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Synthesis of crosslinked polyurethane and Network constrained surface phase separation

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Synthesis of crosslinked polyurethane
and
Network constrained surface phase separation

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

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Synthesis of crosslinked polyurethane and network constrained surface phase separation

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Abstract

To create functional surfaces for soft materials, such as polyurethanes, our approach is to use a semifluorinated surface modifier as minor component to the matrix material. The surface modifier, driving by reduction in surface energy, surface-concentrates to form a functionalized surface layer at the air-polymer interface. In our previous studies, linear PTMO-based polyurethanes were used as the matrix material. These systems undergo slow surface phase separation at room temperature due to the thermodynamically immiscibility of the soft blocks. In this study, chemically crosslinked matrix was developed to provides a steric hindrance to constrain the mobility of surface modifier and to form a kinetically stable surface. The physical property and morphology of base crosslinked matrix has been characterized using DSC, UTT, DMA and AFM. The surface morphology of surface modified crosslinked matrix has been characterized using AFM, DCA and XPS.
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Chapter 1

Introduction

Background. For surfaces of soft polymeric materials it is well known that chain ends and side chains preferentially concentrates at the air-polymer interface. In polyurethanes and similar hard-block/soft-block systems, the soft blocks are preferred at this interface.\textsuperscript{1-7} Given the thermodynamic driving force for soft block surface concentration, we have explored surface modification using soft blocks that surface concentrate a desired function.\textsuperscript{8-11} Our strategy for generating coatings with functional surfaces is directed at novel soft blocks with functionalized side chains. Polyoxetane soft blocks that have a 1,3-propylene oxide main chain with different side chains have been employed with the same hard block as a base polyurethanes.

In our previous studies, linear PTMO-based polyurethanes were used as the matrix material and linear polyurethane surface modifier contained functionalized soft blocks. A general model for this approach to surface modification is shown in Figure 1. Some of these systems undergo slow surface phase separation at room temperature due to soft block immiscibility.\textsuperscript{12,13} This phase separation process was expedited by annealing. In order to create a kinetically stable surface, a chemically crosslinked polyurethane matrix is evaluated in the present study. The hypothesis is that the network structure may constrain the mobility of surface modifier resulting in a kinetically stable surface morphology.

In this study, A chemically crosslinked polyurethane was obtained by substituting a fraction of the difunctional chain extender (butanediol, BD) with a trifunctional hydroxyl polycaprolactone-triol (PCLT). (Figure 1.1) Two processes with different sequences of addition of reagents were investigated. In one sequence, the isocyanate,
PTMO and diol/triol were added simultaneously. Alternatively, a prepolymer was generated from HMDI, and PTMO followed by the later addition of diol/triol. Interestingly, the order of addition of reagents has been found to affect the surface morphologies of the base polyurethane coatings. Below, preliminary observations of gelation at different length scales as a consequence of different processing conditions are described.

After the chemically crosslinked polyurethanes were developed, surface modifier was added in it and crosslinked base polyurethanes were used as the matrix. (details will be discussed in Chapter 2) Due to the low mobility of the surface modifier in the chemically crosslinked network, the phase separation progress was limited. This lead to a surface morphology that is thermodynamically unstable but kinetically stable.

To establish a frame of reference for modified materials, the mechanical and morphological properties of the crosslinked base polyurethanes has been investigated. With the purpose of this study focused on surface morphological effects of matrix crosslinking, the sequence of addition of matrix constituents was studied to investigate the contribution of the matrix to surface morphology. The intention of this study was aimed at obtaining a relatively feature-free surface morphology so that the morphological effects of the surface modifier could be discerned clearly.
Base Polyurethanes: Previously, linear polyurethane was used as matrix material in this study. Linear polyurethanes are segmented block copolymers in the class of thermoplastic elastomers that are composed of alternating hard and soft segments. (Figure 1) The soft segment is typically a low glass transition temperature ($T_g$) polyester, polyether or polyalkyldiol with molecular weights ranging from 400-5000 Da\textsuperscript{14} while the hard segment is derived from diisocyanates linked to a low molecular weight chain extender such as 1,4-butanediol (BD).

Scheme 1.1 shows the sequence of reaction for the “soft block first” preparation of polyurethanes employed in this work. First is the reaction of the polyol with the diisocyanate which produces a diisocyanate capped soft segment. Secondly, the reaction of the diisocyanate caps with hydroxyl groups from the chain extender forms the linear
hard segment of the polyurethane. As seen in Figure 1.2, the urethane groups within these hard segments can form hydrogen bonds with other hard segment urethane groups creating nanocrystalline domains surrounded by an amorphous soft segment region.

The nanoscale ordered hard domains have a high $T_g$ and give the polyurethane mechanical strength while the low $T_g$ amorphous soft segment allows polyurethanes to be flexible. By adjusting the ratio of hard segment and soft segment during synthesis the properties of polyurethanes can vary between very brittle and hard to soft and tacky. If the diisocyanate or the diol chain extender is replaced with a polyisocyanate or polyol with functionalities greater than 2, crosslinked polyurethanes (thermoset elastomers) can be made. A chemically crosslinked polyurethane was obtained by substituting a fraction of the difunctional chain extender (butanediol, BD) with a trifunctional hydroxyl polycaprolactone triol (PCLT). Two processes with different sequences of addition of reagents were investigated. As shown in Scheme 1.2, in simultaneous process, the isocyanate, PTMO and diol/triol were added simultaneously. Alternatively, a prepolymer was generated from HMDI, and PTMO followed by the later addition of diol/triol in sequential process. Interestingly, the order of addition of reagents has been found to affect the surface morphologies of the base polyurethane coatings. Below, preliminary observations of gelation at different length scales as a consequence of different processing conditions are described.
Scheme 1.1. Polyurethane synthesis, prepolymer method

Figure 1.2. Hard segment hydrogen bonding
Differential Scanning Calorimetry (DSC). The thermal properties of polyurethanes are a very important aspect of bulk characterization. To obtain the thermal characteristics of the polyurethanes presented herein, Differential Scanning Calorimetry (DSC) was employed. DSC is a thermal analysis technique based on heating or cooling a sample and reference at a preset rate, while keeping relative temperature the same. As shown in Figure 1.5, the sample and reference are heated in two separate calorimetric chambers by two separate heating circuits that control the average and differential temperatures. The first circuit changes the temperature of the sample and reference at a preprogrammed constant rate. The second heating circuit eliminates any temperature differences between the sample and reference that appear due to exo- or endothermal effects. The amount of heat per unit time needed (heat flux, dq/dt) to keep the sample at
the same temperature as the reference is then measured and plotted as a function of
temperature to produce a DSC thermogram (Figure 1.5). \(^{21}\)

