Interfacial Water at Polyurethane–Sapphire Interface

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ABSTRACT: Infrared–visible sum frequency generation spectroscopy (SFG) was used to directly probe water between polyurethane (PU) and sapphire substrates after exposing samples to liquid water and water vapor. For liquid water, the observation of SFG peaks associated with H$_2$O bands (3000–3400 cm$^{-1}$) and D$_2$O bands (2300–2600 cm$^{-1}$) indicated water molecules diffused to the buried interface and existed in the form of a hydrogen-bonded water network. The water layer disrupted interactions between polyurethane and sapphire. When PU films were exposed to water vapor, the SFG peak intensities of PU hydrocarbon and sapphire hydroxyl groups changed significantly, which suggested water molecules had reached the interface. However, no hydrogen-bonded water bands were present; instead, the H$_2$O peak at 3550 cm$^{-1}$ and D$_2$O peaks (2600–2700 cm$^{-1}$) were observed. We assigned these peaks to low-coordination water molecules or hydroxyl groups hydrogen bonded with carboxyl groups of PU at the interface. The water molecules did not form a uniform layer at the interface and as a consequence did not completely disrupt the PU/sapphire interactions. These results provide important implications for understanding interfacial adhesion, coatings, and corrosion.

INTRODUCTION

The incorporation of water between two solid surfaces plays an important role in many areas, such as interfacial adhesion, corrosion, catalysis, and lubrication. Interfaces between organic polymers and inorganic substrates are important in understanding protective coatings, adhesive joints, and polymer/inorganic composites. When such systems are exposed to liquid water or humid air, water can diffuse to the polymer/substrate interfaces through the polymer film or along the interface. As a result, water interrupts the initial interactions between polymer and substrate and may cause delamination and mechanical failure, which are detrimental to the durability of polymer/substrate systems.

Various nondestructive measurements have been developed for probing water transport in polymer films. Some examples include electrochemical impedance spectroscopy (EIS), Fourier transform infrared multiple internal reflection (FTIR-MIR) spectroscopy, quartz crystal microbalance (QCM), and X-ray and neutron reflectometry (XR and NR). Wormwell and Brasher have utilized EIS to measure the electrical properties of organic coatings after exposure to aqueous environments since the early 1950s. However, the interpretation of EIS data is model-dependent. FTIR-MIR spectroscopy, developed by Nguyen et al., enables in situ and quantitative detection of water in the vicinity of solid substrates. In both this technique and FTIR-ATR (attenuated total reflectance), water penetration to a depth of 1–2 $\mu$m from the interface can be detected, and they are not sensitive to detect interfacial water and also interfacial water with different level of hydrogen bonding. Even though FTIR-MIR is not interface-specific, it provides information on the transport of water in polymer films and the affinity of water/substrate interactions. QCM, XR, and NR have also been used to measure water uptake in polymer films. QCM is sensitive to changes in the mass of nanometer thick films after exposure to water. More recently, Vogt et al. used NR and XR to study the transport of water in multilayered films upon exposure to water vapor. The X-ray reflectometry data were used to determine the concentration profile of water within the polymer film. NR measurements with D$_2$O provide information on concentration of water within each layer and the concentration of water accumulated at the interface. All these techniques used to monitor water transport in polymer-coated systems are important in predicting the barrier properties of polymer coatings and understanding the impact of water on interfacial properties such as adhesion and electrochemistry.

Water penetration through the polymer film depends on the substrate surface chemistry. Nguyen and co-workers pointed out that plasma-treated substrates having enhanced interactions with PMMA led to a decreased amount of water at their interfaces. O’Brien et al. found that for hydrophobically treated solid surfaces water adsorption was greatly suppressed or prohibited. An investigation was conducted by Karul et al. to clarify the effect of polymer chain mobility on water accumulation. They found that rubbery polymers are able to...
suppress the accumulation of moisture at interfaces. This is because of the larger intrinsic mobility of the polymer chains in the rubbery state.16

