydrolysis/condensation cure was used for surface modification of base polyurethanes, HMDI/BD(30)-(PTMO) or U30 and HMDI/BD(50)-(PTMO) or U50 (Fig. 2.1) where the number in parentheses denotes the hard block weight percent. Upon generating a blend of the polyurethane with the modifier, of which the BB-NG is a minor constituent of the blend, phase separation occurs to provide BB-NG as the topmost layer of the coating. The BB-NG phase forms a functional fluorous layer at the surface while the polyurethane concentrates in the bulk effecting good mechanical properties. As described herein, the surface morphology of these hybrid compositions is dependent on the weight percent of the BB-NG phase.

Another focus of this study has been to provide stability to the functionalized surface. This stability is dependent on the extent of network formation on the mesoscale. Enhancement of the siliceous network was sought by means of an additional component. Saegusa and Chujo
conducted the pioneering work of incorporating TEOS, tetraethoxysilane as a precursor to enhancement of the siliceous domain under water-rich conditions.\textsuperscript{53,54} However, TEOS has been found to be volatile under non-aqueous condensation cure conditions and thus a likely safety hazard in a laboratory setting.\textsuperscript{55} Hence, a crosslinking agent, bis (triethoxysilyl ethane) (BTESE)\textsuperscript{56,57} was employed. BTESE, an ethylene bridged alkoxysilane precursor,\textsuperscript{58,59} has been known to complement structural and functional properties primarily by means of crosslinking,\textsuperscript{60} besides having good reactivity during condensation cure. It has also been shown to be non-volatile during cure at high temperatures of 120 °C based on initial tests.

Thus, in addition to a simpler novel hybrid approach to surface modification of conventional polyurethanes, three potential roles of BTESE were investigated in this study-

1. As a mesoscale builder
2. As an aid to siliceous network formation
3. In stabilization and augmentation of the siliceous domain as well as the modifier

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{btese.png}
\caption{BTESE}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{phase_separation.png}
\caption{Model for phase separation in the hybrid coatings}
\end{figure}
2.2. Experimental.

2.2.1. Materials. PolyFOx diols PF-6320, which we designate 3F-5.2 based on $M_n$ (number average molecular weight) was generously provided by OMNOVA Solutions, Inc. 3-isocyanatopropytriethoxysilane (SII 6455) and bis(triethoxysilyl)ethane (SIB 1817, BTESE) were purchased from Gelest, Inc. Methylene bis (4-cyclohexylisocyanate) (HMDI), poly(tetramethylene oxide) (PTMO) and dibutyltin diacetate (DBDTA) were purchased from Aldrich. Tetrahydrofuran, 99.6% (for analysis ACS, stabilized with BHT), 1,4-butanediol (BD) was obtained from Acros Organics.

2.2.2. Purification of 3F diols. For purification of these 3F diols, the liquid-liquid extraction method described in previous work was followed. In brief, as received 3F diols are extracted 8–10 times with hexane to yield 3F-5.2, where $M_n$ is 5.2 kDa and polydispersity is 1.26.

2.2.3. Polyurethane synthesis. Anticipating AFM studies, two bulk polyurethanes were chosen U50 (with 50 wt% hard block) and U30 (with 30 wt% hard block). (HMDI-BD(50)/PTMO) designated as U50 was prepared using the “soft segment first” method described previously, which is illustrated in Scheme 2.1. HMDI and BD were used for the hard segment with PTMO telechelic as a soft segment. 100 g of U50 was prepared by first reacting 40.58 g of HMDI with 50 g of PTMO(1000) in 100 ml dimethyl formamide (DMF) at 40 ºC and stirred continuously under dry nitrogen purge. 2 drops of 10 wt% DBDTA in THF was also added to the reaction mixture to catalyse the preparation of diisocyanate-terminated prepolymer. The reaction was monitored using a Nicolet 400 FT-IR spectrometer to confirm formation of the urethane linkage. After 30 mins, 9.42 g of BD is added drop-wise into the vessel. The reaction is again monitored using FTIR until the NCO peak (2200 cm$^{-1}$) disappeared, which was after 18 hr. The
polyurethane is then purified by precipitating the mixture into water. After precipitation, the polyurethane is filtered with vacuum and dried in a vacuum oven at 60 °C for 48 hr. HMDI-BD(30)/PTMO(2000) or U30 was also prepared in the same manner, with the hard segment constituting 30 wt% of the polyurethane.

![Scheme 2.1. Synthesis of HMDI-BD-PTMO by the prepolymer method](image)

### 2.2.4. Synthesis of fluorous polyoxetane end-capped with -Si(OEt)_3

With reference to Scheme 2.2, a single-step reaction was carried out. In a 250 mL 2-necked flask under dry nitrogen purge, 5 g of 3F-5.2 diol was stirred with 0.58 ml of 3-isocyanatopropyltriethoxysilane in a molar ratio
of 1:2 in 25 mL THF along with 0.04 g of DBDTA as catalyst for 4 hrs at 40 ºC. End-capping was facilitated by adding the 3F-5.2 drop-wise into the flask using an additional funnel. The reaction was monitored by removing a small sample of the reaction mixture at successive time intervals and obtaining an IR spectrum on KBr discs to confirm disappearance of NCO peak (2200 cm\(^{-1}\)) and OH (3200-3600 cm\(^{-1}\), broad) absorption and appearance of the NH (3300-3600 cm\(^{-1}\)) and CO (1700 cm\(^{-1}\), sharp) peak. End capping 3F terminal hydroxyl groups via formation of urethane linkages marks completion of the synthesis. After 4 hr the NCO peak disappeared, signalling complete end-capping to form the modifier, 3F-Si(OEt)\(_3\) (Scheme 2.2).