![Diagram of DSC Calorimetric Chamber Schematic](image)

**Figure 1.5.** General DSC Calorimetric Chamber Schematic. \(^{21}\)

From the thermograms, characteristics such as glass transition temperature \((T_g)\)
and melting temperature \((T_m)\) can be obtained (Figure 1.6). \(^{22}\) The \(T_g\) is identified by a
change in heat flow that appears on the thermogram as a baseline shift. This baseline shift
indicates that there is a large increase in the mobility of the polymer chains. The \(T_m\) is
denoted on the thermogram by an endotherm peak which indicates the disordering of
crystalline regions of the polymer. \(^{23}\)

![Diagram of General DSC Thermogram](image)

**Figure 1.6.** General DSC Thermogram. \(^{22}\)
The observed $T_g$ of the soft block is indicative of the amount of phase separation in the bulk of the polyurethane. Since the $T_g$ of the soft block is sensitive to the purity, a soft segment $T_g$ that is close to that of the pure soft segment polymer shows that there is very good phase separation throughout the bulk of the polymer.

In this study, DSC was employed to investigate polyurethane phase separation and to detect the separate $T_g$s and $T_m$s for the hard and soft segments. Miller et al. demonstrated this in the study of 4,4'-methylenebis(phenyl isocyanate)-butanediol-poly(tetramethylene oxide) (MDI-BD-PTMO) polyurethanes made via single and multistep polymerization. As seen in Figure 1.7, thermal transitions for the hard and soft segment can be clearly discerned in thermograms of the annealed samples as inflections at -50 °C (soft segment) and 150 °C (hard segment). These clearly defined transitions are similar to those pure soft segment (PTMO) and pure hard segment (MDI-BD) and therefore signify that the polyurethane morphology consists of two distinct phases or domains.

A systematical investigation on the influence from different hard block weight percentage to melting endotherm for linear polyurethane with PTMO-2000 soft block was done in previous studies. As seen in Figure 1.8, a PTMO melting endotherm at about 20°C is present for 15 wt%, 20 wt% and 25% hard block polyurethanes, but not for 30 wt% hard block polyurethane. The disappearance of this endotherm on 30 wt% hard block polyurethane indicates that the soft segment domain can not form a crystalline phase due to a high degree of physical crosslink on hard block.
Figure 1.7. DSC curves of multistep polyurethanes; annealing temperatures indicated.\textsuperscript{30}
In this study, the influence from chemical crosslink to melting endotherm for polyurethanes was investigated. HMDI-BD(30wt%)-PTMO (2000) was chosen as reference. Theoretically, no melting endotherm should be observed because chemical crosslink can better constrain the mobility of soft segments compare with physical crosslink. Interestingly, an unexpected effect was observed. Further discussion is provided in discussion section.

**Uniaxial Tensile Test (UTT).** Uniaxial tensile test is performed to investigate how materials respond to stress. The most straightforward method of testing the mechanical properties is the tensile test, where a stress is applied to the material while the change in specimen length is being recorded until the sample breaks. The stress, \( \sigma \) (MPa), applied to the specimen is plotted versus the strain (\( \varepsilon \)), which is the change in specimen length induced by the applied force divided by the original specimen length, to produce the stress-strain curve for that material.
From the stress-strain curves the tensile properties of the material can be obtained. Young’s modulus or modulus of elasticity, $E$, is defined as stress divided by strain within the elastic region of the stress strain curve. Amorphous rubbery polymers are soft, extend reversibly and tend to have a low modulus when compared to semi-crystalline or glassy polymers (Figure 1.9). Some rubbery polymers such as polyurethanes exhibit an increase in stress per unit strain prior to breakage. This increase in stress, known as strain hardening, is due to polymer chains rearranging in the direction of the applied force (Figure 1.10). This strain-induced crystallization increases the tensile strength of the polymer, thereby causing an increase in stress with any further increase in strain.

The different behavior between linear polyurethane and crosslinked polyurethane in uniaxial tensile test was investigated in this study. The discussion will focus on the Young’s modulus at initial point and maximum strain at break.

**Figure 1.9.** General Stress-Strain curve for three classes of polymers.\(^{23}\)
Dynamic Mechanical Analysis (DMA). The DMA is a technique where a small deformation is applied to a sample sinusoidally in a constant frequency. DMA determines changes in sample properties resulting from changes in five experimental variables: temperature, time, frequency, force, and strain.

In DMA, the storage modulus $E'$ and loss modulus $E''$ of polymers are measured as a function of temperature ramping from -100ºC to 100ºC. The storage modulus is the energy stored elastically during deformation. Storage modulus is related to elastic modulus of solids. The loss modulus is the energy converted to heat during deformation. Loss modulus is related to damping and energy dissipation. The storage and loss modulus are defined as follows:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$
Loss modulus: \[ E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \]

Tan (delta): \[ \tan \delta = \frac{E''}{E'} \]

Where

- \( \sigma_0 \) is maximum stress,
- \( \varepsilon_0 \) is maximum strain,
- \( \delta \) is phase lag between stress and strain.

Modulus values change with temperature and transitions in materials can be seen as changes in the \( E' \) or tan delta curves. This includes not only the glass transition and the melt, but also other transitions that occur in the glassy or rubbery plateau, shown in Figure 1.11. This study focus on the comparison of soft block melting point existing on storage modulus.
Rubbery plateau is related to \( M_e \) between cross-links or entanglements. For thermosets, no \( T_m \) occurs. Rubbery plateau (2). In semicrystalline polymers, a crystal-crystal slip, \( T_\alpha^* \) occurs. For purely crystalline materials, \( T_g \) occurs. \( T_g \) is related to molecular mass up to a limiting value. Beta transitions are often related to the toughness. For purely crystalline materials, \( T_m \) or \( T_\eta \) — melting or flow, chain slippage (3) or (2) — (1).

**Figure 1.11.** Polymer transition and relaxation temperatures

**Tapping Mode Atomic Force Microscopy (TM-AFM).** Phase separation in block copolymers was first described by Cooper and Tobolsky in 1966 during their study of styrene-butadiene-styrene triblock copolymers. In their investigation they postulated that the properties of this block copolymer were due to clustering or microphase separation. Thomas and coworkers subsequently used electron microscopy to show microphase separation in polyurethanes while in this work, tapping mode atomic force microscopy (TM-AFM) (Figure 3) was used to investigate the nanoscale phase separation in polyurethanes.

