

Evaluating UV/H₂O₂ Exposure as a DEHP Degradation Treatment for Plasticized PVC

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This document contains additional information about our SFG experimental setup, additional SFG data for a 10 wt% DEHP system exposed to UV/H₂O₂ treatment methods, and additional UV-Vis data with discussion of plastic film degradation, applicability of UV treatment, and plastic thickness.

Expanded Details on Experimental Section:

SFG Setup Details

The EXSPLA SFG system is composed of a pico-second Nd:YAG laser, a harmonic unit with two KD*P crystals, an optical parametric generation (OPG)/optical parametric amplification (OPA) and difference frequency generation (DFG) system based on LBO and AgGaS₂ (or GaSe) crystals and a detection system. The output of the Nd:YAG laser is a 20 Hz 20 ps 1064 nm near-IR beam. The visible input 532 nm beam for SFG experiments is generated by frequency-doubling a portion of this 1064 nm beam. The mid-IR beam is generated from the OPG/OPA and DFG system and can be tuned from 1000 to 4300 cm⁻¹. For SFG experiments, the incident angles of the visible and the IR input are 60° and 55° with respect to the surface normal, respectively. The diameters of both input beams at the surface are about 500 μm. The SFG signal from the surface is collected by a photomultiplier and processed with a gated integrator.

Expanded Data for SFG Studies:

In order to make a direct comparison to our previous studies looking at the surface changes of plasticized PVC after short wave and long wave UV exposure only, we also obtained SFG data of PVC plasticized with a lower weight percentage of DEHP, 10 wt% DEHP samples. These samples were exposed to short wave and long wave UV with 35 wt% H₂O₂ as outlined in the main paper. Results are discussed below.

SFG Analysis of 10 wt% DEHP

In contrast to the dominating signals observed from DEHP in the 25 wt% sample, the intensities of the signals from DEHP and PVC in the 10 wt% sample are virtually the same, indicating the surface contains both PVC and DEHP molecules (Figure S-1). After 30 min of short wave/H₂O₂ treatment, the intensity of the CH₂(s) peak is larger than the CH₃ peaks, and by 5h, the only signal remaining is that of the CH₂(s) peak, indicative that all DEHP has been converted to other molecules. The SFG spectra after 5h of treatment highly resembles the signal from pure PVC but without the peak from the CH₃(s) end group at 2880 cm⁻¹ (see Figure S-1), so it may be possible that the majority of the surface ordering is from PVC groups. Near complete removal or degradation of DEHP at this point would make sense. At this time, the 25 wt% DEHP samples contain few intact phthalate molecules and some smaller degraded ones. With a lower concentration of DEHP than 25 wt%, perhaps most of the DEHP reacted. In contrast, after 5h of long wave/H₂O₂ treatment, there are virtually no changes in the CH₂ to CH₃ ratio, like that seen with the 25 wt% DEHP sample.