![Scheme 2.2. End-capping reaction between 3F-5.2 diol and 3-isocyanatopropyltriethoxysilane giving the modifier, 3F-Si(OEt)\(_3\)](image)

2.2.5. **Coating processing.** The modifier 3F-Si(OEt)\(_3\) (0.2, 0.5, and 1 wt%) was then blended with a 10 wt% base polyurethane (U50) solution in THF (Scheme 2.3). 2 wt% bis (triethoxysilyl ethane) (BTESE) was also added to aid cross-linking and increase the volume fraction of
siliceous domain in the hybrid by generating a complex siliceous network. These blends were stirred for a minimum of 30 min. Viscosity built up in 15 min as hydrolysis/condensation cure is catalyzed by residual DBTDA catalyst. Microscope slides were drip-coated (AFM, ATR-IR) and glass coverslips were dip-coated (DCA). These were solvent-cured at a) ambient temperature for 2-3 hr, b) 60 °C overnight, and c) 120 °C for 2 hr, driving the condensation cure process to completion. Together 3F-Si(OEt)_3 and BTESE are the precursors to the siliceous network. The hybrid coatings were designated as U50-3F-SiO_{1.5}. The “SiO_{1.5}” represents the condensation cure product resulting from the shared oxygen between the alkoxy end groups from the modifier as well as BTESE. The three modified coatings were thus designated as U50-3F-SiO_{1.5}(0.2), U50-3F-SiO_{1.5}(0.5) and U50-3F-SiO_{1.5}(1.0), respectively.

![Scheme 2.3. Hybrid coating preparation](image)
To serve as a control, coatings of the base polyurethane (designated as simply U50) on microscope slides and coverslips were prepared. The entire procedure was repeated using HMDI-BD(30)/PTMO or U30 yielding U30-3F-SiO$_{1.5}$(0.2), U30-3F-SiO$_{1.5}$(0.5), U30-3F-SiO$_{1.5}$(1.0) and U30.

An additional coating was prepared with 1 wt% of the modifier blended with U50 without BTESE. The rest of the processing steps were the same. This coating was designated as U50-3F(1.0). All the coatings were optically transparent.

2.3. Characterization.

2.3.1. Infrared spectroscopy. FT-IR spectra in transmission were obtained using a Nicolet 400 FT-IR spectrometer. Spectra were used to monitor reaction progress for films prepared by solvent evaporation on KBr plates; 32 scans were taken from 500 to 4000 cm$^{-1}$. The spectra were analyzed using Omnic software. The volume of solution evaporated to generate films was kept constant. The y-axis has arbitrary absorbance units.

2.3.2. Wetting Behavior. Static contact angles were obtained using a Rame-Hart goniometer equipped with an LCD camera. A drop was placed on the coated surface and the image was taken immediately. Captured images were analyzed using Dropview image software version 1.4.11.

Dynamic contact angle measurements (Wilhelmy plate method$^{31}$) were performed using Cahn 312 or ThermoScientific Radian 315 instruments. Deionized water was used as probe liquids with an immersion/withdrawal rate of 100 μm/s. Water (Milli-Q, 18 MΩ), surface tension (72.6±0.4 dyne cm$^{-1}$) was checked for purity before each experiment using a flamed glass cover slip. By analyzing the resulting force versus distance curves (fdc’s), advancing (θ$_{adv}$) and receding (θ$_{rec}$) contact angles were obtained. Contact angles (±1−2°) are averages of several
force–distance cycles. Water was tested for purity after each sample reading as well to check for possible leaching of contaminants from the sample.

2.4. Results and Discussion

2.4.1. Synthesis

A new “hybrid” method for end-capping comprises

(1) End-capping 3F-5.2 diol (Scheme 2.2)

(2) Combining the end-capped 3F-Si(OEt)_3 with BTESE (Scheme 2.3) and

(3) Adding 0.2, 0.5 and 1.0 wt% of the modifier to a 10 wt% THF solution of base Polyurethane (U50 or U30)

Reaction progress was monitored using FT-IR during U50 and U30 synthesis at the beginning of the reaction, during the prepolymer formation and during chain extension as well. In the beginning, the FT-IR spectra showed an O-H stretch peak of the PTMO at approximately 3500 cm\(^{-1}\) and an isocyanate peak at approximately 2300 cm\(^{-1}\). Upon reaction of PTMO with HMDI, peaks at 3300 cm\(^{-1}\) and 1724 cm\(^{-1}\) denote formation of urethane amide (N-H) and carbonyl (C=O) groups respectively. During chain extension, the intensity of the isocyanate peak gradually diminished due to the reaction of the prepolymer isocyanate end groups with butanediol.

The extent of reaction between the 3F diol (1) and 3-isocyantaopropyl triethoxysilane (2) was also monitored. Fig. 2.4 shows the IR spectra over a period of 2 hours. FTIR spectrum A (t= 0) has a broad peak at 3500 cm\(^{-1}\) characteristic of terminal -OH for the 3F diol, and a narrow peak at 2250 cm\(^{-1}\) typical of the isocyanate.\(^{62}\) Spectrum B (t= 1 hr) had a small peak at approximately 1700 cm\(^{-1}\) confirming the formation of C=O bond. The isocyanate peak was still
observed, as the reaction was not complete. Spectrum C (t= 2 hr) shows the absence of NCO and OH peaks and the presence of amide NH (3400 cm\(^{-1}\)) along with a more intense C=O absorption. This finding confirms the formation of the modifier with end-capped alkoxy silane moieties.

![FT-IR spectra for the modifier synthesis reaction at time A) t= 0 hr B) t= 1 hr C) t= 2 hr](image)

**Fig 2.4.** FT-IR spectra for the modifier synthesis reaction at time
A) t= 0 hr B) t= 1 hr C) t= 2 hr

2.4.2. **Surface Characterization**

2.4.2.1. **Sessile drop measurement.** Initially, it was thought that end-capped 3F-Si(OEt)\(_3\) could be used alone as a hybrid surface modifier. Fig. 2.5 shows sessile drop contact angles U50-3F(1.0), i.e. U50 with 1 wt% 3F-Si(OEt)\(_3\). On initial contact with water, i.e. at time t= 0, a 93° contact angle was observed, a significant increase from the 82° contact angle for U50. However, at t= 10 seconds, the water spread, with a rapid decrease in contact angle to 85°. Contact angles
were noted every 10 seconds and it was observed that stabilization to 82° occurred after 1 minute.