Atomic force microscopy is in the group of scanning force microscopy techniques. This technique involves the measurement of different forces (include attractive, repulsive,
electrostatic, and van der Waals) between a sharp tip and the sample surface. Imaging is accomplished by measuring the interaction forces via deflection of a cantilever as the tip approaches the surface. Signal generation in AFM is essentially based on interatomic repulsive forces.

Interactions between the tip and sample can be described by force-distance curves. Figure 1.3 shows how the force changes as the tip approaches the surface. At large separations there is no interaction between the tip and the substrate surface and thus the net force is zero. As the tip moves closer to the surface it jumps into contact because of attractive van der Waals interactions. As the tip moves further towards the sample the total force acting on the cantilever becomes repulsive due to shell electron repulsion. As the tip retracts the force is reduced along the line from position 3 to 4. Below the zero force line the net force acting on the cantilever become attractive due to adhesion thus leading to the tip being held to the surface. At position 4 the

![Figure 1.3](image)

**Figure 1.3.** Force distance curve depicting tip interacting with surface. Adhesion force and the cantilever load are just balanced and the tip flips off the surface as it is further retracted from the sample. In contact mode this pull off force leads to
damaging the surface of soft materials such as polyurethanes and produces damage artifacts in images.

To eliminate this problem, tapping mode AFM (TM-AFM) was used for surface analysis of polyurethanes. TM-AFM involves driving the cantilever near its resonance frequency via the use of a piezo oscillator. This allows only intermittent contact between the tip and the sample surface thus reducing lateral shear forces and the chances of scratching the sample surface. In TM-AFM the information is retrieved from the amplitude signal of the oscillating cantilever since the amplitude of the cantilever will change as it comes across certain topographical features.

By increasing the amplitude “tapping” of the cantilever one can get an idea of the morphology just under the polyurethane surface. With softer tapping, if the polyurethane has good phase separation the tip will only be interacting with PTMO chains. This produces a featureless phase image. With harder tapping, the tip will interact more with the near surface HMDI hard segment. This produces an image that contains features whose intensity increases with harder tapping. Changing of the cantilever amplitude or “tapping” is done by decreasing the amplitude setpoint voltage ($A_{set}$). The ratio of the $A_{set}$ to the initial amplitude setpoint voltage ($A_o$) is the setpoint ratio ($r_{sp}$). Thus with a smaller $r_{sp}$ the cantilever taps harder.

An example of this phenomenon is given in a study of polyurethane-urea block morphology via TM-AFM. As seen from Figure 1.4, the featureless images taken at the higher setpoint ratio (soft tapping) is indicative of the amorphous soft segment being dominant at the surface. At the lower setpoint ratio (harder tapping) the near surface hard segment can be seen in the form of ordered domains previously described. This surface
Segregation of the soft segment is typical for polyurethanes due to the soft segment having a lower surface energy than the hard segment.

Figure 1.4. TM-AFM phase images of polyurethane-urea. Scan size = 500 x 500 nm phase angle 25°. A) Amplitude set point ratio ($A_{sp}/A_o$) = 0.9, B) Amplitude set point ratio ($A_{sp}/A_o$) = 0.8.\textsuperscript{36}
Experimental

Materials. Poly(tetramethylene oxide) (PTMO), polycaprolactone triol, 4,4′-Methylenebis(cyclohexyl isocyanate) (HMDI), methylene chloride (CH$_2$Cl$_2$) and tetrahydrofuran (THF) were acquired from Sigma-Aldrich and used as received. 1,4-Butanediol (BD) was from Acros Organics. 10 wt% dibutyltin dilaurate solution (T-12) was used as catalyst.

Preparation of Linear polyurethanes: Polyurethanes were synthesized by modification of the two step, soft block first method described previously. HMDI and BD were used for the hard segment with 3FOx or PTMO telechelics as a soft segment in solutions of THF.

In the first step, a calculated amount of 3FOx polyoxetane (for PSM) or PTMO (for base PU) in THF was added to excess HMDI in a three-neck round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. After addition of T-12 catalyst (2 drops of 10vol% T-12 in THF), the reactants were kept at 70°C for 3 hr to prepare diisocyanate-terminated prepolymer. In the second stage, calculated amount of BD (diluted in THF) was added slowly in 12 hours with heating continued at 70°C. After all the BD is added into the flask, reaction is kept at 70 °C for 4 hours before cooled to 50°C and precipitated into water/methanol (3:1) mixture for purification. After precipitation, the samples were filtered with vacuum and dried in hood for 2 days followed by drying in a vacuum oven at 65 °C for 24hrs.

The calculated amount of 3FOx and base polyurethanes for 0.5 to 10 wt% 3FOx polyurethane composition were dissolved in 10% solutions of THF. The coatings were
then dip- or drip-coated onto glass slides. Solvent was removed by drying in air for 24 hours followed by 24 hours drying in vacuum oven at room temperature.

**Preparation of crosslinked polyurethanes:** Polyols are crosslinkers in the crosslinked polyurethanes. The ratio of the triol to diol determines the functionality (f), which in turn affects the degree of crosslinking. Different ratios of triol and diol were tested. The selected values of f were 2.1, 2.3, and 2.5. As an example, a 5 gram sample with 30% hard block and triol:diol = 9:1 is composed of 3.5000 g PTMO-2000, 0.2309 g BD, 0.0854 g polycaprolactone triol, 1.2429 g HMDI with dibutyltin dilaurate as catalyst. This yields a crosslinked polyurethane with a functionality of 2.1.

Two processes were used to prepare crosslinked coatings: “simultaneous addition” and “triol last” sequences. The simultaneous process is a one-step polymerization by which all components and THF solvent were mixed initially followed by addition of catalyst. Then coatings were prepared by either dip coating or drip coating depending on the characterization method requirements. As cast coatings were dried in air for at least 24 hours before further removal of solvent at reduced pressure at room temperatures.

The “triol last” process is a three-step process with crosslinking occurring after polycaprolactone triol was added in the last step. This method promotes linear chain extension before the crosslinking. Specifically, the polyether telechelic (PTMO) was allowed to react with diisocyanate for 12 hours and then linear chain extender (BD) was added in a second step. After 5 hours the crosslinker (polycaprolactone triol) was added for the final step. The coating preparation is same as that for the simultaneous process.
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Two processes were used to prepare crosslinked coatings: simultaneous addition and “triol last” sequences. The simultaneous process is a one-step polymerization by which all components and THF solvent were mixed initially followed by addition of catalyst. Then coatings were prepared by either dip coating or drip coating depending on the characterization method requirements. As cast coatings were dried in air for at least 24 hours before further removal of solvent at reduced pressure at room temperatures.

