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Interfacial Molecular Restructuring of Plasticized Polymers in Water

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ABSTRACT

Upon water contact, phthalate-plasticized poly(vinyl chloride) (PVC) surfaces are highly unstable because the plasticizer molecules are not covalently bound to the polymer network. As a result, it is difficult to predict how the surface polymer chains and plasticizers may interact with water without directly probing the plastic/water interface *in situ*. We successfully studied the molecular surface restructuring of 10 wt% and 25 wt% bis 2-ethylhexyl phthalate (DEHP)-plasticized and pure PVC films (deposited on solid substrates) *in situ* due to water contact using sum frequency generation vibrational spectroscopy (SFG). SFG spectral signals from both the top and the bottom of the plastic film were obtained simultaneously, so a thin-film model spectral analysis was applied to separately identify the molecular changes of plastics at the surface and the plastic/substrate interface in water. It was found that in water both the structures of the plastic surface and the buried plastic/substrate interface changed. After removing the samples from the water and exposing them to air again, the surface structures did not completely recover. Further SFG experiments confirmed that small amounts of DEHP were transferred into the water. The leached DEHP molecules could reorder and permanently transfer to new surfaces through water contact. Our studies indicate that small amounts of phthalates can transfer from surface to surface through water contact in an overall scope of minutes. This study yields vital new information on the molecular surface structures of DEHP plasticized PVC in water, and the transfer behaviors and environmental fate of plasticizers in polymers.

INTRODUCTION

The use of plasticized poly(vinyl chloride) (PVC) plastic in modern life has both greatly helped advance society and negatively impacted the environment. The use of PVC materials has revolutionized modern technologies in a myriad of aspects including applications across industrial, medical, and home-good fields. However, human produced plastic components continue to permeate natural ecosystems profusely through many means, including the leaching and transfer of plasticizers into the environment.¹⁻⁶ This may occur as the plastic is being used and after it is disposed.⁷⁻¹⁰

Most PVC products are plasticized with phthalates, which plasticize PVC materials through non-covalent interactions between the PVC and phthalate functional groups. These interactions lower the free energy of the PVC/phthalate system, increase the free volume of the polymer system and lower the glass transition temperature of PVC. (See Figure 1 for molecular structures). Although phthalates are known rodent endocrine disruptors, suspected marine toxins and suspected human carcinogens and toxins,^{4, 11-16} they are very efficient plasticizers, and inexpensive to synthesize. As a result, they remain one of the most commonly used PVC plasticizers worldwide.^{17, 18}

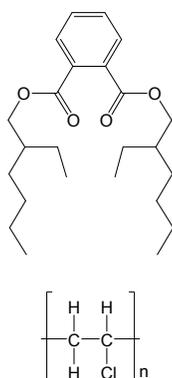


Figure 1. Molecular structures of DEHP (top) and PVC (bottom).

Due to their small size and the lack of covalent bonding to PVC, phthalates are susceptible to leach from the entangled polymer chains. Over the plastic's lifetime, plasticized PVC may be exposed to air and water frequently. Therefore it is important to obtain a molecular-level understanding of the surface structures of phthalate plasticized PVC upon water contact. There are few analytical techniques suitable for studying the molecular behaviors of polymers at aqueous interfaces *in situ*. Cryogenic x-ray photoelectron spectroscopy (cryo-XPS) allows for polymer strands to be effectively frozen in place when in contact with an aqueous environment so that surface compositional changes may be observed.^{19, 20} This can be compared to data from XPS measurements taken in dry conditions. However, XPS is performed under ultra-high vacuum and it is nearly impossible to determine any molecular ordering changes a homo-polymer undergoes over increasing contact time with a liquid. Near Edge X-Ray Absorption Fine Structure (NEXAFS), another very powerful spectroscopic technique, may allow for the determination of molecular orientation changes upon water contact, but the use of a synchrotron is required.²¹⁻²³

Sum Frequency Generation vibrational spectroscopy, or SFG, is a truly surface sensitive vibrational spectroscopic technique capable of probing buried interfaces such as a solid/aqueous interface *in situ* and in real time without physically breaking apart the system of study. The signals detected with SFG are molecular vibrational modes observed only where centrosymmetry is broken, i.e. at surfaces and interfaces, making it an ideal analytical technique to probe the molecular surface functional group behaviors of polymers in air and at buried interfaces like that

of the water/polymer interface.²⁴⁻³³ Although SFG has been used to extensively study other polymers in water, PVC has not yet been studied *in situ* in water at a molecular level.

This paper presents a fundamental study on the behaviors of PVC and phthalate surface functional groups in air, the ordering changes of these CH groups over time when in contact with D₂O (utilized to avoid spectral confusion in the CH region of spectra) and the following CH functional group restructuring in air after water contact using SFG. We compare the behaviors of surface molecular structures on pure PVC films to those on PVC plasticized with 10 wt% and 25 wt% DEHP. In order to obtain molecular vibrational information at the water interface *in situ*, we use a prism experimental geometry, where PVC thin films are spin coated on right angle silica prisms, and D₂O droplets are contacted to the films on the bottom of the prisms (Figure 2). Such an experimental geometry setup yields larger signals when liquids are contacted to substrates (no signals could be obtained with a flat window substrate rather than a prism geometry), but also may lead to interfacial signal interferences and/or different spectra than window geometry, as found in our research.

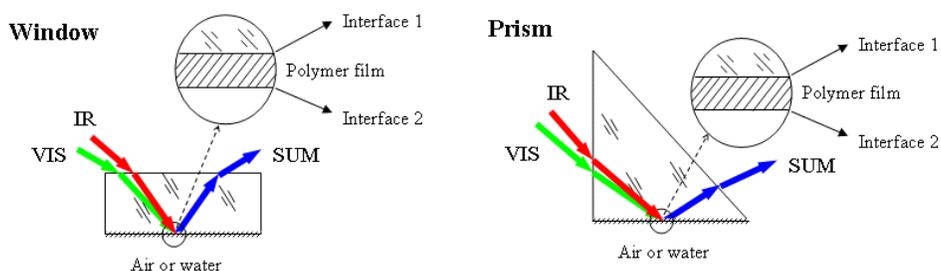


Figure 2. The window and prism geometries for SFG experiments in this study.