Augmenting the coating with 2wt% BTESE resulted in high and stable contact angles as described below. High contact angles were observed for both the U50-3F-SiO$_{1.5}$ as well as U30-3F-SiO$_{1.5}$ hybrid coatings. Static contact angles value for U50-3F-SiO$_{1.5}$(0.2), U50-3F-SiO$_{1.5}$(0.5) and U50-3F-SiO$_{1.5}$(1.0) was found to be 94°, 95° and 96° respectively. These values remained fairly stable in over a minute, with only a 1° change, that is within experimental error. These sessile drop images and contact angles are shown in Fig. 2.6.
The static contact angles for U30-3F-SiO$_{1.5}$(0.2), U30-3F-SiO$_{1.5}$(0.5) and U30-3F-SiO$_{1.5}$(1.0) were 101°, 104° and 105° respectively, considerably higher than the contact angle observed for BP-30 alone (88°). These sessile drop images and contact angles are shown in Fig. 2.7. It is also important to note that these high contact angles did not vary significantly with increasing modifier concentration. The modifier proved to be effective in altering the wetting behavior of the coatings at a concentration as low as 0.2 wt%.

Fig. 2.6. Sessile drop images and contact angles in (°) for:
A) U50; B) U50-3F-SiO$_{1.5}$(0.2); C) U50-3F-SiO$_{1.5}$(0.5); D) U50-3F-SiO$_{1.5}$(1.0)

Fig. 2.7. Sessile drop images and contact angles in (°) for:
A) U30; B) U30-3F-SiO$_{1.5}$(0.2); C) U30-3F-SiO$_{1.5}$(0.5); D) U30-3F-SiO$_{1.5}$(1.0)
The results for 3F hybrid surface modification of U50 and U30 confirmed the hypothesis that the crosslinker BTESE contributed to an enhanced siliceous network and helped stabilize the 3F modifier at the surface. The 3 Si atoms at each end of the crosslinker either shared an oxygen atom with the triethoxy silane, or with each other, helping enhance the siliceous domain near the surface of the coating. The model developed to explain this process of network formation and phase separation is shown in Fig. 2.8.

![Diagram showing network formation and phase separation](image)

**Fig. 2.8.** Physical processes leading to network formation and phase separation from solution to condensation cured coatings (from t= 0 to t ~ 24 hr)

The dynamic wetting behavior of the U50-3F(1.0) is attributed to the surface rearrangement of functionality. In air, the 3F moiety surface concentrates as a consequence of phase separation, giving a low surface energy and thus a high contact angle. In water, however, some of the -SiO$_{1.5}$ groups “flip” to the surface, giving a high surface energy and thus inadequate network formation, resulting in a low contact angle. These processes are thermodynamically driven so as to minimize free energy. It was also interesting to note that when the test was
repeated, the same behavior was observed again, demonstrating that no permanent change had occurred and that the surface dynamics were reversible. A model depicting this phenomenon is shown in Fig. 2.9.

![Model depicting the surface rearrangement of functionality](image)

**Fig. 2.9.** Model depicting the surface rearrangement of functionality
A) at time t= 0 B) at time t> 0

2.4.2.2. **Dynamic Contact Angle Analysis.** DCA measurements were done to analyze further the surface wetting characteristics of the hybrid modified coatings. To determine hydrophobicity of the coated surfaces, water was used as the probe liquid.

The DCA advancing contact angles followed a similar trend to the sessile drop measurements. For U50 alone, advancing contact angles of 85° and receding angle of 66° was observed. For all U50-3F-SiO$_{1.5}$ compositions, advancing contact angles between 94° and 98° and receding angles between 46° and 56° were found. This once again showed that the high contact angles are likely due to the surface concentration of the fluorous moieties as expected. However, a post-DCA water check showed slight hysteresis in fdc’s. The fdc’s of the samples are shown in Fig. 2.10, followed by the corresponding contact angle values in Table 2.1.
Fig. 2.10. DCA Force distance curves of U50-3F-SiO$_1.5$; for Cycles 1-3
A) 0.2 B) 0.5 C) 1.0
Table 2.1. Contact angles $\theta_{\text{adv}}$ (advancing angle) and $\theta_{\text{rec}}$ (receding angle) for U50-3F-SiO$_{1.5}$ compositions

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Contact Angles (°)</th>
<th>U50-3F-SiO$_{1.5}$(0.2)</th>
<th>U50-3F-SiO$_{1.5}$(0.5)</th>
<th>U50-3F-SiO$_{1.5}$(1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{\text{adv}}$</td>
<td>98</td>
<td>98</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>$\theta_{\text{rec}}$</td>
<td>50</td>
<td>46</td>
<td>56</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>$\theta_{\text{adv}}$</td>
<td>98</td>
<td>97</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>$\theta_{\text{rec}}$</td>
<td>50</td>
<td>44</td>
<td>54</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>$\theta_{\text{adv}}$</td>
<td>98</td>
<td>97</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>$\theta_{\text{rec}}$</td>
<td>53</td>
<td>46</td>
<td>56</td>
</tr>
</tbody>
</table>

For all U30-3F-SiO$_{1.5}$ compositions, $\theta_{\text{adv}}$ were between 102° and 106° and $\theta_{\text{rec}}$ between 44° and 48°. The advancing contact angles are much higher than those observed for U30 alone ($\theta_{\text{adv}}$ 93°), clearly indicating a surface concentration by the fluorous moieties. The post-DCA water check showed negligible water contamination. The fdc’s for these coatings are shown in Fig. 2.11, followed by the corresponding contact angle values in Table 2.2.
Fig. 2.11. DCA Force distance curves of U30-3F-SiO$_{1.5}$; for Cycles 1-3
A) 0.2 B) 0.5 C) 1.0
Table 2.2. Contact angles $\theta_{\text{adv}}$ (advancing angle) and $\theta_{\text{rec}}$ (receding angle) for U30-3F-SiO$_{1.5}$ compositions