The “triol last” process is a three-step process with crosslinking occurring after polycaprolactone triol was added in the last step. This method promotes linear chain extension before the crosslinking. Specifically, the polyether telechelic (PTMO) was allowed to react with diisocyanate for 12 hours and then linear chain extender (BD) was added in a second step. After 5 hours the crosslinker (polycaprolactone triol) was added for the final step. The coating preparation is same as that for the simultaneous process.

**Characteraction**

**Fourier Transform-IR Analysis (FT-IR) and Differential Scanning Calorimetry (DSC):** FT-IR and ATR-IR spectra of the linear polyurethane and crosslinked polyurethane were obtained using a Nicolet 400 FT-IR spectrometer.
Differential Scanning Calorimetry was carried out on the TA –Q 1000 Series™ instrument (TA Instruments). Measurements were performed using a standard DSC method where the polymer sample was ramped at a heating rate of 10 ºC/min from -90 ºC to 200 ºC, cooled back to -90 ºC and held isothermally for 5 min. Then the sample was ramped at the same rate from -90 ºC to 200 ºC.

**Dynamic Mechanical Analysis (DMA):** Samples for DMA were 5 mm × 50 mm plaques with thickness from 400-600 µm. A TA instruments RSA 3 dynamic mechanical analyzer was employed using a dynamic temperature ramp test method. During analysis sample temperature was ramped from -100 to 100 ºC at 5 ºC/min while tension cycles were set at 1Hz with maximum strain set to 0.05%. Maximum autotension was set to 2 mm with maximum autotension rate of 0.01 mm/s.

**Uniaxial Tensile Testing (UTT):** Sample preparation and instrument used in Uniaxial tensile testing are the same as them used in dynamic mechanical analysis. The initial sample length before elongation was 5 mm. The elongation rate was set to 10 mm/min. Only the initial portion of the stress strain curve are used to determined the modulus of elasticity. Remarkably, none of the samples were break before 650% strain, which is the upper limit of our testing method.

**Tapping Mode Atomic Force Microscopy (TM-AFM):** One-side coated glass slides were prepared by drip coating either from a 10 wt% solution of PU samples or from the reaction mixture after all components are added. The drying conditions are same as those DCA slides. A Dimension Nanoscope V (Veeco, CA) atomic force microscope was used for morphological analysis of polyurethane film surfaces in air. Images were obtained in tapping mode using silicon crystal cantilevers (40 N/m). The tapping force
was increased from soft to hard by decreasing the setpoint ratio $r_q$ or $A_{\text{exp}}/A_o$, where $A_o$ is free oscillation amplitude and $A_{\text{exp}}$ is the experimental oscillation amplitude. For the crosssection characterization, the coating was fractured after quenched in liquid nitrogen and the fractured surface was sliced and mounted on a glass slide for AFM characterization.

**Results and discussion**

*Synthesis.* Progress of the reaction used to make linear polyurethanes was monitored at the start of the prepolymer stage, during prepolymer formation, and during chain extension. Before the addition of T-12 catalyst, 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$^{-1}$ (Figure 1.12A). Upon the 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 (Figure 1.12B). Since the feed had excess isocyanate, the 2300 cm$^{-1}$ peak remained. During chain extension, the intensity of the isocyanate peak gradually diminished due to the reaction of the prepolymer isocyanate end groups with the butanediol (Figure 1.12C).
Due to the nature of crosslinked polyurethanes that they are not dissolvable in solvent after the reaction is completed, ATR-IT was employed to explore their chemistry. Comparisons of ATR-IR spectra for linear and crosslinked polyurethanes showed that all three crosslinked polyurethane compositions had no residual isocyanate. This indicates complete reaction. Isocyanate peak is not detected in any spectra for both simultaneous and sequential crosslinked polyurethanes. When compared to the linear spectra, all the crosslinked polyurethane spectra display the characteristic carbonyl and amide peaks at 1723 cm\(^{-1}\) and 3300 cm\(^{-1}\) respectively.

**Thermal Analysis.** Differential Scanning Calorimetry, DSC, was used to determine the \(T_g\) and \(T_m\) for linear and crosslinked polyurethanes. According to previous study completed by Dr. Brunson, linear HMDI-BD (30wt\%) - PTMO 2000 does not have melting endotherm for soft block due to a relatively high diisocyanate percentage. When hard block percentage reaches 30\% or higher, the density of hard block associated by

![Figure 1.12. FT-IR Spectra for linear HMDI-BD (30wt\%)-PTMO 2000: A) start of prepolymer reaction, B) 1hr prepolymer reaction, C) 4hrs chain extension](image-url)
hydrogen bond is high enough to eliminate any crystallization in soft block. In this case, no melting endotherm for soft block will be detected for linear HMDI-BD (30wt%)-PTMO 2000. In order to confirm this conclusion, DSC works with various cooling rate for linear HMDI-BD (30wt%)-PTMO 2000 was done in this study. As shown in figure 1.13, no melting endotherm was detected on heating curve and no crystallization exotherm was detected on cooling curve. The glass transition of soft block in linear HMDI-BD (30wt%)-PTMO 2000 was observed at -75 ºC, These values are close to the reported $T_g$ for PTMO. No $T_g$ for hard block was observed.

Figure 1.13. DSC for linear HMDI-BD (30wt%)-PTMO 2000 with different cooling rate A) 2 ºC/min, B) 3 ºC/min, C) 5 ºC/min and D) 10 ºC/min.
Similar as linear HMDI-BD (30wt%)-PTMO 2000, Thermograms for HMDI-
(PCLT/BD-2.3) (30wt%)-PTMO 2000 and HMDI-(PCLT/BD-2.5) (30wt%)-PTMO 2000
crosslinked polyurethanes produced by simultaneous process did not show significant
melting endotherm, and a tiny melting peak was observed on HMDI-(PCLT/BD-2.1)
(30wt%)-PTMO 2000. Interestingly, thermograms for crosslinked polyurethane produced
by sequential process showed significant melting endotherm at 20 ºC. (Figure 1.14) The
heat of fusion, $\Delta H_m$ for linear and crosslinked polyurethanes at soft block melting point is
shown in table 1.1. This indicates that soft segment has relatively higher mobility and is
more capable of crystallizing for crosslinked polyurethanes than for linear polyurethanes,
and mobility of soft segment is significantly affected by process. This result indicates that
diisocyanates in linear HMDI-BD (30wt%)-PTMO can better associate to hard block via
hydrogen bond than them in crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO because the
association of hard block can be interrupted by the branched structure of PCLT
crosslinker. As a result, lower hard block density causes higher soft segment mobility in
crosslinked polyurethanes. Meanwhile, it is clear that the melting endotherm for soft
block is significantly affected by the process that sequential process generated more
melting endotherm than simultaneous process. The reason is that even though hard block
cannot well associated in both sequential process and simultaneous process, the higher
scale of gelation in simultaneous can better decrease the mobility of soft segments. The
detail of gelation formation will be discussed in morphology section.
Figure 1.14. DSC for crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO 2000 produced by A) sequential process and B) simultaneous process.