Therefore, this paper also focuses on resolving SFG signals of the silica/polymer interface from those resulting from the polymer/water or polymer/air interface, allowing us to further understand the molecular-level behaviors of PVC and phthalates in aqueous conditions

and to give a quantitative answer as to why we see different SFG signals for our system in window versus prism geometry. Finally, we briefly study the leaching of DEHP molecules into D₂O and their reorganization at a new interface, demonstrating the instability of the PVC films and furthering our understanding of the surface molecular structural changes of these plastics when in contact with water.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (M_w 62,000; M_n 35,000) in pellet form, tetrahydrofuran (THF) $\geq 99.9\%$ purity, toluene $\geq 99.3\%$ purity, concentrated sulfuric acid (reagent grade), potassium dichromate, and deuterium oxide were obtained from Sigma Aldrich (St. Louis, MO). Bis 2-ethylhexyl phthalate (analytical standard) was purchased from Fluka (St. Louis, MO). Deuterated poly(styrene)-d₈ (PS-d₈) was purchased from Polymer Source, Inc. (Dorval, QC Canada).

Sample Preparation

Right angle fused silica prisms (Altos Photonics, Inc.) and fused silica windows (ESCO Products, Inc.) were used for SFG measurements and were sequentially cleaned using a concentrated sulfuric acid bath saturated with potassium dichromate overnight, rinsed with deionized water, dried with nitrogen gas and then further cleaned by exposing prisms to a glow discharge air plasma for 5 min using a PE-50 series Plasma System (Plasma Etch, Inc.) to remove any excess organic material before sample preparation. PVC pellets were dissolved in THF to prepare the PVC-based thin films. A 30:1 weight ratio of THF/PVC was used for all PVC-based films. DEHP was added by weight percent to PVC. PVC plastic film thicknesses

were ~200 nm. PS-d8 solutions of 1 wt% were prepared by dissolving PS-d8 in toluene. Solutions were mixed using a vortex mixer (Vortex-Genie 2T, Scientific Industries Inc.) until clear.

A P-6000 spin coater (Speedline Technologies) was used to prepare all plastic films. Samples were spin coated at 3000 rpm for 30 s on silica prisms or windows. PVC plastic films were spin coated on both windows and prisms. PS-d8 solutions were spin coated on prisms only.

SFG D₂O Experiments

SFG Model Water Interface Experiments

For SFG experiments, samples were placed film-face down in a custom made sample holder open to air. PVC films were exposed to D₂O for ~1.25 h by contact with a droplet of D₂O in a clean holder pushed upwards to samples using a lab jack. After 1.25 h the jack was lowered and the films were exposed to air to dry for 1 h. SFG spectra were taken before, during D₂O contact, and after 1 h of drying time in air. Two sample geometries, window and prism geometries, were used in this study (Figure 2). *In situ* measurements and measurements before and after D₂O contact were performed with prism geometries (using prism substrates). Window geometries were used for measurements before and after water exposure, but not during. The consequences of using these geometries will be discussed in more detail later.

SFG Phthalate Migration Experiments

For SFG phthalate migration experiments, samples spin coated on windows were contacted to a droplet of D₂O in the same manner as stated above for ~1.5 h. After 1.5 h the jack was lowered and the D₂O holder was transferred to a new prism with a PS-d8 spin coated film. SFG spectra were taken before, during, and after “dirty” D₂O contact to PS-d8.

Instrumentation

SFG

SFG has been widely applied to gather molecular-level information of a variety of surfaces and interfaces such as polymers in aqueous environments.^{24, 34-42} Under the electric dipole approximation, an SFG process is forbidden in centrosymmetric materials but allowed at surfaces or interfaces where the inversion symmetry is broken. Such an advantageous feature makes SFG spectroscopy an ideal analytical tool to study molecular structures at surfaces or interfaces. The details of SFG theory and setup have been extensively outlined in previous papers from our lab,^{29, 43} and some details on our system can be found in the supplemental information file. The SFG experiments conducted for this paper were taken using ssp (s-polarized signal, s-polarized 532 nm input beam and p-polarized tunable frequency IR input beam) and ppp polarization combinations. Further details on SFG signal components can be found in the supplemental information file.

Spectral Deconvolution Analysis

In our SFG experiments, we could not detect SFG ppp signals at the air interface with a face-down window geometry (Figure 2), nor could we generate ssp or ppp signals at the polymer/water interface with a window geometry. Therefore, we obtained SFG spectra using a prism geometry (Figure 2), where both cases (in air and contacting water) generated strong signals. However, the ssp prism air/polymer interface spectra were markedly different from the window air/polymer spectra.

We believe that the spectral differences between spectra obtained on prisms versus windows arise from signal interferences that occurred with prism geometry for this system.

Since a polymer film has two interfaces, whether it is a polymer film on a silica window or a prism, both interfaces (silica/polymer interface and polymer surface in air or polymer/water interface) can generate SFG signals. For SFG spectra of polymers in air, the signal at the air interface is often much larger than at the buried substrate/polymer interface, due to differences in local Fresnel coefficients. It is this local field correction for each interface that determines the relative interfacial SFG signal intensity. However, if signals at the buried substrate/polymer interface are strong, i.e. for the prism geometry when a film thickness is appropriate, it is possible that these signals may dominate the air or water/polymer interfacial signals. Therefore it was vital to complete Fresnel coefficient calculations and use a two interface thin film spectral fitting model to determine if signals at the air or water interface were convoluted with the buried substrate interfacial signals.

For our fitting calculations, we used the ssp SFG spectra in air in window geometry as the basis for plastic surface signal contributions, since the spectra are dominated by surface signals in this geometry. (Evidence to support this claim can be found in our Fresnel coefficient calculations in the supplemental information file). Then, we deduce the ssp SFG signals of the buried polymer/substrate interface generated from the prism geometry in air (which contain signals generated by both the polymer surface in air and the polymer/substrate interface). Finally, knowing the buried polymer/substrate ssp SFG signals and having collected the ssp SFG spectra from the prism geometry in water, we were able to deduce the SFG signals of the polymer surface in water. Similarly, we were able to deduce the SFG ppp spectra from the polymer surface in water, in air and from the buried polymer/substrate interface.⁴⁴⁻⁵¹ More detailed analysis methods of the spectra collected using the window and prism geometries can be found

in the supporting information file. Fitting results in this paper are given in A_q/I_q values (strength of the q_{th} vibrational mode divided by the damping coefficient of the q_{th} vibrational mode), which are generated after fitting peaks and are directly correlated to observed signals. We can directly correlate relative A_q/I_q ratios at the two interfaces to the relative contributions of a functional group at these interfaces (see supplemental file for detailed information on spectral fitting).