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Contact Angles (°)</th>
<th>U30-3F-SiO$_{1.5}$(0.2)</th>
<th>U30-3F-SiO$_{1.5}$(0.5)</th>
<th>U30-3F-SiO$_{1.5}$(1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{\text{adv}}$</td>
<td>106</td>
<td>103</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>$\theta_{\text{rec}}$</td>
<td>47</td>
<td>48</td>
<td>44</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>$\theta_{\text{adv}}$</td>
<td>105</td>
<td>103</td>
<td>102</td>
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<td></td>
<td>$\theta_{\text{rec}}$</td>
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<td>101</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>$\theta_{\text{rec}}$</td>
<td>46</td>
<td>46</td>
<td>44</td>
</tr>
</tbody>
</table>

Advancing angles characterize the hydrophobic dry surface whereas the receding angle corresponds to a hydrophilic wetted surface. Water hydrogen bonding to the −OCH$_2$-CF$_3$ hydrogens has previously been considered to explain the large contact hysteresis for fluorous systems.$^{12,63}$ Contact angle hysteresis was found to be higher for U30-3F-SiO$_{1.5}$ compositions, showing more extensive surface reorganization in comparison to U50-3F-SiO$_{1.5}$ compositions.

The receding angles observed show that the presence of physisorbed water, charge and polar groups result in a hydrophilic surface once the surface has been wetted. In both cases, however, the contribution of base polyurethane hard block to near surface morphology is likely to be low as the base polyurethane $\theta_{\text{adv}}$ is lower and the $\theta_{\text{rec}}$ is higher than the modified surfaces. The slight change in contact angles as a function of immersion cycle must reflect a combination of chemisorption of water and surface rearrangement. Driven by thermodynamically favorable hydrogen bonding with water, it is likely that some area fraction of near surface hard block of the base polyurethane changes place with the 3F moiety of the modifier.
2.5. Conclusions.

A simpler and more economical, novel hybrid approach to surface modification of conventional polyurethanes was shown in the present study. The fluoropolyoxetane, 3F-diol, was used to alter the surface functionality of the HMDI-BD-PTMO polyurethane with 30 wt% and 50 wt% hard block with interesting results. Optically transparent coatings were prepared. From the DCA and the sessile drop measurements, it is clear that these modified coatings present a fluorous near-surface character. The fluorous species were found to surface-concentrate driven by immiscibility and minimization of surface energy, providing functionality. A significant outcome of this study was the establishment of a crosslinking agent as a means of stabilizing the modified polymer surface. BTESE was found to form a siliceous network, augmenting the siliceous domain. Wetting behavior was found to be altered, with the modified U30 showing higher hydrophobicity (14°-18° increase in contact angle) in comparison to the modified U50 (10°-12° increase in contact angle). Slight or negligible contamination of water was observed with these coatings as is evident from the post-DCA water check. It was also interesting to note that a concentration of modifier as low as 0.2 wt% was sufficient to significantly alter wetting behavior. The extent of phase separation and subsequent surface modification was explored by further characterization of the modified coatings, and is explained in the following chapter.
CHAPTER 3

3.1. Introduction.

Phase imaging is a powerful AFM imaging technique that reveals information about surface structure on the microscale and nanoscale. Phase imaging records the phase shift in signal in tapping-mode AFM. The phase signal provides a measure of the energy dissipation involved in the contact between the tip and the sample. The phase shift is a sort of “delay” in the oscillation of the cantilever during the up and down motion contacting the sample. It thus displays contrast between different regions of the sample, helping to analyze heterogeneous surfaces. The phase shift depends on factors including viscoelasticity, adhesion and contact area. The phase can thus be affected by relative softness/hardness of the sample, or even its chemical nature.

Interpretation of a phase contrast image is sometimes challenging but a useful technique for elucidating mechanical and compositional characteristics. As described in the previous chapter, Zhang, et al., described surface modification using fluorous polyurethanes.\textsuperscript{50} Unexpectedly, it was observed that the neat 3F-polyurethanes exhibited complex surface morphologies owing to phase separation. For example, AFM phase images of the neat 3F polyurethane or U30-3F-4.5 showed micropeaks (Fig. 3.1)\textsuperscript{50} that were attributed to early phase separation of high molecular weight components during solvent evaporation.
Previously, the surface morphology of “neat” HDMI based polyurethanes with fluorous soft blocks were found to be typically nanoscale-smooth with near surface hard block domains revealed by hard tapping.\textsuperscript{8,11,64} However, U30-3F-4.5 had a relatively high molecular weight (110 kDa).\textsuperscript{50} The combination of the high molecular weight of the polyurethane and narrow polydispersity (1.1) of the 3F-4.5 soft block contributed to the surface phase separation shown in Fig. 3.1. The model proposed for phase-separated nanodomains is shown in Fig. 3.2.\textsuperscript{50} Individual soft blocks are represented as Janus-like nanostructures created by self-aggregation of 3F blocks.

\textbf{Fig. 3.1.} AFM (100 x 100 µm) images of U-3F-4.5 A) Height(500 nm) B) Phase C) 3D height
With harder tapping, phase contrast is governed mainly by the different mechanical properties of the sample regions or components. In elastomeric systems, stiffer components can be identified by their more positive (brighter) phase contrast in phase images obtained by hard tapping.\textsuperscript{65} The sensitivity of phase imaging to surface heterogeneity is a key feature of the tapping mode in its application to polymers. Contrast in phase images reflects surface modulus and viscoelasticity, from which physical form or compositional differences may be deduced. These characteristics have been further explored in the present study by a nanoindentation method for hardness tests (modulus mapping).

An initial nanoindentation study was conducted on the 3F polyurethane U-3F-4.5 to investigate the relative moduli of the micropeaks and surrounding area (Fig.s 3.1 and 3.2). From surface topography and phase it was clear that there were two distinct areas that comprised the...
surface of the sample (Fig. 3.1). Conventional interpretation of phase images would indicate that the micropeaks observed should have a higher modulus than the surrounding area. However, our nanoindentation mapping showed that that was not the case. Within experimental error, there was no differentiation between modulus of the micropeaks and that of the surrounding surface. Both had moduli of about 32 MPa (Fig. 3.3).