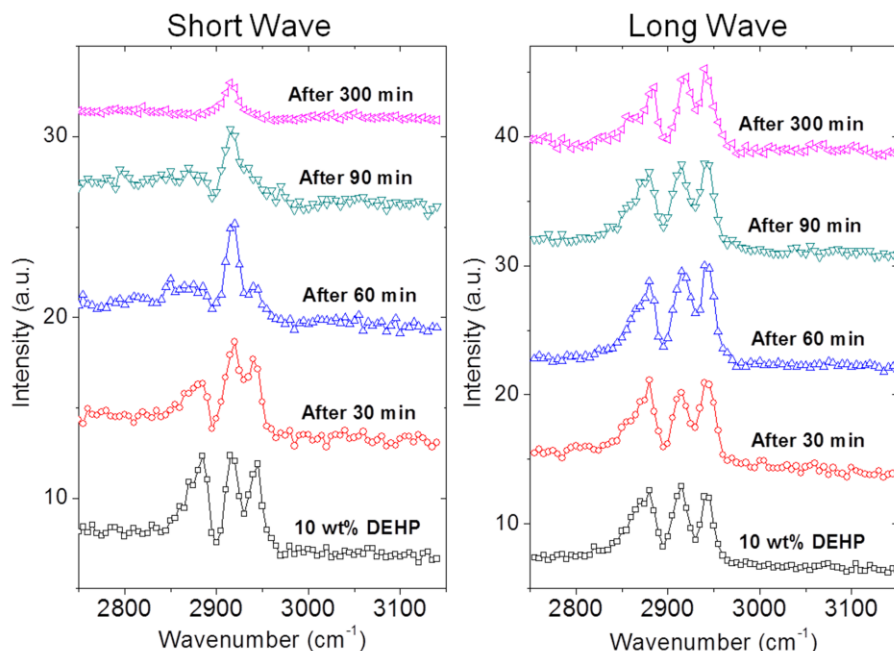


Figure S-1. SFG ssp spectra collected from plasticized PVC with 10 wt% DEHP before and after 30 min, 60 min, 90 min, or 300 min of short (left panel) versus long (right panel) wave UV exposure with H₂O₂.

UV-Vis Data and Analysis

To further understand the chemical changes the plasticized PVC material may undergo due to absorption of UV light and subsequent bond breaking, UV-Vis spectra of 25 wt% DEHP films were obtained before and after 5h exposure of 254 nm UV, as shown in Figure S-2. With a film thickness upwards of 200 nm on all sides of the UV-Vis cuvette (400+ nm total), there is low UV absorbance at 254 nm, indicating that the UV (at 254 nm) penetrates the bulk of the sample.

After short wave UV exposure, there is a decrease in signal intensity in the lower wavelength region, from 190 nm to about 250 nm, and an increase in signal intensity at about 300 nm. The absorbances in the low wavelength region are associated with phenyl ring (possibly in combination with the conjugated C=O) UV absorptions, suggesting that the conjugated bond network in and around some phenyl rings are no longer intact. In turn, the increase in absorption after reaction around 300 nm is associated with an increase in conjugation across PVC chains, strong evidence for double bond formation. Such bonds would result once chlorine was abstracted from the polymer, which is expected to occur from short wave UV exposure. A slight tail of increased absorption is observable towards longer UV wavelengths, which can also be associated with the increased conjugation of the polymer system. It is important to note that not many absorbance changes are observed in the longest UV wavelengths, and although the film does not absorb much long wave UV or short wave visible light, a small amount of absorption is observed at 365 nm, the wavelength utilized for our long wave UV exposure experiments.

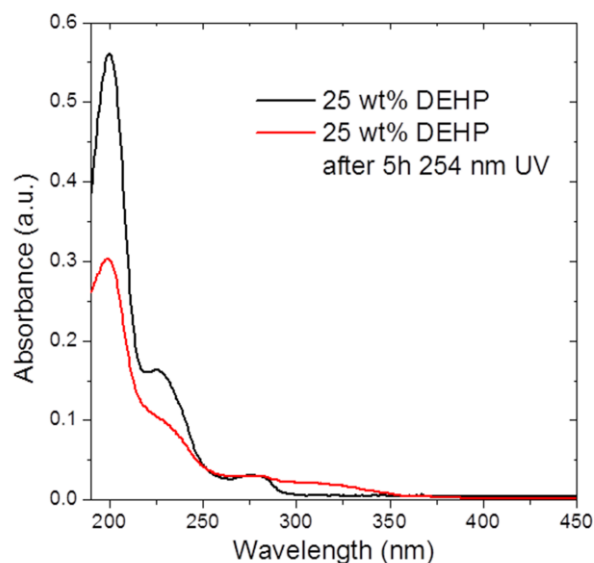


Figure S-2. UV-Vis spectra of a thin film (400 +nm total thickness) of PVC with 25 wt% DEHP before and after 5h of exposure to 254 nm.