Although a variety of studies quantifying interfacial water have been conducted, the structure of such a complex interface is not well understood. Understanding the molecular structure of the polymer/substrate interface in the presence of water can help clarify the mechanism of water-induced interfacial properties. To address this issue, we have built an experimental apparatus to directly probe the water between the polymer film/sapphire (Al2O3) interface using infrared-visible sum frequency generation spectroscopy (SFG) in total internal reflection (TIR) geometry.19 In the dipole approximation, SFG, which is a second-order nonlinear technique, is only active where there is a breakdown in inversion symmetry. This selection rule makes it possible to use SFG to study the structure of molecules near surfaces and interfaces.20−22 Briefly, SFG spectroscopy involves two incident beams: a visible beam and a tunable IR beam overlapping temporally and spatially on the sample and generating a sum frequency signal ($\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$) at the interface. The SFG signals are enhanced when the scanning IR frequency overlaps with the molecular vibrational modes of interfacial molecules that are infrared- and Raman-active. The SFG intensities and the positions of SFG peaks can provide chemical and orientational information on the molecules.24 We can also selectively probe individual interfaces in multilayered systems as SFG output is enhanced 10−100 times when the incidence angles are near the critical angle for TIR.25,26 Taking advantage of this approach, we studied the structure of the polyurethane (PU)/sapphire interface upon exposure to liquid water and water vapor as a function of time.27−29 The SFG spectra were acquired using a picosecond Spectra-Physics laser system with a tunable IR beam, 2000−3800 cm−1, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 100−200 μm, together with a visible beam of 800 nm, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 1 mm.28 The SFG spectra were measured by scanning the IR range from 2000 to 3800 cm−1. We performed experiments at incident angles near the critical angles, calculated using Snell’s law for total internal reflection. The refractive indices of water, air, polyurethane, and sapphire used in the calculation were 1.33, 1.00, 1.51, and 1.76, respectively. We used incident angles (with respect to the surface normal of the sapphire prism face) of 42°, 16°, and 2° to probe the PU/air, PU/H2O (and PU/D2O), and PU/sapphire interfaces, respectively. The incident angle of the visible laser beam was ~1.5° lower than that of the tunable IR laser.9,23,29 The polarization combinations reported in this work are SSP (s-polarized SFG output, s-polarized visible input, and p-polarized IR input) and PPP (p-polarized SFG output, p-polarized visible input, and p-polarized IR input). The SFG signals in the D2O region were weaker than those in the H2O region because of the different sensitivity of the SFG instrumentation in these two regions.24 Therefore, direct comparison of SFG intensities between these two regions is not possible in the current experiment. The spectra were fitted to the Lorentzian equation21

$$I_{\text{SFG}} \propto \left[ I_{\text{eff,NR}} + \sum A_\nu (\omega_{\text{IR}} - \omega_\nu - i\Gamma_\nu)^2 \right]^{-1}$$

(1)

In eq 1, $I_{\text{eff,NR}}$ describes the nonresonant contribution, and $A_\nu$, $\Gamma_\nu$, and $\omega_\nu$ are the amplitude, damping constant, the scanning frequency of the incident IR beam, and frequency of the $\nu$th vibrational resonance, respectively.

**RESULTS AND DISCUSSION**

Figure 3 shows the SFG spectra for the PU/air interface and the PU/sapphire interface, respectively. There are three
characteristic peaks at 2800, 2850, and 2920 cm$^{-1}$ at the PU/air interface. These peaks are assigned to $\alpha$-CH$_2$(s) stretching, CH$_2$(s), stretching and CH$_2$(as) stretching modes, respectively.$^{32 - 35}$ The spectrum of the PU/sapphire interface reveals two peaks at 2940 and 3650 cm$^{-1}$. The 2940 cm$^{-1}$ peak is tentatively assigned to an asymmetric CH$_2$ vibration of the soft segment (PTMO) moiety.$^{36,37}$ The 3650 cm$^{-1}$ peak is assigned to the surface OH of the sapphire in contact with the PU.$^{37}$

The non-hydrogen-bonded sapphire OH peak is at 3720 cm$^{-1}$, and the shift of this peak to lower wavenumbers at the PU/sapphire interface is due to the acid–base interactions between the acidic surface OH groups and the basic groups in the PU.$^{38}$

Figure 4 shows the SFG spectra of the PU/H$_2$O interface. We observed two H$_2$O peaks at 3100 and 3400 cm$^{-1}$, which are assigned to strongly tetrahedrally coordinated and loosely coordinated hydrogen-bond stretch, respectively.$^{24,39}$ The SFG
spectra for the PU/air and the PU/H_2O interfaces in the hydrocarbon region are very different, suggesting restructuring of the PU surface upon contact with water. Interestingly, the same peak at ~2940 cm^{-1} is present at both the PU/H_2O and the PU/sapphire interfaces, reflecting polar interactions. As suggested by other SFG studies such as silica and poly(ethylene oxide) (PEO), the hydrogen bonds between the water and silanol (SiOH) groups (or PEO headgroups) contribute to the ordering of water. We can conclude that there are hydrogen bonds formed between polar groups (including ether, ester, and amine groups) of PU chain and water, which enhances the magnitude of the ~3200 cm^{-1} peak with respect to the ~3400 cm^{-1} water peak at the PU/water interface.