![Nanoindentation results for U-3F-4.5](image)

**Fig. 3.3.** Nanoindentation results for U-3F-4.5 (from left to right) 5x5 μm 3D height, phase (80°) and modulus chart

Following up on the above unexpected result, the focus of this chapter is not only on exploring the level and extent of phase separation by the fluorous species, but also to clarify the relationship between (a) observation of separated features in phase images (Fig. 3.2), attributed to higher moduli, and (b) the nanoindentation study that did not differentiate between the moduli of the micropeaks and the surrounding area. To further explore the extent of phase separation and level of surface modification in the samples (U30-3F-SiO1.5 and U50-3F-SiO1.5) identified and described in Chapter 2, AFM, XPS and nanoindentation experiments were conducted. Additionally, the bulk modulus (of polyurethanes used for this study) was taken into account.
3.2. Experimental.

3.2.1. Materials. PolyFOx diols PF-6320, which we designate 3F-5.2 based on $M_n$ (number average molecular weight) was generously provided by OMNOVA Solutions, Inc. 3-isocyanatopropyltriethoxysilane (SII 6455) and bis(triethoxysilyl)ethane (SIB 1817, BTESE) were purchased from Gelest, Inc. Methylene bis (4-cyclohexylisocyanate) (HMDI), Poly(tetramethylene oxide) (PTMO) and dibutyltin diacetate (DBDTA) were purchased from Aldrich. Tetrahydrofuran, 99.6% (for analysis ACS, stabilized with BHT), 1,4-Butanediol (BD) was obtained from Acros Organics.

3.2.2. Purification of 3F diols, synthesis of polyurethanes and fluorous polyoxetane end-capped with -Si(OEt)$_3$. These have already been described in Chapter 2.

3.2.3. Coating processing. The modifier 3F-Si(OEt)$_3$ (0.2, 0.5, and 1 wt%) was then blended with a 10 wt% base polyurethane (U50) solution in THF (Scheme 2.3). 2 wt% bis (triethoxysilyl ethane) (BTESE) was also added to aid cross-linking and increase the volume fraction of siliceous domain in the hybrid by generating a complex siliceous network. These blends were stirred for a minimum of 30 min. Viscosity built up in 15 min as hydrolysis/condensation cure is catalyzed by residual DBTDA catalyst. Microscope slides were drip-coated (AFM, ATR-IR) and glass coverslips were dip-coated (DCA). These were solvent-cured at a) ambient temperature for 2-3 hr, b) 60 °C overnight, and c) 120 °C for 2 hr, driving the condensation cure process to completion. Together 3F-Si(OEt)$_3$ and BTESE are the precursors to the siliceous network. The hybrid coatings were designated as U50-3F-SiO$_{1.5}$. The “SiO$_{1.5}$” represents the condensation cure product resulting from the shared oxygen between the alkoxy end groups from the modifier as well as BTESE. The three modified coatings were thus designated as U50-3F-SiO$_{1.5}$(0.2), U50-3F-SiO$_{1.5}$(0.5) and U50-3F-SiO$_{1.5}$(1.0), respectively.
To serve as a control, coatings of the base polyurethane (designated as simply U50) on microscope slides and coverslips were prepared. The entire procedure was repeated using HMDI-BD(30)/PTMO or U30 yielding U30-3F-SiO$_{1.5}$(0.2), U30-3F-SiO$_{1.5}$(0.5), U30-3F-SiO$_{1.5}$(1.0) and U30.

3.3. Characterization.

3.3.1. Infrared spectroscopy. FT-IR spectra in transmission were obtained using a Nicolet 400 FT-IR spectrometer. Spectra were used to monitor reaction progress for films prepared by solvent evaporation on KBr plates; 32 scans were taken from 500 to 4000 cm$^{-1}$. The spectra were analyzed using Omnic software. The volume of solution evaporated to generate films was kept constant. The y-axis has arbitrary absorbance units.

3.3.2. X-ray Photoelectron Spectrometry (XPS). Measurements were carried out with a Thermo Fisher Scientific ESCALAB 250 instrument. Analysis utilized monochromatic Al Kα X-rays and with an X-ray spot size of 500mm and a take-off angle of 90°. Pass energy for survey spectra was 150 eV. Pressure in the analytical chamber during spectral acquisition was maintained at 2 × 10$^{-8}$ Torr while an argon electrostatic flood source affected charge neutralization. Cured triblock samples were cut and attached to the surface of a silicon wafer using carbon tape. Data were analyzed with the Thermo Avantage software (v4.40).

3.3.3. Tapping Mode Atomic Force Microscopy (TM-AFM). A Dimension Nanoscope V (Veeco, CA) atomic force microscope with silicon cantilevers (40 N/m) was used for morphological analysis. Unless otherwise noted, imaging was performed in tapping mode at a set point ratio ($r_{sp} = A_{exp}/A_0$) of 0.8, where $A_0$ is free oscillation amplitude and $A_{exp}$ is the experimental oscillation amplitude.
3.3.4. Nanoindentation.

a. Data Collection.

Surface topography and mechanical properties were determined from Atomic Force Microscope (AFM) imaging and nanoindentation (MFP 3D, Asylum Research, Santa Barbara, CA). Images and indentation profiles for each sample were taken with a Multi75DLC tip (Innovative Solutions Bulgaria Ltd., Bulgaria) with a nominal spring constant of 3.54 N/m, Spring constants were measured prior to each experiment using the thermal fluctuation method.66-68 Data analysis was performed using the software Igor Pro 6 (WaveMetrics, Oswego, OR).