RESULTS AND DISCUSSION

Window Geometry: PVC in Air

Figure 3 contains the ssp SFG spectrum of pure PVC in air obtained in window geometry. Similar to previous observations, the largest peak at 2915 cm^{-1} belongs to the methylene symmetric ($\text{CH}_2(\text{s})$) stretch and a small peak at 2880 cm^{-1} is assigned to the end group methyl symmetric stretch ($\text{CH}_3(\text{s})$).^{28, 52, 53} From our previous discussion in the experimental section, we know that such a window spectrum originates from CH groups on the PVC surface in air. Therefore, we know the PVC surface is dominated by methylene groups.

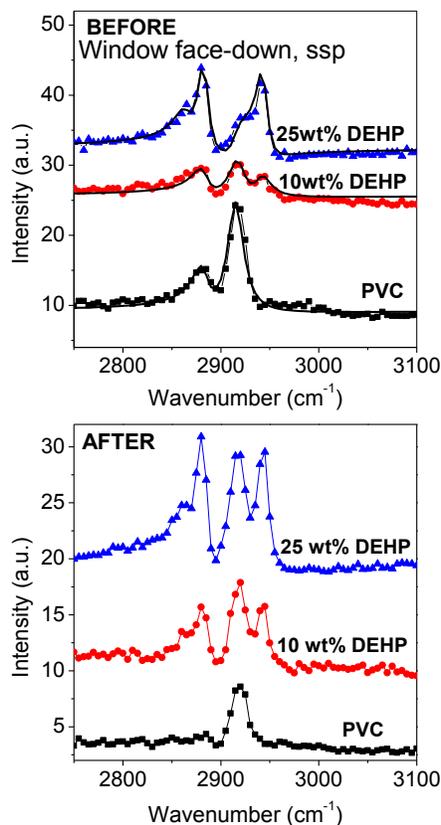


Figure 3. SFG ssp face down window spectra of pure PVC, PVC with 10 wt% DEHP and PVC with 25 wt% DEHP in air before D₂O contact (top) and after D₂O contact (bottom). The spectra before D₂O contact have been fitted. The fits are shown on the spectra in the top panel as solid black lines and the experimental data as points only.

Prism Geometry: PVC in Air

As discussed in the supporting information, the ssp SFG signal (Figure 4) generated from the PVC on silica prism in air may be dominated by the contribution from the buried PVC/silica interface since the absolute Fresnel coefficient of the silica/PVC interface is ~ 2.21 and that of the PVC surface in air is ~ 0.66 (film thickness ~ 200 nm). To obtain the signal contribution from the buried PVC/silica interface, the ssp spectrum of the PVC surface in air is needed, which was

collected from the window geometry. Detailed fitting results are given in Table S-1 in the supplemental information file.

Surprisingly, in addition to the major contribution from the surface methylene signal, only two very weak resonant peaks were determined to originate from the buried silica interface with A_q / I_q ratios of 0.3 and -0.2 (see Table S-2 for more information). So for the ssp spectrum collected from the prism geometry in air, the surface signals dominate the spectrum even though the buried silica interface has a larger Fresnel coefficient than that of the PVC surface in air. This likely occurred because the molecular groups at the silica/PVC interface are highly disordered.

Since no SFG signals were collected from the window geometry in the ppp polarization combination and strong ppp SFG signals were collected from the prism geometry, and since we know the Fresnel coefficients of the buried interface dominate in prism geometry (see supplemental file), we can conclude that strong ppp SFG signals from PVC on prisms in air were only generated from the silica/PVC interface. Unsurprisingly, the spectrum could be fitted using signals from the buried silica interface only (Table S-2). In prism ppp spectra, in addition to the previous PVC peak assignments, we can observe a small peak at 2860 cm^{-1} , assigned to CH/CH₂ contributions in accordance with IR studies^{54,55} (see Figure 4). From all these fitting results, we can conclude that the PVC ssp spectrum on prisms yields information on both the PVC surface in air and the buried PVC/substrate interface, whereas the ppp polarization gives information on the CH functional groups at the buried silica interface. This shows we can use ppp SFG signal in prism geometry to selectively probe the buried PVC/silica interface.

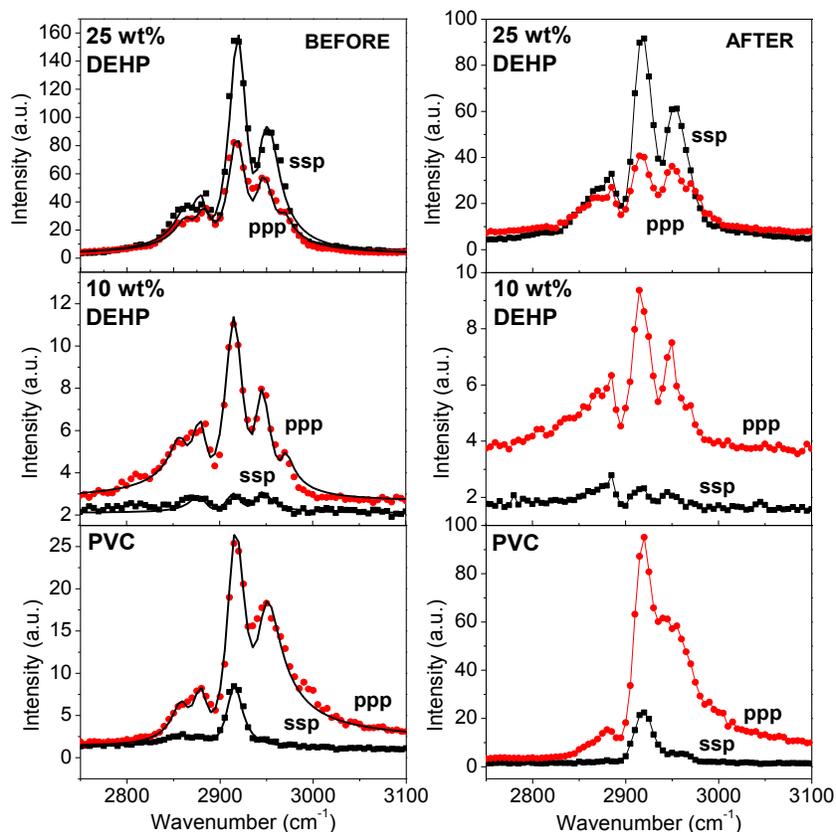


Figure 4. SFG prism spectra of plastics in air before (left side) and after (right side) D₂O exposure with 1h drying time. The spectra before D₂O contact found in the left panel have been fitted. The fits are shown on the spectra as solid black lines and the data as points only.