<table>
<thead>
<tr>
<th>Process</th>
<th>Functionality</th>
<th>Soft segment Tm (°C)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequential</td>
<td>F2.1</td>
<td>21</td>
<td>35</td>
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<tr>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>F2.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.1. Soft block melting endotherm for crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO
**Uniaxial Tensile Testing (UTT).** Tensile testing revealed that the degree of crosslinking affects the modulus. For many applications, such as marine anti-fouling coatings, mechanical properties are extremely important for durability and function of coatings. It is essential to reveal the effect from chemical crosslink and process to mechanical properties of polyurethanes. TA instruments RSA 3 dynamic mechanical analyzer was employed to uniaxial tensile testing.

Figure 1.17 shows the stress/strain curve of crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO produced by sequential process and simultaneous process. Remarkably, none of the samples were breaks before 650% strain, which is the upper limit of our testing method. It suggests that the maximum strain of crosslinked polyurethane is sufficient for most coating applications. Interestingly, the modulus decrease with functionality increases for sequential process and increase with functionality increases for simultaneous process. This result indicates that the degree of crosslinking and the process are two important factors that affect the modulus. The reason for the above results is not clear yet, one assumption is that the crosslinking of polyurethane can result in two major effects, one is the destruction of hard blocks (discussed in thermal analysis section), the other one is the formation of gel (will discuss in morphology section). Such two effects causes reverse influences to modulus, which the destruction of hard block decreases the modulus but formation of gel increases modulus. Because sequential process and simultaneous process generate nanoscale gelation and microscale gelation respectively, and microscale gelation can increase modulus much more significantly than nanoscale gelation. The modulus decrease for sequential process due to the density of hard block decreases. On the other hand, the modulus increase for simultaneous process due to the
The density of microscale gelation domain increases. This conclusion indicates that crosslinking is a very flexible strategy in terms of tuning the mechanical properties of polyurethane.

Figure 1.17 Stress/strain curve for crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO 2000 produced by A) sequential process and B) simultaneous process.
Dynamic mechanical analysis (DMA). As seen in the storage modulus (E’) vs. temperature curve, (Figure 1.18) the inflection in the curve between -80 and -60 ºC indicates that the soft segment glass transition was -70 ºC. The storage modulus curve for sequential process had an inflection at 20 ºC which indicates soft segment melting as observed in DSC (Figure 1.14A). This inflection was not observed for simultaneous which also correlate to the DSC results. The inflection seen in the DMA curve at 20 ºC for sequential process is due to the lack of hard block domain and nanoscale gelation cannot significant constrain the soft segments. On the other hand, Simultaneous did not display an inflection at 20 ºC indicating that the soft segments are not a mobile due to the gelation in microscale (detail will be discussed in morphology section).

Figure 1.17 DMA for crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO 2000 produced by A) sequential process and B) simultaneous process.
**Morphology:** Tapping mode atomic force microscopy (TM-AFM) was utilized to provide information on surface morphology and phase separation between the hard and soft segment of the polyurethane. In the phase images of TM-AFM, a light color indicates a more elastic interaction of the tip with the surface, while a darker color indicates interactions with a soft surface feature such as the soft domain in polyurethane as an usual case.

Figure 1.18 shows the TM-AFM 2D height, phase and 3D height images of linear HMDI-BD (30wt%)-PTMO 2000 (Figure 1.18A), crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by simultaneous process (Figure 1.18B) and crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by sequential process (Figure 1.18C) at setpoint ratio of 0.8. Significant differences can be observed between these three surfaces. On phase images, no distinct feature is observed on the surface of linear HMDI-BD (30wt%)-PTMO 2000 and crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by sequential process in micro-scale, and the surface of crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by simultaneous process is dominated with domains in micro-scale. The source of these features is believed as the high level of gelation generated by simultaneous process. Further magnification to nano-scale indicates that the linear HMDI-BD (30wt%)-PTMO 2000 and crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by sequential process coatings are dominated with two different types of nano-scale domains. The nano-scale domains with irregular shapes shown on linear HMDI-BD (30wt%)-PTMO 2000 surface are well known as hard block and soft block domains for polyurethane. Meanwhile, the nano-scale domains with round shape on crosslinked HMDI-(PCLT/BD-
2.1) (30wt%)-PTMO 2000 produced by sequential process are believed as the gelation domain. As seen in height images, the roughness of linear HMDI-BD (30wt%)-PTMO 2000 and crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by sequential process is similar, while crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by simultaneous process has a much higher. Some distinct features are shown on the surface of HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by simultaneous process. The dimension and shape of these noticed features are corresponded to those on phase image. In the case of linear HMDI-BD (30wt%)-PTMO 2000 and crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by sequential process coatings, the surfaces are relatively smooth. No feature in micro-scale is shown on surface.

Figure 1.18 AFM for A) linear HMDI-BD (30wt%)-PTMO 2000, B) crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by simultaneous process and C) crosslinked HMDI-(PCLT/BD-2.1) (30wt%)-PTMO 2000 produced by sequential process. R_{sp}=0.80
The reason why simultaneous process and sequential process generate micro-scale gelation and nano-scale gelation respectively is that sequential addition process results in longer linear segments before crosslinking compare with simultaneous addition. The length of linear segments in XPU network affects surface morphology significantly. In simultaneous process, diols, triols and diisocyanate react faster to facilitate gelation prior to PTMO reaction and this result in large scale gelation (microgel). However, in sequential process, because long linear segments formed in prior to crosslink, diisocyanate is less concentrated and well spaced when triol is added. As a result, smaller sized and better distributed gel sites (nanogel) form. (Figure 1.19)

Figure 1.19 A)Micro-scale gelation and B) nano-scale gelation in crosslinked HMDI-(PCLT/BD) (30wt%)-PTMO 2000.
Conclusions. Considering the results obtained during this study, it appears that process and the degree of crosslinking are two important factors which affect the physical and morphological properties of crosslinked polyurethanes. Uniaxial tensile testing indicates crosslinking is able to either increase or decrease the modulus depend on process. This result demonstrates that crosslinking is a very flexible strategy to in terms of turning mechanical properties of crosslinked polyurethanes.