Surface topographic images were collected with the AFM operating in non-contact mode in air at room temperature. Randomly chosen areas of 25 µm² were analyzed for each of the various coatings. Indentation profiles were collected after surface topography was imaged by selecting 20 discrete points on the surface per sample that comprised 10 “features”- either of distinct height or depth depending on the sample, and 10 background surface points. The indentation trigger mode was set to a relative force deflection of 1 nN. Indentation force-distance profiles were then collected by indenting 10 nm into the surface at a rate of 10 nm/s followed by withdrawing at the same rate. The modulus of the observed features as well as the background was determined from the analysis of indentation profiles using fitting to the Oliver–Pharr model.

b. Data Analysis/Oliver-Pharr Model

The elastic modulus of surface points was calculated from the Oliver-Pharr model39 using the relation:
$$E_{sample} = \frac{1 - \nu_{sample}^2}{\left(\frac{1}{E_c} - \frac{1 - \nu_{tip}^2}{E_{tip}}\right)}$$  \hspace{1cm} (Eqn. 3.1)

Where $E_{sample}$, $E_{tip}$, $E_c$ are the elastic modulus of the sample, tip, reduced elastic modulus of the sample respectively and $\nu_{sample}$, $\nu_{tip}$ the poisson ratio of the sample and of the tip. The Oliver-Pharr model was selected over the Hertz model, which is often used for nanoindentation analysis,\textsuperscript{41,69} because it is more suited for soft samples, where there are lower loads and higher surface interactions.\textsuperscript{38,67}
3.4. Results and Discussion

3.4.1. Synthesis

A new “hybrid” method for end-capping comprises

(1) End-capping 3F-5.2 diol (Scheme 1.2)

(2) Combining the end-capped 3F-Si(OEt)₃ with BTESE (Scheme 1.3) and

(3) Adding 0.2, 0.5 and 1.0 wt% of the modifier to a 10 wt% THF solution of base Polyurethane (U50 or U30)

Reaction progress was monitored using FT-IR during U50 and U30 synthesis at the beginning of the reaction, during the prepolymer formation and during chain extension as well. In the beginning, the FT-IR spectra showed an O-H stretch peak of the PTMO at approximately 3500 cm⁻¹ and an isocyanate peak at approximately 2300 cm⁻¹. Upon reaction of PTMO with HMDI, peaks at 3300 cm⁻¹ and 1724 cm⁻¹ denote formation of urethane amide (N-H) and carbonyl (C=O) groups respectively. During chain extension, the intensity of the isocyanate peak gradually diminished due to the reaction of the prepolymer isocyanate end groups with butanediol.

The extent of reaction between the 3F diol (1) and 3-isocyanato propyl triethoxysilane (2) was also monitored. Fig. 2.4 (Chapter 2) shows the IR spectra over a period of 2 hours. FTIR spectrum A (t= 0) has a broad peak at 3500 cm⁻¹ characteristic of terminal -OH for the 3F diol, and a narrow peak at 2250 cm⁻¹ typical of the isocyanate. Spectrum B (t= 1 hr) had a small peak at approximately 1700 cm⁻¹ confirming the formation of C=O bond. The isocyanate peak was still observed, as the reaction was not complete. Spectrum C (t= 2 hr) shows the absence of NCO and OH peaks and the presence of amide NH (3400 cm⁻¹) along with a more intense C=O
absorption. This finding confirms the formation of the modifier with end-capped alkoxy silane moieties.

3.4.2. Surface Characterization

3.4.2.1. X-ray Photoelectron Spectroscopy. Atom % F, O, C, N and Si obtained from XPS at a 90° take-off angle at penetration depth of about 10 nm for coatings U50-3F-SiO$_{1.5}$ and U30-3F-SiO$_{1.5}$ have been listed in tables 3.1 and 3.2 respectively. The theoretical atom % for 3F soft block and the modifier (assuming total surface concentration of modifier as a consequence of complete phase separation) is also shown in these tables.

In case of all U50-3F-SiO$_{1.5}$ compositions, fluorine was found at the surface, confirming phase separation of the fluorinated species. However, the F atom % was found to be much lower than the calculated 3F-SiO$_{1.5}$ atom %. For U50-3F-SiO$_{1.5}$(0.2) and U50-3F-SiO$_{1.5}$(1.0), the C and O atom %, on the other hand, were found to be somewhat closer to the calculated values. For U50-3F-SiO$_{1.5}$(0.5), the C atom % was lower than expected, while the O atom % was higher. The Si atom % for all 3 compositions was significantly higher. These findings suggested partial phase mixing at the surface, with the siliceous network not only at the near surface region of the coating but also at the outermost surface.

In case of all U30-3F-SiO$_{1.5}$ compositions as well, fluorine was found to a significant extent at the surface, confirming phase separation of the fluorinated species. The F atom % was found to be higher than that in the U50-3F-SiO$_{1.5}$ compositions. Interestingly, the Si atom % was zero in both the U30-3F-SiO$_{1.5}$(0.2) and the U30-3F-SiO$_{1.5}$(0.5). Overall, the atom % data was quite comparable to the expected values of the 3F-diol alone. These findings suggest greater surface concentration by the fluorous moieties with the siliceous network embedded at a greater depth, possibly 10 nm. The F atom % was found to be quite high for the U30-3F-SiO$_{1.5}$(1.0);
however, the O, N and Si atom % was quite comparable to the calculated values for the 3F-SiO$_{1.5}$.

**Table 3.1.** XPS results for U50-3F-SiO$_{1.5}$ coatings

<table>
<thead>
<tr>
<th>Designation</th>
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<tr>
<td></td>
<td>C</td>
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<tr>
<td>U50-3F-SiO$_{1.5}$(0.2)</td>
<td>60.2</td>
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<tr>
<td>U50-3F-SiO$_{1.5}$(0.5)</td>
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<tr>
<td>U50-3F-SiO$_{1.5}$(1.0)</td>
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<tr>
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<th>Atom percent (%) (calculated)</th>
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<tbody>
<tr>
<td>3F soft block</td>
<td>58.3</td>
</tr>
<tr>
<td>3F-SiO$_{1.5}$</td>
<td>57.6</td>
</tr>
</tbody>
</table>

**Table 3.2.** XPS results for U30-3F-SiO$_{1.5}$ coatings

<table>
<thead>
<tr>
<th>Designation</th>
<th>Atom percent (%) (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>U30-3F-SiO$_{1.5}$(0.2)</td>
<td>58.2</td>
</tr>
<tr>
<td>U30-3F-SiO$_{1.5}$(0.5)</td>
<td>58.5</td>
</tr>
<tr>
<td>U30-3F-SiO$_{1.5}$(1.0)</td>
<td>53.9</td>
</tr>
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<th>Atom percent (%) (calculated)</th>
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<tr>
<td>3F soft block</td>
<td>58.3</td>
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<tr>
<td>3F-SiO$_{1.5}$</td>
<td>57.6</td>
</tr>
</tbody>
</table>
3.4.2.2. **TM-AFM.** Images for U50-3F-SiO\(_{1.5}\) and U30-3F-SiO\(_{1.5}\) coatings were obtained at a medium tapping (\(r_{sp}= 0.8\)) to investigate topology and morphology for these novel hybrid systems. These images were used to investigate the change in surface features, upon addition of the modifier with U50/U30.