Prism Geometry: PVC in D₂O

In order to study the molecular surface changes of PVC from water contact, PVC samples were contacted with D₂O (used in place of water to avoid spectral confusion) and SFG spectra were collected *in situ* in the prism geometry. Figure 5 gives ssp and ppp prism spectra collected from PVC as a function of D₂O contact time. The major signal detected in water for both ssp and ppp spectra is CH₂(s) at 2915 cm⁻¹. Upon contact with deuterated water, the 2915 cm⁻¹ signal

increases slightly in intensity compared to the signal in air. However, as contact time increases, the PVC peaks decrease in intensity and are significantly smaller than those in air for both ssp and ppp spectra. The 2880 cm^{-1} signal from CH_3 disappears immediately. In addition, a new peak at 2970 cm^{-1} appears, which we have previously assigned to the CHCl stretching from PVC.⁵⁶ This peak is barely observable in ssp but visibly present in ppp spectra.

Since we know the buried silica prism/PVC interfacial ssp SFG signal from the study in air (Table S-3), we can obtain the ssp SFG signal contributed from the PVC/silica interface versus the PVC/water interface by fitting the ssp SFG spectrum collected from the PVC on a prism in D_2O (Table S-3). The fitting results indicate the main signal at 2915 cm^{-1} in ssp spectrum for the prism in water (Figure 5) must come from the PVC/water interface since the only contributed resonant signals from the silica/PVC interface are very weak and located at 2860 cm^{-1} and 2880 cm^{-1} with 0.3 and $-0.2 A_q / \Gamma_q$ ratios, respectively. When we apply the same fitting logic for the ppp spectra, the observed resonant signals can only be fit well when accounting for both interfaces (Figure 5, Table S-3), e.g. A_q / Γ_q for $\text{CH}_2(\text{s})$ at the PVC/water interface is -2.4 , whereas it is 1.8 for the silica/PVC interface. Therefore the SFG signals must originate from both the silica/PVC and PVC/water interfaces. Here OH vibration (may be from incomplete deuteration) shifts the line shape.

The decrease in 2915 cm^{-1} intensity over time in ssp spectra (dominated by PVC/water interface contributions) could either indicate a change in methylene group orientation or an increase in surface methylene disorder (or orientation distribution) at the PVC/water interface. Because both ssp and ppp polarizations showed a decrease in methylene signal, it is more likely that the PVC surface continues to disorder with increasing contact time with water. Thus with

the information from our spectral fitting, we can conclude that the observed spectral changes of CH groups in ssp were indicators of increased CH disorder over minutes at the polymer/water interface. The spectra from ppp, which are due to both the water and silica buried interfaces, also indicate increased CH disorder over time. However, some ordering at the polymer/water interface does remain after 90 min of water exposure. We are not able to make definitive statements about ordering changes at the buried polymer/silica interface from water contact with our spectra obtained *in situ* in D₂O. This research indicates that even though we could not detect SFG signals from the PVC/water interface using a window geometry, it is feasible to follow the surface structural changes as a function of time using a prism geometry.

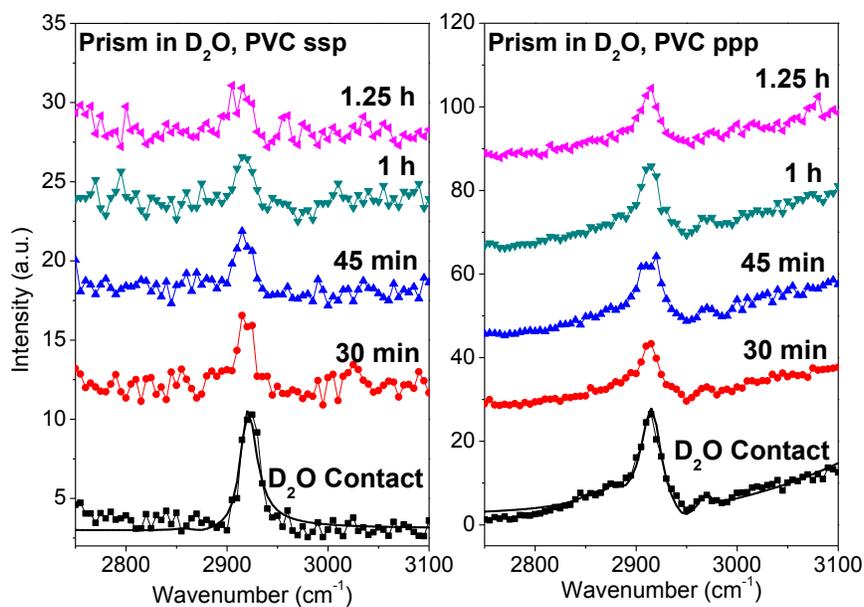


Figure 5. SFG prism spectra of PVC in D₂O interface over increasing contact time from first contact to 1.25 h. On the left is the ssp spectra series and the right the ppp series. The spectral fits of the peaks upon water contact are represented as black lines.

Window Geometry: PVC in Air after D₂O Contact

After exposure to D₂O, the PVC films were dried in air for one hour and SFG spectra were obtained again at the air interface. Spectra were obtained on both windows and prism substrates. The ssp spectra of PVC in air on windows after drying can be observed in Figure 3. Note that the 2915 cm⁻¹ CH₂(s) peak still dominates. However, the 2880 cm⁻¹ CH₃(s) peak is now lower in intensity compared to 2915 cm⁻¹ than previously, suggesting some functional group rearrangement after water contact, and ultimately indicating that the exposure to water contact for hours results in stable surface restructuring changes (on a scale of hours). The more hydrophobic end methyl groups move to the bulk of the PVC sample after water contact.