Figure 4b (lower curve) shows the SFG spectrum of the PU/sapphire interface collected using PPP polarization after the cell was filled with liquid H_2O. We observed two H_2O bands at ~3150 and ~3400 cm^{-1} and a PU peak at 2940 cm^{-1}, which indicates the diffusion of water to the PU/sapphire interface. In addition, we observed a peak at ~3700 cm^{-1} that is associated with water and surface OH groups. The molecular interpretation of this ~3700 cm^{-1} peak is difficult because of contribution from water in contact with PU, water in contact with sapphire, and sapphire in contact with PU. To simplify the analysis, we replaced H_2O with D_2O and measured the SFG spectra of the PU/sapphire interface. This makes spectral interpretation easier because the D_2O peaks are between 2300 and 2800 cm^{-1}. The peaks at 2400 and 2500 cm^{-1} are assigned to strongly tetrahedrally coordinated and loosely coordinated D_2O peaks, which confirms the presence of a water layer between PU and the sapphire substrate. The peak at 3620 cm^{-1} is assigned to sapphire OH in contact with D_2O. This assignment is based on a previous study of the sapphire/D_2O interface where this peak corresponds to surface OH groups in contact with D_2O. The assignment based on a previous study of the sapphire/D_2O interface where this peak corresponds to surface OH groups in contact with D_2O. The sapphire OH peak in contact with PU is at ~3650 cm^{-1}, and a red-shift to 3620 cm^{-1} indicates that the sapphire OH is now in direct contact with D_2O. The original peak is at ~3720 cm^{-1}, and it corresponds to the sapphire free OH.

Figure 5. SFG spectra in PPP polarization. (a) Blank sapphire in the presence of various RH of H_2O vapor. The solid lines joining the data points are provided as a guide. (b) PU/sapphire interface for various RH of H_2O vapor. To minimize any dispersion effects, the various spectra were collected from 2700-3200 and 3200-3800 cm^{-1} and then stitched together. The liquid H_2O spectrum is for comparison. The solid lines are fits to the data points using eq 1. (c) PU/sapphire interface for various RH of D_2O vapor. The various spectra were collected from 2200-2800, 2800-3200, and 3200-3800 cm^{-1} and then stitched together. The liquid D_2O spectrum is for comparison. The solid lines are fits to the data points using eq 1.
In addition to water exposure, it is also of interest to study how water vapor diffuses to the polymer/solid interface. This has particular importance in determining how coatings resist the diffusion of water to the polymer/solid interface. Figure 5 shows the spectra of the blank sapphire/vapor and the PU/sapphire interfaces collected after exposing samples to H₂O and D₂O vapor as a function of relative humidity (RH). Figure 5a shows the SFG spectra for the sapphire/vapor interface. The SFG spectrum for 0% RH shows a sharp peak at 3720 cm⁻¹, which is assigned to the free OH groups of the sapphire. At 17% RH, the SFG signal intensity decreases for the free OH peak and the width broadens. This indicates water molecules adsorb onto the sapphire surface and interact with the surface OH groups. After increasing the RH to 72%, the free OH peak red-shifts to lower wavenumbers and merges with the shoulder at ∼3600 cm⁻¹. An earlier SFG study of water adsorption on mica showed that water coverage reached a full monolayer at ∼90% RH and formed an ordered strongly tetrahedrally coordinated structure due to the negatively charged mica surface. Adsorbed water on silicon oxide has been studied by attenuated total reflection infrared spectroscopy (ATR-IR). The authors observed that an strongly tetrahedrally coordinated water network grew up to three layers as RH increased from 0 to 30%. In the RH range of 30–60%, the transition of the strongly tetrahedrally coordinated structure to loosely coordinated water took place. Above 60% RH, the liquid water grew on top of the ice-like layer. In contrast, our SFG spectra of sapphire in H₂O vapor at varied RH did not show any water peaks in the 3000–3400 cm⁻¹ region. It should be noted that the original peak of the free OH groups returned after exposure to dry N₂ gas (Figure S4). This indicates that water molecules were clearly adsorbed on the sapphire surface but did not form a hydrogen-bonded network.