For U50-3F-SiO\(_{1.5}\) coatings, 100 x 100 µm phase images revealed a remarkably complex near surface morphology due to phase separation (Fig. 3.4). Upon further magnification, 10 x 10 µm phase images show rounded protruding domains attributed to 3F modifier, and a surrounding area representing the siliceous network embedded within the base polyurethane U50 (Fig. 3.5). The latter thus corresponds to the surface depletion of 3F. The surface roughness R\(_q\) is low (6-18 nm) for all the coatings, suggesting smooth surfaces. These smooth surfaces also pave way for nanoindentation studies without surface roughness confounding the results. The phase images at softer tapping (\(r_{sp}= 0.9\)) also show these phase separated domains, albeit less prominently, suggesting that the extent of phase separation is high.

With regard to modifier concentration, the AFM images are more or less the same for all samples, except that features of size 0.2-0.4 µm in diameter were observed for the U50-3F-SiO\(_{1.5}\)(0.5), smaller than compared to those observed for the U50-3F-SiO\(_{1.5}\)(0.2) and the U50-3F-SiO\(_{1.5}\)(1.0), which were at least of size 0.8-1.2 µm in diameter. These results are displayed in Figs. 3.4 and 3.5.
Fig 3.4. Phase and corresponding 3D height (100x100 µm) images of U50-3F-SiO$_{1.5}$ coatings ($r_q=0.8$, phase = 60°, $z=500$ nm) A) 0.2 B) 0.5 C) 1.0
For U30F-SiO$_1.5$, AFM images at 100x100 μm revealed a few scattered micropeaks (Fig. 3.6). At 5x5 μm, images revealed phase separation at the sub-micron level, with irregularly-shaped features (Fig. 3.7). The 3D height images revealed that these features were at a depression with respect to the background. The surface roughness $R_q$ is quite low (1-3 nm) for all these
coatings as well, suggesting smooth surfaces. The lower hard block concentration may have provided less competition to the 3F moieties for surface concentration and thus given way to higher surface concentration of the coating by the fluorinated species. However, judging by the fewer micropeaks, the extent of microscale phase separation was less. Aggregation of the fluorous domains at a microscale level did not occur to a considerable extent. This could be due to lower level of immiscibility between the 3F modifier and the base polyurethane.

Fig 3.6. Phase and corresponding 3D height (100x100 µm) images of U30-3F-SiO$_{1.5}$ coatings ($r_{sp}$ = 0.8, phase = 30°, $z$ = 150 nm) A) 0.2 B) 0.5 C) 1.0
With regard to modifier concentration, the AFM images observed are more or less the same for all three samples.

3.4.2.3. Nanoindentation. Firstly, nanoindentation studies were conducted on the U50-3F-SiO₁.₅ coatings. Phase separation of the 3F soft block was clearly observed from the phase
images. To further elucidate any mechanical differences of the areas nanoindentation was used to characterize the nanomechanical properties of the features. Both the protruding features (2D) as well as the dark surface background as observed earlier with AFM scans were subjected to nanoindentation using an AFM tip to a constant depth of 10 nm. The resulting force-distance curves were analyzed to determine if there was a difference in the elastic modulus of the features. As described earlier, a stiff material would require a larger force to indent to the same depth when compared to a more compliant material. The samples were indented to a depth of only 10 nm to avoid probing further into the bulk on the material as the observed features were all on the order of 10 nm height. Indenting further may have measured features that existed further under the surface than initial AFM imaging revealed.

The calculated moduli revealed that the protruding spherical features had moduli much different than that of the background surface. These results have been illuminated in Fig. 3.8. The moduli of these features were found to be about 6-10 times higher than that of the background surface. The features of U50-3F-SiO_{1.5}(0.2) had an average modulus of 2518 MPa while the background had an average modulus of only 397 MPa. In case of U50-3F-SiO_{1.5}(0.5), the rounded features had an average modulus of 613 MPa with the background having a modulus of 87 MPa. Finally, U50-3F-SiO_{1.5}(1.0) had features of 1522 MPa modulus and background of 144 MPa modulus.
In case of U30-3F-SiO$_{1.5}$ coatings, the results are similar to those obtained for the fluorous polyurethane U-3F-4.5. The phase features which are at a greater depth compared to the rest of the background surface, as revealed by the 5x5 µm phase images discussed earlier, in Fig. 3.7, as well as the background surface were then indented using an AFM tip to a constant depth of 10 nm and the resulting force-distance curve obtained was analyzed to determine if there was a difference in the elastic modulus of the features.

**Fig. 3.8.** Nanoindentation results for U50-3F-SiO$_{1.5}$ (from left to right) 3D height, phase (5x5 µm) and modulus chart A) 0.2 B) 0.5 C) 1.0
The calculated moduli revealed that the irregular features had moduli only slightly higher than that of the background, in case of all three coatings, U30-3F-SiO$_{1.5}$(0.2), U30-3F-SiO$_{1.5}$(0.5) and U30-3F-SiO$_{1.5}$(1.0), on the order of about 20-35 MPa. These results have been illuminated in Fig. 3.9. This is quite comparable to the U-3F-4.5 data, which also showed similar moduli results.