As seen from DMA and DSC, the crosslinked polyurethanes produced by simultaneous possess has better thermal stability at 0-50 ºC. Unlike crosslinked polyurethanes produced by sequential process, the crosslinked polyurethanes produced by simultaneous did not exhibit any melting or other transitions between 0-50 ºC. This type of stability in this temperature range could facilitate the “freezing” of the desired surface morphology and surface chemistry.

On the other hand, TM-AFM data illustrated that the sequential process generates gelation in much smaller scale compare with simultaneous process. The result indicates that crosslinked polyurethane produced by sequential process has much less effect to the surface morphology after polymer surface modifier is incorporated. For abhesion and other surface modification applications, sequential process may be a better option for matrix to investage the behavior and distribution of surface modifier.
Chapter 2

Introduction

Background. The phenomenon of polymer phase separation has garnered great attention in recent years and has been studied both experimentally and through various modeling approaches.\textsuperscript{38-42} Early studies of polymer phase separation relied on solid and liquid phase separation models developed by Holenberg and Halprin.\textsuperscript{43} These proved inadequate however, because polymers have intrinsic viscoelastic properties which allow them to have behavior intermediate between solids and fluids. For short deformation times, the response for polymers is typical of a solid where stress is proportional to applied strain while during long deformation times, polymer exhibit fluid-like behavior where stress is proportional to strain rate. Therefore polymers exhibit phase separation behavior similar to the fluid model at long time scales.\textsuperscript{44}

Phase separation in polymers occurs via spinodal decomposition where in early stages the phase separation is governed by concentration fluctuations and decrease of bulk energy while in the latter stages, phase separation is controlled by material diffusion and the decrease surface energy.\textsuperscript{45} Depending on the control parameters, the morphology of phase separation can vary from interconnected islands, separated dots, pits to line with ordered or disorder spatial orientation with sizes ranging from a few nanometers to microns.\textsuperscript{46,47}

As described in Chapter 1, the functionalization of polymer surfaces via the use of polymer surface modifiers is a method of creating desired surface characteristic without altering their bulk properties. This chapter discusses polyurethane surface phase separation involving a surface modifier and a linear base polyurethane or a crosslinked polyurethane produced by sequential process. The polymer surface modifier (PSM)
consisting of HMDI-BD hard segment and a semifluorinated soft segment polymer which is designated as 3FOx. As discussed in Chapter 1, the objective of this research was to constrain the mobility of polymer surface modifier (PSM) and decrease the level of phase separation by using the crosslinked polyurethane matrix. The distribution and stability of PSM on linear and crosslinked polyurethane will be investigated and compared in this chapter.

The previous chapter discussed the development and evaluation of crosslinked polyurethane. Compared with simultaneous process, sequential process generates much smaller gelation domains (nano-scale gelation). Because this chapter focuses on the morphological study, crosslinked HMDI/BD(30)-PTMO 2000 was chosen as the matrix in this study.

**Experimental**

**Materials.** Poly(tetramethylene oxide) (PTMO), polycaprolactone triol, 4,4’-Methylenebis(cyclohexyl isocyanate) (HMDI), methylene chloride (CH₂Cl₂) and tetrahydrofuran (THF) were acquired from Sigma-Aldrich and used as received. 1,4-Butanediol (BD) was from Acros Organics. 10 wt% dibutyltin dilaurate solution (T-12) was used as catalyst. Poly(3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane) P(3FOx) was generously provided by OMNOVA Solutions, Akron OH.

**Preparation of Linear polyurethanes:** Polyurethanes were synthesized by modification of the two step, soft block first method described previously. HMDI and BD were used for the hard segment with 3FOx or PTMO telechelics as a soft segment in solutions of THF.
In the first step, a calculated amount of 3FOx polyoxetane (for PSM) or PTMO (for base PU) in THF was added to excess HMDI in a three-neck round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. After addition of T-12 catalyst (2 drops of 10vol% T-12 in THF), the reactants were kept at 70°C for 3 hr to prepare diisocyanate-terminated prepolymer. In the second stage, calculated amount of BD (diluted in THF) was added slowly in 12 hours with heating continued at 70°C. After all the BD is added into the flask, reaction is kept at 70 °C for 4 hours before cooled to 50°C and precipitated into water/methanol (3:1) mixture for purification. After precipitation, the samples were filtered with vacuum and dried in hood for 2 days followed by drying in a vacuum oven at 65 °C for 24hrs.

The calculated amount of 3FOx and base polyurethanes for 0.5 to 10 wt% 3FOx polyurethane composition were dissolved in 10% solutions of THF. The coatings were then dip- or drip-coated onto glass slides. Solvent was removed by drying in air for 24 hours followed by 24 hours drying in vacuum oven at room temperature.

**Preparation of crosslinked polyurethanes:** Polyols are crosslinkers in the crosslinked polyurethanes. The ratio of the triol to diol determines the functionality (f), which in turn affects the degree of crosslinking. Different ratios of triol and diol were tested. The selected values of f were 2.1, 2.3, and 2.5. As an example, a 5 gram sample with 30% hard block and triol:diol = 9:1 is composed of 3.5000 g PTMO-2000, 0.2309 g BD, 0.0854 g polycaprolactone triol, 1.2429 g HMDI with dibutyltin dilaurate as catalyst. This yields a crosslinked polyurethane with a functionality of 2.1.

Two processes were used to prepare crosslinked coatings: “simultaneous addition” and “triol last” sequences. The simultaneous process is a one-step
polymerization by which all components and THF solvent were mixed initially followed by addition of catalyst. Then coatings were prepared by either dip coating or drip coating depending on the characterization method requirements. As cast coatings were dried in air for at least 24 hours before further removal of solvent at reduced pressure at room temperatures.