Figure 5b shows the SFG spectra for the PU/sapphire interface. The SFG intensity of the peak at 2940 cm⁻¹ assigned to PU increases as RH increases, while the intensity of the 3650 cm⁻¹ peak decreases with increasing RH. All these changes indicate that H₂O molecules diffuse to the buried interface and interact with the PU and the sapphire substrate. The intensity of the SFG signal between 3100 and 3400 cm⁻¹ increases slightly as RH is increased. However, no obvious ∼3200 or ∼3400 cm⁻¹ peaks were observed in the humidity experiments. This indicates that the water molecules at the PU/sapphire interface do not form a hydrogen-bonded monolayer to completely disrupt the interactions between the PU segments and the surface OH groups. This interpretation is also supported by the existence of a 3650 cm⁻¹ peak in the humidity experiments, in which water at the interface partially disrupts the interaction between the polymer and the sapphire substrate. This is because at the PU/sapphire interface the 3650 cm⁻¹ peak was not observed when the coating was exposed to water (see Figure 4b). The above experimental results were reversible: when the polymer film exposed to 82% RH was taken out and left in a vacuum oven for 1 h, the original 0% spectrum was reproduced (Figure S5).

In the hydrogen-bonded region, we also observed a peak at ∼3550 cm⁻¹ at the PU/sapphire interface in the presence of H₂O vapor. This peak was observed as a shoulder on the main peak at 3650 cm⁻¹ attributed to the acid–base interactions between the surface OH and PU. In order to interpret this peak correctly, we performed humidity experiments using D₂O vapor. Figure 5c shows the SFG spectra for D₂O vapor experiments. The observation of intensity changes in the PU hydrocarbon peak and the sapphire OH peak are consistent with the conclusion reached using the H₂O vapor. In addition, we also observed SFG signals in the D₂O region at ∼2630 and ∼2700 cm⁻¹, which are at higher wavenumbers than those for strongly tetrahedrally coordinated and loosely coordinated D₂O peaks. This is interesting and also consistent with the results that the water molecules do not form a highly coordinated hydrogen-bonded water layer. Wei et al. obtained SFG spectra for the vapor/water interface and suggested that the resonant feature at 3500–3600 cm⁻¹ may be assigned to the bonded OH stretching mode of water molecules with one bonded OH and one dangling OH (low-coordination water). ATR-IR studies of water adsorption in poly(2-methoxyethyl acrylate) films by Morita et al. observed two bands at 3628 and 3558 cm⁻¹. Similar peaks have been reported in the literature. These peaks are attributed to the antisymmetric and symmetric OH stretching modes of water with the C=O···H−O type of hydrogen bond. The three peaks observed at ∼3550, ∼2630, and ∼2700 cm⁻¹ in our spectra may be assigned to low-coordinated water or to water with the C=O···H−O hydrogen bond.

Finally, we would like to reflect on the implications of these results. For adhesion and corrosion, the strong interactions between the polymer and the substrate are important. Upon exposure to liquid water, we have directly observed the disruptions of the polymer/substrate interactions, which could lead to delamination and create an environment that would accelerate corrosion. The results for water vapor were interesting because exposure to high RH did not result in the formation of hydrogen-bonded water networks which could be directly verified by the location of the OH peaks in the SFG experiments. This indicates an early stage of delamination unlike that observed for liquid water. Preventing water penetration is of interest in many industrial applications, and in the future we will be extending this work to study adhesion promoters that are used to maintain adhesion even in the presence of water.

### CONCLUSION

In conclusion, we have studied the diffusion of water to the PU/sapphire interfaces after exposing films to liquid water or water vapor using surface-sensitive sum frequency generation spectroscopy. In the case of the liquid water experiments, water at the PU/sapphire interface forms a highly coordinated hydrogen-bonded layer and disrupts the interactions between PU and the sapphire substrate. However, this water layer may be thin because we also observed the hydrocarbon peak from PU. In the case of exposure to water vapor, we observed that water molecules penetrate to the PU/sapphire interface. However, water molecules are unable to form a uniform monolayer and only partially disrupt the PU/sapphire interactions. Figure 6 shows a simple illustration of the main results of this work. The direct observations of water at the buried interface in liquid water and humidity experiments provide important clues as to the role of water in loss of adhesion. Moreover, our results demonstrate the feasibility of using SFG as a means of testing the ability of a specific polymer coating to delay corrosion.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b03263.

Thickness measurements, calculations of interference, and results of fits (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Edward Laughlin for help in designing and building the humidity apparatus. We are also indebted to Gary Leuty, Mena Klittich, and Dona Foster for helpful discussions. We thank US DoD (FA7000-10-1-0002) for supporting J.Z. and NSF-DMR for supporting E.A.D. and Y.Z.

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