Prism Geometry: PVC in Air after D₂O Contact

When we look at ssp prism spectrum after D₂O contact, the 2915 cm⁻¹ signal dominates, the 2880 cm⁻¹ signal is not observed, and an increase in intensity for the 2950 cm⁻¹ methylene asymmetric (CH₂(as)) peak is clearly observed (Figure 4). We believe that the CH₂(as) peak originates from the surface since the contributions from the buried silica interface before water contact were very small in comparison. The decrease of the CH₃(s) signal and increase of CH₂(as) signal is further evidence that the surface of the material is changed from water contact. For ppp prism spectra, there is an obvious decrease in intensity of the CH₃(s) peak at 2880 cm⁻¹. We determined that this peak originated from CH₃ groups at the silica/polymer interface previously. This indicates that we have buried interface restructuring as well as surface restructuring, which could occur if the water penetrated all the way to the bottom of the film.

In summary, the PVC surface exhibits restructuring upon contacting water. At the PVC/water interface, the plastic surface is still dominated by the methylene groups, but the end methyl groups are not observed. The PVC surface becomes more and more disordered as a

function of water contact time, and the resulting surface restructuring is irreversible; after the removal of PVC from water, the surface is still dominated by the methylene groups, but end methyl groups are no longer ordered on the surface. In addition, irreversible buried film/silica interface restructuring occurred from water contact as well, which indicates that water eventually penetrated the entirety of the plastic.

10 wt% DEHP/PVC in Air and D₂O

Window Geometry: 10 wt% DEHP in Air

For pure DEHP, the following peak assignments apply: the two major peaks at 2880 cm⁻¹ and 2945 cm⁻¹ belong to CH₃(s) and Fermi resonance vibrational modes, respectively. A shoulder around 2860 cm⁻¹ is assigned to the CH₂(s) mode of DEHP. For mixtures of PVC and 10% DEHP by weight, the film/air interfacial ssp spectra on windows contain vibrational resonances from both PVC's CH₂(s) groups at 2915 cm⁻¹ and CH₃(s) at 2880 cm⁻¹. The CH₃(s) from PVC overlaps with the dominating CH₃(s) signal from DEHP at the same wave number. The addition of DEHP also yields a Fermi resonance signal (2945 cm⁻¹), and a 2865 cm⁻¹ CH₂(s) shoulder from DEHP can be resolved as well in Figure 3. The intensities of the methyl DEHP peaks compared to the CH₂(s) peak of PVC are about equal. Therefore the SFG ssp signal detected from the 10% DEHP on window in air shows that the surface in air is covered by both PVC and DEHP. Fitting results for 10 wt% DEHP on windows can be found in Table S-4.

Prism Geometry: 10 wt% DEHP in Air

SFG spectra on prisms appear similar to those on windows (Figure 4) although the peak ratios of methylene to methyl groups vary. In the ssp polarization combination, the CH₃ peaks

are about equally intense compared to PVC's CH₂ peak. However in ppp, the CH₂(s) peak is much larger than the CH₃ peaks. This trend can be explained once again, by fitting the SFG spectra with regards to Fresnel coefficient contributions and the known fitting parameters from the ssp signals in air. As shown in Table S-5, for the ssp polarization combination in air, both interfaces contribute to the spectrum. Again, the silica/PVC interface contribution is small although it has a large Fresnel coefficient. As an example, the A_q / Γ_q ratio of the CH₂(s) peak at the air interface is 2.1 compared to -0.28 at the buried silica interface.

But in the ppp prism spectrum, the CH₂(s) peak is much larger than the CH₃ contribution, because only the silica/PVC interface contributes to the spectrum, according to our fits (Table S-5, A_q / Γ_q ratios only generated for the buried interface). On a mechanistic level, it makes sense that we see larger CH₂ signals at this interface. Likely the CH₂ groups on the PVC chains are more ordered at the buried solid hydrophilic interface than the more hydrophobic CH₃ groups on the small DEHP molecules. Once again, we have an opportunity to determine what happens to both the surface and buried interface of the plastic film from water contact using both ssp and ppp spectra. Before water contact, we know the 10 % DEHP plasticized PVC surface in air is covered by both DEHP and PVC, while at the buried polymer/silica interface, the PVC CH₂ group dominates.

Prism Geometry: 10 wt% DEHP in D₂O

Once the 10 wt% DEHP films on prisms were contacted to D₂O, similar spectral trends as those with PVC in D₂O occur (Figure 6). That is, the 2915 cm⁻¹ CH₂(s) peak increases in intensity upon contact and then decreases over increasing contact time. Once again, the CH₂(s) peak dominates both ssp and ppp spectra the entire 1.25 hours of D₂O contact. The major

difference between pure PVC and the 10 wt% mixture D_2O contact is the overall intensity of the $CH_2(s)$ peak. Looking at the scale on Figures 5 and 6, it is obvious the intensity of the 2915 cm^{-1} peak is greater from the PVC phthalate mixture than the pure PVC in D_2O for both ssp and ppp prism spectra. This may suggest that the $CH_2(s)$ groups were ordered to a higher degree on the surface of the polymer mixture than on the surface of the pure PVC sample.

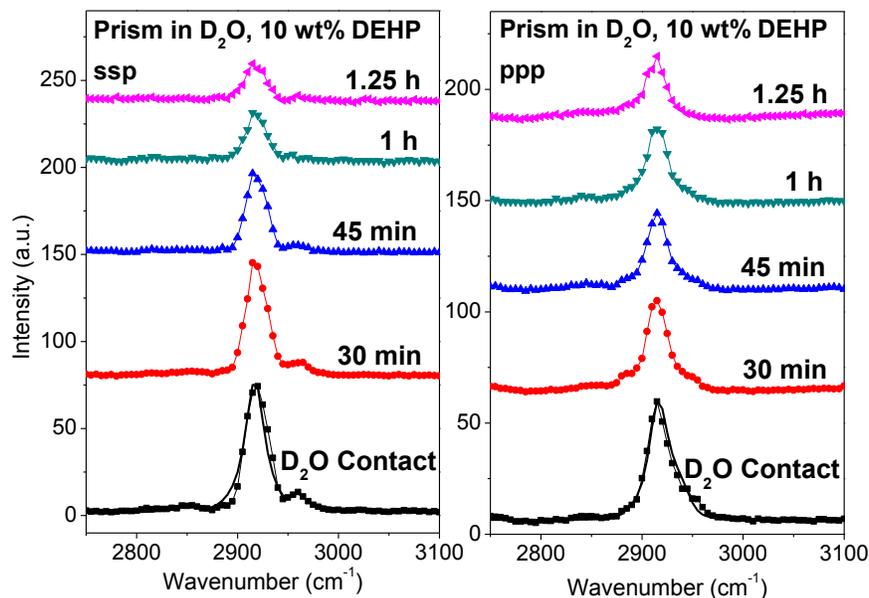


Figure 6. SFG prism spectra of 10 wt% DEHP plasticized PVC in D_2O over increasing contact time from first contact to 1.25 h. On the left is the ssp spectra series and the right the ppp series.