The “triol last” process is a three-step process with crosslinking occurring after polycaprolactone triol was added in the last step. This method promotes linear chain extension before the crosslinking. Specifically, the polyether telechelic (PTMO) was allowed to react with diisocyanate for 12 hours and then linear chain extender (BD) was added in a second step. After 5 hours the crosslinker (polycaprolactone triol) was added for the final step. The coating preparation is same as that for the simultaneous process.

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**Sample preparation.** For linear matrix, PSM blend solutions were prepared by co-dissolving 0.5, 1, 2 or 5 wt% PSM with base linear PU in THF in a fashion similar to Kurt et al.\(^46\) For crosslinked matrix, 0.5, 1, 2 or 5 wt% PSM was dissolved in THF, and was added to the matrix solution right after the crosslinker was added. Samples were dip coated or drip coated on glass slides. Coatings were stored at ambient temperature for overnight annealed at 60 °C for 24 hours.

**Characteraction**

**Tapping Mode Atomic Force Microscopy (TM-AFM):** One-side coated glass slides were prepared by drip coating either from a 10 wt% solution of PU samples or from the reaction mixture after all components are added. The drying conditions are same as those DCA slides. A Dimension Nanoscope V (Veeco, CA) atomic force microscope was used for morphological analysis of polyurethane film surfaces in air. Images were obtained in tapping mode using silicon crystal cantilevers (40 N/m). The tapping force was increased from soft to hard by decreasing the setpoint ratio \(r_{sp} = \frac{A_{exp}}{A_o}\), where \(A_o\)
is free oscillation amplitude and $A_{\text{exp}}$ is the experimental oscillation amplitude. For the crosssection characterization, the coating was fractured after quenched in liquid nitrogen and the fractured surface was sliced and mounted on a glass slide for AFM characterization.

**Dynamic contact angle (DCA):** For linear polyurethane systems, coated slides for (DCA) measurements were made by dip coating glass microscope cover slides (No. 1 ½ 22 x 40 mm glass cover slips) into a 10 wt% solution of PU with desired amount of surface modifier. The dip-coated slides were then dried overnight at room temperature followed by 24-hour drying in a vacuum oven to remove any residual solvent. For crosslinked systems, dip coating process was done 1 hour after addition of all components into the reaction mixture, including surface modifiers, but before the reaction medium reach too high viscosity. Dip-coated slides were left to cure for 24 hours at room temperature. To ensure the removal of residual solvent cured slides were placed in a vacuum oven at ambient temperature for 24 hr. Fully-cured coatings were prepared by heating the above coatings at 60 ºC for 24 hours.

Wetting behavior was analyzed using the Wilhelmy Plate Method via a Cahn Dynamic Contact Angle (DCA) Model 312 Analyzer (Cerritos, CA). The surface tension quantification limit of the instrument is 0.1 dyne/cm. The probe liquid was ~18 MΩ/cm deionized water from a Barnstead (Dubuque, IA) Nanopure system. The surface tension of the probe liquid was checked daily ($72.6 \pm 0.5$ dynes/cm). Beakers used for DCA analysis were cleaned by soaking in an isopropanol/potassium hydroxide base bath for at least 24 hr, rinsed for 30 sec with hot tap water and then rinsed another 30 sec with Nanopure water. In a typical determination, a coated slide was attached to the
electrobalance via a clip and the stage with the beaker of water was automatically raised and lowered to allow the water to impinge upon the slide. By analyzing the resulting force versus distance curves (fdc), advancing ($\theta_{\text{adv}}$) and receding ($\theta_{\text{rec}}$) contact angles were obtained. Unless otherwise noted, the stage speed was 100 $\mu$m/sec and the wetted depth is from 8-15 mm. This was repeated 4 times during the course of analysis for each sample. To ensure the nanopure DI water is clean enough with surface tension at 72.43 mN/m (22 °C) and to examine whether there was contamination from the polymer samples, the wetting medium was tested with a flamed glass slide before and after the testing of the PU samples under the same conditions.
Results and Discussion

Tapping mode atomic force microscopy (TM-AFM) was utilized to provide information on surface morphology and phase separation between the polymer surface modifier and matrix of the surface modified polyurethanes. In the phase images of TM-

Figure 2.1 Model of Dynamic Contact Angle Analysis. A) Equation relating apparent force to contact angle. B) Depiction of DCA samples, C) Depiction of advancing force-distance curve for hydrophobic surface, D) Depiction of advancing force-distance curve for hydrophilic surface.
AFM, a light color indicates a more elastic interaction of the tip with the surface, while a darker color indicates interactions with a soft surface feature such as the soft domain in polyurethane as a usual case⁷.

0.5 wt% PSM. Figure 2.2 shows the TM-AFM phase and 3D height images (100 x 100 µm) of two coatings with 0.5 wt% surface modifier with linear (Figure 1A) or crosslinked (Figure 1B) matrix polyurethanes at setpoint ratio of 0.8. Both coatings showed very smooth surfaces with root mean square roughness (Rₐ) at 3 nm (TPU) and 4 nm (XPU) on height images. However, the phase images show the significant difference between these two in that the coating with XPU matrix is relatively featureless compare to the coating with LPU matrix. LPU matrix showed small features on phase images. These noticed features are shown similar in the 1 x 1 µm images with round. All of these features are shown as a pit in the height image and light color in the phase image. In the case of XPU coating, no distinct features are shown.

Further magnification to 10 x 10 µm indicates the noticeable features at 100 x 100 µm scale become distinct after magnified to 10 x 10 µm. As shown in figure 2.2A, the LPU coating is dominated with domains of features with two different diameters, one is 100-200nm and the other one is 800-1000nm. In contrast, XPU matrix images are still comparably featureless, which indicates the top surface layer is not significantly phase separated.
1 wt% PSM. By doubling the amount of surface modifier in the system, the surface morphology is not significantly different for 1wt % PSM in LPU matrix, but the small features (100-200 nm diameter) in 1 wt% PSM phase images grows up to the big features (800-1000 nm diameter). The difference on height image of LPU matrix is caused by a smaller Z value (10 nm) is Figure 2.3. This result indicates the aggravation of phase separation on LPU matrix. These round shaped shallow colored patterns in the phase images are believed to be the PSM domains since its size increases with increasing concentration of PSM.

For XPU matrix, a significant difference is observed on both phase images and height images that some features with irregular shapes start to show up. Corresponding to this change, it is noticed that $R_q$ increases from 4 and 12 nm for XPU matrix at scan size 100 x 100 µm. This result indicates that the phase separation is initiated on XPU matrix but the level of phase separation is not high enough to form domains in round shapes.