UV-Vis Data for Thick Film Discussion

Many clear PVC plastics contain a large concentration of plasticizers by weight. This includes PVC tubing, medical tubing and bags (which are known to be made with >70 wt% phthalate), PVC films, and PVC utilized for packaging materials. Due to the limits of UV depth penetration, short wave UV cannot be used on all PVC materials to degrade phthalates after plastic disposal. As stated in the main paper, the model UV treatment systems were designed to degrade the bulk of phthalates in clear PVC materials, other opaque thin film PVC products, and to treat the surfaces of decades old PVC materials in which most phthalates have already migrated to the surface layers of the plastic. While determining the exact penetration depth of short wave UV into different types of plastics is beyond the scope of this paper, we utilized UV-Vis to determine if 254 nm UV could penetrate the bulk of a thicker film. 254 nm UV without H₂O₂ was tested since this exposure was determined to be the most effective treatment to degrade phthalates in PVC. The UV-Vis setup used requires that the UV pass through the entirety of the cuvette to reach the detector. As shown in Figure S-3, a 25 wt% DEHP loaded PVC plastic coated 20-30 μm thick on all sides of a quartz cuvette (40-60 μm total), absorbs only about 0.23 absorbance units at 254 nm, compared to 0.04 absorbance units for the 400+ nm film. This indicates that UV light still penetrates through both layers of plastic at roughly 59% transmission. It may be reasonable to apply this technique, therefore, to both sides of clear thin PVC plastics to remove bulk phthalates, or to the surfaces of old PVC plastics.

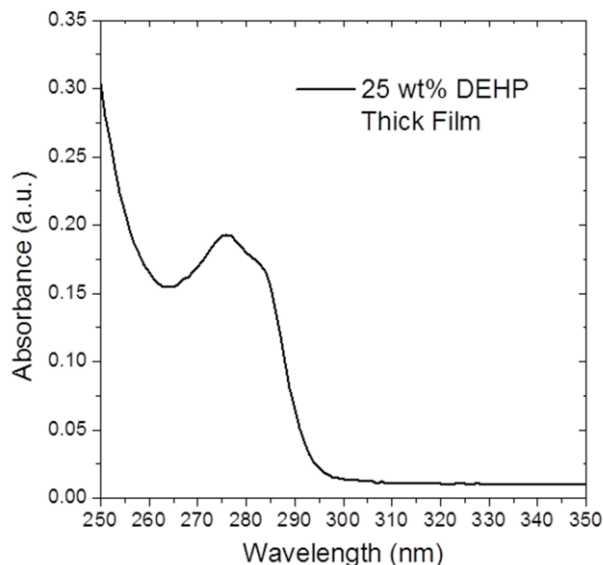


Figure S-2. UV-Vis spectra near 254 nm of a thick film (40-60 μm total thickness) of PVC with 25 wt% DEHP.

UV-Vis Experimental Details

UV-Vis spectra were obtained on a UV-1601PC UV-Vis Shimadzu Spectrophotometer. Thin plastic films were formed on the insides of quartz cuvettes by squirting ~ 1 mL plastic solution inside the cuvettes using a glass pipette and pouring excess solution out. For the thin film preparation, the plastic solution procedure was identical to the method stated in the experimental section of the paper. Thick films were generated by squirting ~ 1 mL of plastic solution into quartz cuvettes two times, and pouring excess solution out. The sample preparation for the plastic solutions were the same as stated in the experimental except the weight ratio of THF:PVC was 10:1. The cuvettes were rinsed with ethanol and Milli-pore deionized water several times, dried with nitrogen gas, and plasma cleaned for 3 min prior to film preparation. For the thin film experiment, one quartz cuvette was subjected to 5h 254 nm UV exposure in an identical manner to the UV experiments outlined in the main paper. Clean quartz cuvettes were used as a background for UV-Vis measurements. The authors thank the members of the Gafni lab at the University of Michigan for allowing us use of and help with their UV-Vis instrument.