The spectral fits of the peaks upon water contact are represented as black lines.

Next, the fitting results for the ssp spectra in D_2O upon water contact (Table S-6) reveal that the dominant $CH_2(s)$ peak originates mainly from the polymer/water interface (A_q/I_q ratio of 3.5 versus -0.28). We believe that the strong CH_3 signals from the 10 wt% DEHP sample present in air before D_2O contact, immediately disappear because of almost immediate disorder of CH_3 DEHP groups at the polymer/water interface. Most barely resolvable residual CH_3

signals upon contact and increasing contact times are from still ordered CH₃ molecules at the other buried silica interface.

Then, looking more closely at the fitting results for the ppp spectra of 10 wt% DEHP in D₂O, we can see that both interfaces contribute to the spectrum. In Table S-6, A_q/Γ_q ratios for 2860, 2880, 2945, and 2970 cm⁻¹ peaks are only generated at the buried silica interface. However, the strong 2915 cm⁻¹ peak mainly arises from the PVC/water interface (A_q/Γ_q ratio -3.5 versus 1.1). And it should be noted, for the CH₂(s) mode, the signs of the signals at the PVC/water interface (-42) and the silica/PVC interface (13) are opposite, indicating the absolute orientations of these functional groups at the two interfaces are different. One is pointing up and the other is pointing down. Once again we can conclude that the addition of water increases and then decreases CH₂ ordering of the PVC molecules at the water interface, and that the CH₃ molecules from DEHP at this interface are almost instantly disordered.

Window Geometry: 10 wt% DEHP in Air after Water Contact

The windows spectrum of 10 wt% DEHP film/air interface after water contact can be found in Figure 3. The ssp window spectrum is remarkably similar to the film/air interface before water contact except for one element: the DEHP CH₃ to PVC CH₂ peak intensity ratio. After water contact, the 2880 cm⁻¹ peak is always lower than the 2915 cm⁻¹ peak, compared to before, when the peak ratios are almost evenly matched, suggesting CH₃ irreversible reorientation, or the dislodging of CH₃ groups from the surface in some form.

Prism Geometry: 10 wt% DEHP in Air after Water Contact

For ssp spectra on prisms, the opposite trend holds true (Figure 4). The 2880 cm⁻¹ peak increases in intensity in comparison to the 2915 cm⁻¹ peak. An increase in molecular disorder on

the surface of the film with minor changes to the buried silica/PVC interface or increased ordering at the buried interface may result in a larger CH_3 to CH_2 intensity ratio after water contact. So this once again suggests that some form of irreversible molecular surface reorientation occurred. And for the prism ppp spectrum, which only contains signals from the buried interface, we can conclude that some, but not many ordering changes occurred. We do see a slight change in the CH_3 to CH_2 intensity ratio after water contact, with an increase in the CH_3 intensity, which corroborates our conclusions with our ssp prism spectra. The CH group reordering changes on the surface of our PVC system were much larger than the changes at the buried silica/film interface.

In summary, the surface of 10 wt% DEHP plasticized PVC in air is covered by both DEHP and PVC functional groups but the buried polymer/silica interface is dominated by PVC methylene groups. The CH_3 groups of DEHP are disordered almost immediately upon contact. As a function of time, PVC surface order decreased as well. After removing the 10 wt% DEHP plasticized PVC from water, there was only partial recovery of surface methyl groups. Some restructuring behavior of the buried polymer/silica interface was also observed.

25 wt% DEHP/PVC in Air and Water

Window Geometry: 25 wt% DEHP in Air

As previously reported, the SFG ssp window spectrum of the PVC/DEHP mixture in air contains signals assigned to both PVC and DEHP functional groups (Figure 3).^{28, 52} The DEHP methyl group signatures dominate the spectrum, and the 2915 cm^{-1} peak for $\text{CH}_2(\text{s})$ appears as a

shoulder. This indicates that DEHP molecules, rather than PVC, dominate the surface. Fitting results for the window geometry can be found in Table S-7.

Prism Geometry: 25 wt% DEHP in Air

Once again, the spectra in air on prisms are different than the ssp spectra on windows as seen in Figure 4. In the ssp polarization, the 2915 cm^{-1} peak is much larger than the 2880 and 2945 cm^{-1} peaks whereas in ppp polarization the 2915 cm^{-1} peak is only slightly larger than the methyl resonances. This time, our fitting results indicate that both the air and buried silica interfaces contribute to ssp spectra, with the silica/PVC interface dominating the spectrum (Table S-8). Here, the $\text{CH}_2(\text{s}) A_q / \Gamma_q$ ratio in air is -2 , but at the buried silica interface it is 5.7 . Once again, this indicates that the PVC methylene groups are more ordered at the hydrophilic silica interface than the hydrophobic air interface.

The ppp spectrum only contains signals from the PVC/silica interface which originate from both PVC methylene groups and DEHP groups. This case is clearly different than pure PVC and 10 wt% DEHP, where we were still able to generate information mainly from the surface in ssp polarization. Here, we have most information arising from the buried interface, which will be very important in our analysis of water penetration into the film later.

Prism Geometry: 25 wt% DEHP in D₂O

The ssp prism spectrum of 25 wt% DEHP upon contact with D₂O shows the appearance of an intense 2915 cm^{-1} $\text{CH}_2(\text{s})$ peak (Figure 7). A second strong peak at 2950 cm^{-1} in ssp spectra is also present, assigned to the $\text{CH}_3(\text{s})$ Fermi resonance. After 30 min of water exposure, almost no peaks can be resolved. This indicates that either the plastic surface first became highly

ordered and then disordered, or that multiple interfacial signals are initially observed, and then disappear with increasing water contact time.