**Fig. 3.9.** Nanoindentation results for U30-3F-SiO$_{1.5}$ (from left to right) 3D height, phase (5x5 µm) and modulus chart A) 0.2 B) 0.5 C) 1.0
Thus, the average moduli of the phase separated features in case of U50-3F-SiO$_{1.5}$ are not only significantly higher than those observed in U30-3F-SiO$_{1.5}$, but also present a stark difference in stiffness when compared to the rest of the background surface.

The anomalous result obtained from analysis of the U30-3F-SiO$_{1.5}$ coatings could be reasoned by considering the fact that areas with only sub-micron level phase separation have been indented during our nanoindentation study. These areas also exhibited a partial phase mixing. Additionally, the presence of micropeaks as a consequence of micron level phase separation was limited and sparsely distributed, as evident from the 100x100 µm images of the U30-3F-SiO$_{1.5}$ coatings (Fig. 3.10). Several sections of the coating were analyzed, finding only areas as shown in Fig. 3.9 above. Hence the detection of moduli differences was limited.

**Fig. 3.10.** 3D height (100x100 µm) AFM images of U30-3F-SiO$_{1.5}$ coatings
A) 0.2 B) 0.5 C) 1.0
On the other hand, 1x1 µm AFM images of U50-3F-SiO$_{1.5}$ coatings were scanned to investigate sub-micron level phase separation. Although nanoscale phase separation was observed (Fig. 3.11), besides the micropeaks, no discrete, individual features could be distinguished that was analysed by nanoindentation.

![AFM phase images](image)

**Fig. 3.11.** AFM phase images (1x1 µm) of U50-3F-SiO$_{1.5}$ coatings ($r_{sp} = 0.8$, phase = 60°)

A) 0.2  B) 0.5  C) 1.0

It is to be noted that in Fig. 3.7, the irregular features were darker than the rest of the background being at a greater depth, whereas in Fig. 3.9, the irregular features were revealed by the phase image as being lighter than the rest of the surface. This difference in phase contrast was perhaps due to phase shift. A negative shift of its resonant frequency is caused by attractive forces acting on the AFM probe; whereas a positive shift is caused due to repulsive forces. A
typical amplitude resonance curve of the AFM cantilever is similar to that of a harmonic oscillator (Fig. 3.12)\textsuperscript{70}. If the phase of the oscillation is measured at the initial resonance frequency, $\omega_0$ (as happens in tapping mode), the phase of the oscillation will be negative (with respect to its level at $\omega_0$) in the attractive force regime and positive in the repulsive force regime. The phase changes reflect the tip–sample force interactions in the tapping mode. Hence, lighter features may appear dark and vice versa. It is important to focus on the phase contrast, rather than the artificial color.

![Amplitude and phase versus frequency curves](image)

**Fig. 3.12.** Amplitude versus frequency and phase versus frequency relationships for harmonic oscillator with resonant frequency $\omega_0$. Attractive forces cause a low-frequency shift of these curves (- - - -), repulsive forces cause a high-frequency shift (--- --- ---)


An interesting aspect of the coatings mechanical properties was the bulk modulus of the polyurethanes used. Using an MTS System uniaxial tensile tester, it was found that U30 and U50 have a bulk modulus of 3.7 MPa and 10.1 MPa respectively.\textsuperscript{71} Higher the hard block weight
percent, lower the toughness and hence higher the modulus. A satisfactory comparison between the modulus values measured by nanoindentation and those measured by the tensile tester cannot be made. Hence the possibility of contribution of the bulk matrix to the surface of the coatings in terms of moduli cannot be elucidated. It is however important to note that U50, having higher modulus, is softer than U30.
3.5. Conclusions.

Surface modification of conventional polyurethanes was achieved using fluorous polyoxetanes via a simpler hybrid approach. Surface characterization of these coatings revealed interesting surface morphology as well as micromechanical properties. Surface aggregation of hybrid fluorous domains as a consequence of phase separation was observed by AFM for both the U50-3F-SiO$_{1.5}$ and U30-3F-SiO$_{1.5}$ coatings. The extent of phase separation was further confirmed by the XPS. Surface concentration of the 3F surface modifier was found to be greater in case of the U30-3F-SiO$_{1.5}$ coatings. Partial phase mixing was observed in both cases by XPS, which probes to a depth of around 10 nm. One of the most intriguing outcomes of this study was the significant difference in moduli observed for the features in the U50-3F-SiO$_{1.5}$ coatings. This supported conventional theory that phase separated domains have higher moduli in comparison to the background. U30-3F-SiO$_{1.5}$ coatings as well as the U-3F-4.5 provided a contrasting result. The moduli of the separated domains were similar or only marginally higher compared to the rest of the surface. This could be the case since the microscale phase separation in case of U30-3F-SiO$_{1.5}$ is much lower; the micropores are more sparsely distributed and the nanoindentation studies were conducted on the areas with sub-micron level phase separation.
CHAPTER 4

4.1. Future Work.

A novel hybrid approach to surface modification of conventional polyurethanes was discussed in the preceding chapters. This study however necessitates further exploration into certain important aspects. It would be supportive to understand the significance of the change in bulk modulus of the hybrid coating and thereby the consequence of the polyurethane matrix differing in hard block weight percent. Nanoindentation studies could be conducted on these polyurethanes U30 and U50 to confirm the values found by tensile testing, 3.7 MPa and 10.1 MPa respectively, and make a comparative study. The U30-3F-SiO$_{1.5}$ coatings may be further tested by nanoindentation on areas with microscale phase separation. Additionally, durability, toughness and strength of the coatings via dynamic mechanical analysis and/or tensile tests should be tested in order to explore their potential in commercial applications. The low receding angles exhibited by all the hybrid coatings could be further investigated as it is an important indicator of adhesive and bonding interactions with other materials. This study could be extended using more combinations of BTESE and modifier concentrations so as to optimize effective surface modification process. For example, BTESE concentration could be increased to test enhanced crosslinking effects, and if this has a direct impact on constrainedness of phase separation. Since modifier concentration as low as 0.2% was sufficient to significantly induce phase separation, perhaps lower amounts of modifier may be used as well.
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