Figure 2.2. Surface morphology of 0.5 wt% PSM in A) LPU and B) XPU; $R_{sp}$=0.80, $Z=100$ nm, 60°; $R_q$ is shown in nanometer.
2 wt% PSM. In Figure 2.4, the AFM images show the systems with 2 wt % 3FOxTPU in both crosslinked and linear matrices. For LPU matrix, the size of PSM domains increases but the density decreases. It suggests that the smaller domains are mergerd into neighbor domains and form larger domain.

Interestingly, it is remarkable that the phase separation observed on 1 wt% PSM images is alleviated. As shown in figure 2.4 B, no distinct domains are observed on 10 × 10 µm images. However, the $R_q$ further increased to 17 nm. It indicates that the phase separation on XPU matrix is in a very low level with 2 wt% PSM.
Figure 2.4. Surface morphology of 2 wt% PSM in A) LPU and B) XPU; \(R_{sp}=0.80; R_q\) is shown in nanometer.

Figure 2.5 shows the topologies and morphologies of the modified surfaces with 5 wt% of the surface modifier. Again LPU surfaces showed very low \(R_q\) and relatively featureless height images even at highly magnified scales (Z ranges are set at 200 nm for the 100 x 100 and 10 x 10 \(\mu m\) images). But the phase image of the surface with linear matrix is striking. Very large and interestingly patterned features are shown in the 100 x 100 \(\mu m\) images. It indicates a high level of phase separation in linear matrix.

The coating with XPU matrix shows relatively large interconnected features and the \(R_q\) is remained the same as it for 2 wt% PSM. This result suggests that 5 wt% is too high that the XPU matrix can no longer disturb the formation of phase separation.
X-ray photoelectron spectroscopy (XPS) was employed to explore the atom ratio for surface modified LPU matrix and XPU matrix. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. In this study, the electron take off angle is fixed at 90°.

Because fluorine only exists in PSM, the atom ratio of fluorine is chosen as the most reference to evaluate the distribution of PSM on surface layer. As shown in table 2.1, the atom ratio of fluorine in XPU matrix maintains in the same level as it in neat PSM (100 wt%). The different between is within the tolerance of instrument error. This result indicates that the surface layer of surface modified XPU matrix is completely dominated by PSM. In contrast, the atom ratio of fluorine in LPU matrix decreases with the concentration of PSM decreases, and even on 5 wt%, the atom percentage of fluorine
for linear matrix is not as high as it for neat PSM. This result indicates that the surface layer of LPU is not completely dominated by PSM. As a result, PSM in LPU matrix cannot surface concentrate as well as it in XPU matrix due to the formation of phase separation.

<table>
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<tr>
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<th>3FOx PU in XPU matrix</th>
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<th>3FOx PU in LPU matrix</th>
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Table 2.1. XPS for surface modified XPU matrix and LPU matrix.
**Dynamic contact angle analysis (DCA).** DCA was utilized to examine the effects of the surface hydrophobicity of surface modified LPU matrix and XPU matrix. DCA provides evidences to evaluate the stability of PSM on the surface of matrix.

**LPU matrix.** Figure 2.6 shows DCA for surface modified LPU matrix. The contact angles for 0.5, 1, 2 and 5 wt% PSM in LPU matrix is essentially the same. The initial advancing contact angle was 112° on average. After four immersion/emersion cycles the advancing contact angle was 106° on average. The average receding contact angle increased from 38° to 43° for the same cycles. In summary, force distance curves (fdc’s) for the linear base polyurethane show that the surface gradually changes from slightly hydrophobic ($\Delta \theta_{adv} > 90^\circ$) to slightly hydrophilic ($\Delta \theta_{adv} < 90^\circ$).

The 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 (AFM) changes place with the PSM soft block.

**Crosslinked polyurethanes.** The XPU matrix also showed changes in contact angle after repeated interrogation cycles. (Figure 2.7) On average, the initial and ending advancing contact angle for XPU matrix is slightly lower than them for LPU contact angle. The average advancing contact angles ranged from 107°-103° while the average receding contact angle range from 51°-53°. In general, the ending contact angles were higher compared to the linear polyurethane.

From comparing the change in the advancing and receding contact angles after four immersion/emersion cycles, an interesting trend in contact angle hysteresis is observed. In general, the decrease in advancing contact angle from cycle one to cycle
four is attributed to the difference in PSM mobility is lower in crosslinked matrix than in crosslinked matrix (table 2.2A). It indicates the LPU matrix lacks chemical crosslinks which allows the PSM chains to have more mobility. Upon wetting, this mobility allows for the polar component of the PSM or near surface matrix to change conformation and interact with the water. This continued interaction over repeated interrogation cycles results in the adsorption of addition water molecules that results in increasing hydrophilicity. For XPU matrix, increased crosslink density decreases the PSM mobility. This decrease in mobility hinders near surface conformational changes of the PSM or near surface matrix and thereby decreases the interaction of the polar components with water. This decreased interaction with water limits the adsorption of water molecules to the surface which results in lower changes in advancing contact angles.

In addition to the change of advancing contact angle, the change of receding contact angle for XPU matrix is also lower than it for LPU matrix (Table 2.2B). This result indicates that less water adsorption XPU. Again, it demonstrates the higher stability for XPU matrix.
Figure 2.6. DCA for LPU matrix; contact angles for cycle 1-4 are shown in (°)
Figure 2.7. DCA for XPU matrix; contact angles for cycle 1-4 are shown in (°)

Table 2.2. Change of A) advancing contact angle and B) receding contact angle for XPU and LPU matrices.
Conclusions: According to AFM images, for 0.5wt% ~ 2wt% PSM, the coating with LPU matrix shows relatively large features in microscale, while the coating with XPU matrix displays much smaller round features in nanoscale. For 5wt% PSM, the coatings with both LPU and XPU matrix show large features in microscale, indicating phase separation starts in the solution. The length scale and degree of phase separation can be tuned by crosslinked network, concentration of surface modifier and other processing parameters. Due to the presence of the chain network in the crosslinked matrix, further modifier phase separation is kinetically impeded, which is not the case for the linear matrix.

XPS data demonstrates that surface modified XPU matrix is completely dominated with PSM at 0.5, 1, 2 and 5 wt%. While the surface concentration of PSM decreases with the overall PSM concentration decreases. Even at 5 wt%, the surface of LPU matrix is not completely dominated by PSM.

DCA shows that the changes of advancing contact angle and receding contact angle are lower for XPU matrix than for LPU matrix. It indicates XPU matrix higher surface stability and lower water adsorption.


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