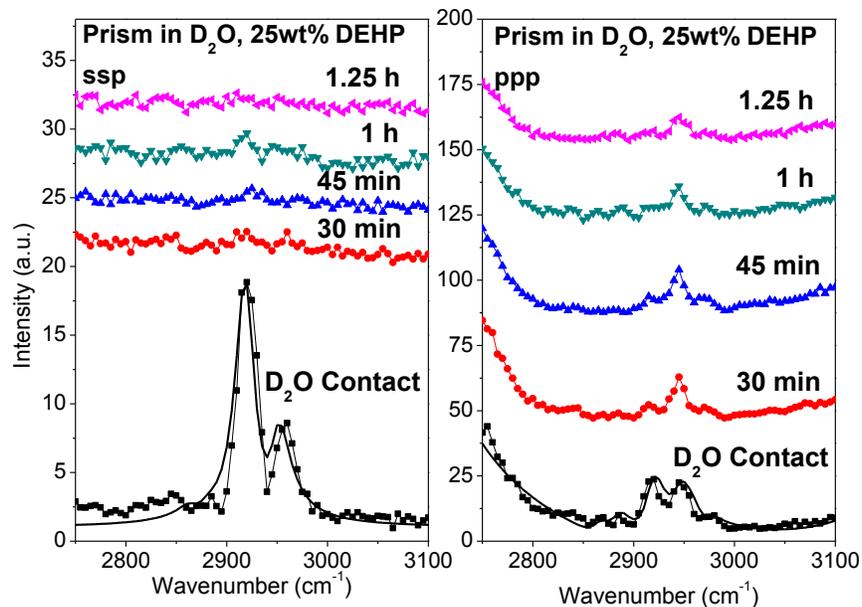


Figure 7. SFG prism spectra of 25 wt% DEHP plasticized PVC in D_2O over increasing contact time from first contact to 1.25 h. On the left is the ssp spectra series and the right the ppp series.

The spectral fits of the peaks upon water contact are represented as black lines.

The ssp spectrum for initial water contact (Table S-9) can be fitted with the fitting parameters of the buried interface in air. As such, we believe that the plastic's surface ordering is destroyed right after contacting water. With increased plasticization from the DEHP molecules, the water quickly diffused to the buried interface and destroyed silica/PVC interfacial ordering as well. This conclusion is also supported by ppp spectra.

In the ppp spectrum upon water contact, the spectrum was fit well with contributions from the buried silica interface with weak surface signal contributions from the water interface (Table S-9), agreeing with the observation of the disappearance of the ssp plastic surface signals

immediately after water contact. The ppp SFG signal also decreases as a function of increasing contact time, which means the silica/PVC interfacial ordering must be destroyed due to increased water diffusion through the plasticized polymer film. Because the plasticizer bulk content is high in this sample, the water can easily diffuse through the film.

Window Geometry: 25 wt% DEHP in Air after D₂O Contact

Previously the changes in CH₃ to CH₂ peak ratios due to water contact were explored with 10 wt% DEHP samples. This trend can be more clearly observed with the ssp window spectrum of 25 wt% DEHP in air after water contact (Figure 3). Before water contact, the CH₂(s) peak of PVC is observed as a shoulder in the 25 wt% DEHP mixture. After water contact, however, a clear large 2915 cm⁻¹ peak is present. This again suggests that there may have been either functional group reorientation or loss of CH₃ groups on the surface.

Prism Geometry: 25 wt% DEHP in Air after D₂O Contact

Prism ssp spectra reveal again, only very small changes before and after water exposure (Figure 4). Since we found that the silica/polymer interface dominates ssp spectra with this sample type, we believe that there were only small ordering changes at this buried interface. The spectrum of ppp prisms after water exposure only slightly changes. Recalling ppp prism spectra, the buried silica interface completely dominates the spectrum. The buried solid interface must undergo slight irreversible ordering changes from water contact. We now know both the surface and the bottom of this plastic film were altered from water contact. It is interesting that this film has roughly the same thickness as the other two sample types (~200 nm), but the signal contributions from the film surface versus buried interfaces are different for the 25 wt% DEHP prisms in air and D₂O compared to the pure PVC and 10 wt% DEHP samples. It can be

reasonably concluded that this occurs because the material with 25 wt% DEHP is intensively plasticized, compared to the other two samples. The increased plasticizer content increases the free volume within the polymer matrix, therefore changing the dynamic reordering behavior of the CH functional groups at the two interfaces.

Nevertheless, our results showed that the surface of the 25 wt% DEHP plasticized PVC undergoes dramatic surface restructuring in water. Both the surface and the buried polymer/silica interface became disordered in water. After the sample was removed from the water, the surface structure did not completely recover. For both plasticized samples, it is not clear yet if the surface signal changes after water contact are due to phthalate or PVC surface reorientation, disorder, or loss of phthalates on the surface to water. As the next section reveals, a combination of all of the above may have taken place.

Phthalate Disorder and Leaching

To test the stability changes of phthalates in PVC/plasticizer mixtures due to contact with water, phthalate-leaching experiments were conducted. A PVC mixture of 45 wt% DEHP and PVC was contacted to D₂O for about 1.5 hours. The D₂O droplet was then contacted to a new clean polymer surface (PS-d8) and SFG spectra were obtained at the PS-d8 interface. The SFG spectra of the clean deuterated polystyrene polymer surface before, during and after “dirty” D₂O contact can be seen in Figure 8. With this system we no longer have to worry about interfacial signal interferences. Any deposited molecules will not form a thick enough film where interface interference will occur, and the deposited PS-d8 yields no SFG signal in the CH stretching frequency range.

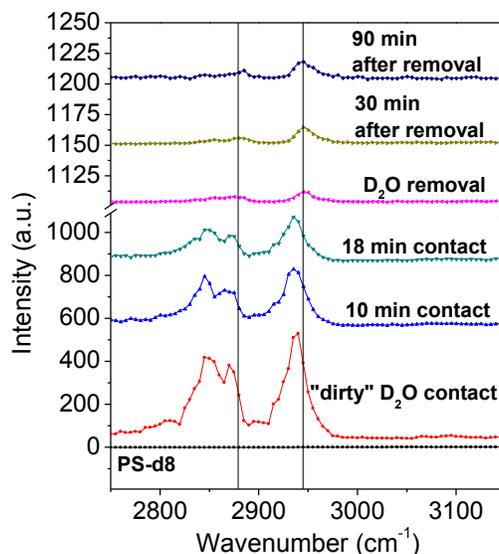


Figure 8. SFG prism ssp spectra of PS-d8 film contacted with “dirty” D₂O containing phthalate molecules for up to 20 minutes and the resulting spectra of the PS-d8 air interface after removal of the D₂O. The two black lines are provided for reference and centered at 2880 and 2945 cm⁻¹.

Upon immediate contact with the “dirty” D₂O, spectral shapes significant of DEHP at the D₂O/polymer interface can be observed. The unique shape of the three major peaks at the PS-d8/dirty D₂O interface matches that of pure DEHP in air, but the peaks are shifted in D₂O: near 2855 cm⁻¹, 2870 cm⁻¹, and 2935 cm⁻¹, rather than 10 cm⁻¹ higher as normal. We found this same frequency shift trend with a solution of known concentration of DEHP in D₂O contacted to a PS-d8 sample (data not shown), confirming that indeed phthalate molecules transferred from the plastic matrix to the water even though the molecules are considered hydrophobic in nature.

In addition, we observe trends in phthalate reordering over time, with decreasing signal at the water/polymer interface, suggesting either disorder or adsorption into the PS matrix. Once the D₂O was removed and the surface was air-dried, clear 2880 cm⁻¹ and a peak around 2945 cm⁻¹ remain at the polymer/air interface. To make sure the signals observed were not from the D₂O

or PS-d8 itself, the experiments were not only repeated numerous times but conducted using pure D₂O as blank experiments. No signals were observed for the blank experiments. Attempts to observe the leaching of phthalates from plastic films using FTIR and ATR-FTIR were unsuccessful (see Figure S-5 for FTIR results before and after water contact), which indicates that the amounts of leached phthalates were too low to be detected using these traditional spectroscopic techniques.

The phthalate leaching studies show the phthalate molecules were not stable upon contact with water even at relatively “short” contact times, and may help explain the differences in peak ratios between CH₃ and CH₂ groups on windows after water contact. DEHP molecules were likely disordered, and some molecules were removed from the water contact. Like most water/polymer SFG studies, the movement of functional groups at the surface likely occurred because of drives to lower the interfacial free energy of the system.

CONCLUSION

The molecular effects of water contact on pure and plasticized PVC surfaces were studied *in situ* using SFG spectroscopy. The surface end CH₃ molecular groups on pure PVC were instantly disordered upon water contact and the dominating CH₂ groups disordered in water over increasing exposure time. Addition of 10 wt% DEHP changed the surface structure, yielding increased CH₂ and CH₃ disorder with increased water exposure time. The surface CH molecular groups on PVC with 25 wt% bulk DEHP disordered almost immediately with water contact. Eventually, water migrated through the plastic bulk of all the films to reach the buried substrate/polymer interface, where water induced CH group disorder. This was most clearly

observed with the 25 wt% DEHP sample, which may indicate that more water penetrated this film than the other two sample types. After removal from water and drying in air, all films demonstrated irreversible surface functional group changes. For the first time, through DEHP leaching tests, it was found that the phthalate molecules are capable of transferring into D₂O and can be transferred from D₂O to reorganize and reorient on new surfaces very quickly (in minutes). Irreversible buried interface reordering was also observed.

During this study, it was found that SFG spectra obtained in prism geometry appeared different from spectra taken in window geometry. It was determined that the spectra obtained in window geometry in air only contained signals from the air interface. Using a deconvolution analysis and the fitted parameters of the window spectra, we quantified the spectral contributions from the buried polymer/silica interface in the prism spectra. We found that prism SFG signals generated from different samples originated from different interferences (either surface signal dominated, buried interface dominated, or a both interfacial signals contributed to spectra, depending on the plastic type and the experimental environment). We therefore were able to generate a very good understanding of molecular ordering changes from water contact at the polymer/water and polymer/silica interfaces at the same time. This method of analysis may be applied to many other thin-film systems analyzed using SFG to identify the interfacial origins of SFG signals and/or study molecular group behaviors at two interfaces simultaneously. Lastly, the films studied were simple models of PVC plastics, but it is well known that many PVC plastics contain leached plasticizers present on surfaces available to contact water. Therefore, the results from these studies suggest that when real PVC plastics are contacted with water, the molecular surfaces of the plastics may change dramatically and if plasticizers are present on the

surface, small amount of plasticizer molecules may escape from the plastic and permanently transfer to other surfaces through water contact.

ACKNOWLEDGMENTS

This research is supported by the National Science Foundation (NSF) (CHE 1111000). The authors thank Dr. Xiaoxian Zhang for insightful discussion and Dr. Xiaofeng Han for his expertise in SFG laser maintenance and repairation. Dr. Xiaolin Lu is also grateful for the National Natural Science Foundation of China (51173169, 21004054), Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education, and Human Resources and Social Security Bureau of Zhejiang Province, China and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions, China (PAPD 1107037001).

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The authors declare no competing financial interest

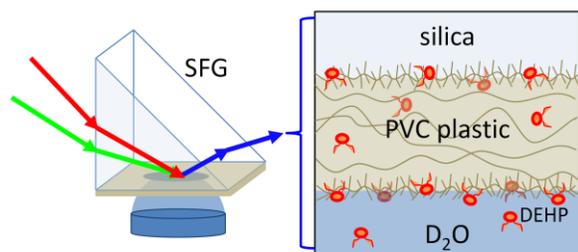
An electronic supplemental information file is associated with this article. The supplemental file includes additional information on the details of the SFG laser system, SFG signal contributions, a discussion on film thickness choice, more details on SFG prism peak fits and the corresponding fitting tables, and details and results of FTIR experiments on plastic films before and after water contact.

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TOC



We present a means to study the molecular changes of the top and bottom of polymers contacted to water simultaneously *in situ*. Plasticizers were found to transfer from polymer surfaces to water in minutes.